



## SEQUENTIAL ELECTRODIALYTIC EXTRACTION OF PHOSPHORUS COMPOUNDS

Viader, Raimon Parés; Mølgaard Ottesen, Lisbeth; Erland Jensen, Pernille

*Publication date:*  
2017

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Viader, R. P., Mølgaard Ottesen, L., & Erland Jensen, P. (2017). SEQUENTIAL ELECTRODIALYTIC EXTRACTION OF PHOSPHORUS COMPOUNDS. (Patent No. WO2017055341).

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## (51) International Patent Classification:

**B01D 61/44** (2006.01)    **C05B 17/00** (2006.01)  
**B09B 3/00** (2006.01)    **C05D 9/00** (2006.01)  
**B09C 1/08** (2006.01)    **C05D 9/02** (2006.01)  
**C02F 1/469** (2006.01)    **C02F 1/66** (2006.01)  
**C02F 11/00** (2006.01)    **C02F 101/20** (2006.01)

## (21) International Application Number:

PCT/EP2016/073094

## (22) International Filing Date:

28 September 2016 (28.09.2016)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

15187370.0 29 September 2015 (29.09.2015) EP

(71) Applicant: **DANMARKS TEKNISKE UNIVERSITET**  
 [DK/DK]; Bygning 101A, Anker Engelunds Vej 1, 2800  
 Kgs. Lyngby (DK).

(72) Inventors: **VIADER, Raimon Parés**; Rolf Krakes Allé 5,  
 2860 Søborg (DK). **MØLGAARD OTTESEN, Lisbeth**;  
 Harløsevej 144, 3400 Hillerød (DK). **ERLAND JENSEN,**  
**Pernille**; Tjørnevænget 55, Lyngby 2800 (DK).

(74) Agent: **HØIBERG P/S**; Adelgade 12, 1304 Copenhagen  
 K (DK).

(81) Designated States (unless otherwise indicated, for every  
 kind of national protection available): AE, AG, AL, AM,  
 AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,  
 BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,  
 DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,  
 HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,  
 KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,  
 MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,  
 OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,  
 SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,  
 TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,  
 ZW.

(84) Designated States (unless otherwise indicated, for every  
 kind of regional protection available): ARIPO (BW, GH,  
 GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,  
 TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,  
 TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,  
 DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,  
 LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,  
 SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,  
 GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: SEQUENTIAL ELECTRODIALYTIC EXTRACTION OF PHOSPHORUS COMPOUNDS

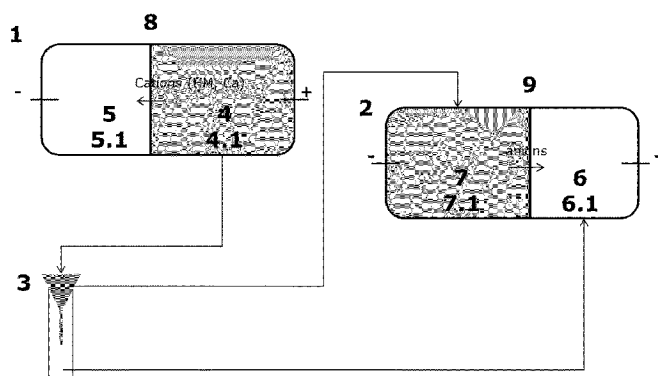


Fig. 1

(57) Abstract: The present invention relates to an apparatus for electrodialytic extraction of phosphorus from a particulate material in suspension and to a method for electrodialytic phosphorus recovery, which uses the apparatus. The method may be applied for wastewater treatment, and/or treatment of particulate material rich in phosphorus. The present invention provides an apparatus for electrodialytic extraction of phosphorus from a particulate material comprising acidic and/or alkaline soluble phosphorus compounds, in suspension, comprising: • a first electrodialytic cell comprising a first anolyte compartment comprising a first anolyte, and a first catholyte compartment comprising a first catholyte, wherein the compartments of the first cell are separated by a cation exchange membrane, wherein the first anolyte is the particulate material in suspension, the first electrodialytic cell configured for exposing the particulate material to acidic conditions; • a second electrodialytic cell comprising a second anolyte compartment comprising a second anolyte, and a second catholyte compartment comprising a second catholyte, wherein the compartments of the second cell are separated by an anion exchange membrane, the second electrodialytic cell configured for exposing the particulate material to alkaline conditions; and • filtration means in fluid communication with the first and second electrodialytic cells, and configured to filter the first anolyte, and transfer the residual into the second catholyte compartment to be comprised in the second catholyte, and transfer the filtrate into the second anolyte compartment to be comprised in the second anolyte.



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**Published:**

— *with international search report (Art. 21(3))*

## Sequential electrodialytic extraction of phosphorus compounds

### Field of invention

5 The present invention relates to an apparatus for electrodialytic extraction of phosphorus from a particulate material in suspension, a method for electrodialytic phosphorus recovery, and the use of the apparatus and the method for wastewater treatment, and/or treatment of particulate material rich in phosphorus.

### Background of invention

10 Phosphorus (P) is a valuable resource; it is an elemental nutrient for agriculture, as well as an element in food, biofuels and biobased materials. The global consumption of phosphorus, and phosphorus compounds such as phosphate ( $\text{PO}_4^{3-}$ ), is increasing, and thus the supply of phosphorus has received increasing attention during recent years. Phosphorus may be extracted from phosphate rock reserves. The reserves are  
15 geographically restricted and a non-renewable resource. The reserves, or primary sources, of phosphorus are estimated to be depleted within a century.

Alternative, also called secondary, phosphorus resources include municipal wastewater and agricultural organic residues, such as livestock manure or digestate from biogas  
20 plants. In the wastewater, the phosphorus occurs as dissolved inorganic phosphates in a liquid fraction and/or as phosphorus bound in a solid fraction, e.g. as inorganic precipitates or complexes, or as complex biochemical molecules.

The purpose of wastewater treatment is to remove contaminants from the wastewater  
25 to produce an environmentally safe fluid for reuse. The solid, or semi-solid, waste from such a process is called sludge, and depending on the processes it may be characterised as industrial sludge or sewage sludge, and the sludge will thus contain the contaminants. The contaminants may be heavy metals as well as phosphorous compounds. Contaminants such as phosphorous compounds are typically removed  
30 from the wastewater by microorganisms combined with chemical precipitation involving the addition of iron (Fe) or aluminium (Al) salts. Thus, sludge typically contains phosphorus bound as inorganic phosphates (Al-, Fe- and Ca-phosphates) and organic bound phosphorus.

The sludge is further typically incinerated to ash, which may be either disposed or reused as e.g. farm fertilizer. However, the ashes containing iron and aluminum phosphates are known to have low fertilizer value, as phosphorus in these chemical forms is not easily accessible for plants. Thus, methods to extract phosphorus from sewage sludge or sewage sludge ashes (also denoted SSA) into phosphorus products with higher fertilizer value are of interest.

Furthermore, in the fertilizer industry it is important to keep the ratios of Al, Fe, and Mg to phosphorus low. This is to obtain industrial phosphoric acid with high concentration, as well as to manufacture common fertilizers like diammonium phosphate (DAP). For this purpose, there is a technical limit called minor element ratio (MER), defined as:

$$MER = \frac{Al_2O_3 + Fe_2O_3 + MgO}{P_2O_5} < 0.085$$

Recently, electrodialysis or electrodialytic remediation has been used to produce phosphorus products from ashes. WO 2015/032903 [1] discloses a two compartment electrochemical cell, where the two compartments are separated by a cation exchange membrane. A particulate suspension, such as an ash comprising heavy metals, is introduced into the anode compartment. When an electric field is applied, protons are generated at the anode, whereby the different metals (Al, Ca, Fe and heavy metals) dissolve and form positively charged cations that will migrate from the anode compartment, through the cation exchange membrane and into the cathode compartment.

Thus, in [1] the heavy metals are separated from the particulate suspension, and the residual particulate suspension which may contain phosphorus, may be used as an agricultural product. However, the concentration of phosphorus in the liquid part of the residual particulate suspension may be low, and its fertilizer value in the solid part of the residual particulate suspension is low if the phosphorus is found as iron and aluminium phosphates in the original ash.

Furthermore, typically the concentration of phosphorus in the liquid part of the residual particulate suspension is low, because the rate of phosphorus extraction to the liquid part is low, since the main driving forces for the extraction is dissolution and diffusion.

Electrodialytic remediation of a phosphorus containing sludge using a two compartment electrochemical cell with an anion exchange membrane, has been described by B. Ebbers et al. [2]. The sludge, which may comprise phosphorus, is in this case introduced into the cathode compartment. When an electric field is applied, hydroxide anions are formed at the cathode, whereby some of the phosphorus bound in the sludge will dissolve and form negatively charged phosphorus compounds (such as  $\text{HPO}_4^{2-}$ ) that will migrate from the cathode compartment, through the anion exchange membrane and into the anode compartment.

Thus, in [2] the phosphorus is separated from the particulate suspension in the cathode compartment, and concentrated in the anode compartment in a readily available form. However, when using this method, not all phosphorus compounds will dissolve and/or form negatively charged compounds. For example, phosphorus bound to calcium (Ca) is expected to remain as insoluble in the cathode compartment. Thus, the method is not suitable for fully, or high degree of recovery of the phosphorus in the ashes.

Furthermore, typically the concentration of phosphorus in the liquid part of the residual particulate suspension is low, because the rate of phosphorus extraction to the liquid part is low, since the main driving forces for the extraction is dissolution and diffusion.

### Summary of invention

The present invention provides an apparatus and a method for high recovery of phosphorus from a particulate material, such as a sludge or a sludge ash. Furthermore, the present invention provide extracted phosphorus in a form that can be easily used to manufacture products with high fertilizer value, such as phosphorus in an aqueous solution.

The inventors of the present invention have surprisingly found that if modifications are made to the earlier established two compartment electrodialytic cell, by combining two separated two compartment cells via filtration means, then an improved remediation method is achieved.

In a first aspect the present invention provides an apparatus for electrodialytic extraction of phosphorus from a particulate material in suspension, comprising:

- a first electrodialytic cell comprising

- a first anolyte compartment comprising a first anolyte, and
- a first catholyte compartment comprising a first catholyte,  
wherein the compartments of the first cell are separated by a cation  
exchange membrane, and wherein the first anolyte is the particulate  
material in suspension;
- a second electrodialytic cell comprising
  - a second anolyte compartment comprising a second anolyte, and
  - a second catholyte compartment comprising a second catholyte,  
wherein the compartments of the second cell are separated by an anion  
exchange membrane; and
- filtration means in fluid communication with the compartments and  
configured to filter the first anolyte, and transfer the residual into the second  
catholyte compartment to be comprised in the second catholyte, and  
transfer the filtrate into the second anolyte compartment to be comprised in  
the second anolyte.

In a further aspect, the present invention provides an apparatus for electrodialytic extraction of phosphorus from a particulate material comprising acidic and/or alkaline soluble phosphorus compounds, in suspension, comprising:

- a first electrodialytic cell, comprising
  - a first anolyte compartment comprising a first anolyte, and
  - a first catholyte compartment comprising a first catholyte,  
wherein the compartments of the first cell are separated by a cation  
exchange membrane,
  - wherein the first anolyte is the particulate material in suspension,  
the first electrodialytic cell configured for exposing the particulate  
material to acidic conditions;
- a second electrodialytic cell comprising
  - a second anolyte compartment comprising a second anolyte, and
  - a second catholyte compartment comprising a second catholyte,  
wherein the compartments of the second cell are separated by an anion  
exchange membrane,  
the second electrodialytic cell configured for exposing the particulate  
material to alkaline conditions; and

filtration means in fluid communication with the first and second electrodialytic cells, and configured to filter the first anolyte and transfer the residual into the second catholyte compartment to be comprised in the second catholyte and transfer the filtrate into the second anolyte compartment to be comprised in the second anolyte.

5

In a second aspect the present invention provides a method for electrodialytic phosphorus recovery, comprising:

- (a) providing a first electrodialytic cell, comprising a first anolyte compartment and a first catholyte compartment, separated by a cation exchange membrane;
- 10 (b) providing a particulate material comprising phosphorus;
- (c) mixing the particulate material with a liquid and use it as an anolyte for the first cell;
- (d) providing an electrolyte solution and use it as a catholyte for the first cell;
- (e) applying a first current to the first cell;
- whereby metal ions are concentrated in the catholyte;
- 15 (f) providing a second electrodialytic cell, comprising a second anolyte compartment and a second catholyte compartment, separated by an anion exchange membrane;
- (g) transferring the treated anolyte from the first cell by filtration means such that the treated anolyte is filtered into a residual and a filtrate;
- (h) transferring the liquid filtrate into the second anolyte compartment thereby forming a
- 20 second anolyte;
- (i) mixing the residual with water, and transferring it into the second cathode compartment thereby forming a second catholyte;
- (j) applying a second current to the second cell;
- whereby phosphorus and phosphorous compounds are concentrated in the second
- 25 anolyte.

In a further aspect, the present invention provides a method for electrodialytic phosphorus recovery, comprising:

- (a) providing a first electrodialytic cell, comprising a first anolyte compartment and a
- 30 first catholyte compartment, separated by a cation exchange membrane;
- (b) providing a particulate material comprising acidic and/or alkaline soluble phosphorus compounds;
- (c) mixing the particulate material with a liquid and use it as an anolyte for the first cell;
- (d) providing an electrolyte solution and use it as a catholyte for the first cell;
- 35 (e) applying a first current to the first cell thereby exposing the particulate material to



acidic conditions,

whereby metal ions are concentrated in the catholyte;

(f) providing a second electrodialytic cell, comprising a second anolyte compartment and a second catholyte compartment, separated by an anion exchange membrane;

5 (g) transferring the treated anolyte from the first cell to filtration means such that the treated anolyte is filtered into a residual and a filtrate;

(h) transferring the liquid filtrate into the second anolyte compartment thereby forming a second anolyte;

10 (i) mixing the residual with water, and transferring the mixture into the second cathode compartment thereby forming a second catholyte;

(j) applying a second current to the second cell thereby exposing the particulate material to alkaline conditions,

whereby phosphorus and phosphorous compounds are concentrated in the second anolyte.

15

A third aspect of the present invention is directed to the use of the apparatus according to the first aspect, and the use of the method according to the second aspect of the invention, for wastewater treatment and/or treatment of particulate material rich in phosphorus, such as incinerated-, gasified-, and pyrolyzed- wastewater sludge ash.

20

### Description of Drawings

The invention will in the following be described in greater detail with reference to the accompanying drawings.

25

**Figure 1** shows an embodiment of the invention comprising a first electrodialytic cell (1), a second electrodialytic cell (2), and filtration means (3). Each cell is a two

compartment electrochemical cell, where the charged electrodes, indicated by plus (anode) and minus (cathode) signs, are placed in respectively the anolyte

compartments (4, 6) and the catholyte compartments (5, 7). The two compartments in

30

the first cell (1) are separated by a cation exchange membrane (8), and the two

compartments in the second cell are separated by an anion exchange membrane (9).

Electrolyte solutions and/or suspensions are circulated in the compartments, and the

electrolyte/suspension in the anolyte compartments is designated anolyte (4.1, 6.1),

and the electrolyte/suspension in the catholyte compartments is designated catholyte

35

(5.1, 7.1).

**Figure 2** shows an embodiment of the invention where the first catholyte (5.1) is recycled as first catholyte (5.1), and/or the second anolyte (6.1) and/or the first filtrate (3.1) is recycled as a part comprised in the first anolyte (4.1). The embodiment also illustrates a second filtration means (10) in fluid communication with the second catholyte compartment (7), wherein the produced second filtrate (10.1) may be recycled as the liquid comprised in the second catholyte (7.1).

**Figure 3** shows the solubility curves of Al-, Fe-, and Ca-phosphates as a function of pH, according to [3].

**Figure 4** shows the solubility curves of calcium orthophosphoric compounds at 37°C, depending on pH in aqueous solution. HAp: hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), TCP: calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ), OCP: octacalcium phosphate ( $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ), DCPA: dicalcium phosphate anhydrous ( $\text{CaHPO}_4$ ), DCPD: dicalcium phosphate dihydrate ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), according to [4].

Figure 5 shows the pH dependence of metal hydroxide solubility, where the considered minerals are  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$ , and  $\text{Zn}(\text{OH})_2$ , as reported by C. Noubactep in Clean-Soil Air Water 41(5) (2013) p. 493-502 [5].

### Detailed description of the invention

The present invention relates to an apparatus and a method for extraction of phosphorus from a particulate material, such as a sludge or a sludge ash. Particulate material such as sludge or sludge ash typically comprise phosphorus bound to Al, Fe and Ca and/or heavy metals. Examples of common phosphorous compounds in sewage sludge and ashes include  $\text{AlPO}_4$ ,  $\text{FePO}_4$ ,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , and  $\text{Ca}_3(\text{PO}_4)_2$ , as well as other less common compounds such as  $\text{CaHPO}_4$ ,  $\text{Ca}_4\text{H}(\text{PO}_4)_3$ , and  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$ .

Phosphorus refers to the chemical element with symbol P and atomic number 15. Compounds comprising phosphorus are referred to as phosphorous compounds, but may also be referred to as phosphorus species, or abbreviated as "P-compounds". Examples of P-compounds include ortho-phosphates with the general formula

$H_xPO_4^{x-3}$ , where x is between 0 and 3, as well as iron-, aluminum-, and Ca-phosphate compounds. By the term “phosphorus” as used herein is meant any material comprising phosphorus in any form, such as elemental form, ionic form, or any compound comprising phosphorus. Thus, the terms “phosphorus compounds” and  
5 “phosphorous compounds” may be used interchangeably.

By the term “phosphorous” as used herein is meant any kind of ionic form, which includes elemental phosphorous, such as for example phosphoric acid ( $H_3PO_4$ ), dihydrogen phosphate ( $H_2PO_4^-$ ), hydrogen phosphate ( $HPO_4^{2-}$ ), phosphate ( $PO_4^{3-}$ ),  
10 phosphorous acid ( $H_3PO_3$ ), dihydrogen phosphonate ( $H_2PO_3^-$ ), hydrogen phosphonate ( $HPO_3^{2-}$ ), phosphonate ( $PO_3^{3-}$ ) and pyrophosphate ( $H_2P_2O_5^{2-}$ ), as well as  $AlPO_4$ ,  $FePO_4$ ,  $Ca_{10}(PO_4)_6(OH)_2$ , and  $Ca_3(PO_4)_2$ . A skilled person would know of any similar ionic forms that phosphorous may be able to form.

15 A suspension is a heterogeneous mixture of solid particles or particular matter dispersed or suspended in a fluid or liquid phase. By the term “particulate matter” as used herein is meant any kind of particulate material that can be suspended and subjected to the novel process of the present invention.

20 In some embodiments the particulate material originates from waste products. Such products often need to be deposit at a secured waste deposit because of the toxic heavy metals. Hence, if the particulate material can be treated before disposal so that the heavy metals are removed prior to depositing, as well as removal of any valuable elements such as phosphorus, then a smaller amount of waste product needs to be  
25 deposited.

Examples of waste products that can be subjected to the electrodialytic process of the present invention include sludge ash, manure ash, soil and soil sludge, municipal solid waste incineration air pollution control residue, harbor sediment, sewage sludge,  
30 sewage sludge ash (SSA), mine tailings, low quality P-ore, freshwater sediment, slag, bottom ash, fly ash, bioash and industrial/agricultural sludge. In a preferred embodiment the particulate material is a material selected from the group consisting of sludge ash, manure ash, soil and soil sludge, municipal solid waste incineration air pollution control residue, harbor sediment, sewage sludge and sewage sludge ash. In a

particular preferred embodiment the particulate material is sewage sludge ash containing heavy metals as well as calcium-, iron- and/or aluminum phosphates.

By the term “heavy metal” as used herein is meant any metal or metalloid that is toxic and thereby dangerous to the health of human beings and animals as well as to the environment. Hence, the term refers to metals that need to be removed from materials before said materials are safe to use as for example agricultural products or the like. Typical examples of heavy metals include As, Ba, Se, Sb, Mo, Cd, Cr, Cu, Ni, Pb, Zn, Sn, Ta, Nb, Zr and any of the lanthanides, as well as Hg.

By the term “alkaline soluble phosphorus compounds” is meant phosphorus compounds with a high solubilisation at alkaline pH, i.e. at a pH value above 10. Examples of alkaline soluble phosphorus compounds include Al phosphates and Fe(III) phosphates as seen in Figure 3.

By the term “acidic soluble phosphorus compounds” is meant phosphorus compounds with a high solubilisation at acidic pH, i.e. at pH value below 4. Examples of acidic soluble phosphorus compounds include Ca phosphates (e.g.  $\text{Ca}_3(\text{PO}_4)_2$ ) as seen in Figures 3-4, and Mg phosphates.

The particulate material to be treated may comprise phosphorus bound in various forms depending on the origin and treatment.

Sewage sludge ash from low-T gasification as used in Examples 1-4 typically comprise phosphorus bound to Ca, Al, and Fe. The phosphorus bound to Fe and Al is mainly formed after chemically treatment of the sludge, where Fe and Al salts are typically used for treatment and for capturing phosphorus in the sludge.

The sludge may be turned into ash by gasification, such as low-T gasification, or by incineration.

The phosphorus compounds typically remains upon gasification, i.e. the Al-P and Fe(III)-P compounds are still present. However, incineration may affect the phosphorus compounds, such that the phosphorus bound to Al and Fe(III) is decomposed and instead forms Ca-P compounds.

Thus, in these cases the particulate material to be electrodialytically treated may comprise phosphorus bound to Ca, Al, and Fe, or mainly phosphorus bound as Ca-P. Sewage sludge may also be chemically treated with other chemicals than Al salts and/or Fe-salts, such as  $\text{AlCl}_3$ , and  $\text{FeCl}_3$ . An examples of another chemical is  $\text{Ca}(\text{OH})_2$ . Thus, the particulate material to be electrodialytically treated may comprise phosphorus bound to Al, and/or Fe, and/or Ca.

Examples 1-4 describes electrodialytic treatment of a particulate materials comprising P bound to Ca, Al, and Fe.

Example 5 describes electrodialytic treatment of a particulate materials comprising P bound to mainly Ca.

Example 6 describes electrodialytic treatment of a particulate materials comprising P bound to mainly Ca and Al.

Example 7 describes electrodialytic treatment of a particulate materials comprising P bound to mainly Ca and Fe(III).

Example 8 describes electrodialytic treatment of a particulate materials comprising P bound to mainly Al.

Example 9 describes electrodialytic treatment of a particulate materials comprising P bound to mainly Fe(III).

Even though the starting particulate material comprises mainly phosphorus bound to Ca, phosphorus bound to other components may be formed before or during the electrodialytic treatment. For example part of the Ca-P compounds that are dissolved during electrodialytic treatment at low pH, may reprecipitate as new Al-P or Fe-P compounds.

Similarly, for a starting material comprising no Ca-P compounds, Ca-P compounds may be formed before or during the electrodialytic treatment if Ca is present isolated or as other compounds. Ca may be present since it is used as a sludge stabilizer.

The P-compounds formed before or during the electrodialytic treatment may be due to Al, Fe, and/or Ca being present either isolated or as other compounds used during previous steps of the sludge or wastewater treatment. For example, Al salts may be used in the flocculation step at the wastewater treatment plant, or may be present due to the zeolites present in the wastewater. Similarly, Fe(III) may be present since Fe (III)

salts may be used in the flocculation step at the wastewater treatment plant. Also, Ca may be present due to the use of lime as stabilizer at the wastewater treatment plant.

Thus, to ensure maximum potential P recovery, it is advantageous that phosphorus  
5 bound to Al, and/or Fe, and/or Ca, formed at various steps of the material treatment.  
can be recovered.

#### Sequential electrodialytic extraction

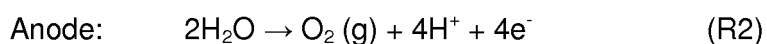
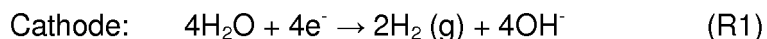
10 In an aspect of the current invention, the extraction of phosphorus from a particulate  
material process is performed sequentially by combining two separated electrodialytic  
two compartment cells via filtration means. By using the sequential approach, a high  
degree of the bound phosphorus are extracted, and optionally heavy metals are  
extracted too.

15 The sequential method for electrodialytic phosphorus recovery, comprises the steps of:  
(a) providing a first electrodialytic cell (1), comprising a first anolyte compartment (4)  
and a first catholyte compartment (5), separated by a cation exchange membrane (8);  
(b) providing a particulate material comprising phosphorus or phosphorous  
compounds;  
20 (c) mixing the particulate material with a liquid and use it as an anolyte for the first cell  
(4.1);  
(d) providing an electrolyte solution and use it as a catholyte (5.1) for the first cell;  
(e) applying a first current to the first cell (1);  
whereby metal ions are concentrated in the catholyte (5.1);  
25 (f) providing a second electrodialytic cell, comprising a second anolyte compartment (6)  
and a second catholyte compartment (7), separated by an anion exchange membrane  
(9);  
(g) transferring the treated anolyte (4.1) from the first cell (1) by filtration means such  
that the treated anolyte is filtered into a residual and a filtrate (3.1);  
30 (h) transferring the liquid filtrate (3.1) into the second anolyte compartment (6) thereby  
forming a second anolyte (6.1);  
(i) mixing the residual with water, and transferring the mixture into the second cathode  
compartment (7) thereby forming a second catholyte (7.1);  
(j) applying a second current to the second cell (2);

whereby phosphorus and phosphorous compounds are concentrated in the second anolyte (6.1).

An illustration of an embodiment of the invention is shown in Figure 1. Figure 1 shows a first electro dialytic cell (1), a second electro dialytic cell (2), and filtration means (3). Each cell is a two compartment electrochemical cell, where the charged electrodes, indicated by plus (anode) and minus (cathode) signs, are placed in respectively the anolyte compartments (4, 6) and the catholyte compartments (5, 7). The two compartments in the first cell (1) are separated by a cation exchange membrane (8), and the two compartments in the second cell are separated by an anion exchange membrane (9). Electrolyte solutions and/or suspensions are circulated in the compartments, and the electrolyte/suspension in the anolyte compartments is designated anolyte (4.1, 6.1), and the electrolyte/suspension in the catholyte compartments is designated catholyte (5.1, 7.1).

During the extraction process, an electric field in the form of a direct current is applied to the electrodes of the first cell, and then subsequently to the second cell. In each cell, the current will result in the following electrolytic half-reactions at the electrodes (reaction R1 and R2):



From the half-reactions it follows that the pH near a cathode will increase (due to the produced hydroxide ions), and the pH near an anode will decrease (due to the produced protons), when a current is supplied.

In Figure 1, a suspension of particulate material is provided as anolyte (4.1), and a solution is provided as catholyte (5.1), in the respective compartments of the first cell (1). During electrolysis, the pH in the anolyte will decrease due to the reaction (R2). As the pH decreases, metals bound in the particulate material dissolve and will be released as cations. Due to the charge of the electrodes, the released cations will migrate to the catholyte (5.1). The released cations typically include calcium ions, and/or heavy metals (HM), and/or other cations.

In an embodiment of the invention, the heavy metals include Ba, Se, Sb, Mo, Cd, Cr, Cu, Ni, Pb, Zn, Sn, and Hg. In a further embodiment the heavy metals include Cd, Cr, Cu, Pb, Ni and Zn. In a further embodiment of the present invention the heavy metals include metals that upon dissolution form positively charged ions that are capable of migrating into the cathode compartment during the remediation process. Some heavy metals may form positively charged ions and/or negatively charged ions upon dissolution. For example, As, Sb, Cr, and Mo may form negatively charged ions upon dissolution, e.g.  $\text{AsO}_4^{3-}$ .

10 The type of released cations will depend on the pH, and the complexing affinity of the cations. Figures 3 and 4 show the solubility of Al-, Fe-, and Ca-phosphates as a function of pH. Figure 5 show the solubility of metal hydroxides, such as Al- and Fe-hydroxides.

15 From Figure 3 it is seen that under acidic conditions, Ca-phosphates are the most easily dissolved, and they will dissolve and be released as Ca cations and phosphate ions.

20 The Al- and Fe-phosphates are seen to be less easy to dissolve. However, under alkaline conditions, only Al- and Fe-phosphates are soluble, whereas most Ca-phosphates are insoluble. The solubility as a function of pH of other calcium orthophosphoric compounds are also seen in Figure 4.

25 From Figure 5 it follows that the dissolution of the Al- and Fe-phosphates under alkaline environment results in negative ions of phosphorous (e.g.  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ), and the dissolved Al- and Fe-components may form insoluble hydroxides,

30 Under acidic conditions, the cations from calcium phosphates will be released and occur mainly as simple cations ( $\text{Ca}^{2+}$ ). In contrast, the released Al and Fe ions are known to form positively charged Al-P and Fe-P complexes. Examples of such complexes can be  $\text{Al}(\text{HPO}_4)^+$ ,  $\text{Fe}(\text{H}_2\text{PO}_4)^+$ ,  $\text{Fe}(\text{H}_2\text{PO}_4)^{2+}$  and  $\text{Fe}(\text{HPO}_4)^+$ .

Thus, as the electrolysis proceeds, first Ca ions and optionally heavy metals (HM) will be released and migrate into the first catholyte (5). Subsequently, Al-P and Fe-P



complexes are formed, and due to their charge, they will also migrate into the first catholyte (5.1).

From the successive migration it follows that the migration of the phosphorus complexes (Al-P and Fe-P) during the electrolysis process may be controlled and avoided by the electrolysis parameters such as the pH, current load and time. In an embodiment of the invention, the electrolysis process of the first cell (1) is controlled such that only calcium ions, and optionally heavy metals, will be released and migrate into the first catholyte (5.1). The embodiment is illustrated in Figure 1.

In an embodiment of the invention, the metal ions concentrated in step (e) comprises calcium ions and/or heavy metal ions.

Subsequent to the electrolysis in the first electrodialytic cell (1), the treated particulate material, i.e. the anolyte (4.1), is transferred to filtering means (3) as illustrated in Figure 1. From the filtering means, the solid residual and the liquid filtrate is further transferred to the second electrodialytic cell (2). The residual is transferred to the catholyte compartment (7) of the second cell to be comprised in the second catholyte (7.1), and the filtrate is transferred to the anolyte compartment (6) of the second cell to be comprised in the second anolyte (6.1). The residual will comprise the particulate material including the phosphorus bound as Al- and Fe-phosphates, and the filtrate will comprise the released phosphate ions originally bound to Ca.

When electrolysis in the second electrodialytic cell (2) is carried out, negatively charged species will migrate into the second anolyte (6.1). Furthermore, according to the electrode reaction (R1), the pH in the catholyte compartment will increase during the electrolysis. The increase will result in the dissolution of the Al- and Fe- phosphates, as seen from Figure 3, and thus the release of the negatively charged phosphorous species, which will migrate to the anolyte (6.1). The increased pH could also cause any present calcium to precipitate as Ca-phosphates, as seen from Figures 3 and 4. However, if calcium has been removed in the first electrodialytic cell, Ca-P-precipitates are avoided.

The sequential process results in a high degree of phosphorus being mobilised from a particulate material, as well as the mobilised phosphorus being made available for

extraction and recovery. In addition any heavy metals may be removed. In an embodiment of the invention, the method is used for combined electrodialytic phosphorus recovery and heavy metal removal.

5 In the first electrodialytic cell, the pH conditions are configured such that phosphorus bound to calcium is mobilised and extracted to a liquid phase. In the second electrodialytic cell, the pH conditions are configured such that phosphorus bound to aluminium and iron is mobilised and extracted to the same liquid phase as the phosphorus originally bound to calcium, by the use of filtration means.

10

The high phosphorus recovery of the invention is obtained by both a high degree of mobilisation of phosphorus compounds, as well as mobilisation into a form that can be extracted. Thus, phosphorus bound to Ca as well as phosphorus bound to Fe and Al can be mobilised and extracted to the same liquid based product.

15

Control of the electrodialytic treatment parameters is essential to obtain a high phosphorus recovery. Furthermore, the treatment parameters will depend on the amount of ash to be treated.

20

In an embodiment of the invention, the first and second currents, of respectively the first and second electrodialytic cell, are below 3 mA/g ash, more preferably below 2 mA/g ash, and most preferably below 1.5 mA/g ash. In a further embodiment, the first and second currents are supplied for between 1.25 to 4.5 h/g ash, more preferably between 1.25 to 2.25 h/g ash.

25

In another embodiment of the invention, the first and second currents are supplied for a time relative to the amount of particulate material, and wherein the time is between 1.25 to 4.5 h/g particulate material, more preferably between 1.25 to 2.25 h/g particulate material.

30

An embodiment of the apparatus illustrated in Figures 1-2 for the sequential electrodialytic extraction of phosphorus from a particulate material in suspension, comprises: a first electrodialytic cell (1) comprising a first anolyte compartment (4) comprising a first anolyte (4.1), and a first catholyte compartment (5) comprising a first catholyte (5.1), wherein the compartments of the first cell (4, 5) are separated by a

35

cation exchange membrane (8), and wherein the first anolyte (4.1) is the particulate material in suspension; a second electro dialytic cell (2) comprising a second anolyte compartment (6) comprising a second anolyte (6.1), and a second catholyte compartment (7) comprising a second catholyte (7.1), wherein the compartments of the second cell (6, 7) are separated by an anion exchange membrane (9); and  
5 filtration means (3) in fluid communication with the compartments (4, 6, 7) and configured to filter the first anolyte (4.1), and transfer the residual into the second catholyte compartment (7) to be comprised in the second catholyte (7.1), and transfer the filtrate (3.1) into the second anolyte compartment (6) to be comprised in the second  
10 anolyte (6.1).

Larger quantities of phosphorus may be extracted from large quantities of particulate material by repeating the described sequential process any number of times to treat further particulate material. In an embodiment of the invention, the sequential process  
15 is repeated one or more times times, to treat further particulate material.

For any of the repetitions, one or more of the electrolytes, or parts thereof, may be recycled. By re-using or recycling the anolytes and/or catholytes, or parts thereof, the operational cost can be reduced, as the required amounts of liquid are reduced, as well  
20 as the amount of current to decrease or increase the pH to a certain degree, will be reduced.

For recycling of the fluids, the apparatus comprises circulation means as indicated in Figure 2. Any type of circulations means known to the skilled person may be applied,  
25 such as pumps.

In an embodiment of the invention, the apparatus further comprises circulation means for transferring a fluid comprised in one unit (3-7,10) to the same or another unit (3-7,10), such that the apparatus is configured for recycling fluids, and wherein the  
30 circulation means optionally are pumps.

In an embodiment of the invention, the apparatus further comprises circulation means for recycling fluids, such as the first catholyte (5.1), second anolyte (6.1), and filtrates (3.1, 10.1). In a further embodiment of the invention, the circulation means are pumps.  
35

In an embodiment of the invention, the sequential process is repeated one or more times, and wherein the first catholyte (5.1) is recycled, and/or the first filtrate (3.1) is recycled, and/or the filtrate of the second catholyte (10.1) is recycled, and/or the second anolyte (6.1) is recycled.

5

In a further embodiment of the invention, the sequential process is repeated one or more times, and wherein the first catholyte (5.1) is recycled to be comprised in the first catholyte (5.1), and/or the first filtrate (3.1) is recycled to be comprised in the first anolyte (4.1), and/or the second anolyte (6.1) is recycled to be comprised in the first anolyte (4.1), and/or the second filtrate (10.1) is recycled to be comprised in the second catholyte (7.1).

10

In a further embodiment of the invention, the sequential process is repeated on a further batch of particulate material (i.e. not treated previously), and/or on the particulate material of step (j) to subject the treated material to a second cycle, thereby extracting any phosphorus that have not been recovered from the first cycle.

15

In an embodiment of the invention, the particulate material provided in step (b) is a further batch of particulate material, and step (c)-(j) is repeated thereby defining a second cycle, and optionally wherein the liquid provided in repeated step (c) is recycled first filtrate (3.1), and/or the filtrate of the second catholyte (10.1), and/or the second anolyte (6.1) from the first cycle, and optionally wherein the electrolyte solution of repeated step (d) is the first catholyte from the first cycle.

20

In a further embodiment of the invention, the particulate material provided in step (b) is the particulate material of step (j) or a further batch of particulate material, and step (c)-(j) is repeated thereby defining a second cycle,, and optionally wherein the liquid provided in repeated step (c) is recycled first filtrate (3.1), and/or the filtrate of the second catholyte (10.1), and/or the second anolyte (6.1) from the first cycle, and optionally wherein the electrolyte solution of repeated step (d) is the first catholyte from the first cycle.

25

30

#### First electrodialytic cell

The anolyte (4.1) of the first electrodialytic cell (the first anolyte) may comprise a particulate material comprising heavy metals and phosphorus or phosphorous

35

compounds, from which the phosphorus is extracted to be recovered, and optionally also the heavy metals are extracted and removed.

5 Particulate material from waste products are known to comprise significant amounts of heavy metals and phosphorus. In an embodiment of the invention, the particulate material of the first anolyte (4.1) is selected from the group consisting of ash, ash from the thermal treatment of biomass, manure ash, sewage sludge ash, incinerated sewage sludge ash, gasified sewage sludge ash, chemically precipitated sewage sludge, biologically precipitated sewage sludge, or a combination thereof.

10

In another embodiment of the invention, the particulate material of the first anolyte (4.1) comprises phosphorous compounds, wherein the phosphorus is chemically bonded to calcium (Ca), and/or aluminum (Al), and/or iron (Fe).

15

In another embodiment of the invention, the particulate material of the first anolyte (4.1) comprises above 0.5 wt% P bonded to Ca, and/or Al, and/or Fe, more preferably above 1 wt% or 1.5 wt%, and most preferably above 2 wt% or 2.5 wt%.

20

For faster and more homogeneous extraction of the phosphorus and/or heavy metals, the particulate material is suspended in a liquid. In an embodiment of the invention, the particulate material of the first anolyte (4.1) is suspended in a liquid selected from the group consisting of distilled water, tap water, recycled second anolyte (6.1) and recycled filtrate (3.1), diluted acid, such as  $H_3PO_4$ , and any combination thereof.

25

The diluted acid may be phosphoric acid ( $H_3PO_4$ ), or any other acid.

30

The recycling of the second anolyte (6.1) or the first filtrate (3.1) in a repeated process are illustrated in Figure 2. By re-using or recycling the second anolyte (6.1) or first filtrate (3.1) as the liquid comprised in the first anolyte (4.1), the operational cost of the apparatus can be limited. The required amounts of liquid and current, to provide acidic conditions, will be reduced when the second anolyte is recycled.

35

The extraction process may also depend on the solid load of particulate material in the suspension. The solid load may be indicated by the liquid/solid ratio (L/S) of the suspended particulate material.

In an embodiment of the invention, the liquid/solid ratio (L/S) of the suspended particulate material in the first anolyte (4.1) is above 30, more preferably equal to or above 20, and most preferably equal to or above 10, or equal to or above 2.

5

A key parameter determining the type and amounts of released cations and anions from the particulate material is the pH. In an embodiment of the invention, the pH of the first anolyte (4.1) is controlled by a first eletrodialytic current, and wherein the pH decreases during the first electrodialytic treatment. In a further embodiment of the invention, the pH of the first anolyte (4.1) is below 4, more preferably below 2.5, and most preferably below 2. In a further embodiment of the invention, the pH is further controlled by the type of liquid added to the first anolyte (4.1), such as diluted acid. In a further embodiment, the apparatus is configured such that the pH of the first anolyte (4.1) is controlled by a first electrodialytic current, and configured such that the pH decreases during the first electrodialytic treatment, and/or wherein the pH of the first anolyte (4.1) is below 4, more preferably below 2.5, and most preferably below 2.

10

15

The catholyte (5.1) of the first electrodialytic cell (the first catholyte) may be any electrolyte facilitating the electrodialytic process of the first cell.

20

In an embodiment of the invention, the first catholyte (5.1) is an electrolyte solution. In a further embodiment of the invention, the first catholyte (5.1) is selected from the group consisting of solutions of sodium nitrate ( $\text{NaNO}_3$ ), solutions of sodium chloried, solutions of nitric acid, solutions of hydrochloric acid, distilled water, tap water, and recycled first catholyte (5.1).

25

The recycling of the first catholyte (5.1) as first catholyte (5.1) in a repeated process is illustrated in Figure 2. By re-using or recycling, the operational cost of the apparatus can be limited.

30

The first electrodialytic cell (1) comprise a cation exchange membrane (8) as shown in Figures 1-2. The cation exchange membrane is a semipermeable membrane, which allows the passage of the positive charges (cations), while preventing the passage of negative charges (anions). The released cations (calcium and optionally heavy metals)

will migrate through the cation exchange membrane (8) and into the catholyte (5.1) in the cathode compartment (5), due to the polarity of the electrodes.

#### Stirring means

5 To avoid sedimentation of the suspended particulate material, and for efficient operation of the electrodialytic processes in the electrodialytic cells, it is advantageous that the catholytes and/or anolytes in the compartments are stirred. In an embodiment of the invention, one or more of the compartments (4, 5, 6, 7) further comprises stirring means. In a further embodiment, the first anolyte compartment (4) and/or the second  
10 catholyte compartment (7) comprises stirring means.

Stirring means suitable for electrodialytic cells are known to the skilled person. In an embodiment of the invention, the stirring means are selected from the group consisting of overhead stirrer, magnetic stirrer, and stirring by gas bubbling, such as air or CO<sub>2</sub>  
15 bubbling.

#### Heating means

To control or accelerate the extration process further, it may be advantageous that the electrolytes (i.e. anolytes and catholytes) are heated. In an embodiment of the  
20 invention, one or more of the compartments (4, 5, 6, 7) further comprises heating means. In a further embodiment of the invention, the temperature of one or more of the anolytes and/or catholytes (4.1, 5.1, 6.1, 7.1) is above room temperature. In a further embodiment of the invention, the temperature of the one or more electrolyte(s) is above 30 °C, more preferably above 40 °C or 50 °C.

25 The apparatus of the invention may be used in a wastewater treatment plant, where waste heat in the form of heat streams are known to be present. In an embodiment of the invention, the heating means are driven by the waste heat streams from a wastewater treatment plant. The conversion of waste heat for use as heating means for  
30 electrolytes in an electrodialytic cell are known to a person skilled in the art.

#### Filtration means (3,10)

Filtration is a mechanical operation for the separation of solids from fluids. The operation may be carried out using a filter or a membrane, which allows the fluid to  
35 pass through or flow through, and prevents the solids from passing through. The liquid

that passes through is called the filtrate, and the resident particles are called the residual.

5 Filtration means may be a filter with a defined mesh size, where the mesh size describes the size of the openings. Filtration through multiple filters may be carried out, and the filtration may further be assisted by use of vacuum, i.e. vacuum filters. Figure 2 illustrates an embodiment of the invention, where the filtration means (3) comprises two filtration means, a filter and a vacuum filter.

10 In an embodiment of the invention, the filtration means is selected from the group of filter paper, vacuum filters, and a combination thereof.  
In a further embodiment of the invention, the filter mesh size is equal to or below 50  $\mu\text{m}$ , more preferably equal to or below 45  $\mu\text{m}$ , and most preferably equal to or below 40  $\mu\text{m}$ , and optionally combined with a vacuum filter. In a further embodiment of the  
15 invention, the vacuum filter has a filter mesh size equal to or below 10  $\mu\text{m}$ , more preferably equal to or below 1  $\mu\text{m}$ , and most preferably equal to or below 0.45  $\mu\text{m}$ .

#### Second electro dialytic cell

20 The anolyte (6.1) of the second electro dialytic cell (the second anolyte) is the filtrate (3.1) from the first filtration means (3), and corresponds to the produced liquid of the first anolyte, as illustrated in Figures 1-2. The second anolyte may be further recycled as a liquid for the first anolyte (4.1) as illustrated in Figure 2.

25 The catholyte (7.1) of the second electro dialytic cell (the second catholyte) comprises the residual from the filtration means, which corresponds to the particulate material of the first anolyte, as illustrated in Figures 1-2. The catholyte (7.1) may further comprise additional liquid such that the residual becomes suspended in the liquid to further facilitate the electro dialytic extraction process. In an embodiment of the invention, the second catholyte (7.1) comprises the residual from the first filtration means and a  
30 further liquid phase. In a further embodiment of the invention, the further liquid phase is selected from the group consisting of water, distilled water, tap water, sodium hydroxide (NaOH), recycled filtrate from the second filtration means (10.1), and any combination thereof.



During the electrodialytic operation in the second electrodialytic cell, the pH of the second catholyte (7.1) increases thereby facilitating the dissolution Al- and Fe-phosphates, and thus release of phosphate ions. The pH is therefore a key parameter for controlling the extration process of phosphorus. It further follows from Figure 5 that the dissolution of the Al- and Fe-phosphates under alkaline environment results in negative ions of phosphorous (e.g.  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ), and the dissolved Al- and Fe-components will form insoluble hydroxides.

In an embodiment of the invention, the pH of the second catholyte (7.1) is controlled by a second electrodialytic current, and wherein the pH increases during the second electrodialytic treatment. In a further embodiment, the apparatus is configured such that the pH of the second catholyte (7.1) is controlled by a second electrodialytic current, and configured such that the pH increases during the second electrodialytic treatment.

The electrodialytic treated second catholyte (7.1) may also be recycled as illustrated in Figure 2. The second catholyte may be transferred to a second filtration means (10), where it is filtered into a second residual and a second filtrate. In an embodiment of the invention, the apparatus further comprises second filtration means (10) in fluid communication with the second catholyte compartment (7) configured to filter the second catholyte (7.1) into a second residual and a second filtrate (10.1). In a further embodiment of the invention, the second filtrate is recycled as the further liquid in the second catholyte (7.1) as illustrated in Figure 2. In a further embodiment, the filtration means is a filter with a mesh size of equal to or below 50  $\mu\text{m}$ , more preferably equal to or below 45  $\mu\text{m}$ , and most preferably equal to or below 40  $\mu\text{m}$ , and optionally combined with a vacuum filter.

The second residual from the second filtration means (10) may be deposited as waste. In cases where the heavy metals and phosphorus are removed, the waste may be deposited without environmental concerns. Furthermore, the clean waste may be recycled as raw material for rockwool, concrete or brick production.

The second electrodialytic cell (2) comprises an anion exchange membrane (9) as shown in Figures 1-2. The anion exchange membrane is a semipermeable membrane, which allows the passage of the negative charges (anions), while preventing the

passage of positive charges (cations). The anions will migrate through the anion exchange membrane and into the anolyte in the anode compartment (6), due to the polarity of the electrodes.

## 5 Examples

### Example 1: High P recovery (70%)

10 Ash resulting of thermally treating sludge from Randers Centralrenseanlæg by means of Pyroneer technology (low-T gasification). The P of the sludge was captured 50% biologically and 50% chemically (using Fe and Al salts). The ash initially contained around 2.7% P, 1.0% Al, 3.1% Ca and 5.5% Fe.

The membrane of the cell was Ionics (GE): ANION,AR204SZRA, and CATION,CR67.

#### 15 *First electrodialytic cell*

35 g of ash was mixed with 350 mL of distilled water in the first ED cell in the anolyte. 500 mL of the electrolyte solution (0.01 M  $\text{NaNO}_3$ , pH=2) was placed in the catholyte, and a 50 mA current was applied until the anolyte reached a pH of 1.7, (52.5 hours). The decrease of pH in the anolyte involved the dissolution of Ca, P and heavy metals.

20

#### *Filtration means*

At the end of this experiment, the anolyte and the bulk SSA (sewage sludge ash) were separated through a filtration at atmospheric pressure with a filter paper of 40  $\mu\text{m}$ . In order to maximize the effective separation of P, 200 mL of distilled water was flushed  
25 through the SSA in the filter, resulting in a filtrate with a total volume of 470 mL. The total P extracted from the ash was around 27.3%, whereas 23.7% of P (0.24 g) was mobilized to the filtrate, and thus recovered. The filter paper with the SSA was dried overnight. After this treatment, the resulting ash weighted 31.4 g and had a content of around 2.3% of P.

30

#### *Second electrodialytic cell*

25.1 g of the ash resulting from the first ED treatment was mixed with 300 mL of distilled water in the catholyte of the second ED cell with 8 mL of NaOH 1 M. The 470 mL of the filtrate liquid from the first ED cell was vacuum filtrated through a filter of 0.45  
35  $\mu\text{m}$  and used as electrolyte solution in the anolyte of this second ED cell. A current was applied at 50 mA for 3 days. The pH of the catholyte at the end of the experiment

was 12.2. Surprisingly around 63.4% of the P content was mobilized to the anolyte allowing an overall P-recovery of around 70%:

$$\text{recovered } P = \overbrace{23.7\%}^{\text{1st ED recovery}} + \left( \overbrace{100\% - 27.3\%}^{\substack{\text{P remaining after the first ED} \\ \text{1st ED extraction}}} \right) \times \left( \overbrace{63.4\%}^{\text{2nd ED recovery}} \right) = 69.8\%$$

5 The total amount of P recovered in this example was 0.6 g. This was obtained with the electrical current applied for a total of 124.5 hours (i.e. 52.2 hours in the first cell, and 3 days in the second cell). This is considerably higher than what was extracted in the single two-compartment ED cell setup (i.e. not a sequential setup) disclosed in [1] for a similar period (cf. Example 4) . The final ash weighted 22.8 g and the P content was  
10 around a 0.8%. The content of the anolyte solution at the end of the experiment was as follows:

P: 1.3 g/L Fe: 0.03 g/L Al: 0.03 g/L As: 0.15 mg/L, Cd<0.02 mg/L,  
Cr<0.02 mg/L, Cu: 0.2 mg/L, Ni:0.02 mg/L, Pb: 0.06 mg/L, Zn: 1 mg/L

This corresponds to a MER value of 0.04.

15

The consumption of chemicals was:

- For the pH regulation in first cell:

$$\begin{aligned} & \frac{13 \text{ mL } HNO_3 5 \text{ M}}{\left( 35 \text{ g ash} \cdot \frac{2.7 \text{ g P} \cdot 23.7\% \text{ recovered P}}{100 \text{ g ash}} + 25.1 \text{ g ash} \cdot \frac{2.3 \text{ g P} \cdot 63.4\% \text{ recovered P}}{100 \text{ g ash}} \right) \cdot \frac{1 \text{ mole P}}{31 \text{ g P}}} \\ &= 3.42 \frac{\text{mole } HNO_3}{\text{mole P}} \end{aligned}$$

20

- For the NaOH used in the second cell:

$$\begin{aligned} & \frac{8 \text{ mL NaOH } 1 \text{ M}}{\left( 35 \text{ g ash} \cdot \frac{2.7 \text{ g P} \cdot 23.7\% \text{ recovered P}}{100 \text{ g ash}} + 25.1 \text{ g ash} \cdot \frac{2.3 \text{ g P} \cdot 63.4\% \text{ recovered P}}{100 \text{ g ash}} \right) \cdot \frac{1 \text{ mole P}}{31 \text{ g P}}} \\ &= 0.42 \frac{\text{mole NaOH}}{\text{mole P}} \end{aligned}$$

Example 2: Electrodialytic treatment time

The experiment from Example 1 was repeated, i.e treating an ash from the same origin as Example 1 and with a similar composition (around 3.5% P, 1.2% Al, 4.1% Ca and 6.6% Fe), but where the electrodialytic (ED) treatment time of the first electrodialytic cell was prolonged. The first ED step was continued until the pH was 1.5 (5 days and 6 hours approximately).

This resulted in extraction of 29.1% of P, and mobilization of around 23.1% of P into the first anolyte. This corresponded to 0.29 g P recovered, which is not significantly higher than the 0.24 g recovered in the first step of Example 1.

Thus, significant longer electrodialytic treatment time did not improve the total phosphorus recovery significantly.

#### Example 3: Solid load

The example is carried out as Example 1, but where the liquid/solid ratio (L/S) of the suspension to be treated is increased from L/S=10, to L/S=20. Thus, in the latter case, 350 mL of distilled water is mixed with 17.5 g of ash.

#### Example 4: P recovery using the non-sequential setup disclosed in [1]

Starting material, i.e. treated ash from the same origin (i.e. sewage sludge ashes from low-T gasification) as for Example 1, was used, having a similar composition (around 3.5% P, 1.2% Al, 4.1% Ca and 6.6% Fe).

The starting material was exposed to P recovery as described in Example 1, but where the recovery was stopped after the first electrolytic cell. Thus, the setup was not sequential as described in Example 1, but corresponds to first electrolytic cell, which is identical to the setup disclosed in [1].

The electrodialytic treatment was continued until the pH was 1.5. The current was applied for 125 hours, which is similar to the total remediation time of Example 1 (124.5 hours).

During the treatment, heavy metals are dissolved into positive ions, which are separated from the sludge by migration into the catholyte. Phosphorous from the particulate material may also be dissolved in the anolyte during the process.

Phosphorus is mainly dissolved into ions with negative charge, which will stay mobilised in the anolyte. However, a minor part (ca. 6.5% as reported in [1]) of the phosphorus may be dissolved and form positive charged complexes, which will migrate into the catholyte.

5

This resulted in extraction of 29.1% of P, and mobilization of around 23.1% of P into the anolyte. This corresponded to 0.29 g P recovered, which is significantly lower than the 70% recovery in Example 1.

10 The lower P recovery for the non-sequential setup is ascribed to the presence of Al- and Fe- phosphates which are not fully dissolved and mobilised in the acidic environment.

15 Thus, for particulate material comprising phosphorus bound to alkaline soluble compounds, a high recovery of phosphorus is not obtained with the non-sequential setup. High P recovery with the non-sequential setup can only be obtained for particulate material with low contents of only alkaline soluble compounds, such as ash from sewage sludge with a low content of Al- and Fe-phosphates.

20 Thus, significant longer electrodialytic treatment time with the setup according to [1] resulted in much lower phosphorus recovery of the treated material.

Moreover, the proportions of Al and Fe to P in the anolyte were considerably higher than in Example 1, and consequently MER was higher (0.129), making it a product not  
25 suitable for the production of common fertilizers like DAP.

Example 5: Electrodialytic treatment of particulate material comprising phosphorus bound to Ca

30 The starting particulate material is incineration sewage sludge ashes where P is precipitated with  $\text{Ca}(\text{OH})_2$ . The ash further contains Al due to the use of Al salts in the flocculation step at the wastewater treatment plant, or the zeolites present in the wastewater. The ash contains 5% Al, 10% Ca and 5% P, and P is mainly bound to Ca in the ash (i.e. the original ash state).

35

Non-sequential electrodialytic treatment according to [1] may result in low P recovery, The Ca-P compounds are dissolved in the non-sequential setup, however the released P is likely to form Al-P compounds, which are less soluble than Ca-P bindings in acidic pH as seen from Figure 3. All dissolved P from the Ca-phosphates may be reprecipitated as Al-phosphates, which are not recovered using the non-sequential electrodialytic treatment. Thus, using the non-sequential method results in lower P recovery.

The sequential electrodialytic treatment according to the present invention may result in a higher P recovery, since the Al-phosphates formed may be dissolved and recovered in the second electrodialytic cell under alkaline conditions.

Example 6: Electrodialytic treatment of particulate material comprising phosphorus bound to Ca and Al

The starting particulate material is incineration sewage sludge ashes where P is precipitated using 50% with  $\text{Ca}(\text{OH})_2$  and 50% with  $\text{AlCl}_3$ . The ash further contains Al due to the use of Al salts in the flocculation step at the wastewater treatment plant, or the zeolites present in the wastewater. The ash contains 5% Al, 5% Ca and 5% P, and P is essentially 50% bound to Ca and 50% to Al in the ash.

Non-sequential electrodialytic treatment according to [1] may result in low P recovery. The Ca-P bindings are dissolved, however, in this treatment new Al-P bindings could be formed from dissolved Al and P, which are less soluble than Ca-P bindings in acidic pH (cf. Figure 3). In the worst case scenario, all dissolved P from Ca-phosphates would be re-precipitated as Al-phosphates, which are not recovered using the non-sequential electrodialytic treatment.

The sequential electrodialytic treatment according to the present invention may result in a higher P recovery, since the Al-phosphates formed may be dissolved and recovered in the second electrodialytic cell under alkaline conditions.

Example 7: Electrodialytic treatment of particulate material comprising phosphorus bound to Ca and Fe(III)

The starting material is gasification sewage sludge ashes where P is precipitated 50% with  $\text{Ca}(\text{OH})_2$  and 50% with  $\text{FeCl}_3$ . The ash further contains Fe(III) due to the use of Fe(III) salts in the flocculation step at the wastewater treatment plant. The ash contains 5% Ca, 10% Fe and 5% P, and the P is essentially 50% bound to Ca and 50% to Fe(III) in the ash.

Non-sequential electrodialytic treatment according to [1] may result in low P recovery. The Ca-P bindings are dissolved, however, in this treatment new Fe(III)-P bindings could be formed from dissolved P and Fe(III), which are less soluble than Ca-P bindings in acidic pH (cf. Fig. 3). In the worst case scenario, all dissolved P from Ca-phosphates would be re-precipitated as Fe(III)-phosphates, which are not recovered using the non-sequential electrodialytic treatment.

The sequential electrodialytic treatment according to the present invention may result in a higher P recovery, since the Fe(III)-phosphates formed may be dissolved and recovered in the second electrodialytic cell under alkaline conditions.

Example 8: Electrodialytic treatment of particulate material comprising phosphorus bound to Al

The starting material is incineration sewage sludge ashes where P is precipitated with  $\text{AlCl}_3$ . The ash further contains Ca due to the use of lime as stabilizer at the wastewater treatment plant. The ash contains 5% Al, 10% Ca and 5% P, and P is essentially bound to Al in the ash.

Non-sequential electrodialytic treatment according to [1] may result in low P recovery. The Al-P bindings may only be dissolved to a limited degree under acidic conditions. Thus, the P is not recovered using the non-sequential electrodialytic treatment.

The sequential electrodialytic treatment according to the present invention may result in a higher P recovery. Any P compounds dissolved, may form Ca-P compounds. The Ca-phosphates formed may be dissolved and recovered in the first electrodialytic cell under acidic conditions, and the Al-P compounds may be dissolved and recovered in the second electrodialytic cell under alkaline conditions.

Example 9: Electrodialytic treatment of particulate material comprising phosphorus bound to Fe(III)

5 The starting material is gasification sewage sludge ashes where P is precipitated with  $\text{FeCl}_3$ . The ash further contains Ca due to the use of lime as stabilizer at the wastewater treatment plant. The ash contains 10% Ca, 10% Fe and 5% P, and P is essentially bound to Fe(III) in the ash.

10 Non-sequential electrodialytic treatment according to [1] may result in low P recovery. The Fe-P bindings may only be dissolved to a limited degree under acidic conditions. Thus, the P is not recovered using the non-sequential electrodialytic treatment.

15 The sequential electrodialytic treatment according to the present invention may result in a higher P recovery. Any P compounds dissolved, may form Ca-P compounds. The Ca-phosphates formed may be dissolved and recovered in the first electrodialytic cell under acidic conditions, and the Fe-P compounds may be dissolved and recovered in the second electrodialytic cell under alkaline conditions.

**Items**

20 The invention can be further described by the items listed below.

Item 1

An apparatus for electrodialytic extraction of phosphorus from a particulate material in suspension, comprising:

- 25       - a first electrodialytic cell (1) comprising
- a first anolyte compartment (4) comprising a first anolyte (4.1), and
  - a first catholyte compartment (5) comprising a first catholyte (5.1), wherein the compartments of the first cell (4, 5) are separated by a cation exchange membrane (8), and wherein the first anolyte (4.1) is the
- 30       particulate material in suspension;
- a second electrodialytic cell (2) comprising
- a second anolyte compartment (6) comprising a second anolyte (6.1), and
  - a second catholyte compartment (7) comprising a second catholyte
- 35       (7.1),



wherein the compartments of the second cell (6, 7) are separated by an anion exchange membrane (9); and  
filtration means (3) in fluid communication with the compartments (4, 6, 7) and configured to filter the first anolyte (4.1), and transfer the residual into the second catholyte compartment (7) to be comprised in the second catholyte (7.1), and transfer the filtrate (3.1) into the second anolyte compartment (6) to be comprised in the second anolyte (6.1).

Item 1a

- 10 An apparatus for electrodialytic extraction of phosphorus from a particulate material comprising acidic and/or alkaline soluble phosphorus compounds, in suspension, comprising:
- 15 a first electrodialytic cell (1) comprising
    - a first anolyte compartment (4) comprising a first anolyte (4.1), and
    - 15 a first catholyte compartment (5) comprising a first catholyte (5.1),
    - wherein the compartments of the first cell (4, 5) are separated by a cation exchange membrane (8),
    - wherein the first anolyte (4.1) is the particulate material in suspension,
    - the first electrodialytic cell configured for exposing the particulate
    - 20 material to acidic conditions;
  - a second electrodialytic cell (2) comprising
    - a second anolyte compartment (6) comprising a second anolyte (6.1),
    - and
    - a second catholyte compartment (7) comprising a second catholyte
    - 25 (7.1),
    - wherein the compartments of the second cell (6, 7) are separated by an anion exchange membrane (9),
    - the second electrodialytic cell configured for exposing the particulate material to alkaline conditions; and
  - 30 filtration means (3) in fluid communication with the first and second electrodialytic cells (1, 2), and configured to filter the first anolyte (4.1) and transfer the residual into the second catholyte compartment (7) to be comprised in the second catholyte (7.1) and transfer the filtrate (3.1) into the second anolyte compartment (6) to be comprised in the second anolyte (6.1).

## Item 2

The apparatus according to item 1 or 1A, further comprising circulation means for recycling fluids, such as the first catholyte (5.1), second anolyte (6.1), and filtrates (3.1, 10.1).

5

## Item 2A

The apparatus according to items 1 or 1A, further comprising circulation means for transferring a fluid comprised in one unit (3-7,10) to the same or another unit (3-7,10), such that the apparatus is configured for recycling fluids, and wherein the circulation means optionally are pumps.

10

## Item 3

The apparatus according to item 2, wherein the circulation means are pumps.

15

## Item 4

The apparatus according to any of the preceding items, wherein the particulate material of the first anolyte (4.1) is selected from the group consisting of ash, ash from the thermal treatment of biomass, manure ash, sewage sludge ash, incinerated sewage sludge ash, gasified sewage sludge ash, chemically precipitated sewage sludge, biologically precipitated sewage sludge, or a combination thereof.

20

## Item 5

The apparatus according to any of the preceding items, wherein the particulate material of the first anolyte (4.1) comprises phosphorous compounds, wherein the phosphorus is chemically bonded to calcium (Ca), and/or aluminium (Al), and/or iron (Fe).

25

## Item 6

The apparatus according to any of the preceding items, wherein the particulate material of the first anolyte (4.1) comprises above 0.5 wt% P bonded to Ca, and/or Al, and/or Fe, more preferably above 1 wt% or 1.5 wt%, and most preferably above 2 wt% or 2.5 wt%.

30

## Item 7

The apparatus according to any of the preceding items, wherein the particulate material of the first anolyte (4.1) is suspended in a liquid selected from the group consisting of

35

distilled water, tap water, recycled second anolyte (6.1) and recycled filtrate (3.1), diluted acid, and any combination thereof.

Item 8

- 5 The apparatus according to any of the preceding items, wherein the liquid/solid ratio (L/S) of the suspended particulate material in the first anolyte (4.1) is above 30, more preferably equal to or above 20, and most preferably equal to or above 10, or equal to or above 2.

10 Item 9

The apparatus according to any of the preceding items, wherein the pH of the first anolyte (4.1) is controlled by a first electrodialytic current, and wherein the pH decreases during the first electrodialytic treatment.

15 Item 9A

The apparatus according to any of the preceding items, configured such that the pH of the first anolyte (4.1) is controlled by a first electrodialytic current, and configured such that the pH decreases during the first electrodialytic treatment, and/or wherein the pH of the first anolyte (4.1) is below 4, more preferably below 2.5, and most preferably below 2.

20

Item 10

The apparatus according to any of the preceding items, wherein the pH of the first anolyte (4.1) is below 4, more preferably below 2.5, and most preferably below 2.

25

Item 11

The apparatus according to any of the preceding items, wherein the first catholyte (5.1) is an electrolyte solution.

30 Item 12

The apparatus according to any of the preceding items, wherein the first catholyte (5.1) is selected from the group consisting of solutions of sodium nitrate, solutions of nitric acid, distilled water, tap water, and recycled first catholyte (5.1).

35 Item 12A

The apparatus according to any of the preceding items, wherein the first catholyte (5.1) is an electrolyte solution, preferably selected from the group consisting of solutions of sodium nitrate, solutions of sodium chloride, solutions of nitric acid, solutions of hydrochloric acid, distilled water, tap water, and recycled first catholyte (5.1).

5

Item 13

The apparatus according to any of the preceding items, wherein one or more of the compartments (4, 5, 6, 7) further comprises stirring means.

10

Item 14

The apparatus according to item 13, wherein the stirring means are selected from the group consisting of overhead stirrer, magnetic stirrer and stirring by gas bubbling.

Item 15

15

The apparatus according to any of the preceding items, wherein one or more of the compartments (4, 5, 6, 7) further comprises heating means.

Item 16

20

The apparatus according item 15, wherein the temperature of one or more of the anolytes and/or catholytes (4.1, 5.1, 6.1, 7.1) is above room temperature.

Item 17

The apparatus according to any of items 15-16, wherein the temperature is above 30 °C, more preferably above 40 °C or 50 °C.

25

Item 18

The apparatus according to any of the preceding items, wherein the filtration means is selected from the group of filter paper, vacuum filters, and any combination thereof.

30

Item 19

The apparatus according to item 18, wherein the filter mesh size is equal to or below 50  $\mu\text{m}$ , more preferably equal to or below 45  $\mu\text{m}$ , and most preferably equal to or below 40  $\mu\text{m}$ , and optionally combined with a vacuum filter.

35

Item 20

The apparatus according to any of items 18-19, wherein the vacuum filter has a filter mesh size equal to or below 10  $\mu\text{m}$ , more preferably equal to or below 1  $\mu\text{m}$ , and most preferably equal to or below 0.45  $\mu\text{m}$ .

5      Item 21

The apparatus according to any of the preceding items, wherein the second catholyte (7.1) comprises the residual from the filtration means and a further liquid phase.

Item 22

- 10      The apparatus according to item 21, wherein the further liquid phase is selected from the group consisting of water, distilled water, tap water, sodium hydroxide (NaOH), recycled filtrate from the second filtration means (10.1), and any combination thereof.

Item 23

- 15      The apparatus according to any of the preceding items, wherein the pH of the second catholyte (7.1) is controlled by a second electrodynamic current, and wherein the pH increases during the second electrodynamic treatment.

Item 23A

- 20      The apparatus according to any of the preceding items, configured such that the pH of the second catholyte (7.1) is controlled by a second electrodynamic current, and configured such that the pH increases during the second electrodynamic treatment.

Item 24

- 25      The apparatus according to any of the preceding items, further comprising second filtration means (10) in fluid communication with the second catholyte compartment (7) configured to filter the second catholyte (7.1) into a second residual and a second filtrate (10.1).

30      Item 25

The apparatus according to item 24, wherein the second filtrate is recycled as the further liquid in the second catholyte (7.1) according to items 21-22.

Item 26

A method for electrodialytic phosphorus recovery, comprising:

- (a) providing a first electrodialytic cell (1), comprising a first anolyte compartment (4) and a first catholyte compartment (5), separated by a cation exchange membrane (8);
- (b) providing a particulate material comprising phosphorus;
- 5 (c) mixing the particulate material with a liquid and use it as an anolyte for the first cell (4.1);
- (d) providing an electrolyte solution and use it as a catholyte (5.1) for the first cell;
- (e) applying a first current to the first cell (1);
- whereby metal ions are concentrated in the catholyte (5.1);
- 10 (f) providing a second electrodialytic cell, comprising a second anolyte compartment (6) and a second catholyte compartment (7), separated by an anion exchange membrane (9);
- (g) transferring the treated anolyte (4.1) from the first cell (1) by filtration means such that the treated anolyte is filtered into a residual and a filtrate (3.1);
- 15 (h) transferring the liquid filtrate (3.1) into the second anolyte compartment (6) thereby forming a second anolyte (6.1);
- (i) mixing the residual with water, and transferring the mixture into the second cathode compartment (7) thereby forming a second catholyte (7.1);
- (j) applying a second current to the second cell (2);
- 20 whereby phosphorus and phosphorous compounds are concentrated in the second anolyte (6.1).

#### Item 26A

A method for electrodialytic phosphorus recovery, comprising:

- 25 (a) providing a first electrodialytic cell (1), comprising a first anolyte compartment (4) and a first catholyte compartment (5), separated by a cation exchange membrane (8);
- (b) providing a particulate material comprising acidic and/or alkaline soluble phosphorus compounds;
- (c) mixing the particulate material with a liquid and use it as an anolyte for the first cell
- 30 (4.1);
- (d) providing an electrolyte solution and use it as a catholyte (5.1) for the first cell;
- (e) applying a first current to the first cell (1) thereby exposing the particulate material to acidic conditions,
- whereby metal ions are concentrated in the catholyte (5.1);
- 35 (f) providing a second electrodialytic cell, comprising a second anolyte compartment (6)

and a second catholyte compartment (7), separated by an anion exchange membrane (9);

(g) transferring the treated anolyte (4.1) from the first cell (1) to filtration means such that the treated anolyte is filtered into a residual and a filtrate ;

5 (h) transferring the liquid filtrate into the second anolyte compartment (6) thereby forming a second anolyte (6.1);

(i) mixing the residual with water, and transferring the mixture into the second cathode compartment (7) thereby forming a second catholyte (7.1);

10 (j) applying a second current to the second cell (2) thereby exposing the particulate material to alkaline conditions,  
whereby phosphorus and phosphorous compounds are concentrated in the second anolyte (6.1).

#### Item 27

15 The method according to items 26 or 26, wherein the metal ions concentrated in in step (e) comprises calcium ions and/or heavy metal ions.

#### Item 28

20 The method according to any of items 26-27, wherein the first and second currents relative to the amount of particulate material are below 3 mA/g particulate material, more preferably below 2 mA/g particulate material, and most preferably below 1.5 mA/g particulate material.

#### Item 29

25 The method according to any of items 26-28, wherein the first and second currents are supplied for a time relative to the amount of particulate material, and wherein the time is between 1.25 to 4.5 h/g particulate material, more preferably between 1.25 to 2.25 h/g particulate material.

#### Item 30

30 The method according to any of items 26-29, wherein step (a)-(j) is repeated one or more times, and wherein the first catholyte (5.1) is recycled, and/or the first filtrate (3.1) is recycled, and/or the filtrate of the second catholyte (10.1) is recycled, and/or the second anolyte (6.1) is recycled.

## Item 30A

The method according to any of items 26-29, wherein the particulate material provided in step (b) is a further batch of particulate material, and step (c)-(j) is repeated thereby defining a second cycle,, and optionally wherein the liquid provided in repeated step (c) is recycled first filtrate (3.1), and/or the filtrate of the second catholyte (10.1), and/or the second anolyte (6.1) from the first cycle, and optionally wherein the electrolyte solution of repeated step (d) is the first catholyte from the first cycle.

## Item 31

Use of the apparatus according to any of items 1-25 for wastewater treatment, and/or treatment of particulate material rich in phosphorus.

## Item 32

Use of the methods according to any of items 26-30 for wastewater treatment, and/or treatment of particulate material rich in phosphorus.

**References**

- [1] WO 2015/032903.
- [2] B. Ebberts et al., Abstract no. O131, 13<sup>th</sup> Symp. EREM, 7<sup>th</sup>-10<sup>th</sup> September 2014, Malaga, Spain.
- [3] W. Stumm and J. J. Morgan, Aquatic chemistry : Chemical equilibria and rates in natural waters: Wiley, 1996.
- [4] K. Kuroda and M. Okido, "Hydroxyapatite Coating of Titanium Implants Using Hydroprocessing and Evaluation of Their Osteoconductivity", Bioinorganic Chemistry and Applications v.2012 (2012).
- [5] C. Noubactep, "Relevant reducing agents in remediation Fe<sup>0</sup>/H<sub>2</sub>O systems", Clean-Soil Air Water 41(5) (2013) p. 493-502.



## Claims

1. An apparatus for electrodialytic extraction of phosphorus from a particulate material comprising acidic and/or alkaline soluble phosphorus compounds, in suspension, comprising:
- a first electrodialytic cell (1) comprising
    - a first anolyte compartment (4) comprising a first anolyte (4.1), and
    - a first catholyte compartment (5) comprising a first catholyte (5.1), wherein the compartments of the first cell (4, 5) are separated by a cation exchange membrane (8), wherein the first anolyte (4.1) is the particulate material in suspension, the first electrodialytic cell configured for exposing the particulate material to acidic conditions;
  - a second electrodialytic cell (2) comprising
    - a second anolyte compartment (6) comprising a second anolyte (6.1), and
    - a second catholyte compartment (7) comprising a second catholyte (7.1), wherein the compartments of the second cell (6, 7) are separated by an anion exchange membrane (9), the second electrodialytic cell configured for exposing the particulate material to alkaline conditions; and
  - filtration means (3) in fluid communication with the first and second electrodialytic cells (1, 2), and configured to filter the first anolyte (4.1) and transfer the residual into the second catholyte compartment (7) to be comprised in the second catholyte (7.1) and transfer the filtrate (3.1) into the second anolyte compartment (6) to be comprised in the second anolyte (6.1).
2. The apparatus according to claim 1, further comprising circulation means for transferring a fluid comprised in one unit (3-7,10) to the same or another unit (3-7,10), such that the apparatus is configured for recycling fluids.
3. The apparatus according to any of the preceding claims, wherein the particulate material of the first anolyte (4.1) is selected from the group consisting of ash,

ash from the thermal treatment of biomass, manure ash, sewage sludge ash, incinerated sewage sludge ash, gasified sewage sludge ash, chemically precipitated sewage sludge, biologically precipitated sewage sludge, or a combination thereof.

5

4. The apparatus according to any of the preceding claims, wherein the particulate material of the first anolyte (4.1) comprises phosphorus compounds, wherein the phosphorus is chemically bonded to calcium (Ca), and/or aluminium (Al), and/or iron (Fe), and/or wherein the particulate material of the first anolyte (4.1) comprises above 0.5 wt% P bonded to Ca, and/or Al, and/or Fe, more preferably above 1 wt% or 1.5 wt%, and most preferably above 2 wt% or 2.5 wt%.  
10
5. The apparatus according to any of the preceding claims, wherein the particulate material of the first anolyte (4.1) is suspended in a liquid selected from the group consisting of distilled water, tap water, recycled second anolyte (6.1) and recycled filtrate (3.1), diluted acid, and any combination thereof.  
15
6. The apparatus according to any of the preceding claims, configured such that the pH of the first anolyte (4.1) is controlled by a first electrodialytic current, and configured such that the pH decreases during the first electrodialytic treatment.  
20
7. The apparatus according to any of the preceding claims, wherein the first catholyte (5.1) is an electrolyte solution, preferably selected from the group consisting of solutions of sodium nitrate, solutions of sodium chloride, solutions of nitric acid, solutions of hydrochloric acid, distilled water, tap water, and recycled first catholyte (5.1).  
25
8. The apparatus according to any of the preceding claims, wherein one or more of the compartments (4, 5, 6, 7) further comprises stirring means, and optionally wherein the stirring means are selected from the group consisting of overhead stirrer, magnetic stirrer and stirring by gas bubbling, and/or wherein one or more of the compartments (4, 5, 6, 7) further comprises heating means, and/or wherein the temperature of one or more of the anolytes and/or catholytes (4.1, 5.1, 6.1, 7.1) is above room temperature, and optionally wherein the temperature is above 30 °C, more preferably above 40 °C or 50 °C.  
30  
35

- 5 9. The apparatus according to any of the preceding claims, wherein the filtration means is selected from the group of filter paper, vacuum filters, and any combination thereof, and optionally wherein the filter mesh size is equal to or below 50  $\mu\text{m}$ , more preferably equal to or below 45  $\mu\text{m}$ , and most preferably equal to or below 40  $\mu\text{m}$ , and optionally further combined with a vacuum filter, and optionally wherein the vacuum filter has a filter mesh size equal to or below 10  $\mu\text{m}$ , more preferably equal to or below 1  $\mu\text{m}$ , and most preferably equal to or below 0.45  $\mu\text{m}$ .
- 10 10. The apparatus according to any of the preceding claims, wherein the second catholyte (7.1) comprises the residual from the filtration means and a further liquid phase, and optionally wherein the further liquid phase is selected from the group consisting of water, distilled water, tap water, sodium hydroxide (NaOH), recycled filtrate from the second filtration means (10.1), and any combination thereof.
- 15 11. The apparatus according to any of the preceding claims, configured such that the pH of the second catholyte (7.1) is controlled by a second electro dialytic current, and configured such that the pH increases during the second electro dialytic treatment.
- 20 12. The apparatus according to any of the preceding claims, further comprising second filtration means (10) in fluid communication with the second catholyte compartment (7) configured to filter the second catholyte (7.1) into a second residual and a second filtrate (10.1).
- 25 13. A method for electro dialytic phosphorus recovery, comprising:
- 30 (a) providing a first electro dialytic cell (1), comprising a first anolyte compartment (4) and a first catholyte compartment (5), separated by a cation exchange membrane (8);
- (b) providing a particulate material comprising acidic and/or alkaline soluble phosphorus compounds;
- (c) mixing the particulate material with a liquid and use it as an anolyte for the first cell (4.1);
- 35 (d) providing an electrolyte solution and use it as a catholyte (5.1) for the first cell;

- (e) applying a first current to the first cell (1) thereby exposing the particulate material to acidic conditions,  
whereby metal ions are concentrated in the catholyte (5.1);  
(f) providing a second electroalytic cell, comprising a second anolyte compartment (6) and a second catholyte compartment (7), separated by an anion exchange membrane (9);  
(g) transferring the treated anolyte (4.1) from the first cell (1) to filtration means such that the treated anolyte is filtered into a residual and a filtrate ;  
(h) transferring the liquid filtrate into the second anolyte compartment (6) thereby forming a second anolyte (6.1);  
(i) mixing the residual with water, and transferring the mixture into the second cathode compartment (7) thereby forming a second catholyte (7.1);  
(j) applying a second current to the second cell (2) thereby exposing the particulate material to alkaline conditions,  
whereby phosphorus and phosphorous compounds are concentrated in the second anolyte (6.1).
14. The method according to claim 13, wherein the metal ions concentrated in step (e) comprises calcium ions and/or heavy metal ions.
15. The method according to any of claims 13-14, wherein the particulate material provided in step (b) is a further batch of particulate material, and step (c)-(j) is repeated thereby defining a second cycle,, and optionally wherein the liquid provided in repeated step (c) is recycled first filtrate (3.1), and/or the filtrate of the second catholyte (10.1), and/or the second anolyte (6.1) from the first cycle, and optionally wherein the electrolyte solution of repeated step (d) is the first catholyte from the first cycle.

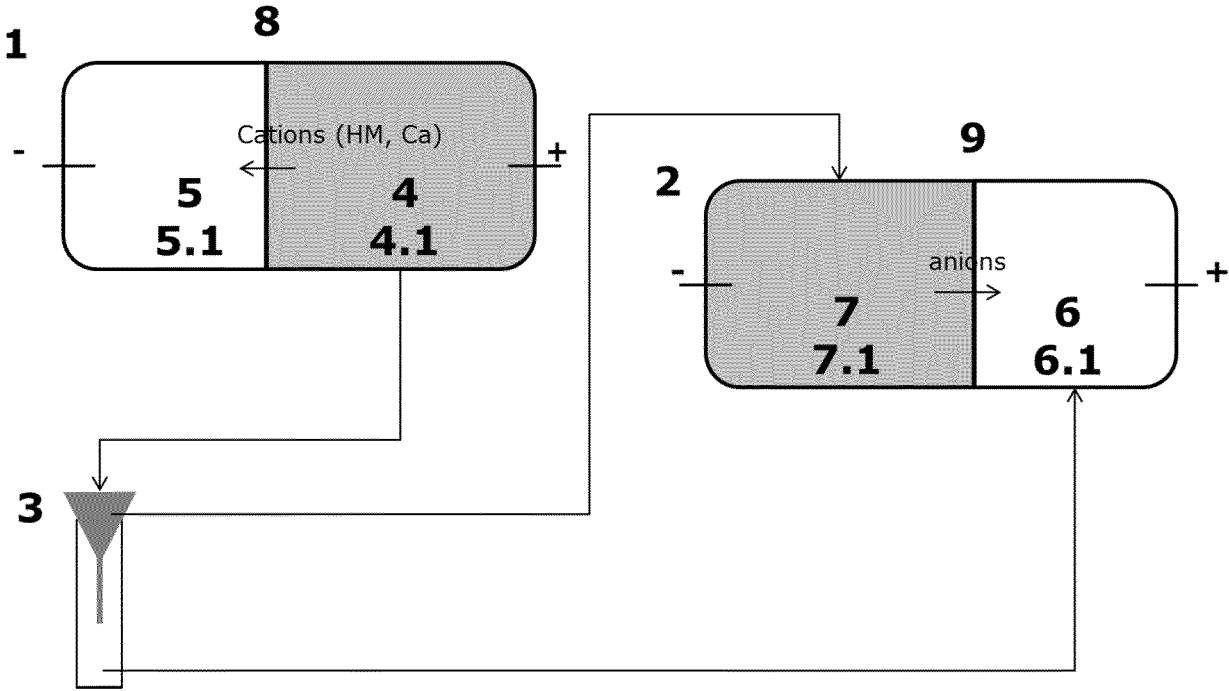


Fig. 1

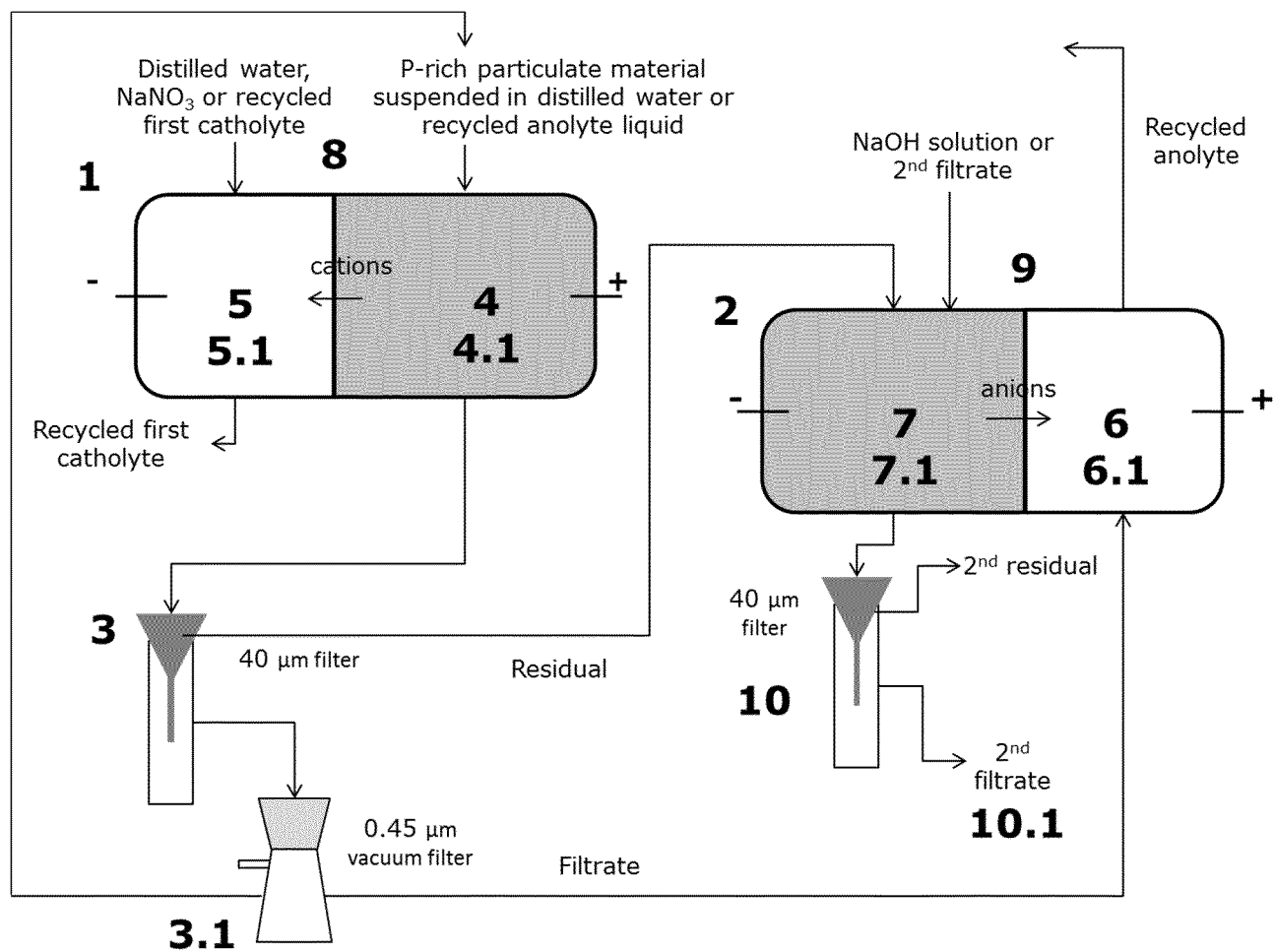


Fig. 2

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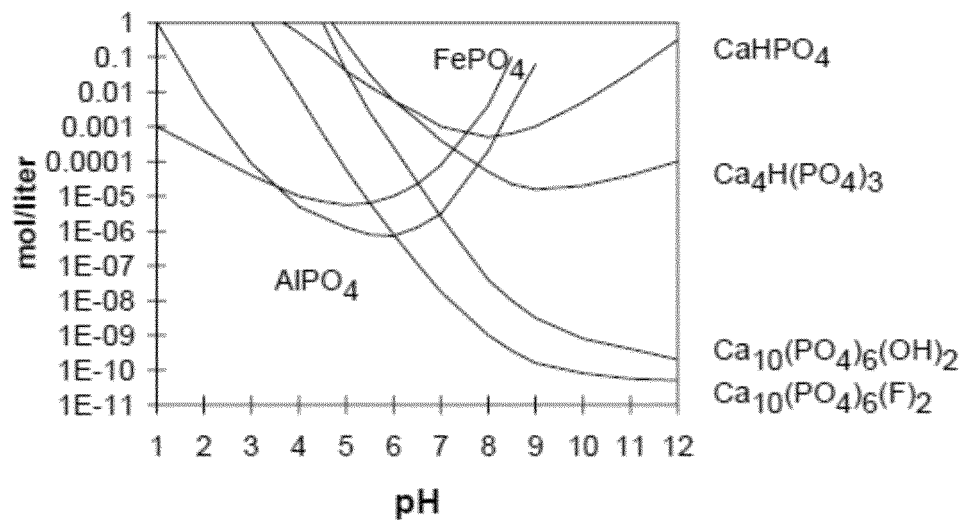


Fig. 3

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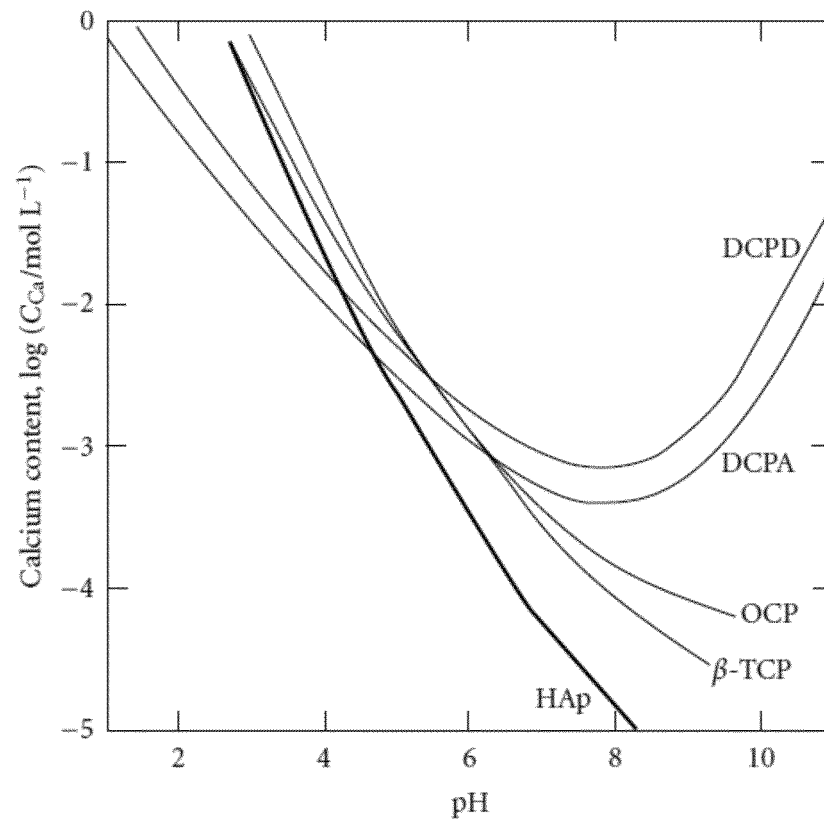


Fig. 4



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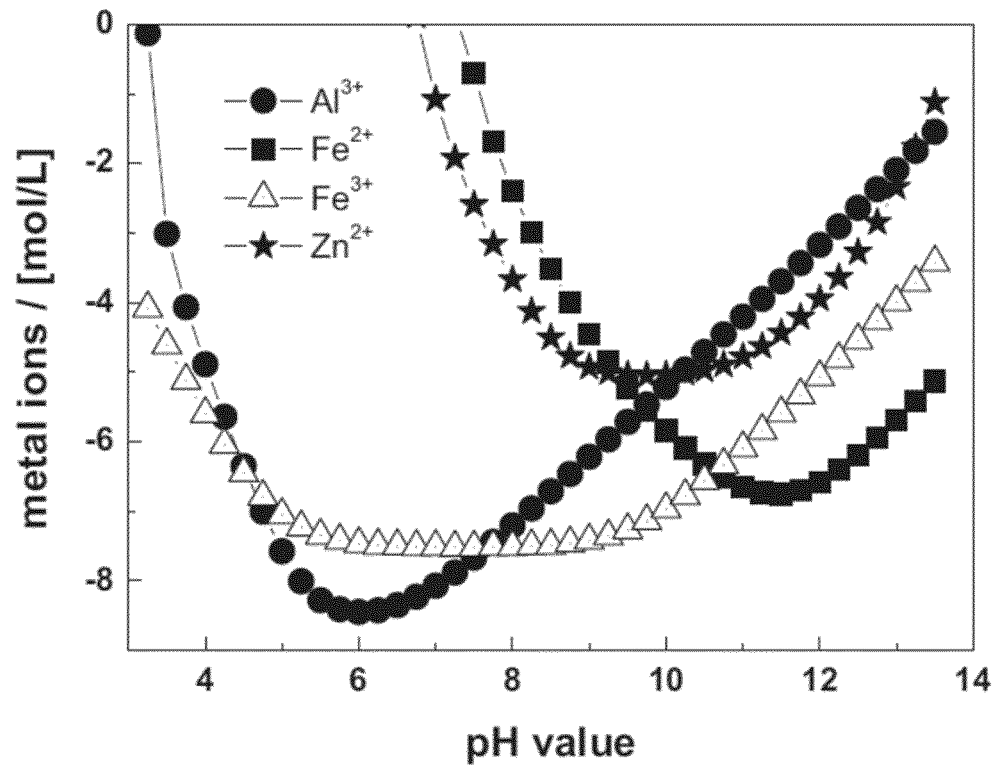


Fig. 5

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2016/073094

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D61/44 B09B3/00 B09C1/08 C02F1/469 C02F11/00  
C05B17/00 C05D9/00 C05D9/02  
ADD. C02F1/66 C02F101/20

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)

B01D B09B B09C C02F C05B C05D

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

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

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2015/032903 A1 (UNIV DENMARK TECH DTU [DK]) 12 March 2015 (2015-03-12) cited in the application figures 1-4 page 5, line 21 - page 11, line 4 page 13, line 15 - page 14, line 29 table 1a	1-15
A	----- EBBERS BENJAMIN ET AL: "Electrodialytic treatment of municipal wastewater and sludge for the removal of heavy metals and recovery of phosphorus", ELECTROCHIMICA ACTA, vol. 181, 22 April 2015 (2015-04-22), pages 90-99, XP029302243, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2015.04.097 the whole document -----	1-15

☐

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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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

16 November 2016

Date of mailing of the international search report

25/11/2016

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European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Châtellier, Xavier

## INTERNATIONAL SEARCH REPORT

### Information on patent family members

International application No

PCT/EP2016/073094

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