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Description

Technical field

The present invention relates to the reclamation of ash originating from waste incineration. In particular, the present invention relates to the reclamation of ash originating from the incineration of sewage sludge, bone, liquid manure or household waste.

Technological background of the invention

Given the increasingly severe environmental and ecological constraints, the reclamation of waste or residues, irrespective of their origin, has become all the more pertinent. Waste is generally incinerated to form two types of residues: solid non-combustible materials, referred to as clinker or slag, which may contain high concentrations of pollutants such as heavy metals, which are likely to be released when exposed to water; and fume purification residues, which are made up of ash from dust removal and fume detoxification residues originating from the gas treatment. The reclamation of these types of waste may be complex, depending on their composition. Some of these are used in construction or in the preparation of bituminous mixtures.

For example, US 5,521,132 describes the reclamation of ash via the production of ceramic materials. The ash is brought into contact with borax and a calcium compound, and is then heated to very high temperatures (of approximately 1000°C) to form ceramics.

EP 0 743 079 also describes the treatment of ash originating from a waste incinerator for stabilising the heavy metals contained in the ash. The ash is subjected to a phosphating reaction at a high temperature (of between 500°C and 1200°C) in order to convert the toxic metal chlorides into phosphate salts.

Moreover, WO 97/31874 discloses a method for making ash inert by its reaction with a phosphate mixture in order to form a paste that is fully calcined at a temperature of more than 600°C. The obtained residue is mixed with water and a hydraulic binder such as cement.

These different processes are mainly aimed at encapsulating or confining the heavy metals present in the ash in ceramics or cement, in order to ultimately prevent them from spreading into the environment. These processes therefore result in a significant increase in the mass of the waste, without adding value to the components thereof, which are simply trapped in the cement or ceramics before being disposed of in specific waste facilities.

JP H11-92122 describes a method for extracting phosphorous from materials containing phosphorous, such as ash from the incineration of sludge. However, the method involves digestion by sulphuric acid.

In addition, JP H11-33594 discloses a method for treating sewage sludge by a phosphoric acid solution at a temperature of 40°C. This method does not provide for optimal purification of sewage sludge.

The object of the present invention is to overcome these drawbacks and reclaim at least some of the components of ash originating from waste incineration.

Summary of the invention

The present invention relates to a method for reclaiming ash originating from wet waste incineration. The ash mainly originates from the incineration of sewage sludge, bone, liquid manure or household waste.

As described in claim 1, the present invention provides a method for treating ash originating from waste incineration, comprising:

a) digesting ash by a leaching liquor containing phosphate ions in solution, in order to form a first solid phase comprising impurities and a first liquid phase comprising phosphate ions,

b) separating said first liquid phase comprising phosphate ions from said first solid phase.

Said first liquid phase is thereby isolated from said first solid phase, and this makes it easier to reclaim later. Said first liquid phase comprises phosphate ions from said leaching liquor, but also comprises metals in the form of metal ions or other elements originating from the ash. The solubilisation of these metals, which are initially present in the ash, will help in their subsequent treatment and recycling. In this way, the present method makes it possible to reclaim several metals that are present in the ash, specifically by extracting at least some of them. Moreover, the final residue, i.e. said first solid phase, can be reused in the fields of construction. The present invention provides a method for treating ash that is more eco-friendly than the methods known from the prior art. Indeed, the present method consumes less energy as it does not comprise a high-temperature treatment step or a calcining step. Moreover, the present method generates significantly less waste, since it allows the components of the ash to be extracted so as to be subsequently used in specific recycling facilities or directly as a solution for the market for diverse and varied applications (agriculture, food, construction, soil stabilisation, etc.).

Step a) can be executed at a temperature of between 20°C and 95°C, advantageously between 20°C and 80°C, preferably between 50°C and 80°C, in particular between 50°C and 65°C.

Advantageously, said leaching liquor containing phosphate ions in solution has a weight percentage of phosphate ions of between 1% and 85%, advantageously between 7% and 55%, preferably between 7% and 50%, in particular between 7% and 40%, more preferably between 13% and 28%, by weight of phosphate ions, based on the total weight of the leaching liquor. The phosphate ions taken into consideration for determining the above weight percentage of phosphate ions are phosphate ions in the form H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}.

Preferably, said leaching liquor containing phosphate ions in solution is a phosphoric acid solution, preferably an aqueous solution of phosphoric acid. The use of a leaching liquor containing phosphate ions, preferably an aqueous solution of phosphoric acid, makes it possible to improve the extraction yield of different elements (in particular phosphorous, calcium, magnesium, aluminium or iron) present in the ash, and to reduce the number of steps to be in the method. Preferably, the leaching liquor does not contain any other acid in addition to the phosphoric acid. In fact, the presence of another acid will promote the production of other salts that are soluble or insoluble salts in water. The removal of these salts, and their separation from the phosphate salts, will require additional liquid-liquid, chemical precipitation or mechanical separation extraction steps. Thus, the use, in step a), of a phosphoric acid solution as the leaching liquor makes it possible to optimise the number of steps in the method and to make said method more economically viable.

Said separation, implemented in step b), can be executed by filtration. The filtrate recovered after filtration corresponds to said first liquid phase comprising phosphate ions and free of impurities that remain solid in said first solid phase. The impurities that do not dissolve in the leaching liquor are then recovered in said first solid phase and can be reused as raw materials in the preparation of construction materials or soil stabilisation, or for any other application that requires a composition of this kind that mainly comprises sand and gypsum. The residue has the advantage of being a stable residue, i.e. it is stable in leaching conditions and can therefore be used without negatively affecting the environment, for example in soil amelioration.

A brief description of the figures

Fig. 1 shows a block diagram of the method according to a particular embodiment of the present invention.

Detailed description of the invention

The present invention relates to a method for treating ash originating from waste incineration. As mentioned above, the ash can originate from the incineration of various kinds of waste. Nevertheless, the invention is particularly suitable for ash originating from the incineration of sewage sludge, bone, liquid manure or household waste, preferably for ash originating from the incineration of sewage sludge, bone or liquid manure. The ash may comprise salts or oxides of metals such as metals from columns 1 to 16 of the periodic table of elements, including the rare earths, lanthanides and actinides, as well as salts or oxides of the following elements Si, P, S or As. Preferably, the metals from columns 1 to 16 mentioned above can be Na, K, Li, Rb, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag, Zn, Cd, Al, Ge, Sn, In, Sb, Pb or Bi. The method according to the present invention makes it possible to extract all or some of these different metals or elements in the form of water-soluble phosphate salts. These salts can then be separated and reclaimed independently of one another. By virtue of the method according to the present invention, even said first solid phase recovered in step b) can be reclaimed and used as a raw material for other applications. Therefore, the ash treated using the present method is no longer stored but reclaimed to preserve the environment and reduce the amount of waste that is stored or in landfills.

The present method comprises the following steps:

a) digesting ash by a leaching liquor containing phosphate ions in solution, in order to form a first solid phase comprising impurities and a first liquid phase comprising phosphate ions,

b) separating said first liquid phase comprising phosphate ions from said first solid phase.

After separation, said first liquid phase comprising phosphate ions can be recovered and/or isolated. In addition to phosphate ions, the first liquid phase can comprise metal ions originating from salts or oxides of metals such as metals from columns 1 to 16 of the periodic table of elements, including the rare earths, lanthanides and actinides, or ions originating from the following elements Si, P, S or As. The metal ions may be ions originating from the following metals: Na, K, Li, Rb, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag, Zn, Cd, Al, Ge, Sn, In, Sb, Pb or Bi. In particular, the present method can make it possible to extract and thus reclaim all or some of aluminium, calcium, magnesium, iron, sodium, potassium, zinc, rare earths, copper, mercury, lead, phosphorous or any one of the metals mentioned above and contained in the ash, if there are any of said metals in said ash.

Said leaching liquor containing phosphate ions in solution can have a weight percentage of phosphate ions of between 1% and 85%, advantageously between 7% and 55%, preferably between 7% and 50%, in particular between 7% and 40%, more preferably between 13% and 28%, by weight of phosphate ions, based on the total weight of the leaching liquor. Surprisingly, the present method provides a high extraction yield (of more than 80%) of one or more components of the ash, for example phosphorous, aluminium, calcium, magnesium or iron, when a leaching liquor containing phosphate ions in solution has a weight percentage of phosphate ions of between 7% and 50%, in particular between 7% and 40%, preferably between 13% and 28%, by weight of phosphate ions, based on the total weight of the leaching liquor.

Preferably, the leaching liquor containing phosphate ions in solution is a preferably aqueous phosphoric acid solution. Said phosphoric acid solution used can be diluted, preferably in water, in order to obtain a leaching liquor having a weight percentage of phosphate ions of between 1% and 85%, advantageously between 7% and 55%, preferably between 7% and 50%, in particular between 7% and 40%, more preferably between 13% and 28%, by weight of phosphate ions, based on the total weight of the leaching liquor. The phosphoric acid solution can be diluted before, at the same time as or after it is brought into contact with said ash treated in step a). Thus, a phosphoric acid solution (for example 85% by weight H_3PO_4) can be brought into contact with the ash and then a sufficient quantity of water is added to obtain a leaching liquor having a weight percentage of phosphate ions as mentioned above. Alternatively, a phosphoric acid solution (for example 85% by weight H_3PO_4) can be brought into contact with the ash at the same time as when the quantity of water necessary to obtain a leaching liquor having a weight percentage of phosphate ions as mentioned above is added. Alternatively, a phosphoric acid solution (for example 85% by weight H_3PO_4) can be diluted with water to obtain a leaching liquor having a weight percentage of phosphate ions as mentioned above, said leaching liquor then being added to the ash in order to implement step a) of the present method.

Preferably, the leaching liquor containing phosphate ions in solution comprises at least 50% by weight of phosphoric acid, advantageously at least 75% by weight of phosphoric acid, preferably at least 90% by weight of phosphoric acid, in particular at least 98.5% by weight of phosphoric acid, more particularly at least 99% by weight of phosphoric acid.

Preferably, the weight ratio between said leaching liquor containing phosphate ions in solution and the ash can be greater than or equal to 2, advantageously greater than 4, preferably greater than 5, in particular greater than 5.5. The weight ratio between said leaching liquor containing phosphate ions in solution and the ash can also be between 2 and 100, advantageously between 4 and 50, preferably between 5 and 50, in particular between 5 and 25. The weight of ash to be taken into consideration is the weight of the ash before digestion, i.e. before it is brought into contact with the leaching liquor. This has the advantage of forming, in step a), a slightly viscous reaction medium in which the ash or residues originating from the digestion are suspended. When the leaching liquor is a phosphoric acid solution, the weight of the leaching liquor is determined from the weight of the phosphoric acid solution used in step a), and optionally from the weight of the water added if the phosphoric acid solution is diluted. Thus, increases in mass or the formation of a viscous and mostly unusable paste are avoided. The separation executed in step b) is thus made easier.

Preferably, before implementing step b), the weight ratio between said first liquid phase comprising phosphate ions and the ash is greater than or equal to 2, advantageously greater than 4, preferably greater than 5, in particular greater than 5.5. The weight ratio between the said first liquid phase and the ash can also be between 2 and 100, advantageously between 4 and 50, preferably between 5 and 25. The weight of ash to be taken into consideration is the weight of the ash before digestion, i.e. before it is brought into contact with the leaching liquor. Thus, the leaching liquor and the ash can temporarily form a paste or a slurry, but a sufficient quantity of water is added before implementing step b) of the present method in order to obtain the weight ratio between said first liquid phase and the ash mentioned above. The separation executed in step b) is therefore made easier and the reclamation of the ash is improved.

Step a) of the present method can be executed at a temperature of between 20°C and 95°C, advantageously between 20°C and 80°C, preferably between 50°C and 80°C, in particular between

50°C and 65°C. Implementing the digestion of the ash at between 50°C and 80°C makes it possible to control the viscosity of the reaction medium and to prevent processing problems related to the leaching of the ash, and mainly increases in the mass of the reaction medium.

Step b) of the present method can be executed at a temperature of between 20°C and 95°C, advantageously between 20°C and 80°C. Step b) of the present method can be executed at a temperature of more than 40°C, preferably between 50°C and 80°C, in particular between 50°C and 65°C. The implementation of step b) of the present method at a temperature of between 50°C and 80°C also improves the quality of the separation of the phases and the overall effectiveness of the method.

The ash is digested by the leaching liquor containing phosphate ions in solution for a duration of between 5 minutes and 8 hours, advantageously between 5 minutes and 4 hours, preferably between 5 minutes and 2 hours. The ash is digested by the leaching liquor containing phosphate ions in solution for a duration of between 5 minutes and 45 minutes, more particularly between 30 minutes and 45 minutes. Extremely high extraction yields, for example of > 90% for phosphorous, are observed even when the duration of the digestion step is between 5 minutes and 2 hours, advantageously between 5 minutes and 45 minutes. This makes it possible to improve the economic and industrial viability of the present method.

Advantageously, the present method is applicable to the treatment of ash originating from the incineration of sewage sludge, bone or liquid manure. The ash treated by the present method has a phosphorous content, expressed in percentage by weight of PO_4 phosphates in the ash, of at least 7%, preferably between 7% and 67.5%, in particular between 7% and 47%, more particularly between 20% and 47%. Phosphorous contents in the ash of at least 7% by weight of phosphates, preferably between 7% and 67.5%, in particular between 7% and 47%, more particularly between 20% and 47%, can be present in particular in the ash originating from the incineration of sewage sludge, bone or liquid manure.

Preferably, when the ash comprises phosphorous, the absolute mass of phosphorous, expressed in g of PO_4, in said first liquid phase comprising phosphate ions obtained in step b) is greater than the absolute mass of phosphorous, expressed in g of PO_4, in said leaching liquor containing phosphate ions in solution initially used in step a) of the present method to digest the ash. Thus, the phosphorous contained in the ash is extracted and rendered soluble by the leaching liquor, which allows said first liquid phase to be enriched with phosphates. Preferably, when the leaching liquor is a phosphoric acid solution, said first liquid phase obtained in step b) is a phosphoric acid solution enriched with phosphates.

The present method has a high extraction yield of at least some of the metals contained in the ash, mostly in the form of water-soluble phosphate salts. For example, at least 80%, advantageously at least 90%, preferably at least 95%, of the calcium or magnesium present in the ash is digested in step a) and recovered in said first liquid phase comprising phosphate ions, which is obtained in step b). Similar values are also obtained for aluminium, iron or other metals present in the ash. In particular, the present method has a high extraction yield of phosphorous contained in the ash, if there is any. At least 85%, advantageously at least 90%, preferably at least 95%, in particular at least 98%, of the phosphorous present in the ash is digested in step a) and recovered in said first liquid phase in the form of phosphate ions.

Said first liquid phase comprising phosphate ions and obtained in step b) can be recovered and may form a phosphoric acid solution. Said first liquid phase can be used as a raw material for the production of fertilisers. Said first liquid phase may also comprise metal phosphate salts, such as aluminium phosphate, calcium phosphate, iron phosphate or magnesium phosphate salts. This phosphoric acid solution obtained in step b) can be used as such. Depending on the composition of the ash, said first liquid phase can also comprise sulphate salts, such as aluminium sulphate, calcium sulphate, iron sulphate or magnesium sulphate salts.

According to a preferred embodiment, step a) of the present method can be executed in a first co-current reactor comprising one or more compartments, advantageously between 2 and 12 compartments, preferably between 2 and 5 compartments, in particular between 3 and 5 compartments. The compartments are arranged in series and are in communication with one another from their base. The ash and the leaching liquor containing phosphate ions can, for example, be introduced in a first compartment. The thus formed sludge then passes through each of the other compartments, which can thus be used to modulate or control the reaction time and optimise the mixture of the compounds. The last compartment of said first co-current reactor of step a) is connected to a means for separating the first liquid phase from the first solid phase resulting from the step. Preferably, the first liquid phase and the first solid phase are separated using filtration. Thus, the last compartment of said first co-current reactor of step a) is connected to a filter via a pipe, which makes it possible to transport the reaction medium obtained at the end of step a) to the filter where step b) of the present method is executed. Optionally, a buffer storage tank can be placed between the last compartment of the first co-current reactor used for implementing step a) and the filter used for implementing step b). In this case, the reaction medium obtained at the end of step a) is transferred from the buffer tank to the filter of step b).

The present method may also comprise a step c) of purifying said first liquid phase comprising phosphate ions obtained in step b), in order to form a second liquid phase comprising phosphate ions. The purification of said first liquid phase comprising phosphate ions makes it possible to reduce in particular the content of one or more metal ions present in said first liquid phase and mentioned above, i.e. the metal ions originating from the metals from columns 1 to 16 of the periodic table, preferably Na, K, Li, Rb, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag, Zn, Cd, Al, Ge, Sn, In, Sb, Pb or Bi, or ions originating from the following elements Si, S or As, in particular, Ca, Mg, Fe or Al. The purification may also make it possible to separate the different metal ions present in said first liquid phase, in order to reclaim them independently of one another. According to a particular embodiment, said second liquid phase can therefore be a purified phosphoric acid solution, i.e. a solution in which the contents of different metal ions such as calcium, magnesium, aluminium, iron or other metal ions can be reduced by comparison with the contents of these ions in said first liquid phase, it also being possible for said first liquid phase to be a phosphoric acid solution according to a particular embodiment.

Purification step c) can be a purification by liquid-liquid extraction. Thus, step c) of said first liquid phase comprising phosphate ions includes:

(i) extracting the phosphate ions contained in said first liquid phase with an organic solvent, in order to form an organic extraction phase containing phosphate ions and an aqueous extraction phase containing impurities;

(ii) re-extracting said organic extraction phase by an aqueous re-extraction agent, in order to form an aqueous re-extraction phase and an organic phase with a low content of phosphate ions;

(iii) separating the aqueous re-extraction phase containing phosphate ions and the organic phase, said aqueous re-extraction phase containing phosphate ions being said second liquid phase.

The organic solvent is preferably selected from the group consisting of methyl isobutyl ketone, butanol, pentanol, organic solvents in C_4 to C_7, and mixtures thereof. The purification step can also include, preferably before the extraction or re-extraction of the organic extraction phase containing phosphate ions, the steps consisting of:

- washing said organic extraction phase containing phosphate ions with an aqueous solution in order to obtain a washed organic phase containing phosphate ions and an aqueous phase containing impurities and a particular quantity of phosphate ions;
- separating the obtained washed organic phase containing phosphate ions. This organic phase is suitable for said re-extraction. The purification by liquid-liquid extraction may also include steam distillation of traces of organic extraction agent from said second liquid phase. Step c) of purification by liquid-liquid extraction may also comprise the addition of a strong acid to said first liquid phase comprising phosphate ions, which was obtained in step b), before step (i) mentioned above. This makes it possible to increase the extraction yield.

Alternatively, the purification of said first liquid phase, executed in step c), comprises the application of ion exchange to produce said second liquid phase. By comparison with liquid-liquid extraction, purification by application of ion exchange provides for a better yield of phosphate ions in said second liquid phase. The application of ion exchange can be executed using one or more resins for the exchange of ions, advantageously cations or anions or a mixture thereof, preferably cations. Preferably, the ion-exchange resins comprise acid functional groups. In particular, the acid functional groups contained in the ion-exchange resins have a pKa of less than the pKa of the acid-base pair of which the conjugate base is formed by the phosphate ions obtained in step b). Advantageously, the resins for the exchange of ions, preferably cations, comprise acid functional groups having a pKa that is less than the pKa of the $H_3PO_4/H_2PO_4^-$ pair. The application of ion exchange may comprise the application of an anion-exchange resin in order to recover any arsenic oxides that may be generated during the implementation of the present method.

Said one or more cation-exchange resins can be regenerated independently of one another by an acid solution, advantageously hydrochloric acid, nitric acid or sulphuric acid. Said acid can be a strong acid. The regeneration of the ion-exchange resins produces an aqueous solution comprising metal salts trapped by the resins. These salts can be chloride, nitrate or sulphate salts. Preferably, said one or more cation-exchange resins can be regenerated independently of one another by a hydrochloric acid solution or a sulphuric acid solution, or a mixture thereof. An aqueous solution comprising one or more chloride salts or one or more sulphate salts or a mixture thereof may be formed. The salts may be metal chloride salts selected from among the metals from columns 1 to 16 of the periodic table (metals and transition metals, rare earths, As) or metal sulphate salts selected from among the metals from columns 1 to 16 of the periodic table (metals and transition metals, rare earths, As).

In general, the ash used in the present method mainly comprises calcium, magnesium, aluminium, iron, silicon or phosphorous in varying contents, depending on the origin of the ash. Silicon is mainly recovered in said first solid phase. Preferably, phosphorous is recovered in said first liquid phase or said second liquid phase in the form of phosphoric acid. When said one or more cation-exchange resins are regenerated independently of one another by a hydrochloric acid solution, an aqueous solution comprising calcium chloride, magnesium chloride, aluminium chloride or iron chloride, or mixtures thereof, is formed for each of the cation-exchange resins. These aqueous solutions can be recovered and isolated for later reuse in various technical fields, such as construction and the treatment of waste water in water purification plants. These aqueous solutions can also be dried and concentrated in order to obtain a commercial product. The salts can also be precipitated according to processes that are known to a person skilled in the art. This method is also applicable for recovering all or some of the other metals present in the ash. This is made possible by multiplying the number of ion-exchange resins. Thus, aqueous solutions comprising salts of metals, such as Na, K, Li, Rb, Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Cr, Mo, Mn, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag, Zn, Cd, Al, Ge, Sn, In, Sb, Pb or Bi, can be obtained during the regeneration of said ion-exchange resins. The present method therefore makes it possible to extract all or some of the different metals contained in the ash and to recover said metals, preferably in the form of chloride salt solutions. Alternatively, if said ion-exchange resins are regenerated by a sulphuric or nitric acid solution, aqueous solutions of nitrate or sulphate salts are obtained instead of aqueous solutions of chloride salts.

The present method thus allows the ash as described in the present invention to be reclaimed, in particular by extracting all or some of the aluminium, calcium, magnesium, iron or phosphorous present in the ash. Depending on the initial composition of the ash, other metals may be extracted and recovered. Preferably, phosphorous is recovered in the form of an aqueous solution of phosphoric acid. As mentioned above, all or a some of the aluminium, calcium, magnesium or iron can be recovered in the form of an aqueous solution of calcium chloride, aluminium chloride, magnesium chloride or iron chloride.

The present method may also comprise a step of concentrating said first liquid phase comprising phosphate ions or said second liquid phase comprising phosphate ions.

The present method may also comprise a step of treating said first liquid phase comprising phosphate ions obtained in step b) or said second liquid phase comprising phosphate ions obtained in step c) using activated carbon. This treatment makes it possible to remove all or some of the dioxin or mercury that may be present in said first liquid phase comprising phosphate ions obtained in step b) or said second liquid phase comprising phosphate ions obtained in step c).

According to a particular embodiment of the invention, said second liquid phase comprising phosphate ions, obtained in step c), is a phosphoric acid solution. This can be obtained by using, in step a), a phosphoric acid solution as the leaching liquor comprising phosphate ions in solution.

According to a preferred embodiment, a part of said first liquid phase or said second liquid phase comprising phosphate ions is recycled for use in step a) as a leaching liquor containing phosphate ions in solution. The method can therefore be executed continuously.

According to a particular embodiment of the invention, the leaching liquor is a phosphoric acid solution and the present method may comprise:

a) digesting ash having a phosphorous content, expressed in percentage by weight of PO_4 in the ash, of at least 1% by a first phosphoric acid solution, in order to form a first solid phase comprising impurities and a first liquid phase comprising phosphate ions, the weight ratio between said first phosphoric acid solution and the ash being greater than or equal to 2, advantageously greater than 4, preferably greater than 5,

b) separating said first liquid phase comprising phosphate ions from said first solid phase,

b') optionally treating the first liquid phase comprising phosphate ions using activated carbon,

c) purifying said first liquid phase comprising phosphate ions, preferably by the application of ion exchange or by liquid-liquid extraction, in order to obtain a second phosphoric acid solution,

c') optionally treating said phosphoric acid solution using activated carbon. The weight of said first phosphoric acid solution is determined by the weight of the phosphoric acid solution and the weight of the added water if said first phosphoric acid solution is diluted before, during or after it is brought into contact with the ash. Preferably, the digestion is executed at a temperature of between 20°C and 95°C, advantageously between 20°C and 80°C, preferably between 50°C and 80°C, in particular between 50°C and 65°C; and advantageously for a duration of between 5 minutes and 8 hours, advantageously between 5 minutes and 4 hours, preferably between 5 minutes and 2 hours, in particular between 15 minutes and 45 minutes, more preferably between 30 and 45 minutes. Preferably, the first phosphoric acid solution has a weight percentage of phosphate ions of between

7% and 50%, in particular between 7% and 40%, preferably between 13% and 28%, by weight of phosphate ions, based on the total weight of the first phosphoric acid solution. The phosphate ions taken into consideration for determining the above weight percentage of phosphate ions are phosphate ions in the form H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}.

According to another aspect of the invention, when the ash contains phosphorous, it can be used to increase the absolute mass of phosphates of an aqueous solution of phosphoric acid. Indeed, by applying the present method in which the leaching liquor containing phosphate ions in solution is a phosphoric acid solution, said first liquid phase comprising phosphate ions or said second liquid phase comprising phosphate ions obtained is a phosphoric acid solution in which the absolute mass of phosphates (in g of PO_4) was increased by comparison with the absolute mass of phosphates in the leaching liquor (in g of PO_4).

The present method can be applied to ash that mainly contains aluminium, iron, calcium or magnesium or mixtures thereof, and little phosphorous (less than 1% by weight of PO_4). In this case, said first liquid phase will comprise aluminium, calcium, iron or magnesium phosphate salts or mixtures thereof. The implementation of purification step c), for example by the application of ion exchanges or by liquid-liquid extraction, will make it possible to recover a second liquid phase comprising phosphate ions in solution, e.g. a phosphoric acid solution if the leaching liquor used in step a) was a phosphoric acid solution. Moreover, the regeneration of the ion-exchange resins will make it possible to mainly recover aqueous solutions of aluminium, calcium, magnesium or iron salts or mixtures thereof, and possibly other aqueous solutions of metal salts originating from the metals that may be present in the ash, such as Na, K, Li, Rb, Sr, Ba, Sc, Y, Ti, Zr, V, Nb, Cr, Mo, Mn, Ru, Co, Rh, Ni, Pd, Cu, Ag, Zn, Cd, Ge, Sn, In, Sb, Pb or Bi.

Fig. 1 is a block diagram of the method according to a particular embodiment of the present invention. The ash 1 and a phosphoric acid solution 2 is fed to the digestion reactor 3. After the ash 1 has been digested according to the conditions of the present method, the reaction medium is filtered by a filter press 4 in order to separate the first solid phase 5 from the first liquid phase 6 comprising phosphate ions in solution. The first liquid phase is treated in 7 with activated carbon 8. The solid residue resulting from this treatment is removed in 8’ and the liquid phase 9 resulting from this treatment is treated with three cation-exchange resins, 10, 10’ and 10”, placed in series. The number of cation-exchange resins is limited to three in this example for the sake of clarity and conciseness; in practice, however, at the industrial level, the number of cation-exchange resins can be increased, for example to between 20 and 100 cation-exchange resins, depending on the degree of purity of said second liquid phase and the number of metals to be recovered. The liquid phases 9', 9" and 9"' correspond to the liquid phases at the output of the corresponding cation-exchange resin. The liquid phases 9', 9" and 9"' are phosphoric acid solutions, the purity of which is improved as and when they pass through the cation-exchange resins. All or some of the phosphoric acid solution obtained in 9"' can be recovered or stored in 14 or recycled so as to be supplied to the digestion reactor 3. The ion-exchange resins 10, 10', 10" are regenerated independently of one another by a hydrochloric acid solution 11, 11' or 11". The aqueous solution 12 recovered after the regeneration of the exchange resin 10 mainly comprises calcium chloride or magnesium chloride or a mixture of the two. The aqueous solutions 12' and 12" recovered after the regeneration of the exchange resin 10' and 10" mainly comprise aluminium chloride or iron chloride or a mixture of the two.

Procedure for determining the metal contents

The metal contents in a sample are determined using optical emission spectrometry (ICP-OES: Inductively coupled plasma optical emission spectrometry) using an Agilent 710 Axial series ICP optical emission spectrometer equipped with a nebuliser (One Neb insert concentric ICP) and a plasma torch (lo-flw, Quartz, inlet tbg, axial). The samples and standards are prepared in containers that are cleaned beforehand with a diluted nitric acid solution (193 g of nitric acid at 96%, diluted to 1000 mL with distilled water). The equipment is calibrated using the following protocol, using standard solutions of $Pb(NO_3)_2$ with a lead concentration of 100 mg/L, of $Cd(NO_3)_2$ with a cadmium concentration of 100 mg/L, of $Hg(NO_3)_2$ with a mercury concentration of 100 mg/L, of H_3AsO_4 with an arsenic concentration of 100 mg/L, and of $Y(NO_3)_3$ with a yttrium concentration of 100 mg/L. From each of the solutions of $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Hg(NO_3)_2$ and H_3AsO_4, a series of 7 samples with calibrations of 0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm, 1 ppm and 5 ppm are prepared. In each sample, 200 µL of the standard solution of $Y(NO_3)_3$ is added and then each sample is diluted with the above diluted nitric acid solution, until a volume of 100 mL is obtained. The samples to be analysed by ICP-OES are prepared by mixing 10 g of the sample to be analysed and 200 µL of the standard solution of $Y(NO_3)_3$ in a 100 mL flask containing 50 mL of the diluted nitric acid solution, as prepared above. The volume is then adjusted to 100 mL by adding the diluted nitric acid solution. The thus obtained solution is shaken vigorously.

Example 1

A leaching liquor was prepared, comprising a phosphoric acid solution at 20.7% by weight of phosphate ions, from 481.1 g of a phosphoric acid solution at 85% by weight of H_3PO_4 and 1510.1 g of water. In a digestion reactor, 100 g of ash originating from the incineration of sewage sludge was brought into contact with the phosphoric acid solution at 20.7% by weight of phosphate ions, as prepared above. The ash comprised 36.2% of phosphorous (expressed in percentage % by weight in the form of PO_4). The ash was digested for 30 minutes at 60°C. The reaction mixture was filtered by a filter press. The filtrate was purified by applying 6 cation-exchange resins (Lewatit® S2568H - Lanxess) arranged in series. The aqueous solution of phosphoric acid recovered at the output of the sixth cation-exchange resin comprised 98% of the phosphates initially present in the digestion reactor, i.e. of the phosphates initially present in the ash and in the leaching liquor. This phosphoric acid solution was concentrated in order to obtain a solution at 54% by weight of P_2O_5. The application of the cation-exchange resins allowed the phosphoric acid solution to be purified. The above table 1 summarises the different metal contents that were contained in the phosphoric acid solution before purification and at the output of each of the ion-exchange resins.

Table 1 - Metal content (ppm) in the phosphoric acid solution

Metals	Ash	Before purification	1st column	2nd column	3rd column	4th column	5th column	6th column
Al	39000	1101	915	426	152	73	n.d.	41
As	32	1.6	1.56	1.73	1.67	1.75	1.64	1.78
Ca	78000	4048	275	39	<	<	<	<
Cd	2	0.5	<	<	<	<	<	<
Cr	90	4.2	3.74	3.81	3.23	2.96	2.53	2.5
Fe	110000	2144	1942	1758	1588	1475	1143	1009
K	13200	897	92	43	10	2	n.d.	n.d.
Mg	14100	1012	193	8	1	<	<	<
Mn	1456	73	15	1	0.1	<	<	<
Mo	17	1.4	1.35	1.5	1.43	1.48	1.49	1.61
Na	3600	229	45	<	<	<	<	<
Ni	126	4.9	0.6	<	<	<	<	<
Pb	169	12	1	0.35	<	<	<	<
Sr	454	29	1.45	0.12	<	<	<	<

Zn	1598	100	14.5	0.1	<	<	<	<
Si	140000	<250	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

** the symbol "<" indicates that the content is lower than the detection threshold.*

The application of the resins for the exchange of ions, preferably of cations, made it possible to remove some of the metals present in the phosphoric acid solution obtained after step b) of the present method. The magnesium, calcium, aluminium or iron contents were significantly reduced. The different columns were regenerated independently of one another by a hydrochloric acid solution at 5%. The aqueous solutions recovered after the regeneration of columns 1 and 2 comprised magnesium chloride, calcium chloride, iron chloride and aluminium chloride. The aqueous solutions recovered after the regeneration of columns 3 to 6 mainly comprised iron chloride and aluminium chloride.

Example 2

Example 1 was reproduced using phosphoric acid solutions of different concentrations for digesting the ash. Four phosphoric acid solutions, respectively at 9.9% by weight of phosphate ions, 13.8% by weight of phosphate ions, 27.6% by weight of phosphate ions, and 34.5% by weight of phosphate ions, were prepared using a phosphoric acid solution at 85% by weight of H_3PO_4.

Table 2 - results of the digestion of ash by phosphoric acid solutions of different concentrations

Example	Ash (g)	Weight % of phosphate ions in the leaching liquor	Weight % of phosphate ions in the filtrate	Yield (%)
2A	100	9.9	11.1	90
2B	100	13.8	15.4	95.5
2C	100	20.7	22.2	98
2D	100	27.6	29.0	99
2E	100	34.5	36.6	98

As shown by the results summarised in table 2, the phosphate content in the solution obtained after filtration (after step b) of the present method is greater than the phosphate content of the leaching liquor. The phosphorous present in the ash was extracted and reclaimed in the form of a phosphoric acid solution. The yield, mentioned in table 2, corresponds to the quantity of phosphates recovered in the filtrate of step b) of the present method, by comparison with the quantity of phosphates present initially, i.e. in the ash and in the leaching liquor. This yield was excellent when the ash was digested in the leaching liquor used in examples 2C, 2D or 2E.

Example 3

Ash (100g) mainly comprising 18.1% by weight of silicon, 8.7% by weight of aluminium, 15.7% by weight of calcium, 2.3% of iron, 1.5% by weight of magnesium was treated with 1992 g of a phosphoric acid solution (20.7% by weight of phosphate ions) at 60°C for 45 minutes. The ash contained less than 1% by weight of phosphorous (expressed in % by weight of PO_4). The reaction medium was filtered by a filter press. The liquid phase was purified by the application of 5 ion-exchange resins placed in series (Lewatit® S2568H - Lanxess). A phosphoric acid solution with a low metal ion content was recovered after this purification. The ion-exchange resins were regenerated with a hydrochloric acid solution at 5% and five aqueous solutions were recovered. The extraction yields for aluminium, calcium, magnesium and iron were respectively 95%, 98%, 98% and 81%.

Patentkrav

1. Fremgangsmåde til behandling af aske stammende fra forbrænding af affald, i særdeleshed fra forbrændingen af spildevandsslam, knogle eller gylle, omfattende trinnene:

a) at nedbryde aske med en udvaskningsopløsning indeholdende phosphationer i opløsning for at danne en første fast fase omfattende urenheder og en første flydende fase omfattende phosphationer, hvor nævnte udvaskningsopløsning indeholder phosphationer i opløsning med en vægtprocent af phosphationer på mellem 1 % og 85 %,

b) at separere nævnte første flydende fase omfattende phosphationer fra nævnte første faste fase,

kendetegnet ved, at asken har et phosphorindhold i asken, udtrykt i vægtprocent af phosphater i formen af PO_4, på mindst 7 %, og **ved, at** trin a) udføres i en periode på mellem 5 minutter og 45 minutter og ved en temperatur på mere end 40 °C.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** nævnte fremgangsmåde yderligere omfatter et trin c) at oprense nævnte første flydende fase omfattende phosphationer, for at danne en anden flydende fase omfattende phosphationer, hvor nævnte oprensning udføres ved væske-væske ekstraktion eller ved anvendelse af ionbytning.

3. Fremgangsmåde ifølge krav 1 eller 2, **kendetegnet ved, at** vægtforholdet mellem nævnte udvaskningsopløsning indeholdende phosphationer i opløsning og asken er større end eller lig med 2, fordelagtigt større end 4, fortrinsvis større end 5.

4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** nævnte udvaskningsopløsning indeholdende phosphationer i opløsning har en vægtprocent af phosphationer på mellem 7 % og 55 %, fortrinsvis mellem 7 % og 50 %, i særdeleshed mellem 7 % og 40 % efter vægt af phosphationer, baseret på den samlede vægt af udvaskningsopløsningen.

5. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** udvaskningsopløsningen indeholdende phosphationer i opløsning er en phosphorsyreopløsning, fortrinsvis en opløsning omfattende mindst 98,5 % efter vægt af phosphorsyre.

6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** asken nedbrydes i trin a) af udvaskningsopløsningen indeholdende phosphationer i opløsning i løbet af en periode på mellem 30 minutter og 45 minutter.

7. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** asken nedbrydes i trin a) af udvaskningsopløsningen indeholdende phosphationer i opløsning ved en temperatur på mellem 50 og 80 °C, fortrinsvis mellem 50 og 65 °C.

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** asken har et phosphorindhold i asken, udtrykt i vægtprocent af phosphater i formen af PO_4, på mindst 7 %, fortrinsvis på mellem 7 % og 67,5 %,
og fortrinsvis mindst 85 % af phosphor til stede i asken nedbrydes i trin a) og genvindes i den nævnte første flydende fase omfattende phosphationer og opnås i trin b), fordelagtigt mindst 90 %, fortrinsvis mindst 95 %, i særdeleshed mindst 98 %.

9. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** trin a) udføres i en medstrømsreaktor omfattende mellem 2 og 12 rum, fortrinsvis mellem 2 og 5 rum, i særdeleshed mellem 3 og 5 rum.

10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav 2 til 9, **kendetegnet ved, at** trin c) udføres ved anvendelse af ionbytning, under anvendelse af en eller flere ionbytterresiner.

11. Fremgangsmåde ifølge det foregående krav, **kendetegnet ved, at** nævnte ene eller flere ionbytterresiner regenereres uafhængigt af hinanden ved hjælp af en syreopløsning.

12. Fremgangsmåde ifølge det foregående krav, **kendetegnet ved, at** syren er saltsyre eller svovlsyre eller en blanding deraf, og en eller flere vandige opløsninger omfattende chloridsalte eller sulfatsalte eller en blanding deraf genvindes under regenereringen af nævnte ionbytterresiner.

13. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** nævnte anden flydende fase omfattende phosphationer opnået i trin c) er en phosphorsyreopløsning.

14. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** en del af nævnte første flydende fase omfattende phosphationer eller af nævnte anden flydende fase omfattende phosphationer genbruges til anvendelse i trin a) som en udvaskningsopløsning indeholdende phosphationer i opløsning.

15. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** nævnte fremgangsmåde omfatter trinnene:

a) at nedbryde aske stammende fra forbrændingen af spildevandsslam, knogler eller gylle, med et phosphorindhold, udtrykt i procent efter vægt af PO4 i asken, på mindst 7 %, med en første phosphorsyreopløsning, for at danne en første fast fase omfattende urenheder og en første flydende fase omfattende phosphationer, hvor vægtforholdet af den nævnte første phosphorsyreopløsning til asken er større end eller lig med 2, fordelagtigt større end 4, fortrinsvis større end 5, hvor nævnte første phosphorsyreopløsning fortrinsvis har en vægtprocent i phosphationer på mellem 7 % og 55 % efter vægt af phosphationer, baseret på den samlede vægt af udvaskningsopløsningen, hvor nedbrydelsen udføres i løbet af en periode på mellem 5 minutter og 45 minutter og ved en temperatur på mellem 50 °C og 65 °C;

b) at separere nævnte første flydende fase omfattende phosphationer fra nævnte første faste fase,

b') eventuelt, at behandle den første flydende fase omfattende phosphationer under anvendelse af aktivt kul,

c) at oprense nævnte første flydende fase omfattende phosphationer, fortrinsvis ved anvendelse af ionbytning eller ved væske-væske ekstraktion, for at opnå en anden phosphorsyreopløsning,

c') eventuelt, at behandle nævnte phosphorsyreopløsning under anvendelse af aktivt kul,

hvor trin a) fortrinsvis udføres i en medstrømsreaktor omfattende mellem 2 og 12 rum, fortrinsvis mellem 2 og 5 rum, i særdeleshed mellem 3 og 5 rum.

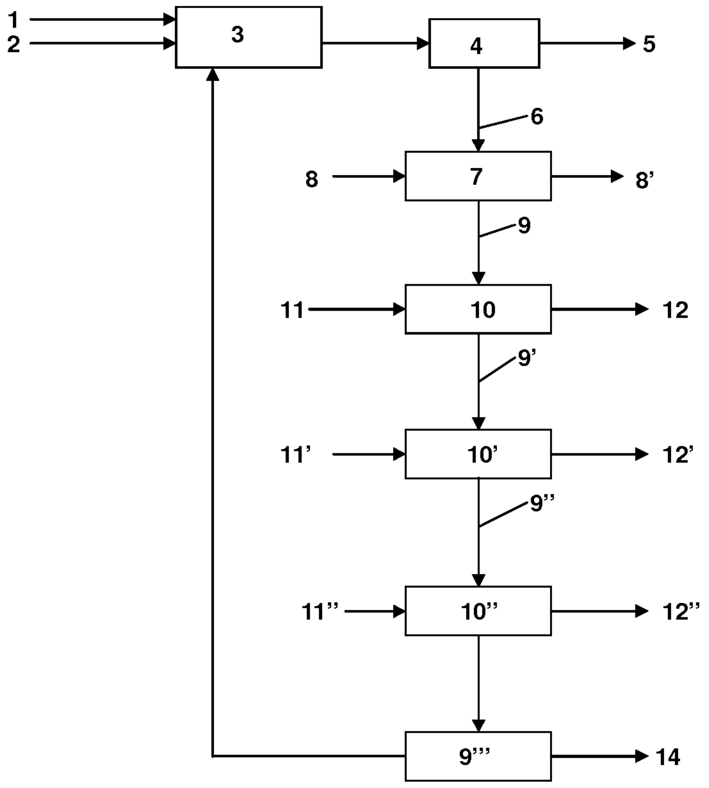

Fig. 1