⑲ **Octrooicentrum Nederland**

⑪ **2016484**

⑫ B1 **OCTROOI**

㉑ Aanvraagnummer: **2016484**

㉒ Aanvraag ingediend: **24/03/2016**

(51) Int. Cl.:
A62D 3/33 (2016.01) **A62D 3/38** (2016.01) **A62D 101/24** (2016.01) **A62D 101/43** (2016.01)

㊶ Aanvraag ingeschreven:
02/10/2017

㊸ Aanvraag gepubliceerd:
03/10/2017

㊼ Octrooi verleend:
05/10/2017

㊺ Octrooischrift uitgegeven:
06/10/2017

(73) Octrooihouder(s):
Stichting Energieonderzoek Centrum Nederland te Petten.

(72) Uitvinder(s):
Kamuran Yasadi te Petten.
Joris Jasper Dijkstra te Petten.
Andre van Zomeren te Petten.

(74) Gemachtigde:
ir. M.F.J.M. Ketelaars c.s. te Den Haag.

(54) Prevention of Sb leaching from bottom ash.

(57) The invention relates to an improved process for the treatment of bottom ash, which prevents excessive leaching of Sb and render them suitable for open application. In the process according to the invention, bottom ash is treated by (a) providing an aqueous suspension of the bottom ash; (b) mixing the bottom ash suspension originating from step (a) with green rust and allowing Sb(V) to be reduced to Sb(III); and (c) introducing O_2 into the mixture originating from step (b). The invention also concerns a mixture of bottom ash and green rust, for example as obtainable by step (b), and the treated bottom ash as obtainable by step (c), as well as the use of said bottom ash.

Prevention of Sb leaching from bottom ash

[0001] The present invention relates to an improved process for the prevention of leaching of antimony (Sb) from bottom ash, and a system for performance of the process.

Background

[0002] In industrialised countries, each inhabitant produces about 1 ton of municipal solid waste per year. Incineration is a common technique for treating municipal waste, accounting for some 30-40% of municipal waste treatment. Incineration of municipal solid waste can reduce waste mass by some 70% and can provide energy from the waste to generate electricity. Municipal solid waste incineration (MSWI) produces two types of ash: fly ashes and bottom ashes. Bottom ashes can be used in the building industry, in road constructions etc. Such use, however, is hampered by the fact that harmful elements of the bottom ash, such as antimony, are leached out from the building material into the environment by rain and/or ground water. Sb compounds are hazardous to the environment as well as to public health. Nowadays, the leaching of Sb is an important reason why bottom ash from many incinerator facilities cannot be used in the environment without protective means. Bottom ash is sealed with a liner system and the composition of the groundwater is continuously monitored.

[0003] Various processes for improving the quality, in particular reducing the leaching properties, of bottom ashes are known in the art. These include washing, leaching, carbonation, electrochemical processes and thermal treatments. NL 1026346 discloses a process for binding heavy metals in bottom ash by water extraction, followed by carbonation and addition of acidified iron oxide. WO 2012/169882 describes a process for purifying bottom ash wherein the bottom ash is rinsed with saturated salty scouring water. NL 1002461 teaches a bottom ash treatment with water vapour to reduce leaching of heavy metal atoms. CO_2 treatment of bottom ash has also been used for reducing leaching. Dijkstra et al., *Environ. Sci. Technol.* **2006**, 40, 4481-4487, teach the treatment of freshly quenched, humid bottom ash with CO_2-enriched air to reduce the leaching of fulvic acid, Cu and Mo. Rendek et al., *J. Hazardous Materials*, **2006**, B128, 73-79, teach carbonation of humidified bottom ash with pure CO_2 for pacification of the bottom ash. However, certain anions, such as antimonate, are still relatively mobile and can thus be leached out of the treated bottom ash. Moreover, CO_2 treatment even increases antimonate leaching, as it slightly lowers the pH which liberates Sb ions. Therefore, there is a need for a process of treating waste incineration bottom ash in such a way that antimonate is immobilised and does not leach out of the treated bottom ash.

[0004] Reducing the extent of antimonate leaching from bottom ash has been investigated. Especially oxyanions of Sb(V), i.e. $Sb(OH)_6^-$, are known to leach significantly from bottom ash. Adding Fe(II) minerals to bottom ash has been found to promote the reduction of Sb(V) to Sb(III), of which $Sb(OH)_3$ is dominant, which is bound much more strongly within the bottom ash matrix than Sb(V). This reduction thus reduces the leaching of Sb. However, the kinetics of the reduction of Sb(V) are unfavourable, as the reaction is very slow. Such processes of treating bottom ash with Fe(II) is known from e.g. NL1026346. Also the use of Fe(III) oxide is known from the prior art. Meima and Comans, *J. Geochemical Exploration*, **1998**, 62, 299-304 and Comans et al., *Waste Management*, **2000**, 20, 125-133, disclose the addition of Fe(III) or Al(III) salts to increase the sorptive capacity of MSWI bottom ash, which in turn reduces Sb leaching. Outside the field of bottom ash treatment, the use of the Fe(II)/Fe(III) mixed-oxide green rust to reduce Sb(V) to Sb(III) is disclosed by Mitsunobu (*Chemosphere* **2008,** *70*, 942-947).

[0005] Further means with the aim to reduce leaching of i.a. antimony include washing and addition of activated carbon to the bottom ash. EP 1769856 described a process wherein bottom ash is first subjected to a washing process and subsequently activated carbon and an inorganic hydraulic binder are added. Activated carbon binds primarily metal cations that are bound to dissolved organic ligands, such as copper. However, in bottom ash antimony is primarily present in the form of anionic or neutral Sb(V) (Cornelis et al., *Waste Management.* **2012**, *32* (2), 278-286). Any reduction of the leaching of antimony in this process is primarily due to the washing step, as activated carbon itself is not an effective scavenger of antimony. A hydraulic binder encapsulates the MSWI bottom ash as a whole in a cementitious matrix, which essentially changes the MSWI bottom ash into a monolithic product. The bottom ash immobilized with a hydraulic binder is then not suitable anymore for most of its present (open) applications in e.g. construction. WO 2007/035101 describes the immobilization of contaminants in a composition comprising bottom ash and steel slag by including 0.1 – 10 wt% active charcoal in the composition. The addition of steel slag in this process causes a high pH which will lower the solubility of antimony. However, when the pH is lowered again, e.g. due to the reaction of bottom ash with carbon dioxide, the antimony will leach again at its original level before the treatment.

[0006] However, even after treatment with Fe(II) or active carbon, the extent of Sb-leaching is still too high to enable use or storage of bottom ash without the need for protective means. Such protective means prevent the leaching of Sb to the environment, which is undesirable in view of its toxicity and also prohibited by law. These protective means are usually based on low water-permeable materials, such as geosynthetic clay liners. These liner systems, that are very expensive, prevent the bottom ash from contact with water and are prescribed by law for applications with bottom ash that do not fulfil the leaching limit values for open application. Hence, a need in the art remains for a process for treating bottom ash to reduce Sb leaching to such an extent that the thus treated bottom ash can be used or stored without the need for protective means (in the Dutch Soil Quality Decree this is referred to as the so-called open application). The present invention provides in this need, as the bottom ash obtained by the process exhibits Sb leaching below regulatory limits for open application.

Summary of the invention

[0007] The invention relates to an improved process for the prevention of leaching of antimony from bottom ash. The process according to the invention comprises:

(a) providing an aqueous suspension of the bottom ash;

(b) mixing the bottom ash suspension originating from step (a) with green rust and allowing Sb(V) to be reduced to Sb(III);

(c) introducing O_2 into the mixture originating from step (b).

[0008] Using the process according to the invention, Sb is immobilized into the bottom ash in such an efficient way that the bottom ash according to the invention may be used for open applications, i.e. without the need of protective measures that prevent leaching of Sb into the environment. The process according to the invention readily accomplishes 90 – 97 % reductions in Sb leaching, compared to untreated bottom ash. Without being bound to a theory, it is believed that the anoxic conditions together with the use of green rust, having a structure that is ideally suited to fix Sb, and oxidation of the green rust, together lead to optimal fixation of antimony in Sb(III) form, which is less soluble as the commonly present Sb(V) form of antimony.

[0009] Further aspects of the invention concern the intermediary product obtainable in step (b) of the process according to the invention, i.e. a composition comprising bottom ash and green rust, the bottom ash obtainable by the process according to the invention, and the use of the bottom ash according to the invention in a variety of (open) applications.

List of preferred embodiments

1. A process for reducing leaching of antimony from bottom ash, comprising:
    (a) providing an aqueous suspension of the bottom ash;
    (b) mixing the bottom ash suspension originating from step (a) with green rust and allowing Sb(V) to be reduced to Sb(III);
    (c) introducing O_2 into the mixture originating from step (b).
2. Process according to embodiment 1, wherein the bottom ash is municipal solid waste incineration bottom ash.
3. Process according to embodiment 1 or 2 , wherein in step (b) green rust is added in an amount of 0.1 – 15 wt% Fe, based on dry weight of the bottom ash.
4. Process according to any one of embodiments 1 to 3, wherein the green rust contains Fe(II) and Fe(III) cations in an atomic ratio of 1.5 – 2.5, preferably 1.9 – 2.
5. Process according to any one of embodiments 1 to 4, wherein allowing Sb(V) to be reduced to Sb(III) involves taking steps to avoid environmental O_2 from contacting the bottom ash suspension originating from step (a), preferably by placing the suspension in an air-tight environment, wherein gaseous components are prevented from entering the environment.
6. Process according to any one of embodiments 1 to 5, further comprising an O_2 removal step prior to step (b), wherein
    - the bottom ash suspension is subjected to O_2 removal by (i) adding an agent that replaces O_2, preferably an inert gas, (ii) providing an agent that reacts with O_2, preferably Al(0) and/or Fe(II) salt, or (iii) adding a substrate for aerobic microorganisms containing sugar, or
    - the bottom ash suspension is provided in deoxygenated form.
7. Process according to embodiment 6, wherein Al(0) is provided that originates from the bottom ash itself.
8. Process according to any of one embodiments 1 to 7, wherein step (b) is performed by mixing the suspension of bottom ash with a suspension of green rust.

9. Process according to any of one embodiments 1 to 8, wherein step (c) is performed by draining a suspension of bottom ash and green rust and allowing air to contact the drained suspension.
10. Composition comprising bottom ash and green rust.
11. Composition according to embodiment 10, wherein the amount of green rust is such that it contributes 0.1 – 15 wt% Fe, based on dry weight of the bottom ash.
12. Composition according to embodiment 10 or 11, wherein the bottom ash is municipal solid waste incineration bottom ash.
13. Bottom ash obtainable by the process according to any one embodiments 1 – 9.
14. Bottom ash according to embodiment 13, wherein the atomic ratio of Sb(III)/Sb(V) is at least 9, preferably at least 100.
15. Use of the bottom ash according to embodiment 13 or 14 for open applications.

Detailed description

[0010] The present invention relates in a first aspect to an improved process for the prevention of leaching of antimony from bottom ash. The second aspect of the invention concerns to a composition comprising bottom ash and green rust, which is in important intermediary product of the process according to the first aspect. In a third aspect, the invention concerns the bottom ash obtainable by the process according to the first aspect. The invention further concerns in a fourth aspect the use of the bottom ash according to the third aspect in a variety of applications.

PROCESS

[0011] The process according to the invention is for the prevention of leaching of antimony from bottom ash. The process may also be referred to as a process for immobilizing antimony in bottom ash or for enhancing the leaching resistance of bottom ash, in particular to leaching of antimony, or for reducing leaching of antimony from bottom ash or for treating bottom ash. The process according to the invention comprises:

(a) providing an aqueous suspension of the bottom ash;
(b) mixing the bottom ash suspension originating from step (a) with green rust and allowing Sb(V) to be reduced to Sb(III);
(c) introducing O_2 into the mixture originating from step (b).

[0012] The skilled person knows how to determine the amount of Sb that can be leached from bottom ash, e.g. using the percolation test (NEN7373) and with the pH dependence test (EN 14997). The percolation test provides a value for Sb leaching at the natural pH of the bottom ash, which is typically in the range of 10 – 12, while the pH dependence test allows the determination of Sb leaching at a specific pre-set pH. Typically, Sb leaching from bottom ash is highest at a pH of (close to) 8.

[0013] Although the process according to the invention is applicable to any type of bottom ash, it is preferred that the bottom ash is incinerated bottom ash, most preferably municipal solid waste incineration (MSWI) bottom ash. MSWI bottom ash contains significant amounts of Sb. The bottom ash to be treated typically contains Sb, also referred to as "leachable Sb", which would leach into the environment if not treated. Leachable Sb is typically in the form of Sb(V). Preferably, the bottom ash to be treated according to the invention comprises aluminium, which further improves the reduction in Sb leaching by the process according to the invention, especially in view of step (a). The bottom ash to be used in the process according to the invention typically has a content of 1 – 100 g aluminium per kg bottom ash, such as 20 – 75 g/kg or most typically about 50 g/kg. Typically, a small fraction of the aluminium, such as 0.1 – 2 wt% based on total aluminium, is in metallic form. Typically, the content of metallic aluminium is 0.01 – 0.1 g Al(0) per kg bottom ash. Such amounts of Al(0) suffice for optimally performing step (a). However, MSWI bottom ash from which the (majority of) metallic aluminium is removed, e.g. in case the incineration plant has an efficient recovery system for metals that are separated from the fresh bottom ash, is also advantageously treated according to the process according to the invention. Such bottom ash, in particular the small particle size fractions (e.g. 0-2 mm), may still contain sufficient amounts of metallic aluminium for performing step (a). Bottom ash without (significant amounts of) metallic aluminium present may be treated according to the present invention.

[0014] In one embodiment, the pH of the bottom ash suspension that is subjected to step (a) is in the range of 7 – 13, preferably 7 – 9, more preferably 7.5 – 8.5, most preferably the pH is about 8. In case the pH of the bottom ash is above 10, e.g. 10 – 12, the pH may be lowered prior to step (a) by any means known in the art. In one embodiment, the bottom ash is carbonated as known in the art, prior to being subjected to step (a).

Step (a)

[0015] In step (a), an aqueous suspension of the bottom ash is provided. Suspending is typically performed by mixing the bottom ash with water to obtain an aqueous suspension of the bottom ash, herein also referred to as the bottom ash suspension. Mixing with water is preferably accomplished using water in an amount of 0.2 – 50 L per kg bottom ash, more preferably 1 – 25 L/kg, more preferably 4 – 20 L/kg, even more preferably 7 – 15 L/kg, most preferably about 10 L/kg bottom ash.

[0016] In one embodiment, the bottom ash suspension is provided in deoxygenated form, e.g. using deoxygenated water to prepare the suspension. Deoxygenated water may be prepared as known in the art, e.g. by flushing with an inert gas.

Step (b)

[0017] In step (b), green rust is added to the bottom ash suspension originating from step (a), or in other words the bottom ash originating from step (a) is mixed with green rust. Step (b) affords a mixture of the bottom ash and green rust, which is also referred to as the composition according to the invention (see below for a detailed description of the composition according to the invention). Typically, the green rust is added in the form of a suspension. Any means known in the art to mix two components, may be used in step (b). However, it is recommended to add the green rust in the form of a suspension, preferably having an as high as possible green rust concentration. Preferred concentrations of the green rust suspensions are in the range of 10 – 200 g Fe per L, more preferably 30 – 100 g/L, most preferably 50 – 75 g/L. Such green rust concentrations are especially preferred in case synthetic green rust is used, since further components that originate from the iron salt(s) that are used as starting material(s), such as sulphate and/or chloride anions, will be present in the suspension in dissolved state, and the addition thereof to bottom ash is desirably kept as low as possible. Such components may also provide leaching issues when the bottom ash is applied. To this end, the green rust suspension is preferably allowed to settle, until the solid green rust particles are sufficiently separated from the liquid that contains a high concentration of dissolved chloride and/or sulphate.

[0018] Green rust is known in the art and refers to a Fe(II)/Fe(III) mixed oxide. It may be classified as a layered double hydroxide, having layers of positively charged iron cations and relatively loosely bound anions located between the layers. It typically contains, in addition to the Fe(II) and Fe(III) cations, OH^- and O^{2-} anions, and CO_3^{2-}

anions may also be present. In green rust, the atomic ratio of Fe(II) to Fe(III) is typically about 2, but some deviation from the ideal ratio is tolerated by the process of the invention. Preferably, the atomic ratio of Fe(II) to Fe(III) is in the range of 1.5 – 2.5, more preferably 1.9 – 2, most preferably about 2. Green rust from natural sources, such as fougèrite, can be used as well as synthetic green rust, which can be prepared by mixing Fe(II) and Fe(III) (hydr)oxides in the appropriate ratio. Processes to obtain green rust are known in the art. Preferably, green rust that is prepared via the method of Schwertmann and Fechter (*Clay Mineralogy*, **1994**, 29, 87-92), or via similar methods, is used.

[0019] During step (b), the Sb(V) present in the bottom ash is allowed to be reduced to Sb(III). Herein, the green rusts reacts with the Sb(V) to for Sb(III) and at the same time Fe(II) present in green rust is oxidized to (Fe(III). However, as green rust is not stable towards O_2, it is essential that step (b) is performed under O_2-poor conditions. In other words, contact with O_2 from the environment is prevented as best as possible. As will be appreciated by the skilled person, allowing the Sb(V) to be reduced to Sb(III) involves taken necessary steps or means to avoid additional O_2 from the environment from contacting the suspension. Such means are known in the art. In the context of this invention, this may be referred to as placing the bottom ash suspension in a closed or air-tight environment, which means that gaseous components such as air may be capable of exiting the closed environment, but are prevented from entering the environment. Any means to afford such an air-tight environment as known in the art may be used, including the use of an overpressure within the environment or the use of air-tight seals. Herein, the environment is typically a container. Most conveniently, the bottom ash suspension is placed in an air-tight container. Placing of the bottom ash under such O_2-poor conditions, such as an air-tight environment, may be performed prior to or after mixing with the green rust. In order to avoid unnecessary loss of green rust by reaction with O_2, it is preferred that the suspension is placed under O_2-poor conditions as soon as possible after the mixing with the green rust, preferably not later than 1 h, more preferably not later than 30 min or not later than 15 min, most preferably not later than 5 min after the mixing with the green rust. Such exposure times to environmental O_2 does not hamper the efficacy of the present process.

[0020] The duration of step (b), during which the bottom ash is allowed to react with the added green rust and Sb(V) is allowed to be reduced to Sb(III), typically lasts for a period of 15 min – 48 hours, preferably 1 – 36 h, more preferably 16 – 30 h, most preferably about 24 hours. During this time, Sb(V) is allowed to reduce to Sb(III). During the duration of step (b), the entrance of oxygen into the bottom ash suspension should be kept limited, in order to prevent oxidation of the green rust to Fe(III) oxides. The durations as defined herein thus commence when the green rust is mixed with the bottom ash suspension or when the bottom ash suspension is placed under O_2-poor conditions, whichever occurs latest.

[0021] The mixing of bottom ash and green rust may for example occur in a closed (air-tight) tank and/or in an environment of inert gas, and is thus readily combined with existing bottom ash treatment process. The presence of oxygen during the mixing is not problematic, as this oxygen is quickly consumed by reaction with green rust. It could be needed that some additional green rust is added in step (b) to account for this loss by reaction with oxygen. The amount of green rust that is added may vary depending on the Sb(V) content of the bottom ash, but is preferably such that the added amount of Fe is 0.1 – 15 %, more preferably 0.5 – 10 %, more preferably 1 – 5 %, most preferably about 2 % on a dry mass basis, compared to the original dry bottom ash. Thus, most preferably, the content of green rust is such that 20 g Fe/kg dry bottom ash is added. In case no O_2 removal step as defined below is implemented prior to step (b), the amount of green rust that is added may be somewhat higher, typically 0.1 – 10 wt% higher, preferably 0.5 – 5 wt% higher, most preferably 1 – 2 wt% higher. Such an excess of a reactant is also referred to in the art as a sacrificial excess.

[0022] In one embodiment, no separate O_2 removal step is implemented and synthetic green rust having an atomic ratio Fe(II)/Fe(III) in the range of 1.90 – 1.99, preferably 1.95 – 1.98, is used in the process according to the invention. O_2 removal is thus performed simultaneously with step (b) by addition of this synthetic green rust. As such, the green rust will oxidize to reduce the O_2 content of the bottom ash suspension, to obtain an Fe(II)/Fe(III) ratio of about 2, which is then ideally suited to perform step (b). During the synthesis of green rust, the Fe(II)/Fe(III) ratio is easily controlled by measuring the redox potential of the suspension (see also the formation of green rust in example 1). It should be noted that addition of a Fe(II) salt to a bottom ash suspension to in situ oxidize this to green rust is not possible. The presence of bottom ash, containing many different components, prevents the formation of green rust.

[0023] The inventors found that green rust is surprisingly active in immobilizing antimony within bottom ash. Whereas prior art processes typically employ Fe(II) oxides, which slowly convert Sb(V) to Sb(III), the mixture of Fe(II) and Fe(III) in the specific structure of green rust accelerates this conversion (see also Mitsonobu et al., *Chemosphere* **2008,** *70*, 942-947). Without being bound to a theory, it is envisioned that the structure of green rust is ideally suited to accommodate Sb(V) ions, and thus could be seen as a sorbent for Sb(V). As Fe(II) ions are abundantly present within the green rust matrix, any absorbed Sb(V) atom is converted into Sb(III). Sb(III) binds stronger to the bottom ash matrix due to sorption and/or mineral formation, and is thus immobilized within the bottom ash matrix. Fe(III)-oxyhydroxides on the other hand may serve as sorbent for antimonate, but do not promote the conversion of Sb(V) to Sb(III) (Mitsonobu et al., *Environ. Sci. Technol.* **2010,** 44, 3712-3718). Moreover, when other mixtures of Fe(II) and Fe(III) are used, any conversion of Sb(V) to Sb(III) by Fe(II) remains undesirably slow. Magnetite, a Fe(II) mineral, is known to convert Sb(V) to Sb(III) (Kirsch et al., *Mineralogical Magazine* **2008,** *72* (1), 185-189), but even at high amounts of magnetite the conversion is slow (7 – 30 days). Only when such mixtures have the specific structure of green rust, the Sb(V) cations are readily absorbed and the conversion of Sb(V) to Sb(III) is significantly accelerated. Moreover, green rust is stable at a pH around 8, which is the typical pH of carbonated bottom ash. The leaching of Sb typically has a maximum at pH 8 (see: Cornelis et al., Waste Manage. 2012, 32 (2), 278-286). Green rust is thus applicable in the process according to the invention, wherein the Sb leaching of optionally carbonated bottom ash is reduced, without any problem. It should be noted that the process according to the invention also works at other pH values, including higher pH values as typically for untreated bottom ash.

[0024] Sb leaching was found to be reduced by a factor 3.3 – 9.6 by implementation of step (b), depending on the amount of green rust added (1 – 5 % Fe addition based on dry weight, respectively). Notably, this reduction ion Sb leaching does not take into account the additional effect of the optional separate O_2 removal step as defined below. This is much higher than disclosed by Mitsonobu (*Chemosphere* **2008,** *70*, 942-947), who found, using laboratory chemicals (i.e. not in context of bottom ash), that only about 25% of the Sb(V) in the solid phase and about 14% of the Sb(V) in the solution phase could be reduced to Sb(III), after which the reduction of Sb(V) stopped. The reduction percentages taught by Mitsonobu are too low for a sufficient reduction of Sb leaching, such that open application would not be possible. The present inventors found that the reduction of Sb(V) in the solid and the solution phase of a bottom ash suspension after the addition of green rust is in the order of 70 % (based on a 1 % Fe addition), which is much more complete than disclosed in Mitsonobu, even though the ratio of added green rust and total amount of Sb(V) in Mitsonobu is comparable. It is envisioned that the conditions or other components in the bottom ash or in the bottom ash suspension are much more favourable for Sb(V) reduction than can be expected based on Mitsonobu. Without being bound to a theory, it is envisioned that the specific chemical composition of the bottom ash accelerates the reduction of Sb(V). Bottom ash itself contains significant amounts of sulphate and iron, which may form additional green rust when the conditions are favourable, such as a low oxygen content and the addition of a certain amount of green rust.

Optional O_2 removal step

[0025] In a preferred embodiment, the O_2 content of the bottom ash is lowered or reduced prior to step (b). Such reduction of the O_2 content prior to the mixing with green rust enables the use of a lower amount of green rust, as less or even no green rust is lost to reaction with O_2. In other words, it is preferred that the bottom ash is subjected to O_2 removal. O_2 removal may be performed on the bottom ash suspension originating from step (a), or the bottom ash suspension is provided in deoxygenated form. Preferably, the O_2 removal is performed on the bottom ash suspension originating from step (a). The O_2 removal step affords deoxygenated or anoxic bottom ash.

[0026] The O_2 removal step can be performed in various manners, which all lead to the desired result of anoxic bottom ash. In case the O_2 removal step is performed on the bottom ash suspension, i.e. in between steps (a) and (b), O_2 may be removed by (i) adding an agent that replaces O_2, preferably an inert gas, (ii) providing an agent that reacts with O_2, preferably Al(0) and/or Fe(II) salt, or (iii) adding an agent that indirectly reduced the O_2 content, preferably a substrate for aerobic microorganisms containing sugar. Alternatively, the bottom ash suspension is provided in deoxygenated form, e.g. using deoxygenated water to prepare the suspension. Deoxygenated water may be prepared as known in the art, e.g. by flushing with an inert gas.

[0027] In embodiment (i), the suspension is flushed with an agent that replaces O_2, such as an inert gas, typically nitrogen, e.g. by bubbling the inert gas through the suspension. In embodiment (ii), an agent is provided that is capable of reacting with oxygen to obtain an oxidised species, which consumes O_2. This agent may be present within the bottom ash, such as metallic aluminium, or may be added to the bottom ash, either before, after or together with suspending the bottom ash in water. A preferred agent is green rust, since this would conveniently combine the O_2 removal step with step (b). The preferred mode for carrying out the O_2 removal step may depend on the composition of the bottom ash. In case substantial amounts of Al(0) are present in the bottom ash, it is preferred that the bottom ash is mixed with water in step (a) and subsequently placed in an air-tight environment. This allows Al(0) to react with water and oxygen that is dissolved in water, during which hydrogen gas and Al(III) oxides are formed (Vargel, C., **2004**, *Corrosion of Aluminium*, 1 ed. Elsevier Ltd, London, UK). During oxidation to Al(III), the redox potential of the bottom ash suspension is lowered. Under sufficiently low reducing conditions, the dissolved Sb(V) present in the bottom ash suspension is already partially reduced to Sb(III). Thus, step (a) is able to create reducing conditions within the bottom ash, which promotes Sb(III) formation. As Sb(V) is the main component of Sb leaching, and Sb(III) is more strongly bound to the bottom ash matrix, the implementation of step (a) already reduces the extent of leaching of Sb.

[0028] It is thus preferred that the bottom ash contains Al(0) as defined above. However, also in case no or only low levels of Al(0) would be present, the process according to the invention is capable of dramatically reducing the leaching of Sb from bottom ash. O_2 removal may then be performed by addition of an agent capable of reacting with O_2. In other words, a reducing agent is added. Preferred agents in this respect are Al(0) and Fe(II) salts, and mixtures thereof. In view of process economy, the use of Fe(II) salts is most preferred. These will react with oxygen to form Al(III) and/or Fe(III) oxides. When Al(0) is added, the same advantages are obtained, including some initial conversion of Sb(V) to Sb(III), as for the situation wherein Al(0) is present in the bottom ash to be treated. When Fe(II) salts are added to the bottom ash, they react to Fe(III) at the expense of O_2, thus reducing the O_2 content of the suspension. Any Fe(II) salt could be used to lower the O_2 content. The reducing agent in the O_2 removal step and the green rust in step (b) may be added to the suspension consecutively, equally positive results can be obtained wherein they are added to the bottom ash suspension in one go.

[0029] In embodiment (iii), the agent that is added indirectly reduces the O_2 content. Herein, the agent is a substrate (feed) for aerobic microorganisms, which is added to the bottom ash suspension. Such microorganisms are typically present in bottom ash, but may also be added together with the feed. The bottom ash suspension is kept at conditions that allow these aerobic microorganisms to convert O_2 and the substrate into energy (e.g. ATP). The substrate typically contains sugar (e.g. monomeric and/or dimeric carbohydrates), such as glucose. Oxygen is consumed by the microorganisms when they are stimulated to grow, i.e. by addition of the substrate, which thus lowers the O_2 content of the bottom ash. The O_2 content may be reduced to such an extent that the microorganisms die, which does not negatively affect the remaining of the process according to the invention.

[0030] The amount of the agent to be added depends on the amount of oxygen that needs to be removed from the bottom ash suspension. As the O_2 (almost) exclusively originates from the water that is used to prepare the suspension, the amount of O_2 present is readily calculated from the solubility thereof in water at the given conditions, which is typically about 5 – 20 mg/L.

[0031] In whatever manner the O_2 removal step is performed, the skilled person will appreciate how long this step should be continued. As the O_2 content is preferably as low as possible at the end of the O_2 removal step, this step may continue as long as desired. Typical durations of step (a) are 15 min – 48 h, such as 1 – 36 h, preferably 16 – 30 h.

[0032] Implementing the O_2 removal step ensures that green rust that is needed in step (b) is not deactivated by oxidation. Alternatively, the bottom ash suspension is deoxygenated *in situ* during step (b), by addition of additional green rust that will react with O_2 to lower the content thereof. During step (b), the O_2 content is preferably at most 0.3 mg/L of the suspension of even at most 0.1 mg/L of the suspension. In addition, making the suspension anoxic the O_2 removal step, has the advantage to allow metallic aluminium to react with water and to lower the redox potential, such that Sb(V) is already partially reduced to Sb(III). The inventors found that the O_2 removal step alone, when conducted in the presence of Al(0), either as present in the bottom ash and/or externally added, typically results in lowering of Sb leaching by a factor 2. However, the O_2 removal step alone does not lead to sufficient reduction of Sb leaching such that open application is always possible.

Step (c)

[0033] In step (c), O_2 is introduced in the mixture of bottom ash and green rust originating from step (b), or in other words the mixture is aerated. Preferably, air is introduced in the mixture. In a preferred embodiment, the mixture of green rust and bottom ash is in the form of a suspension, from which the water may be drained in step (c). As such, air is able to contact the mixture which thus leads to introduction of oxygen. Typically, the drained bottom ash is dried to enable further application thereof as known in the art.

[0034] Green rust is not stable towards O_2 and oxidises during step (c). During step (c), the oxidation state of the iron cations increases and structures like hydrous ferric oxides (HFO), goethite and lepidocrocite are formed. Such oxides are typically already present in bottom ash, such that no further (polluting) components are introduced in the bottom ash by the process according to the invention. Surprisingly, under these oxidised conditions, the re-oxidation of Sb(III) to Sb(V) was not observed. This is particularly surprisingly in light of the presence of newly formed Fe(III) minerals. Without being bound to a theory, the Sb(III) ions, which are absorbed in the green rust matrix, are believed to be incorporated into the inner structures of these newly formed iron oxides, and being embedded therein are fixed and not capable of leaching. Moreover, since these newly formed iron oxides are hardly soluble in water, even prolonged storage in a humid environment, e.g. in direct contact with rain water, does not lead to significant Sb leaching. The fixing of Sb in the bottom ash according to the process according to the invention was found to be irreversible.

[0035] The inventors found that implementing step (c) following step (b) could further reduce Sb leaching by a factor 3 to 3.5 compared to the product of step (b). In total, after step (c) the inventors found that the Sb leaching is reduced with 90 to 97%, depending on the added mount of green rust in step (b). It should be noted that the reduction in Sb leaching reported herein could not be obtained when only one of steps of (b) and (c) was performed. The interplay of the chemical processes that occur during these steps is essential for the dramatic reduction in Sb leaching.

[0036] The bottom ash that is obtained by the process according to the invention is characterized by a greatly reduced extent of Sb leaching, compared to prior art bottom ash. The bottom ash obtained herein is also referred to as the bottom ash according to the invention and is further defined below.

COMPOSITION

[0037] An important intermediary product of the process according to the invention is the mixture of bottom ash and green rust, preferably as obtainable in step (b) of the process according to the invention. The invention thus also concerns a composition comprising bottom ash and green rust. Preferably, the amount of green rust is such that it contributes 0.1 – 15 %, more preferably 0.5 – 10 %, more preferably 1 – 5 %, most preferably about 2 % Fe, based on dry weight of the bottom ash. In one embodiment, the composition is a suspension and further comprises water.

[0038] The bottom ash preferably originates from an incineration process, and may thus be referred to as incineration bottom ash, more preferably originates from municipal solid waste incineration (MSWI), and may thus be referred to as MSWI bottom ash. As the bottom ash is preferably deoxygenated prior to step (b), the mixture obtainable in step (b) may be deoxygenated. Thus, in one embodiment of the composition according to the invention, the bottom ash is deoxygenated bottom ash, more preferably the deoxygenated bottom ash obtainable by the O_2 removal step described above. Alternatively, the composition according to the invention may be referred to as a deoxygenated composition. In one embodiment, the content of oxygen, typically of dissolved oxygen, is below 1 mg/L, more preferably below 0.5 mg/L or below 0.1 mg/L, most preferably below 0.01 mg/L.

BOTTOM ASH

[0039] Because of their unprecedented low extent of Sb leaching, the bottom ash that is obtained by the process according to the first aspect of the invention distinguishes from prior art bottom ashes. In a third aspect, the invention thus concerns this bottom ash, that is obtainable by or obtained by the process according to the invention. The bottom ash according to the invention may also be referred to as “treated bottom ash”, “Sb-fixed bottom ash” or “Sb-immobilized bottom ash”. The bottom ash according to the invention preferably originates from an incineration process, and may thus be referred to as incineration bottom ash, more preferably originates from municipal solid waste incineration (MSWI), and may thus be referred to as MSWI bottom ash. The bottom ash may also be characterized as exhibiting a Sb leaching of at most 0.32 mg/kg bottom ash, preferably at most 0.25 mg/kg, more preferably at most 0.18 mg/kg and most preferably at most 0.10 mg/kg, as determined by the percolation test (NEN7373). More preferably, these values for Sb leaching are exhibited at a pH of 8, as determined by the pH dependence test (EN 14997). Most preferably, these values for Sb leaching are exhibited at all pH values in the range 4 – 12, as determined by the pH dependence test (EN 14997).

[0040] In one embodiment, the bottom ash according to the invention is defined by a reduction in Sb leaching compared to the untreated bottom ash. Such a reduction in Sb leaching is readily obtained from determining the Sb leaching of untreated bottom ash (i.e. the bottom ash that is subjected to a treatment) and of the treated bottom ash (i.e. the bottom ash that is obtained by a treatment). The Sb leaching may be determined as described herein, most preferably by the percolation test of NEN7373. Preferably, the Sb leaching is reduced by at least 90 %, more preferably by at least 95 %, most preferably by at least 99 %.

[0041] The bottom ash according to the invention typically has a significant content of Sb(III) compared to untreated ash, in which Sb is mainly present as Sb(V). After treatment, a significant portion of the Sb in the sample is present in the form of Sb(III) whereas in untreated samples the amount of Sb(III) is negligible. The atomic ratio of Sb(III)/Sb(V) in the treated bottom ash according to the invention is typically at least 9 (i.e. 90 % of Sb is Sb(III)), preferably at least 15 or at least 25 or even at least 50 or at least 100. The Sb(III)/Sb(V) atomic ratio is preferably as high as possibly, but the ratio typically does not exceed 10000. For solid bottom ash samples, the Sb(III)/Sb(V) ratio can for instance be tested with X-ray adsorption Near Structure (XANES) according to Mitsunobu (*Chemosphere* **2008,** *70*, 942-947 and *Environ. Sci. Technol.*, **2009**, 43(2), 318–323). The distribution of Sb(V) over Sb(III) in treated bottom ash is confirmed by geochemical modelling (see example 2).

[0042] The process according to the invention ensures that Sb, which is Ca-bound in untreated bottom ash, becomes Fe-bound. In other words, the bottom ash obtainable by the process according to the present invention contains Sb that is associated with Fe, typically with Fe(III). Such association may take the form of Fe-particles enriched with Sb or coated with an Sb-containing layer, or in the form of a solid solution of Sb in Fe (particles containing homogenously distributed Sb and Fe ions). Preferably, at least 90 % of the Sb present in the bottom ash according to the invention is Fe-bound, preferably at least 95 %, most preferably at least 99 %. The content of Fe-bound Sb can be determined by electron microscopy in combination with EDS spectroscopy.

USES

[0043] The bottom ash according to the invention is suitable to be used in "open application", which means that no protective measures are needed for application of the bottom ash in the environment as Sb is sufficiently contained within the bottom ash matrix. Hence, in a fourth aspect, the invention concerns the use of the bottom ash according to the invention in open applications, i.e. without the use of protective measures, such as a protective liner.

[0044] The bottom ash is especially suitable to be used in the construction industry in granular form and in open application, e.g. for the construction of embankments for roads, for parking lots, or as a filling material. It can also be mixed with a cementitious binder to obtain a monolithic product, that can be used for e.g., the construction of buildings.

Figures

[0045] Figure 1 depicts the leaching of Sb in mg/L, according to the pH dependence test EN 14997, of the bottom ash of example 1. The light gray line at 0.032 mg/L indicates the upper limit of Sb leaching for open application (recalculated from mg/kg bottom ash to mg/L suspension), as set by the Dutch Soil Quality Decree ("Besluit Bodemkwaliteit", 2007). U = untreated bottom ash at a range of different pH values. Experimental values of Sb leaching obtained in example 1 for 1%, 2 % and 5 % green rust (GR) are depicted, both for the bottom ash obtained in step (b) and obtained in step (c). These are obtained at pH = 8. Lines M depict the results of geochemical modelling experiment of example 2. Solid line M (ox) depicts the Sb leaching under oxidizing conditions as in untreated bottom ash and dashed line M (red) depicts the Sb leaching under highly reducing conditions.

[0046] Figure 2 depicts the predicted distribution of total dissolved Sb over Sb(V) and Sb(III) species, as determined by the model of example 2. Sb(III) = sum of dissolved Sb(III) species under oxidizing conditions as in untreated bottom ash (M(ox)) or under highly reducing conditions (M(red)); Sb(V) = sum of dissolved Sb(V) species under oxidizing conditions as in untreated bottom ash (M(ox)) or under highly reducing conditions (M(red)).

Examples

[0047] 15 g of bottom ash from municipal solid waste incineration plants was mixed with 150 ml of water at a liquid solid ratio (L/S) of 10 L/kg in a reactor vessel. The reactor was equipped with an acid-base titration system to control the pH at 8. This so-called pH-stat procedure follows the procedure of EN 14997. While NEN7373 is the designated test method in the Dutch Soil Quality Decree, the results from EN14997 (carried out at L/S 10) and the cumulative result of NEN7373 are mutually comparable when concentrations in mg/L from EN 14997 at the natural pH of the ash are multiplied with the L/S ratio to obtain mg/kg (e.g., Van der Sloot and Dijkstra, **2004**, ECN report no. ECN-C-04-060; Energy Research Centre of the Netherlands (ECN), Petten, The Netherlands). The EN14997 test is performed for the untreated ash at pH 2, 4, 6, 7, 8, 10.5 (natural pH without acid or base addition) and 12. The effect of the treatment on the leaching of antimony is measured using EN14997 at a single pH value (pH 8). With this system the following experiments were performed.

EXAMPLE 1

[0048] A representative sample of MSWI bottom ash (particle size up to 16 mm) was used with a typical Sb leaching of 1.19 mg/kg at the natural pH of this sample (pH 10.5) and a leaching of 2.29 mg/kg measured at pH 8, as measured with EN14997 (Figure 1). At both pH values, this emission is higher than the 0.32 mg/kg emission that is set by Dutch Soil Quality Decree. After the determination of the leaching of Sb of the untreated bottom ash, the suspension (1 kg bottom ash in 10 L water) was kept under an N_2-rich atmosphere for 24 h to create anoxic circumstances (step a). This sample did not contain reactive metallic aluminium, and the Sb leaching after 24 h was determined to be 2.36 ± 0.06 mg/kg which is not a significant change. Green rust was synthesized by dissolving $FeSO_4$ in water and maintaining the pH of the suspension with addition of NaOH to 7 – 8. The suspension was stirred while exposed to air. O_2 from the air oxidized 1/3 of the Fe(II) to Fe(III) such that an atomic ratio of Fe(II)/Fe(III) of 2 was obtained. Stirring was continued until the suspension turned green. Oxidation of 1/3 of the Fe was confirmed by measuring the redox potential (Eh) of the suspension using a Ag/AgCl-electrode. The suspension was closed to exclude O_2 when Eh rose above -0.05 V. At this redox potential, the Fe(II) in green rust starts to oxidize into Fe(III) (see: *Solid State Sciences* **2003,** *5*, 327-334). From then onwards, the suspension was kept closed from O_2 until it was used. The total Fe-concentration in the green rust-suspension was 60 g Fe per L. For step (b), 2.5, 5 and 12.5 ml of the green rust-suspension was mixed with the bottom ash suspension to achieve a total amount of added Fe of 1 wt%, 2 wt% and 5 wt%, based on dry weight of the bottom ash. The green rust was reacted for 24 h with the bottom ash. After these 24 h, the Sb leaching had decreased to 0.723, 0.592 and 0.237 mg/kg, respectively. In step (c), N_2-supply was stopped and the reactor was exposed to air. Under continuous stirring, $O_2(g)$ dissolved into the suspension. After 24 h, the Sb leaching had dropped even lower, to values of 0.240, 0.165 and 0.080 mg/kg respectively. These emissions are well below the emission limit value of 0.32 mg/kg. The treatment of the bottom ash with green rust was found to reduce the leaching of Sb by 90, 93 and 97 %, respectively, compared to the original Sb leaching.

EXAMPLE 2

[0049] The anticipated distribution of Sb(III) and Sb(V) in treated bottom ash of example 1 is confirmed by equilibrium geochemical modelling using the platform Orchestra (Meeussen, *Environ. Sci. Technol.* **2003,** *37*, 1175-1182). The modelling was performed for wide pH range to obtain information on the pH dependency of Sb leaching in the relevant pH range. The overall model approach is similar to that of Dijkstra et al. (*Applied Geochemistry*, **2008**, 23 (6), 1544-1562). Input for the model is the “available” concentration of Sb in the untreated ash, which is estimated at pH 2 (Figure 1). The solution speciation of antimony, solubility products of antimony minerals, and surface complexation parameters for sorption of Sb(V) to hydrous ferric oxides were adopted from Cornelis et al. (*Waste Management*, **2012**, 32 (2), 278-286). Furthermore, estimated surface complexation parameters for the adsorption of Sb(III) to Fe (hydr)oxides were adopted from Vithanage et al. (*J. Colloid Interface Sci.*, *2013*, 406, 217-224). Amounts of reactive iron (hydr)oxide assumed representative for MSWI bottom ash were adopted from Dijkstra et al. (*Applied Geochemistry*, **2008**, 23 (6), 1544-1562). The model prediction as depicted in Figure 1 denoted with M(ox) is calculated for oxidising redox conditions (pH+pe=15) and represents the model prediction for the untreated ash. Of the Sb in the solution phase, Sb is present almost entirely in the form of Sb(V) (Figure 2). Its solubility is controlled by the romeite-type mineral of Cornelis et al. (*Waste Management*, **2012**, 32 (2), 278-286) which is allowed to precipitate in the model, based on dissolved concentrations of Ca that are fixed to the measured value at each pH value. The dashed model curve denoted by M(red) represents the predicted equilibrium conditions after the addition of green rust (step (b)), based on the measured redox potential in the experiment (pH+pe=3.8). The predicted equilibrium dissolved concentrations of Sb under these conditions are orders of magnitude lower than under oxidised conditions (Figure 1) and consist almost entirely of Sb(III) (Figure 2), which sorbs strongly to the bottom ash matrix. The romeite-type Sb(V) mineral is predicted to be completely dissolved under these conditions.

[0050] The results of example 1 are in line with this predicted pattern but do not reach fully the predicted low concentrations. Apparently, the reaction to Sb(III) may not be complete. After oxidation in step (c), the observed leached Sb is further reduced and demonstrates that the process is irreversible. This additional effect could not be predicted by this geochemical model, as the mechanism is yet unknown.

EXAMPLE 3

[0051] In the present example, bottom ash is treated that originates from a power plant, which is the fine particle size fraction (0-2 mm) obtained as left-over after a physical separation technology. This bottom ash would normally not be used for post-treatment and application, as it is characterized by an atypical high leaching of many metals, such that it is not suitable for open application. For example, the leaching of Sb was determined to be 5.034 mg/kg at pH 8.

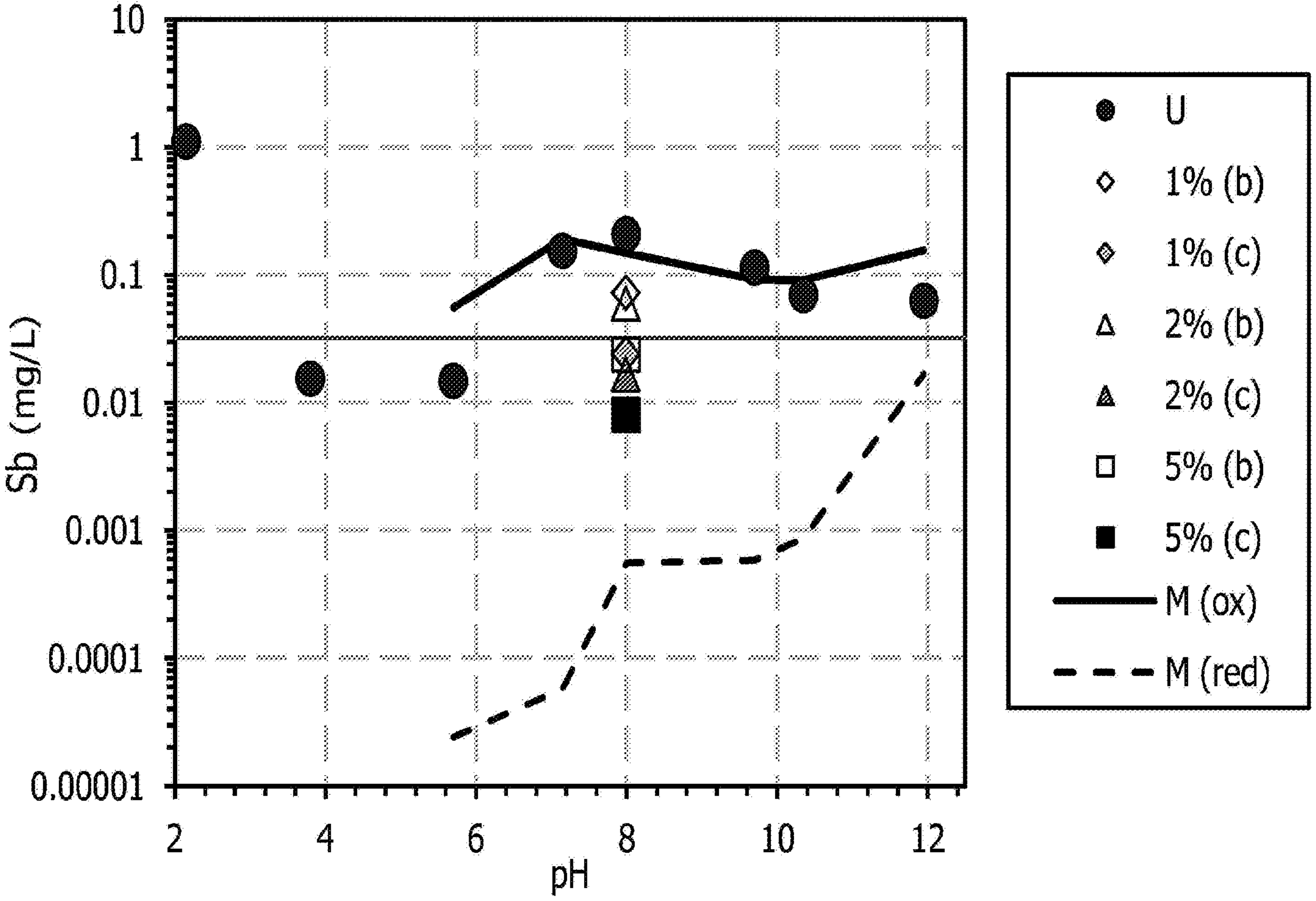
[0052] In step (a), the suspension was prepared and kept under N_2-atmosphere for 24 h as described for Example 1. In this period, Al reacted and the Sb emission reduced to 2.912 mg/kg of bottom ash. For step (b), 0.3 g of green rust, prepared according to Example 1, was added to the bottom ash suspension to achieve a total amount of added Fe of 2 wt%. The green rust was allowed to react for 24 h with the bottom ash, after which the Sb leach was decreased to 1.165 mg/kg. In step (c), N_2-supply was stopped and the reactor was exposed to air. Under continuous stirring, O_2(g) dissolved from the air into the suspension, giving oxidation of green rust to form ferric oxyhydroxides. After 24 h of oxidation, the emission of Sb was dropped to 0.988 mg/kg. The three-step treatment of the bottom ash with green rust was found to reduce the emission by 80%, which is a great improvement over prior art process for reducing leaching of bottom ash, in particular given the fact that the bottom ash sample treated herein exhibited exceptional high leaching of Sb.

Conclusies

1. Werkwijze voor het verlagen van antimoonuitloging uit bodemas, omvattende:
   (a) het verschaffen van een waterige suspensie van de bodemas;
   (b) het mengen van de bodemassuspensie afkomstig uit stap (a) met groene roest en het laten reduceren van Sb(V) tot Sb(III);
   (c) het introduceren van O_2 in het mengsel afkomstig uit stap (b).
2. Werkwijze volgens conclusie 1, waarbij de bodemas afkomstig is uit een afvalverbrandingsinstallatie.
3. Werkwijze volgens conclusie 1 or 2, waarbij de hoeveelheid groene roest zodanig is dat in stap (b) 0.1 – 15 wt% Fe, gebaseerd op drooggewicht van de bodemas, wordt toegevoegd.
4. Werkwijze volgens één der conclusies 1 tot 3, waarbij de groene roest Fe(II) en Fe(III) kationen in een atoomverhouding in het traject 1.5 – 2.5, bij voorkeur 1.9 – 2, omvat.
5. Werkwijze volgens één der conclusies 1 tot 4, waarbij het laten reduceren van Sb(V) tot Sb(III) het nemen van stappen om contact van de bodemassuspensie afkomstig uit stap (a) met O_2 uit de omgeving te vermijden, bij voorkeur het plaatsen van de suspensie in een luchtdichte omgeving waarbij voorkomen wordt dat gasvorming componenten de omgeving binnentreden, omvat.
6. Werkwijze volgens één der conclusies 1 tot 5, welke verder een O_2-verwijderstap voorafgaand aan stap (b) omvat, waarbij
   - de bodemassuspensie onderworpen wordt aan O_2-verwijdering door middel van (i) het toevoegen van een agens dat O_2 vervangt, bij voorkeur een inert gas, (ii) het verschaffen een agens dat met O_2 reageert, bij voorkeur Al(0) en/of een Fe(II) zout, of (iii) het toevoegen van een voedingsstof voor aerobe micro-organismen welke suiker omvat, of
   - de bodemassuspensie in zuurstof verarmde vorm verschaft wordt.
7. Werkwijze volgens conclusie 6, waarbij Al(0) uit de bodems zelf verschaft wordt.
8. Werkwijze volgens één der conclusies 1 tot 7, waarbij stap (b) uitgevoerd wordt door het mengen van de bodemassuspensie met een suspensie van groene rust.
9. Werkwijze volgens één der conclusies 1 tot 8, waarbij stap (c) uitgevoerd wordt draineren van een suspensie van bodemas en groene roest en lucht in contact laten komen me de gedraineerde suspensie.
10. Samenstelling omvattende bodemas en groene roest.

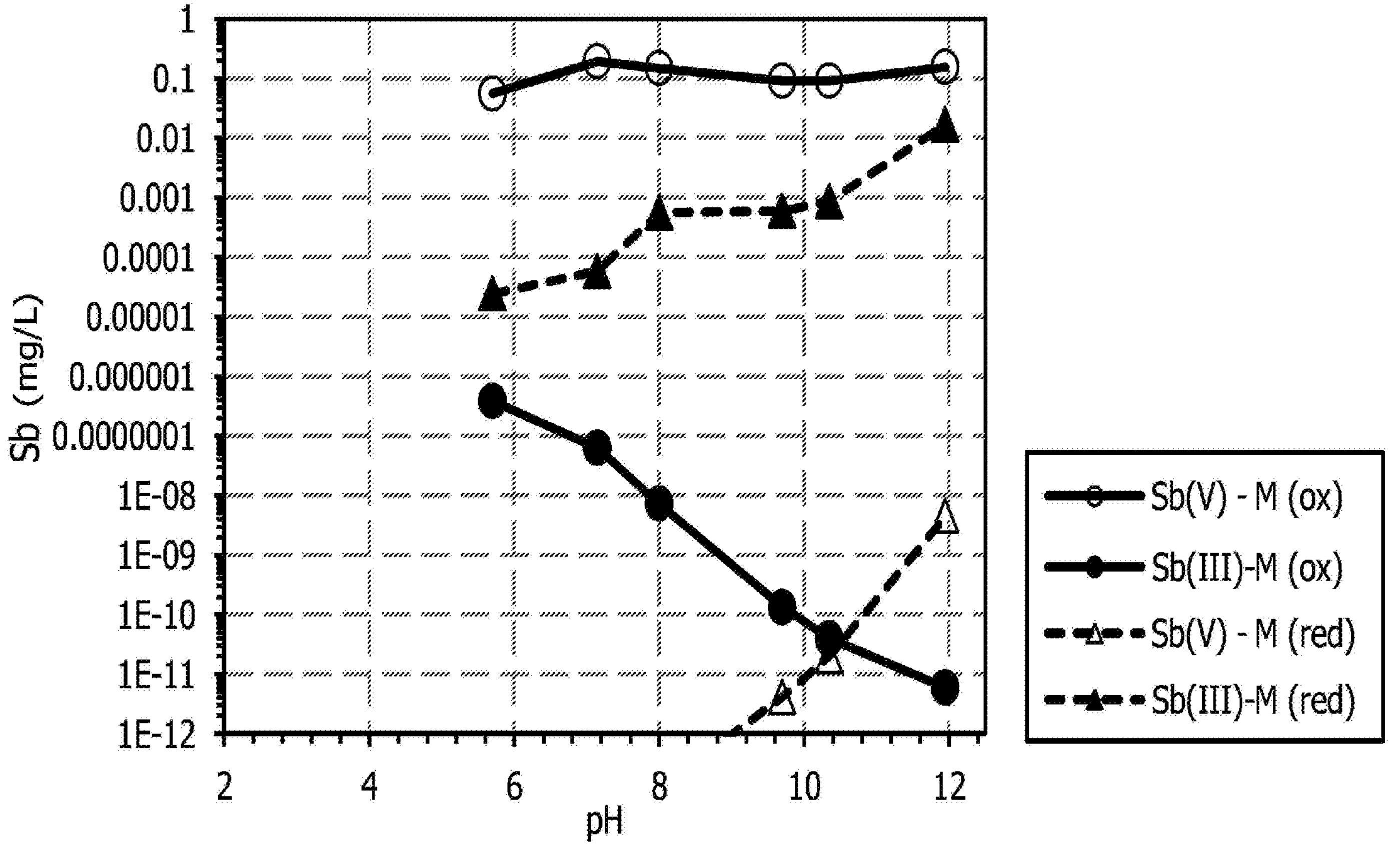
11. Samenstelling volgens conclusie 10, waarbij de hoeveelheid groene roest zodanig is dat het 0.1 – 15 wt% Fe, gebaseerd op drooggewicht van de bodemas, verschaft.
12. Samenstelling volgens conclusie 10 of 11, waarbij de bodemas afkomstig is uit een afvalverbrandingsinstallatie.
13. Bodemas verkrijgbaar door de werkwijze volgens één der conclusies 1 – 9.
14. Bodemas volgens conclusie 13, waarbij de atoomratio Sb(III)/Sb(V) ten minste 9, bij voorkeur ten minste 100 is.
15. Toepassing van een bodemas volgens conclusie 13 of 14 voor open toepassing.

Fig. 1



10
1
0.1
0.01
0.001
0.0001
0.00001
Sb (mg/L)
2
4
6
8
10
12
pH
● U
◇ 1% (b)
◈ 1% (c)
△ 2% (b)
▲ 2% (c)
□ 5% (b)
■ 5% (c)
M (ox)
M (red)

Fig. 2



Sb (mg/L)
1
0.1
0.01
0.001
0.0001
0.00001
0.000001
0.0000001
1E-08
1E-09
1E-10
1E-11
1E-12
2
4
6
8
10
12
pH
Sb(V) - M (ox)
Sb(III)-M (ox)
Sb(V) - M (red)
Sb(III)-M (red)

Abstract

The invention relates to an improved process for the treatment of bottom ash, which prevents excessive leaching of Sb and render them suitable for open application. In the process according to the invention, bottom ash is treated by (a) providing an aqueous suspension of the bottom ash; (b) mixing the bottom ash suspension originating from step (a) with green rust and allowing Sb(V) to be reduced to Sb(III); and (c) introducing O_2 into the mixture originating from step (b). The invention also concerns a mixture of bottom ash and green rust, for example as obtainable by step (b), and the treated bottom ash as obtainable by step (c), as well as the use of said bottom ash.

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE **P6058849NL**
Nederlands aanvraag nr. **2016484**	Indieningsdatum **24-03-2016**
	Ingeroepen voorrangsdatum

Aanvrager (Naam)

Stichting Energieonderzoek Centrum Nederland

Datum van het verzoek voor een onderzoek van internationaal type **31-05-2016**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN66470**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

A62D3/33;A62D3/38;A62D101/24;A62D101/43

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen
IPC	**A62D**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III. ☐ **GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES** (opmerkingen op aanvullingsblad)

IV. ☐ **GEBREK AAN EENHEID VAN UITVINDING** (opmerkingen op aanvullingsblad)

Form PCT/ISA 201 A (11/2000)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2016484

A. CLASSIFICATIE VAN HET ONDERWERP
INV. A62D3/33 A62D3/38
ADD. A62D101/24 A62D101/43

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimum documentatie (classificatie gevolgd door classificatiesymbolen)
A62D

Onderzochte andere documentatie dan de minimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data, CHEM ABS Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	WO 2005/102942 A1 (MITSUBISHI MATERIALS CORP [JP]; HAYASHI HIROSHI [JP]; TAKEUCHI HITOSHI) 3 november 2005 (2005-11-03)	1-9
Y	* bladzijde 11, regel 13 - bladzijde 12, regel 10; conclusie 8 * * bladzijde 17, regel 25 - bladzijde 18, regel 16 * ------	10-15
Y	NL 1 026 346 C2 (INSULINDE RECYCLING & MILIEU B [NL]) 25 juli 2005 (2005-07-25) * tabel 3 * ------	10-15

-/--

☒ Verdere documenten worden vermeld in het vervolg van vak C.

☒ Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

° Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid

30 november 2016

Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type

Naam en adres van de instantie

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

1

De bevoegde ambtenaar

Dalkafouki, A

Formulier PCT/ISA/201 (tweede blad) (Januari 2004)

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A	SATOSHI MITSUNOBU ET AL: "[mu]-XANES Evidence for the Reduction of Sb(V) to Sb(III) in Soil from Sb Mine Tailing", ENVIRONMENTAL SCIENCE & TECHNOLOGY, deel 44, nr. 4, 15 februari 2010 (2010-02-15), bladzijden 1281-1287, XP055324593, US ISSN: 0013-936X, DOI: 10.1021/es902942z * het gehele document * -----	1,10,13
A	SATOSHI MITSUNOBU ET AL: "Interaction of Synthetic Sulfate Green Rust with Antimony(V)", ENVIRONMENTAL SCIENCE & TECHNOLOGY, deel 43, nr. 2, 15 januari 2009 (2009-01-15), bladzijden 318-323, XP055324595, US ISSN: 0013-936X, DOI: 10.1021/es8026067 * het gehele document * -----	1,10,13
A,D	MITSUNOBU ET AL: "Abiotic reduction of antimony(V) by green rust (Fe4(II)Fe2(III)(OH)12SO4.3H2O)", CHEMOSPHERE, PERGAMON PRESS, OXFORD, GB, deel 70, nr. 5, 24 november 2007 (2007-11-24), bladzijden 942-947, XP022360846, ISSN: 0045-6535 in de aanvraag genoemd * het gehele document * -----	1,10,13
A	LEUZ AK ET AL: "Sorption of Sb(III) and Sb(V) to goethite: Influence", ENVIRONMENTAL SCIENCE & TECHNOLOGY, AMERICAN CHEMICAL SOCIETY, US, deel 40, nr. 23, 1 januari 2006 (2006-01-01), bladzijden 7277-7282, XP008182432, ISSN: 0013-936X * het gehele document * -----	1,10,13
A	SATOSHI MITSUNOBU ET AL: "Antimony (V) Incorporation into Synthetic Ferrihydrite, Goethite, and Natural Iron Oxyhydroxides", ENVIRONMENTAL SCIENCE & TECHNOLOGY, AMERICAN CHEMICAL SOCIETY, US, deel 44, nr. 10, 1 januari 2010 (2010-01-01), bladzijden 3712-3718, XP008182398, ISSN: 0013-936X, DOI: 10.1021/ES903901E [gevonden op 2010-04-28] * het gehele document * ----- -/--	1,10,13

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2016484

C.(Vervolg). VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A	SATOSHI MITSUNOBU ET AL: "Behavior of Antimony(V) during the Transformation of Ferrihydrite and Its Environmental Implications", ENVIRONMENTAL SCIENCE & TECHNOLOGY, deel 47, nr. 17, 5 augustus 2013 (2013-08-05), bladzijden 9660-9667, XP055324305, US ISSN: 0013-936X, DOI: 10.1021/es4010398 * het gehele document * -----	1,10,13

1

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek

NL 2016484

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
WO 2005102942 A1	03-11-2005	AU 2005235472 A1	03-11-2005
		CA 2555564 A1	03-11-2005
		CN 1926071 A	07-03-2007
		EP 1740504 A1	10-01-2007
		HK 1098120 A1	10-01-2014
		KR 20070004650 A	09-01-2007
		KR 20080024247 A	17-03-2008
		KR 20090007493 A	16-01-2009
		MY 148255 A	29-03-2013
		US 2007209989 A1	13-09-2007
		US 2009289016 A1	26-11-2009
		US 2010000924 A1	07-01-2010
		WO 2005102942 A1	03-11-2005
NL 1026346 C2	25-07-2005	GEEN	

WRITTEN OPINION

File No. SN66470	Filing date *(day/month/year)* 24.03.2016	Priority date *(day/month/year)*	Application No. NL2016484

International Patent Classification (IPC)
INV. A62D3/33 A62D3/38 ADD. A62D101/24 A62D101/43

Applicant
Stichting Energieonderzoek Centrum Nederland

This opinion contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the application
☐	Box No. VIII	Certain observations on the application

Examiner
Dalkafouki, A

Form NL237A (Dekblad) (July 2006)

WRITTEN OPINION

Application number
NL2016484

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	10-15
	No:	Claims	1-9
Inventive step	Yes:	Claims	
	No:	Claims	1-15
Industrial applicability	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 WO 2005/102942 A1 (MITSUBISHI MATERIALS CORP [JP]; HAYASHI HIROSHI [JP]; TAKEUCHI HITOSHI) 3 november 2005 (2005-11-03)

D2 NL 1 026 346 C2 (INSULINDE RECYCLING & MILIEU B [NL]) 25 juli 2005 (2005-07-25)

Independent claims 1,10,13

Claim 1.

The present application does not meet the criteria of patentability, because the subject-matter of claim 1 is not new.

D1 discloses (bladzijde 11, regel 13 - bladzijde 12, regel 10; conclusie 8; bladzijde 17, regel 25 - bladzijde 18, regel 16)

a method for treating wastewater to remove Sb and other heavy metals comprising :

1. adding green rust slurry in the wastewater under a non-oxidising atmosphere
2. separating the formed precipitate, further adding an alkaline compound to adjust a pH to 11 to 13 to form a strong alkaline iron-based precipitate; a step I of adding the strong alkaline iron-based precipitate to an aqueous solution of a ferrous salt
3. transforming the green rust containing the Sb ions in the more stable ferrite by oxidation.

Claims 10,13.

The subject matter of claims 10 and 13 differs from D1 which is considered to be the closest prior art, in that they claim a bottom ash treated by the method of claim 1.

The problem to be solved by the present invention may therefore be regarded as how to provide a method for eliminating Sb in bottom ash.

D2 describes a method of eliminating Sb from bottom ash by reacting that with iron hydroxide containing material

The skilled person would therefore regard it as a normal option to include this feature in the D1 described in D2 in order to solve the problem posed.

Therefor the subject-matter of claim 10 and 13 does not involve an inventive step.

Dependent claims 2-9, 11,12,14,15:

Dependent claims 2-9, 11,12,14,15 do not appear to contain any additional features which, in combination with the features of any claim to which ithey refer, meet the requirements of novelty and/or inventive step, the reasons being as follows: all the technical features are known from the prior art or are results of normal optimisation experiments