A METHOD OF TREATING AN ASH COMPOSITION

CROSS REFERENCE TO RELATED APPLICATION

The present application claims priority to Singapore application number 10202102558W filed on 12 March 2021 with the Intellectual Property Office of Singapore, the contents of which are incorporated by reference.

TECHNICAL FIELD

The present disclosure relates generally to a method of treating an ash composition. The present disclosure also relates to a method of forming a treated ash composition comprising geopolymers and the treated ash composition comprising geopolymers formed according to the method as described herein. The present disclosure also relates to a method of forming a treated ash composition comprising a plurality of core-shell particles and the treated ash composition comprising the plurality of core-shell particles formed according to the method as described herein. The present disclosure also relates to a method of preparing geopolymers from an ash composition and the geopolymers prepared according to the method as described herein. The present disclosure also relates to a method of preparing core-shell particles from an ash composition and the core-shell particles prepared according to the method as described herein.

BACKGROUND

Ashes generated from incineration in Singapore are in large amounts and are landfilled in Semakau, which is expected to be full by 2035, thus necessitating alternative disposal strategies. The dump at the landfill includes ashes from incinerating waste and non-incinerable waste as well. The ashes as such have toxic components such as heavy metals, dioxins, PAHs, PCBs etc. and hence have to be detoxified to avoid leaching issues, where the soluble toxic ash components run off into water bodies and contribute to environmental toxicity.

Conventional detoxification methods include physical, chemical, thermal and mechanical treatments, which remove or fix the heavy metals and other toxins in the ashes as to reduce leaching. Heavy metals are a big concern given their number and lethal effects and have tight

restrictions on their leaching limits with more than 15 different heavy metals being present in an ash composition.

Geopolymers are polymeric networks of mostly aluminium and silica and have been around for some time now as greener alternatives for Ordinary Portland Cement (OPC) in terms of relatively lesser CO_2 production. They are conventionally produced from suitable precursors such as ashes or slag through alkali activated reactions mostly through of sodium hydroxide or sodium silicate solutions. Another conventional method uses acid based geopolymerisation, which have been found to have superior mechanical properties. This method uses phosphoric acid mostly, which causes disposal issues post-treatment, where large quantity of phosphoric acid is health hazardous.

Acids have been used for extracting heavy metals from ashes as to minimise leaching with both organic and mineral acids having been explored. Acids like sulfuric acid, hydrochloric acid and nitric acid, citric acid etc. have been used. The problem with using such acid treatment is the use of strong acids that they are highly hazardous in nature. oxidizing, non-biodegradable or with their salts being water-insoluble.

Material coating has been tried out with ash for its treatment to facilitate its applications. Conventional coating methods use materials such as chitosan or aluminium hydroxide. The coating material used in conventional methods are unstable under different pHs and degrade under unfavourable conditions, thus, this is only workable in a narrow working range (a range of about 1-2 pH units). Chitosan is an organic polymer with a low thermal stability. It can be cleaved at a low pH. Metal hydroxides (such as aluminium hydroxide) are also pH sensitive, as they start to dissolve at a low pH. A conventional method coats rice husk ash with fluoroalkyl silane as a treatment of ashes and to convert it to a superhydrophobic material for application. However, fluorine is a highly hazardous element by itself and care has to be exercised.

Accordingly, there is a need to provide for a method of converting ashes that address one or more of the problems as described above. There is a need to provide for a method of preparing geopolymers that does not have disposal issues or require long-term exposure to high concentrations of acids. There is a need to provide for a method of leaching out heavy metal from ashes that makes use of an acid that is easier to handle, preferably non-oxidising, biodegradable or with its salts being water-soluble. There is a need to provide for a suitable and optimised coating method for ash that makes it a robust and specific adsorbent.

SUMMARY

In one aspect, the present disclosure relates to a method of treating an ash composition comprising the steps of: a) mixing said ash composition, an acid catalyst, a solvent and optionally an organosilane to form a mixture, wherein the acid catalyst is an organic acid; and b) heating the mixture of step (a) to form a treated ash composition.

Advantageously, the method may reduce the total amount of ashes, thus reducing or eliminating the need to clean ashes.

Further advantageously, the method is safe to the environment and easy to operate as an organic acid is used. The organic acid may be safely disposed. In addition, the organic acid does not require long-term exposure of the ash to it at high concentrations, given its high acid strength.

In another aspect, the present disclosure relates to a method of forming a treated ash composition comprising geopolymers, the method comprising the steps of: a) mixing an ash composition, an acid catalyst and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and b) heating the mixture of step (a) to form the treated ash composition comprising geopolymers.

Advantageously, the method may reduce the total amount of ashes, thus reducing or eliminating the need to clean ashes.

Further advantageously, the method is safe to the environment and easy to operate as an organic acid is used. The organic acid may be safely disposed. In addition, the organic acid does not require long-term exposure of the ash to it at high concentrations, given its high acid strength.

In another aspect, the present disclosure relates to a method of forming a treated ash composition comprising a plurality of core-shell particles, the method comprising the steps of: a) mixing an ash composition, an acid catalyst, an organosilane and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and b) heating the mixture of step (a) to form the treated ash composition comprising the plurality of core-shell particles.

Advantageously, the method may be used to prepare core-shell particles using ash as the ash composition that has little or no cost.

Further advantageously, the method may reduce the total amount of ashes, thus reducing or eliminating the need to clean ashes.

Still further advantageously, the method is safe to the environment and easy to operate as an organic acid is used. The organic acid may be safely disposed. In addition, the organic acid

does not require long-term exposure of the ash to it at high concentrations, given its high acid strength.

In another aspect, the present disclosure relates to a treated ash composition comprising geopolymers formed according to the method as described herein.

In another aspect, the present disclosure relates to a treated ash composition comprising a plurality of core-shell particles formed according to the method as described herein.

In another aspect, the present disclosure relates to a method of preparing geopolymers from an ash composition, comprising the steps of: a) mixing an ash composition, an acid catalyst and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and b) heating the mixture to form geopolymers.

Advantageously, the method may be used to prepare geopolymers using ash that has little or no cost.

Further advantageously, the method may reduce the total amount of ashes, thus reducing or eliminating the need to clean ashes.

Still further advantageously, the method is safe to the environment and easy to operate as an organic acid is used. The organic acid may be safely disposed. In addition, the organic acid does not require long-term exposure of the ash to it at high concentrations, given its high acid strength.

In another aspect, the present disclosure relates to a method of preparing core-shell particles from an ash composition, comprising the steps of: a) mixing an ash composition, an acid catalyst, an organosilane and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and b) heating the mixture to form core-shell particles.

Advantageously, the method may be used to prepare core-shell particles using ash as the ash composition that has little or no cost.

Further advantageously, the method may reduce the total amount of ashes, thus reducing or eliminating the need to clean ashes.

Still further advantageously, the method is safe to the environment and easy to operate as an organic acid is used. The organic acid may be safely disposed. In addition, the organic acid does not require long-term exposure of the ash to it at high concentrations, given its high acid strength.

In another aspect, the present disclosure relates to geopolymers prepared according to the method as described herein.

In another aspect, the present disclosure relates to core-shell particles prepared according to the method as described herein.

DEFINITIONS

As used herein, the term "alkyl group" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 40 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, and the like.

The term "cycloalkyl" as used herein refers to cyclic saturated aliphatic groups and includes within its meaning monovalent ("cycloalkyl"), and divalent ("cycloalkylene"), saturated, monocyclic, bicyclic, polycyclic or fused polycyclic hydrocarbon radicals having from 3 to 40 carbon atoms. Examples of cycloalkyl groups include but are not limited to cyclopropyl, 2-methylcyclopropyl, cyclobutyl, cyclopentyl, 2-methylcyclopentyl, 3-methylcyclopentyl, cyclohexyl, and the like.

The term "alkoxy" as used herein refers to straight chain or branched alkyloxy groups. Examples include methoxy, ethoxy, n-propoxy, isopropoxy, tert-butoxy, and the like.

The term "geopolymers" as used herein refers to an inorganic polymeric structure of alumino-silicates having long-range, covalently bonded, non-crystalline networks.

The term "core-shell particles" as used herein refers to particles having a solid inner core in the centre and a porous layer outside of, and enclosing the core.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value,

more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

DETAILED DESCRIPTION OF OPTIONAL EMBODIMENTS

The present disclosure relates to a method of treating an ash composition comprising the steps of:

a) mixing said ash composition, an acid catalyst, a solvent and optionally an organosilane to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture of step (a) to form a treated ash composition.

The ash composition may comprise particles having a size in the range of about 1 μm to about 5 mm, about 10 μm to about 5 mm, about 100 μm to about 5 mm, about 1 mm to about 5 mm, about 1 μm to about 1 mm, about 1 μm to about 100 μm or about 1 μm to about 10 μm.

The ash composition may comprise elements selected from the group consisting of aluminium, arsenic, barium, calcium, magnesium, silicon, strontium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium, zinc, molybdenum, titanium, zirconium, carbon, sulfur, phosphorous, sodium, potassium, beryllium, boron, cadmium, mercury, selenium, thallium and combinations thereof.

The ash composition may comprise oxides or metal salts. Non-limiting examples of the metal salts include metal halides, metal sulfates, metal nitrates or combinations thereof. The oxides may be an oxide of any of the element(s) defined above, while the metal salt may be a salt of any of the element(s) defined above which can be classified as a metal.

Therefore, the ash composition may be regarded as a composition comprising any of the element(s) defined above, oxide(s) thereof (where appropriate), salt(s) thereof (where appropriate) or a combination of at least one element(s), with at least one oxide(s) and/or at least one salt(s).

The ash composition may be derived from or regarded as "ash". Therefore, in the context of this description, the phrase "ash composition" and "ash" can be regarded as being interchangeable.

The ash composition may be an incinerated ash or an ash obtained from oil refinery. The oxides may be formed when the ash composition was being incinerated. Non-limiting examples of the ash composition include coal fly ash, wood fly ash, sewage sludge ash or combinations thereof.

The acid catalyst may have a formula of R-Y(O)-OH,

wherein R is an alkyl group or a cycloalkyl group, and

wherein Y is a -C-, -S-, or -S(O)-. Advantageously, the use of the organic acid as the acid catalyst may be less hazardous to the environment than using an inorganic acid.

The acid catalyst may be methanesulfonic acid, acetic acid or combinations thereof.

The organosilane may have a formula of $(HO\text{-}A\text{-})_2N\text{-}B\text{-}SiZ_3$,

wherein A and B are independently an alkyl group, and

wherein Z is selected from the group consisting of chlorine, bromine, iodine, an alkoxy group or combinations thereof.

Non-limiting examples of the organosilane include 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane, 3-[Bis(2-hydroxyethyl)amino]propyl-trimethoxysilane, 3-[Bis(2-hydroxyethyl)amino]propyl-trichlorosilane or combinations thereof.

The organosilane may be 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane.

When the organosilane is used, the heating step (b) may form a shell on the particles making up the ash composition such that the treated ash composition comprises a plurality of core-shell particles. The organosilane may react with the ash composition to form the core-shell particles having a core of the ash composition and a shell of the organosilane.

When the organosilane is not used, the particles making up the ash composition may condense in the heating step (b) with the elimination of water molecules and reorganise during the heating step (b), thus forming geopolymers in the presence of the acid catalyst.

Therefore, when the ash composition is treated according to this method, it results in core-shell particles or geopolymers. The treated ash composition may be more stable than an untreated ash, thus leaching its components more slowly. The treated ash composition may also have a lower

amount of toxic components after being treated according to this method. Hence, the treated ash is more environmental-friendly.

The present disclosure relates to a method of forming a treated ash composition comprising geopolymers, the method comprising the steps of:

a) mixing an ash composition, an acid catalyst and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture of step (a) to form the treated ash composition comprising geopolymers.

The ash composition may comprise particles having a size in the range of about 1 μm to about 5 mm, about 10 μm to about 5 mm, about 100 μm to about 5 mm, about 1 mm to about 5 mm, about 1 μm to about 1 mm, about 1 μm to about 100 μm or about 1 μm to about 10 μm.

The ash composition may comprise elements selected from the group consisting of aluminium, arsenic, barium, calcium, magnesium, silicon, strontium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium, zinc, molybdenum, titanium, zirconium, carbon, sulfur, phosphorous, sodium, potassium, beryllium, boron, cadmium, mercury, selenium, thallium or combinations thereof.

The ash composition may comprise oxides or metal salts. Non-limiting examples of the metal salts include metal halides, metal sulfates, metal nitrates or combinations thereof. The oxides may be an oxide of any of the element(s) defined above, while the metal salt may be a salt of any of the element(s) defined above which can be classified as a metal.

Therefore, the ash composition may be regarded as a composition comprising any of the element(s) defined above, oxide(s) thereof (where appropriate), salt(s) thereof (where appropriate) or a combination of at least one element(s), with at least one oxide(s) and/or at least one salt(s).

The ash composition may be an incinerated ash or an ash obtained from oil refinery. The oxides may be formed when the ash composition was being incinerated. Non-limiting examples of the ash composition include coal fly ash, wood fly ash, sewage sludge ash or combinations thereof.

The ash composition may be a combination of coal fly ash and wood fly ash at a weight ratio in the range of about 1:1 to about 5:1, about 2:1 to about 5:1, about 3:1 to about 5:1, about 1:1 to about 3:1, about 1:1 to about 2:1 or about 2:1 to about 3:1.

The acid catalyst may have a formula of R-Y(O)-OH,

wherein R is an alkyl group or a cycloalkyl group, and

wherein Y is a -C-, -S-, or -S(O)-.

Advantageously, the use of the organic acid as the acid catalyst may be less hazardous to the environment than using an inorganic acid.

The acid catalyst may be methanesulfonic acid.

The solvent may dissolve the acid or a salt thereof. Non-limiting examples of the solvent include water, ethanol or combinations thereof.

The ash composition and the acid catalyst may be provided at a weight ratio in the range of about 5:1 to about 20:1, about 10:1 to about 20:1 or about 5:1 to about 10:1. The ash composition and the acid catalyst may be provided at a weight ratio of about 10:1.

The ash composition and the solvent may be provided at a weight ratio in the range of about 1:5 to about 1:20, about 1:10 to about 1:20 or about 1:5 to about 1:10. The ash composition and the solvent may be provided at a weight ratio of about 1:10.

The mixing step (a) may be undertaken for a duration in the range of about 0.5 hour to about 5 hours, about 1 hour to about 5 hours, about 3 hours to about 5 hours, about 0.5 hour to about 3 hours or about 0.5 hour to about 1 hour to form the mixture.

The method may further comprise a step of adding a co-catalyst to the mixture of step (a) and stirring the mixture after the mixing step (a) but before the heating step (b).

The co-catalyst may help to expedite the preparing of geopolymers. Non-limiting examples of the co-catalyst include acetic acid, propanoic acid or combinations thereof.

In the adding step, the acid catalyst and the co-catalyst may have a weight ratio in the range of about 5:1 to about 20:1, about 10:1 to about 20:1 or about 5:1 to about 10:1. The ash composition and the acid catalyst may be provided at a weight ratio of about 10:1.

After adding the co-catalyst, the mixture may have a pH value in the range of about 4 to about 6, about 4.5 to about 6, about 5 to about 6, about 5.5 to about 6, about 4 to about 5.5, about 4 to about 5, about 4 to about 4.5 or about 4.5 to about 5.5.

The stirring may be undertaken for a duration in the range of about 1 hour to about 5 hours, about 3 hours to about 5 hours, about 1 hour to about 3 hours or about 2 hours to about 4 hours.

The heating step (b) may be undertaken at a temperature in the range of about 200 °C to about 400 °C, about 300 °C to about 400 °C, about 200 °C to about 300 °C or about 250 °C to about 350 °C.

The temperature of the heating step (b) may be reached at a ramping rate in the range of about 1 °C/minute to about 10 °C/minute, about 3 °C/minute to about 10 °C/minute, about 5 °C/minute to about 10 °C/minute, about 1 °C/minute to about 5 °C/minute or about 1 °C/minute to about 3 °C/minute.

The heating step (b) may be undertaken for a duration in the range of about 1 hour to about 5 hours, about 3 hours to about 5 hours, about 1 hour to about 3 hours or about 2 hours to about 4 hours.

In the heating step (b), the particles making up the ash composition may join together, thus forming geopolymers.

The method may further comprise a step of washing and drying the treated ash composition after the heating step (b). The treated ash composition may be washed with water.

The drying step may be undertaken at a temperature in the range of about 70 °C to about 150 °C, about 90 °C to about 150 °C, about 110 °C to about 150 °C, about 130 °C to about 150 °C, about 70 °C to about 130 °C, about 70 °C to about 110 °C, about 70 °C to about 90 °C or about 100 °C to about 120 °C.

The drying step may be undertaken for a duration in the range of about 1 hour to about 20 hours, about 5 hours to about 20 hours, about 10 hours to about 20 hours, about 15 hours to about 20 hours, about 1 hour to about 15 hours, about 1 hour to about 10 hours, about 1 hour to about 5 hours or about 10 hours to about 15 hours.

The treated ash composition comprising geopolymers may be derived from a reaction between the ash composition and the acid catalyst. The reaction at least partially converts the ash composition into aluminosilicates, which may be regarded as geopolymers.

The present disclosure relates to a method of forming a treated ash composition comprising a plurality of core-shell particles, the method comprising the steps of:

a) mixing an ash composition, an acid catalyst, an organosilane and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture of step (a) to form the treated ash composition comprising the plurality of core-shell particles.

The ash composition may comprise particles having a size in the range of about 1 μm to about 5 mm, about 10 μm to about 5 mm, about 100 μm to about 5 mm, about 1 mm to about 5 mm, about 1 μm to about 1 mm, about 1 μm to about 100 μm or about 1 μm to about 10 μm.

The ash composition may comprise elements selected from the group consisting of aluminium, arsenic, barium, calcium, magnesium, silicon, strontium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium, zinc, molybdenum, titanium, zirconium, carbon, sulfur, phosphorous, sodium, potassium, beryllium, boron, cadmium, mercury, selenium, thallium or combinations thereof.

The ash composition may comprise oxides or metal salts. Non-limiting examples of the metal salts include metal halides, metal sulfates, metal nitrates or combinations thereof. The oxides may be an oxide of any of the element(s) defined above, while the metal salt may be a salt of any of the element(s) defined above which can be classified as a metal.

The ash composition may be regarded as a composition comprising any of the element(s) defined above, oxide(s) thereof (where appropriate), salt(s) thereof (where appropriate) or a combination of at least one element(s), with at least one oxide(s) and/or at least one salt(s).

The ash composition may be an incinerated ash or an ash obtained from oil refinery. The oxides may be formed when the ash composition was being incinerated. Non-limiting examples of the ash composition include coal fly ash, wood fly ash, sewage sludge ash or combinations thereof.

The method may further comprise a step of leaching the ash composition before the mixing step (a).

In the leaching step, the ash composition may be mixed with a leaching agent in a leaching solvent. The leaching agent may be an organic acid.

The leaching agent may dissolve the metal elements in the ash to form salts thereof. The salts may be soluble in water.

Non-limiting examples of the leaching agent include methanesulfonic acid, citric acid or combinations thereof.

In the leaching step, the ash composition and the leaching agent may have a weight ratio in the range of about 5:1 to about 20:1, about 10:1 to about 20:1 or about 5:1 to about 10:1. The ash composition and the acid catalyst may be provided at a weight ratio of about 10:1.

In the leaching step, the leaching solvent may dissolve the salts of the metal elements. The leaching solvent may be water.

In the leaching step, the ash and the leaching solvent may have a weight ratio in the range of about 1:5 to about 1:20, about 1:8 to about 1:20, about 1:12 to about 1:20, about 1:15 to about 1:20, about 1:5 to about 1:15, about 1:5 to about 1:12, about 1:5 to about 1:8 or about 1:8 to about 1:12.

The leaching step may be undertaken for a duration in the range of about 2 hours to about 24 hours, about 10 hours to about 24 hours, about 20 hours to about 24 hours, about 2 hours to about 20 hours or about 2 hours to about 10 hours.

The leaching step may further comprise a step of washing and drying the ash composition after leaching.

The washing and drying step may be undertaken by washing the ash composition with water after leaching and drying the ash composition after washing at a temperature in the range of about 40 °C to about 100 °C, about 60 °C to about 100 °C, about 80 °C to about 100 °C, about 40 °C to about 80 °C or about 40 °C to about 60 °C.

In the method, the acid catalyst may have a formula of R-Y(O)-OH,

wherein R is an alkyl group or a cycloalkyl group, and

wherein Y is a -C-, -S-, or -S(O)-.

Advantageously, the use of the organic acid as the acid catalyst may be less hazardous to the environment than using an inorganic acid.

In the method, the acid catalyst may be selected from the group comprising acetic acid, propionic acid, butanoic acid, succinic acid, glutaric acid, adipic acid, levulinic acid or combinations thereof.

In the method, the acid catalyst may be acetic acid.

In the method, the solvent may have a polarity index in the range of about 12 to about 5, about 8 to about 5 or about 12 to about 8 as calculated from the solvent's dielectric constant.

Non-limiting examples of the solvent include water, isopropanol or combinations thereof.

The solvent may be a combination of water and isopropanol at a weight ratio in the range of about 90:10 to about 70:30, about 85:15 to about 70:30, about 80:20 to about 70:30, about 75:25 to about 70:30, about 90:10 to about 75:25, about 90:10 to about 80:20, about 90:10 to about 85:15 or about 85:15 to about 75:25.

The acid catalyst may be miscible with the solvent.

The organosilane may react with the ash composition to form core-shell particles having a core of the ash composition and a shell of the organosilane.

The organosilane may have a formula of $(HO\text{-}A\text{-})_2N\text{-}B\text{-}SiZ_3$,

wherein A and B are independently an alkyl group, and

wherein Z is selected from the group consisting of chlorine, bromine, iodine, an alkoxy group or combinations thereof.

Non-limiting examples of the organosilane include 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane, 3-[Bis(2-hydroxyethyl)amino]propyl-trimethoxysilane, 3-[Bis(2-hydroxyethyl)amino]propyl-trichlorosilane or combinations thereof.

In the method, the organosilane may be 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane.

In the method, the ash composition and the solvent may be provided at a weight ratio in the range of about 1:5 to about 1:20, about 1:10 to about 1:20 or about 1:5 to about 1:10. The ash and the solvent may be provided at a weight ratio of about 1:10.

In the method, the ash composition and the organosilane may be provided at a weight ratio in the range of about 2:1 to about 10:1, about 3:1 to about 10:1, about 5:1 to about 10:1, about 2:1 to about 5:1, about 2:1 to about 3:1 or about 3:1 to about 5:1.

In the method, the organosilane and the acid catalyst may be provided at a weight ratio in the range of about 10:1 to about 30:1, about 15:1 to about 30:1, about 20:1 to about 30:1, about 25:1 to about 30:1, about 10:1 to about 25:1, about 10:1 to about 20:1, about 10:1 to about 15:1 or about 15:1 to about 25:1.

In the method, the mixing step (a) may be undertaken for a duration in the range of about 30 minutes to about 2 hours, about 1 hour to about 2 hours or about 30 minutes to about 1 hour to form the mixture.

The mixing step (a) may further comprise tuning the mixture to have a pH value of about 4.

In the method, the heating step (b) may be undertaken at a temperature in the range of about 40 °C to about 100 °C, about 60 °C to about 100 °C, about 80 °C to about 100 °C, about 40 °C to about 80 °C or about 40 °C to about 60 °C.

In the method, the temperature of the heating step (b) may be reached at a ramping rate in the range of about 1 °C/minute to about 5 °C/minute, about 3 °C/minute to about 5 °C/minute or about 1 °C/minute to about 3 °C/minute.

In the method, the heating step (b) may be undertaken for a duration in the range of about 2 hours to about 24 hours, about 10 hours to about 24 hours, about 20 hours to about 24 hours, about 2 hours to about 20 hours or about 2 hours to about 10 hours.

The heating step (b) may form a shell on the particles making up the ash composition such that the treated ash composition comprises a plurality of core-shell particles. The organosilane may react with the ash composition to form the core-shell particles having a core of the particles in the ash composition and a shell of the organosilane.

The present disclosure relates to a treated ash composition comprising geopolymers formed according to the method as described herein. As mentioned above, the treated ash composition comprising geopolymers may be derived from a reaction between the ash composition and the acid catalyst. The reaction at least partially converts the ash composition into aluminosilicates, which may be regarded as geopolymers.

The present disclosure relates to a treated ash composition comprising a plurality of core-shell particles formed according to the method as described herein. As mentioned above, the core-shell particles have a core of the ash composition and a shell of the organosilane.

The present disclosure relates to a method of preparing geopolymers from an ash composition, comprising the steps of:

a) mixing an ash composition, an acid catalyst and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture to form geopolymers.

The ash composition may comprise particles having a size in the range of about 1 μm to about 5 mm, about 10 μm to about 5 mm, about 100 μm to about 5 mm, about 1 mm to about 5 mm, about 1 μm to about 1 mm, about 1 μm to about 100 μm or about 1 μm to about 10 μm.

The ash composition may comprise elements selected from the group consisting of aluminium, arsenic, barium, calcium, magnesium, silicon, strontium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium, zinc, molybdenum, titanium, zirconium, carbon, sulfur, phosphorous, sodium, potassium, beryllium, boron, cadmium, mercury, selenium, thallium or combinations thereof.

The ash composition may comprise oxides or metal salts. Non-limiting examples of the metal salts include metal halides, metal sulfates, metal nitrates or combinations thereof. The oxides may be an oxide of any of the element(s) defined above, while the metal salt may be a salt of any of the element(s) defined above which can be classified as a metal.

Therefore, the ash composition may be regarded as a composition comprising any of the element(s) defined above, oxide(s) thereof (where appropriate), salt(s) thereof (where appropriate) or a combination of at least one element(s), with at least one oxide(s) and/or at least one salt(s).

The ash composition may be an incinerated ash or an ash obtained from oil refinery. The oxides may be formed when the ash composition was being incinerated. Non-limiting examples of the ash composition include coal fly ash, wood fly ash, sewage sludge ash or combinations thereof.

The ash composition may be a combination of coal fly ash and wood fly ash at a weight ratio in the range of about 1:1 to about 5:1, about 2:1 to about 5:1, about 3:1 to about 5:1, about 1:1 to about 3:1, about 1:1 to about 2:1 or about 2:1 to about 3:1.

The acid catalyst may have a formula of R-Y(O)-OH,

wherein R is an alkyl group or a cycloalkyl group, and

wherein Y is a -C-, -S-, or -S(O)-.

Advantageously, the use of the organic acid as the acid catalyst may be less hazardous to the environment than using an inorganic acid.

The acid catalyst may dissolve the metal elements in the ash composition to form salts thereof. The salts may be soluble in water.

The acid catalyst may be methanesulfonic acid.

The solvent may dissolve the acid catalyst or a salt thereof. Non-limiting examples of the solvent include water, ethanol or combinations thereof.

The ash composition and the acid catalyst may be provided at a weight ratio in the range of about 5:1 to about 20:1, about 10:1 to about 20:1 or about 5:1 to about 10:1. The ash composition and the acid catalyst may be provided at a weight ratio of about 10:1.

The ash composition and the solvent may be provided at a weight ratio in the range of about 1:5 to about 1:20, about 1:10 to about 1:20 or about 1:5 to about 1:10. The ash composition and the solvent may be provided at a weight ratio of about 1:10.

The mixing step (a) may be undertaken for a duration in the range of about 0.5 hour to about 5 hours, about 1 hour to about 5 hours, about 3 hours to about 5 hours, about 0.5 hour to about 3 hours or about 0.5 hour to about 1 hour to form the mixture.

The method may further comprise a step of adding a co-catalyst to the mixture of step (a) and stirring the mixture after the mixing step (a) but before the heating step (b).

The co-catalyst may help to expedite the preparing of geopolymers. Non-limiting examples of the co-catalyst include acetic acid, propanoic acid or combinations thereof.

In the adding step, the acid catalyst and the co-catalyst may have a weight ratio in the range of about 5:1 to about 20:1, about 10:1 to about 20:1 or about 5:1 to about 10:1. The ash and the acid catalyst may be provided at a weight ratio of about 10:1.

After adding the co-catalyst, the mixture may have a pH value in the range of about 4 to about 6, about 4.5 to about 6, about 5 to about 6, about 5.5 to about 6, about 4 to about 5.5, about 4 to about 5, about 4 to about 4.5 or about 4.5 to about 5.5.

The stirring may be undertaken for a duration in the range of about 1 hour to about 5 hours, about 3 hours to about 5 hours, about 1 hour to about 3 hours or about 2 hours to about 4 hours.

The heating step (b) may be undertaken at a temperature in the range of about 200 °C to about 400 °C, about 300 °C to about 400 °C, about 200 °C to about 300 °C or about 250 °C to about 350 °C.

The temperature of the heating step (b) may be reached at a ramping rate in the range of about 1 °C/minute to about 10 °C/minute, about 3 °C/minute to about 10 °C/minute, about 5

°C/minute to about 10 °C/minute, about 1 °C/minute to about 5 °C/minute or about 1 °C/minute to about 3 °C/minute.

The heating step (b) may be undertaken for a duration in the range of about 1 hour to about 5 hours, about 3 hours to about 5 hours, about 1 hour to about 3 hours or about 2 hours to about 4 hours.

The method may further comprise a step of washing and drying the geopolymers after the heating step (b). The geopolymers may be washed with water.

The drying step may be undertaken at a temperature in the range of about 70 °C to about 150 °C, about 90 °C to about 150 °C, about 110 °C to about 150 °C, about 130 °C to about 150 °C, about 70 °C to about 130 °C, about 70 °C to about 110 °C, about 70 °C to about 90 °C or about 100 °C to about 120 °C.

The drying step may be undertaken for a duration in the range of about 5 hours to about 20 hours, about 10 hours to about 20 hours, about 15 hours to about 20 hours, about 5 hours to about 15 hours, about 5 hours to about 10 hours or about 10 hours to about 15 hours.

The present disclosure relates to a method of preparing core-shell particles from an ash composition, comprising the steps of:

a) mixing an ash composition, an acid catalyst, an organosilane and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture to form core-shell particles.

The ash composition may comprise particles having a size in the range of about 1 μm to about 5 mm, about 10 μm to about 5 mm, about 100 μm to about 5 mm, about 1 mm to about 5 mm, about 1 μm to about 1 mm, about 1 μm to about 100 μm or about 1 μm to about 10 μm.

The ash composition may comprise elements selected from the group consisting of aluminium, arsenic, barium, calcium, magnesium, silicon, strontium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium, zinc, molybdenum, titanium, zirconium, carbon, sulfur, phosphorous, sodium, potassium, beryllium, boron, cadmium, mercury, selenium, thallium or combinations thereof.

The ash composition may comprise oxides or metal salts. Non-limiting examples of the metal salts include metal halides, metal sulfates, metal nitrates or combinations thereof. The oxides may be an oxide of any of the element(s) defined above, while the metal salt may be a salt of any of the element(s) defined above which can be classified as a metal.

The ash composition may be regarded as a composition comprising any of the element(s) defined above, oxide(s) thereof (where appropriate), salt(s) thereof (where appropriate) or a combination of at least one element(s), with at least one oxide(s) and/or at least one salt(s).

The ash composition may be an incinerated ash or an ash obtained from oil refinery. The oxides may be formed when the ash composition was being incinerated. Non-limiting examples of the ash composition include coal fly ash, wood fly ash, sewage sludge ash or combinations thereof.

The method may further comprise a step of leaching the ash composition before the mixing step (a).

In the leaching step, the ash composition may be mixed with a leaching agent in a leaching solvent. The leaching agent may be an organic acid.

The leaching agent may dissolve the metal elements in the ash composition to form salts thereof. The salts may be soluble in water.

Non-limiting examples of the leaching agent include methanesulfonic acid, citric acid or combinations thereof.

In the leaching step, the ash composition and the leaching agent may have a weight ratio in the range of about 5:1 to about 20:1, about 10:1 to about 20:1 or about 5:1 to about 10:1. The ash composition and the acid catalyst may be provided at a weight ratio of about 10:1.

In the leaching step, the leaching solvent may dissolve the salts of the metal elements. The leaching solvent may be water.

In the leaching step, the ash composition and the leaching solvent may have a weight ratio in the range of about 3:1 to about 20:1, about 5:1 to about 20:1, about 3:1 to about 10:1, about 3:1 to about 5:1, about 5:1 to about 10:1 or about 10:1 to about 20:1

The leaching step may be undertaken for a duration in the range of about 2 hours to about 24 hours, about 10 to 24 hours, about 20 to 24 hours, about 2 to 20 hours or about 2 to 10 hours.

The leaching step may further comprise a step of washing and drying the ash composition after leaching.

The washing and drying step may be undertaken by washing the ash composition with water after leaching and drying the ash composition after washing at a temperature in the range of about 40 °C to about 100 °C, about 60 °C to about 100 °C, about 80 °C to about 100 °C, about 40 °C to about 80 °C or about 40 °C to about 60 °C.

The acid catalyst may have a formula of R-Y(O)-OH,

wherein R is an alkyl group or a cycloalkyl group, and

wherein Y is a -C-, -S-, or -S(O)-.

Advantageously, the use of the organic acid as the acid catalyst may be less hazardous to the environment than using an inorganic acid.

The acid catalyst may be selected from the group comprising acetic acid, propionic acid, butanoic acid, succinic acid, glutaric acid, adipic acid, levulinic acid or combinations thereof.

The acid catalyst may be acetic acid.

The solvent may have a polarity index in the range of about 12 to about 5, about 8 to about 5 or about 12 to about 8 as calculated from the solvent's dielectric constant.

Non-limiting examples of the solvent include water, isopropanol or combinations thereof.

The solvent may be a combination of water and isopropanol at a weight ratio in the range of about 90:10 to about 70:30, about 85:15 to about 70:30, about 80:20 to about 70:30, about 75:25 to about 70:30, about 90:10 to about 75:25, about 90:10 to about 80:20, about 90:10 to about 85:15 or about 85:15 to about 75:25.

The acid catalyst may be miscible with the solvent.

The organosilane may react with the ash to form core-shell particles having a core of the ash and a shell of the organosilane.

The organosilane may have a formula of $(HO\text{-}A\text{-})_2N\text{-}B\text{-}SiZ_3$,

wherein A and B are independently an alkyl group, and

wherein Z is selected from the group consisting of chlorine, bromine, iodine, an alkoxy group or combinations thereof.

Non-limiting examples of the organosilane include 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane, 3-[Bis(2-hydroxyethyl)amino]propyl-trimethoxysilane, 3-[Bis(2-hydroxyethyl)amino]propyl-trichlorosilane or combinations thereof.

The organosilane may be 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane.

The ash composition and the solvent may be provided at a weight ratio in the range of about 1:5 to about 1:20, about 1:10 to about 1:20 or about 1:5 to about 1:10. The ash composition and the solvent may be provided at a weight ratio of about 1:10.

The ash composition and the organosilane may be provided at a weight ratio in the range of about 2:1 to about 10:1, about 3:1 to about 10:1, about 5:1 to about 10:1, about 2:1 to about 5:1, about 2:1 to about 3:1 or about 3:1 to about 5:1.

The organosilane and the acid catalyst may be provided at a weight ratio in the range of about 10:1 to about 30:1, about 15:1 to about 30:1, about 20:1 to about 30:1, about 25:1 to about

30:1, about 10:1 to about 25:1, about 10:1 to about 20:1, about 10:1 to about 15:1 or about 15:1 to about 25:1.

The mixing step (a) may be undertaken for a duration in the range of about 30 minutes to about 2 hours, about 1 hour to about 2 hours or about 30 minutes to about 1 hour to form the mixture.

The mixing step (a) may further comprise tuning the mixture to have a pH value of about 4.

The heating step (b) may be undertaken at a temperature in the range of about 40 °C to about 100 °C, about 60 °C to about 100 °C, about 80 °C to about 100 °C, about 40 °C to about 80 °C or about 40 °C to about 60 °C.

The temperature of the heating step (b) may be reached at a ramping rate in the range of about 1 °C/minute to about 5 °C/minute, about 3 °C/minute to about 5 °C/minute or about 1 °C/minute to about 3 °C/minute.

The heating step (b) may be undertaken for a duration in the range of about 2 hours to about 24 hours, about 10 hours to about 24 hours, about 20 hours to about 24 hours, about 2 hours to about 20 hours or about 2 hours to about 10 hours.

The present disclosure relates to geopolymers prepared according to the method as described herein. As mentioned above, the treated ash composition comprising geopolymers may be derived from a reaction between the ash composition and the acid catalyst. The reaction at least partially converts the ash composition into aluminosilicates, which may be regarded as geopolymers.

The present disclosure relates to core-shell particles prepared according to the method as described herein. As mentioned above, the core-shell particles have a core of the ash composition and a shell of the organosilane.

In one embodiment, there is provided a method of developing geopolymers from coal ash and fly ash, comprising the steps of:

a) dissolving a catalyst in a solvent to form a clear solution;

b) adding coal ash and fly ash to the clear solution of step (a) to form a mixture and stirring the mixture;

c) adding a co-catalyst to the mixture of step (b) and stirring the mixture to obtain an added mixture;

d) heating the added mixture of step (c) to obtain a heated mixture;

e) washing the heated mixture of step (d) with water to obtain a washed mixture; and

f) drying the washed mixture of step (e) to obtain geopolymers.

In one embodiment, the adding step (b) comprises providing the ash and the catalyst at a weight ratio of 10:1.

In one embodiment, the adding step (b) comprises stirring the mixture for 1 hour.

In one embodiment, the adding step (c) comprises providing the catalyst and the co-catalyst at a weight ratio of 1:0.1.

In one embodiment, the adding step (b) comprises providing the ash and the solvent at a weight ratio of 1:10.

In one embodiment, the added mixture of step (c) may have a pH value of about 5.

In one embodiment, the adding step (c) comprises stirring the mixture for 3 hours.

In one embodiment, the heating step (d) is undertaken wherein the ramping rate is 5 °C/minute.

In one embodiment, the heating step (d) comprises heating the added mixture of step (c) at 300 °C.

In one embodiment, the heating step (d) comprises heating the added mixture of step (c) for 3 hours.

In one embodiment, the heating step (d) comprises heating the added mixture of step (c) at a ramping range in the range of 1 to 5 °C/minute.

In one embodiment, the heating step (d) is undertaken in an autoclave.

In one embodiment, the coal ash and fly ash of the adding step (b) are obtained from an oil refinery.

In one embodiment, the catalyst of the dissolving step (a) is methanesulfonic acid.

In one embodiment, the co-catalyst of the adding step (c) is acetic acid.

In one embodiment, the solvent of the dissolving step (a) is selected from the group consisting of water, ethanol and combinations thereof.

In one embodiment, the drying step (f) is undertaken at 110 °C.

In one embodiment, there is provided a method of forming a core-shell ash from a leached ash, comprising the steps of :

a) leaching an ash by a leaching agent to obtain a leached ash;

b) mixing the leached ash of step (a) and a silane agent in a solvent to obtain a mixture;

c) adding a catalyst to the mixture of step (b) and stirring the mixture for an hour to obtain a crude ash; and

d) heating the crude ash to obtain the core-shell ash.

In one embodiment, the leaching step (a) comprises providing the ash and the leaching agent at a weight ratio of 1:0.1.

In one embodiment, the mixing step (b) comprises providing the ash and the silane agent at a weight ratio of 1:0.25.

In one embodiment, the silane agent of the mixing step (b) is 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane.

In one embodiment, the catalyst of the adding step (c) is acetic acid.

In one embodiment, the solvent of the mixing step (b) is selected from the group consisting of water, isopropanol or combinations thereof.

In one embodiment, the combination of the solvent of the mixing step (b) consists of two solvents provided at a weight ratio of 80:20.

In one embodiment, the heating step (d) comprises heating at a ramping rate in the range of 1 °C to 5 °C.

In one embodiment, the heating step (d) is undertaken at 50 °C.

In one embodiment, the heating step (d) is undertaken for 4 hours.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate a disclosed embodiment and serve to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of limits of the invention.

Fig. 1 shows a schematic diagram of methods of processing ashes (2) using a green acid (4). Under the catalysis of the green acid (4), such as methanesulfonic acid, ashes (2) may be made into geopolymers via a hydrothermal reaction. The green acid (4) may further be used to catalyse coating of a coating material (6), such as an orgranosilane, onto the ashes (2) to lock metals from the ashes (2) into core-shell particles (8). The core-shell particles (8) may be used to remove specific metal pollutants from waste (14). The core-shell particles (8) would then be bound to the specific metal pollutants to form a bound structure (10).

Fig. 2 shows scanning electron microscope (SEM) images of (a) coal fly ash (CFA); (b) wood fly ash (WFA); (c) sewage sludge ash (SSA); (d) geopolymers (GP); (e) coal fly ash leached by methanesulfonic acid (A-CFA); (f) wood fly ash leached by methanesulfonic acid (A-WFA); (g) sewage sludge ash leached by methanesulfonic acid (A-SSA); (h) coal fly ash coated with an organosilane (C-CFA); (i) wood fly ash coated with an organosilane (C-WFA); and (j) sewage

sludge ash coated with an organosilane (C-SSA). The SEM images shown in this figure were taken with 2000 × magnification. All scale bars correspond to 10 μm.

Fig. 3 shows transmission electron microscope (TEM) images of (a) coal fly ash (CFA); (b) wood fly ash (WFA); (c) sewage sludge ash (SSA); (d) coal fly ash coated with an organosilane (C-CFA); (e) wood fly ash coated with an organosilane (C-WFA); and (f) sewage sludge ash coated with an organosilane (C-SSA). The TEM images shown in this figure were taken with 4000x magnification.

Fig. 4 shows Fourier-transform infrared (FTIR) spectroscopy images of coal fly ash (CFA); wood fly ash (WFA); and geopolymers (GP).

Fig. 5 shows Fourier-transform infrared (FTIR) spectroscopy images of untreated, methanesulfonic acid leached or organosilane coated ash. Curves in Fig. 5(a) are coal fly ash (CFA); coal fly ash leached by methanesulfonic acid (A-CFA); and coal fly ash coated with an organosilane (C-CFA). Curves in Fig. 5(b) are wood fly ash (WFA); wood fly ash leached by methanesulfonic acid (A-WFA); and wood fly ash coated with an organosilane (C-WFA). Curves in Fig. 5(c) are sewage sludge ash (SSA); sewage sludge ash leached by methanesulfonic acid (A-SSA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 6 shows X-ray diffraction (XRD) patterns of (a) coal fly ash (CFA); (b) wood fly ash (WFA); (c) geopolymers (GP); and (d) sewage sludge ash (SSA). The peak labels correspond to feldspar (F), whitlockite (W), quartz (Q), mullite (M), alumina (Al), calcium sulfate (CS), calcium hydrogen phosphate hydrate (CHP), halite (H), albite (A), gehlenite (G), and calcite (C).

Fig. 7 shows X-ray diffraction (XRD) patterns of (a) coal fly ash (CFA); (b) wood fly ash (WFA); (c) sewage sludge ash (SSA); (d) coal fly ash leached by methanesulfonic acid (A-CFA); (e) wood fly ash leached by methanesulfonic acid (A-WFA); (f) sewage sludge ash leached by methanesulfonic acid (A-SSA); (g) coal fly ash coated with an organosilane (C-CFA); (h) wood fly ash coated with an organosilane (C-WFA); and (i) sewage sludge ash coated with an organosilane (C-SSA).

Fig. 8 shows a thermogravimetric analysis graph of untreated and processed ash. Curves in the graph are coal fly ash (CFA); wood fly ash (WFA); sewage sludge ash (SSA); coal fly ash leached by methanesulfonic acid (A-CFA); wood fly ash leached by methanesulfonic acid (A-WFA); sewage sludge ash leached by methanesulfonic acid (A-SSA); coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 9 shows elemental compositions of leachates from untreated, methanesulfonic acid-leached or organosilane-coated ash.

Fig. 10 shows a chart of marine toxicity testing results, measured as the relative portion of barnacle or artemia that died after treating with untreated or treated ash. Barnacle and artemia were treated with seawater (control); coal fly ash (CFA); wood fly ash (WFA); sewage sludge ash (SSA); coal fly ash leached by methanesulfonic acid (A-CFA); wood fly ash leached by methanesulfonic acid (A-WFA); sewage sludge ash leached by methanesulfonic acid (A-SSA); coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 11 shows charts of percentage removal of metal elements from solutions of single metal ions (Fig. 11(a) to Fig. 11(c)) or mixed metal ions (Fig. 11(d) and Fig. 11(e)) after treating with 10 mg ash or geopolymers. All metal ions had a concentration of 100 ppm before treating. The solutions were treated with (a) coal fly ash (CFA); (b) wood fly ash (WFA); or (c) geopolymers (GP). "As1" and "As2" are arsenite (+3 oxidation state) and arsenate (+5 oxidation sate), respectively. Fig. 11(d) shows a chart of percentage removal of metal cations after treating with ash or geopolymers. Fig. 11(e) shows a chart of percentage removal of metal anions after treating with ash or geopolymers.

Fig. 12 shows charts of percentage removal of metal elements from solutions of single metal ions after treating with 10 mg untreated ash or treated ash. All metal ions had a concentration of 100 ppm before treating. The solutions were treated with (a) coal fly ash (CFA); (b) wood fly ash (WFA); (c) sewage sludge ash (SSA); (d) coal fly ash leached by methanesulfonic acid (A-CFA); (e) wood fly ash leached by methanesulfonic acid (A-WFA); (f) sewage sludge ash leached by methanesulfonic acid (A-SSA); (g) coal fly ash coated with an organosilane (C-CFA); (h) wood fly ash coated with an organosilane (C-WFA); and (i) sewage sludge ash coated with an organosilane (C-SSA). "As1" and "As2" are arsenite (+3 oxidation state) and arsenate (+5 oxidation state), respectively.

Fig. 13 shows charts of percentage removal of metal elements from solutions (a) a mixture of metal cations; or (b) a mixture of metal anions after treating with 10 mg untreated ash or treated ash. All metal ions had a concentration of 100 ppm before treating. The solutions were treated with coal fly ash (CFA); wood fly ash (WFA); sewage sludge ash (SSA); coal fly ash leached by methanesulfonic acid (A-CFA); wood fly ash leached by methanesulfonic acid (A-WFA); sewage sludge ash leached by methanesulfonic acid (A-SSA); coal fly ash coated with an organosilane (C-

CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 14 shows charts of percentage adsorption from solutions of single elements in their cationic form using (a) C-CFA (Fe, Pb, As and Zn); (b) C-WFA (Fe, Pb, Ag and Co); or (c) C-SSA (Fe, Pb, Cd and Zn) after varying durations of 1, 3, 5, 10, 20 and 30 minute(s) and 1, 2, 3, 6 12, 18 and 24 hour(s). All ions had a concentration of 100 ppm before treating. The solutions were treated with coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 15 shows charts of percentage adsorption of: Fe and Pb by (a) C-CFA, (b) C-WFA and (c) C-SSA from a solution of multiple metal elements in their cationic form (Al, Cd, Co, Cu, Fe, Pb, Mn, Ni and Zn); and Cr and Mo by (d) C-CFA, (e) C-WFA and (f) C-SSA from a solution of multiple elements in their anionic form (As, Se, Cr and Mo) after varying durations of 1, 3, 5, 10, 20 and 30 minute(s) and 1, 2, 3, 6 12, 18 and 24 hour(s). All ions had a concentration of 100 ppm before treating. The solutions were treated with coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewagesludge ash coated with an organosilane (C-SSA).

Fig. 16 shows charts of percentage adsorption of Fe and Pb from solutions of single metal elements in their cationic form using 3 different coated size fractions: (a) C-CFA (< 50 μm, 50 to 75 μm and 75 to 100 μm); (b) C-WFA (< 100 μm, 100 to 500 μm and 500 to 1000 μm); and (c) C-SSA (< 100 μm, 100 to 500 μm and 500 to 1000 μm) for a duration of 3 hours. All metal ions had a concentration of 100 ppm before treating. The solutions were treated with coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 17 shows charts of percentage adsorption of: (a) to (c) Fe and Pb from a solution of multiple metal elements in their cationic form (Al, Cd, Co, Cu, Fe, Pb, Mn, Ni and Zn); and (d) to (f) Cr and Mo from a solution of multiple elements in their anionic form (As, Se, Cr and Mo) using 3 different coated size fractions. Fig. 17(a) and 17(d) are results from treatment by C-CFA (< 50 μm, 50 to 75 μm and 75 to 100 μm); Fig. 17(b) and 17(e) are results from treatment by C-WFA (< 100 μm, 100 to 500 μm and 500 to 1000 μm); and Fig. 17(c) and 17(f) are results from treatment by C-SSA (< 100 μm, 100 to 500 μm and 500 to 1000 μm) for a duration of 3 hours. All ions had a concentration of 100 ppm before treating. The solutions were treated with coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 18 shows charts of percentage adsorption of Fe, Pb, Cr and Mo from a solution of single metal elements in their cationic form in the presence of common interfering anions. Anions for Fe are nitrate (NO_3^-), chloride (Cl^-) and sulfate (SO_4^{2-}); anions for Pb are nitrate (NO_3^-), chloride (Cl^-) and acetate (OAc^-); anions for Cr are nitrate (NO_3^-), acetate (OAc^-) and sulfate (SO_4^{2-}); and anions for Mo are nitrate (NO_3^-), chloride (Cl^-) and sulfate (SO_4^{2-}). The solutions were treated for a duration of 3 hours. All metal ions had a concentration of 100 ppm before treating. The solutions were treated with coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

Fig. 19 shows charts of percentage adsorption of: Fe and Pb by (a) C-CFA, (b) C-WFA and (c) C-SSA from a solution of multiple metal elements in their cationic form (Al, Cd, Co, Cu, Fe, Pb, Mn, Ni and Zn) and Cr and Mo by (d) C-CFA, (e) C-WFA and (f) C-SSA from a solution of multiple elements in their anionic form (As, Se, Cr and Mo). The solutions were treated for a duration of 3 hours for 5 cycles of adsorption after the adsorbent was regenerated using NaOH. All ions had a concentration of 100 ppm before treating. The solutions were treated with coal fly ash coated with an organosilane (C-CFA); wood fly ash coated with an organosilane (C-WFA); and sewage sludge ash coated with an organosilane (C-SSA).

EXAMPLES

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1: Synthesis of Geopolymers from Ash

Coal fly ash (received from Sembcorp Industry, Singapore) and wood fly ash (received from Sembcorp Industry, Singapore) were mixed (10 g, 7:3 weight ratio) with methanesulfonic acid (MSA, 30 mL, purchased from Sigma Aldrich Pte Ltd, Singapore) at 200 °C for 4 hours to facilitate acid activated alumina-silicate geopolymer formation through a hydrothermal process. The geopolymers thus formed were washed with 200 mL of water for 4 times and dried in an oven at 100 °C for 4 hours.

Example 2: Silane Coating of Ash

Coal fly ash, wood fly ash and sewage sludge ash (sewage sludge ash was received from Eco Special Waste Management, Singapore, 4 g of each ash was used) were treated with 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane (purchased from Sigma Aldrich Pte Ltd, Singapore, 5 mL) using isopropanol (purchased from Sigma Aldrich Pte Ltd, Singapore, 80 mL) and water (obtained from Milli Q water system, 20 mL) as solvent and glacial acetic acid (purchased from Sigma Aldrich Pte Ltd, Singapore, 0.5 mL) as catalyst for coating reactions. The reactions were kept at pH 4 using HCl (1 M, diluted from 37 weight % HCl purchased from Sigma Aldrich, Singapore) for optimal reactivity.

Comparative Example 1: Synthesis of Acid-Leached Ash

Coal fly ash, wood fly ash and sewage sludge ash (10 g) were leached using methanesulfonic acid (1 M, 100 mL) at 25 °C for 12 hours for removal of heavy metals. The acid-leached ash was washed with 200 mL of water for 4 times and dried in an oven at 100 °C for 4 hours.

Example 3: Morphology and Chemistry of Untreated and Treated Ash

Surface area of the untreated coal fly ash, wood fly ash and sewage sludge ash and treated ash according to the Examples above was measured using Quantachrome Autosorb iQ C-XR. All samples were degassed at 300 °C for 6 hours before the N_2 sorption analysis (see Table 1). Functional groups of the samples were analyzed by Fourier-transform infrared (FTIR) spectra, which were measured at wavenumbers between 4000 and 400 cm^{-1} on a Bruker Vertex 70 spectrometer with a Platinum attenuated total reflection (ATR) module. X-ray diffraction (XRD) patterns were characterized on a Bruker D8 Advance powder X-ray diffractometer. The morphology of the samples was examined by field-emission scanning electron microscope (FESEM) (JEOL, JSM-7610F) at an accelerating voltage of 20 kV, and high resolution field-emission transmission electron microscope (FETEM) (JEM-2100F) at an accelerating voltage of 200 kV. An elemental analyzer (EA, ThermoFisher Scientific FlashSmart CHNS Elemental Analyser) was used to investigate the composition of the samples. Thermal stability of the materials was measured at temperatures increasing from 30 to 750 °C at a ramping rate of 10 °C min^{-1} under nitrogen atmosphere on a Perkin Elmer SII (Diamond series).

Ashes from difference sources were converted to non-hazardous materials for applications as described herein (see Fig. 1). Fig. 2 shows that coal fly ash before treatment consisted of spherical micron (a few tens) sized particles (Fig. 2(a)), while the wood fly ash was more fibrous

in nature with a few spherical particles also present (Fig. 2(b)). The geopolymer was a mixture of structures predominated by spherical particles because of the high ratio of coal fly ash used in the reacting mixture (Fig. 2(d)). Sewage sludge ash has a bigger particle size distribution in the range of a hundreds of microns with particles measuring up to a few mm in size (Fig. 2(c)). The MSA treated (Fig. 2(e) to Fig. 2(g)) and organosilane coated ashes (Fig. 2(h) to Fig. 2(j)) displayed similar morphology and size to the untreated ash.

The particle size and morphology of the coal fly ash (CFA) and wood fly ash (WFA) were examined using HR-TEM as well and it could be seen that the CFA was clearly spherical, dense and about a few microns in size (Fig. 3(a)), while WFA was elongated with strands in the size range of a few tens of microns and of low density (Fig. 3(b)). Sewage sludge ash (SSA) had a dense network structurally with no particle shape (Fig. 3(c)). The organosilane coated ashes (CFA, Fig. 3(d); WFA, Fig. 3(e); and SSA, Fig. 3(f)) resembled their respective untreated ashes morphologically (CFA, Fig. 3(a); WFA, Fig. 3(b); and SSA, Fig. 3(c)).

Table 1. Surface Area of Untreated, Acid-Leached and Coated Ash.

Sample	Surface Area (m^2/g)
CFA	2.014
WFA	17.863
SSA	5.327
GP	31.411
A-CFA	0.064
A-WFA	58.710
A-SSA	64.252
C-CFA	2.121
C-WFA	17.793
C-SSA	6.859

In Table 1, CFA represents coal fly ash; WFA represents wood fly ash; SSA represents sewage sludge ash; GP represents geopolymers; A-CFA represents coal fly ash leached by methanesulfonic acid; A-WFA represents wood fly ash leached by methanesulfonic acid; A-SSA represents sewage sludge ash leached by methanesulfonic acid; C-CFA represents coal fly ash coated by an organosilane; C-WFA represents wood fly ash coated by an organosilane; and C-SSA represents sewage sludge ash coated by an organosilane.

As can be seen from Table 1, CFA had a very low surface area. WFA had a surface area of about 8.5 times that of CFA and for SSA the surface area was 2.5 times higher than that of CFA.

The geopolymers exhibited a high surface area because of the hydrothermal conditions used and also the use of MSA which removed heavy metals apart from its catalytic role. As for the acid-treated ash, the surface area increased multiple folds (except for coal fly ash) due to the degradative nature of acid action, which could be due to partial removal of materials such as calcite and dissolution of alkali based compounds while coated samples exhibited a slight increase in surface area due to introduction of the organosilane groups.

FTIR spectra of the CFA, WFA and GP are shown in Fig. 4. A peak at 450 cm^{-1} corresponded to Si-O-Si bending; peaks at 770 and 610 cm^{-1} were due to Si-O-Si and Al-O-Si symmetric stretching and a peak at 1050 cm^{-1} was attributed to Si-O-Si and Al-O-Si asymmetric stretching, the presence of geopolymerisation was identified through the appearance of a peak at around 995 cm^{-1}, which could be due to the partial substitution of Si by Al. Peaks at around 3450 cm^{-1} were due to O-H vibrations.

In Fig. 5, FTIR spectra of SSA showed characteristic peaks at 460 and 610 cm^{-1}, corresponding to Si-O-Si bending and Si-O-Al stretching vibration similar to CFA & WFA. Peaks at 1042 cm^{-1} were due to Si-O-Si and Al-O-Si asymmetric stretching and multiple small peaks below 900 cm^{-1} were due to metal-O vibrations, because oxides and hydroxides were mostly present in ashes due to the incineration process.

FTIR spectra of the treated ashes showed no modifications of the functional groups on the ashes and both the acid leached and the coated ashes exhibit similar FTIR patterns as the untreated ashes (Fig. 5(a) to Fig. 5(c)).

As can be seen from Fig. 6, CFA had the following minerals in it: silica, aragonite ($CaCO_3$) and aluminium oxide, albite and mullite, while WFA showed quartz, calcium carbonate, calcium sulfate, calcium hydrogen phosphate. X-ray diffractogram of the geopolymers showed the presence of aluminosilicates like gehlenite ($Ca_2Al_2SiO_7$) (an indicator for the formation of geopolymers) apart from albite ($NaAlSi_3O_8$), that was already present in CFA. In SSA (Fig. 6(d)), XRD showed the presence of the following minerals: calcite ($CaCO_3$) at 23, 40 and 50, quartz (27,47 and 60), and other minerals such as whitlockite (calcium phosphate) at 22, 28 and 33; alumina (Al_2O_3), feldspar (aluminum based silicate) and gypsum (calcium sulphate). A peak at 68 was due to the alumina, gypsum, maghemite and feldspar. These were characteristic peaks of sewage sludge ash that have been observed in previous studies.

XRD of the methanesulfonic acid leached ashes showed that there were no new mineral phases formed post-treatment (Fig. 7). The leached ashes showed a similar XRD pattern to that of

untreated ash, which was expected as acid leaching dissolved heavy metals purely, rather than affecting the crystalline phases.

The thermal stability of ashes is shown in Fig. 8. Untreated coal fly ash, acid-leached coal fly ash, Untreated sewage sludge ash and acid-leached sewage sludge ash did not show any weight loss when heated at temperatures up to 800 °C due to the absence of thermally decomposed organic moieties. After the coating with 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane over untreated coal fly ash or sewage sludge ash, the decomposition of organic groups present over the ashes started at 150 °C up to 550 °C with weight loss of up to 4 to 6 %. This clearly indicated the coating of organosilane groups over the ash. The decomposition of untreated wood fly ash and leached wood fly ash started at 150 °C due to the organic content present in the ashes and had around 15 % of weight loss after heating. After the coating with organosilane the weight loss percentage increased when heating between 150 °C and 550 °C, which was due to the coated organic components. The thermal stability of the coating material over ashes was sufficiently high to withstand heating at temperatures up to 150 °C, thus the coated ashes were sufficiently stable for use as an adsorbent for water treatment application.

Example 4: Leaching of Untreated and Acid-Leached Ash

Untreated and treated ashes were subjected to leaching using DI water (obtained from Milli Q water system) and seawater (at 27 Practical Salinity Unit (PSU)) at a liquid-to-solid (L/S) ratio of 10, based on EN 12457-2 to determine heavy metal contents. The seawater was obtained from Tropical Marine Science Institute (TMSI) at St Johns Island, Singapore. The seawater had been aged in the dark for at least one month and subsequently filtered with a 0.2 µm sterilized filter before being used in this example. Leachates were filtered through a 0.45 µm membrane filter using vacuum pump and were acidified to pH <2 by adding concentrated HNO_3 (1 M, diluted from 70 weight % HNO_3 purchased from Sigma Aldrich, Singapore) and tested for various cations (Agilent ICP-OES 5100 and Agilent ICP-MS 7700x).

Table 2. Elemental analysis of the Untreated and Acid-Leached Ash.

Wt%	CFA	WFA	SSA	A-CFA	A-WFA	A-SSA
Al	2.04	0.219	5.99	5.6413	3.8838	5.5336
As	ND	0.023	0.0019	0.0005	0.00493	0.0015
Ba	0.05	0.091	0.04	0.0054	0.1656	0.0637
Ca	1.08	3.447	5.24	0.1311	4.8107	0.1999
Mg	0.05	0.387	1	0.0901	0.4353	0.6013
Sr	0.04	0.038	0.0266	0.0023	0.0214	0.0028
Cd	0	<0.01	0.0015	0	0.0009	0.0002

Cr	0.01	0.019	0.03	0.005	0.009	0.006
Co	<0.01	<0.01	0.002	0.0005	0.0008	0.0032
Cu	<0.01	0.04	0.053	0	0.1861	0.0087
Fe	3.99	2.193	0.002	0.0066	0.0432	0.014
Pb	<0.01	0.099	0.008	0	0.1861	0.0087
Mn	0.05	0.09	0.03	0.0066	0.0432	0.014
Ni	<0.01	<0.01	0.02	0.0015	0.0046	0.0283
V	0.01	<0.01	0.005	0.003	0.0102	0.0049
Zn	<0.01	0.686	0.22	0.0015	0.1388	0.2556
Sb	ND	0.01	0.0015	0.0001	0.0024	0.0004
Mo	<0.01	<0.01	0.002	0	0.0022	0.0025
Si	16.42	6.753	0.0056	10.54	3.23	0
Ti	0.97	0.515	0.5266	0.0592	0.0542	0.059
Zr	0.02	<0.01	0.0166	0.0021	0.006	0.0023

In Table 2, CFA represents coal fly ash; WFA represents wood fly ash; SSA represents sewage sludge ash; A-CFA represents coal fly ash leached by methanesulfonic acid; A-WFA represents wood fly ash leached by methanesulfonic acid; and A-SSA represents sewage sludge ash leached by methanesulfonic acid. ND represents not detected.

Table 2 shows that the hazardous elements in coal, wood and sewage ash lowered significantly after acid-leaching, especially for the highly toxic elements such as arsenic, cadmium, cobalt, vanadium and chromium. This is critical for environmental applications of leached ashes such as its use as a soil additive or construction materials. The silica, aluminium and calcium present in the leached ashes demonstrated the leached ash's potential to be used as construction materials, lightweight composites, and reaction catalyst, respectively.

With regard to heavy metals, elements such as As, Ba, Cr, Pb, Mo and Sr leached less in acid-leached and coated ashes as compared to untreated ash. Elements such as Cd, Cu, Fe, Mn, V and Zn leaches less from untreated ashes (Fig. 9(a) and Fig. 9(b)). A mixed leaching profile was observed, which was because of the unique nature of every metal ion and its solubility in the leaching solvent. Heavy metals such as Sn, Ti, Zr, Bi, Se, Co are found in ND levels in the leachate. The ND levels were <0.02 for Se, <0.024 for Sn, <0.0007 for Co, <0.0003 for Ti, <0.0004 for Zr, and <0.0106 for Bi (all units in ppm). With regard to leaching of light metals, the leaching of calcium reduced for acid leached ashes and organosilane coated ash, while for magnesium, aluminium and silicon, it was the other way around (Fig. 9(c)).

Example 5: Marine Toxicity Tests

Brine shrimp (artemia, purchased from Aquafauna Bio-Marine) and barnacle nauplii (collected from a mangrove at Kranji Road, Singapore) toxicity assay are widely used benchmarks

in ecotoxicity testing. Various species of brine shrimps are present which vary in their toxicity response to the test material and here the marine species was used. Barnacle nauplii are the more sensitive of the two organisms used and this is reflected in the relative toxicity of the species.

Barnacle nauplii toxicity assay: Seawater (FSW) used in all experiments were aged for at least one month and 0.2 µm filter sterilized. The salinity was adjusted to 27 PSU with deionized water. The pH of FSW (control) was measured and leachates were adjusted accordingly with weak base and acid to obtain similar pH readings of 7.2 (± 0.2) units. The barnacles (Amphibalanus amphitrite) were collected from a mangrove at Kranji Road, Singapore and subsequently maintained in seawater flow through tank at St John's Island National Marine Laboratory. Stage II nauplii were spawned from adult barnacles and transferred into FSW. Density of nauplii was adjusted to approximately 25-30 individuals in 50 µl of FSW. To 950 µl of test solution in 2 ml shell vial, 50 µl of nauplii solution was introduced giving a final test volume of 1000 µl (1 ml) and a resultant 5% dilution. For each treatment, four replicates were set up. The assay was incubated at 27°C with 12 hours: 12 hours day and night regime for 24 hours. After 24 hours, the assay was terminated. The test solution was dispensed onto a Bogorov tray. The number of dead and living nauplii were enumerated for each replicate. Moribund nauplii were scored as dead.

Brine shrimp toxicity assay: Artemia cysts (Brand: Aquafauna Bio-Marine) were hatched according to manufacturer's instructions 24 hours prior to start of assay. The brine shrimps were harvested and density adjusted to approximately 25-30 individuals in 150 µl FSW. To 2850 µl of test solution in 7 ml shell vial, 150 µl of nauplii solution was introduced, giving a final test volume of 3000 µl (3 ml). This solution constitutes a 5% dilution of the raw leachate. For each treatment, four replicates were set up. The assay was incubated at 27°C with 12 hours: 12 hours day and night regime for 24 hours. At 24 hours, the assay was terminated. The test solution was dispensed onto a Bogorov tray and the numbers of dead/alive nauplii were scored for each replicate. Moribund nauplii were scored as dead.

The toxicity fraction for both the artemia and the barnacle assay is defined as: Toxicity Fraction (for a particular treatment) = Number of Dead Individuals / Number of Seeded Individuals

CFA leachate was found to be non-toxic to both barnacles and artemia, while the wood fly ash leachate is highly toxic for both organisms. Acid leaching and coating were found to lower the toxicity of the ashes significantly (Fig. 10) for the barnacle samples while the artemia were found to be more tolerant towards toxicity, given the more robust nature of the organism.

Example 6: Adsorption of Untreated, Acid-Leached and Treated Ash

Untreated, acid-leached and treated ash samples (10 mg each) were added to 10 mL of various heavy metal solutions (100 ppm, purchased from Sigma Aldrich, Singapore and diluted with distilled water) in a 50 mL polypropylene tube for adsorption studies. The adsorption experiments were carried out in a mechanical shaker for 15 hours at 250 rpm. The adsorption was then probed for various durations such as: 1, 3, 5, 10, 20 and 30 minute(s) and 1, 2, 3, 6 12, 18 and 24 hours so as to find the saturation time point for adsorption. The coal fly ash, wood fly ash and sewage sludge ash were size-sieved into 3 different fractions which were then silane-coated and tested for their adsorption profile. The effect of common interfering anions such as nitrate, sulfate, chloride and acetate on adsorption profile of metals of interest was then tested. Regeneration of the adsorbent was done using 0.5M NaOH (purchased from Sigma Aldrich, Singapore) and was tested for up to 5 cycles of adsorption. After adsorption, the insoluble particles were separated by centrifugation and the concentration of free heavy metal(s) in solution was analyzed using ICP-OES.

It was found that coal fly ash and wood fly ash adsorbed many heavy metals with selenium being the only heavy metal not adsorbed by either. Iron and lead were adsorbed to the highest levels by both ash samples with wood fly ash showing 100% adsorption of both iron and lead (Fig. 11(a) and Fig. 11(b)). The geopolymers produced however showed specific heavy metal adsorption towards iron and lead with some amount of arsenic also being adsorbed (Fig. 11(c)).

When the untreated ashes and the geopolymers were incubated in a mixed solution of cationic heavy metals, iron and lead were observed to be adsorbed the most from the single metal adsorption profile, while for the anionic mixed solution (salt forms of chromium, arsenic and molybdenum), chromium is adsorbed the highest by the untreated ashes and for the geopolymer, arsenic and molybdenum also being adsorbed to an extent (Fig. 11(d) and 11(e)).

Acid-leaching removed the heavy metals found in the untreated ashes as can be seen from Table 2 and also the other elemental content due to acid action resulting in lowered Ca, Mg, Sr, Ti contents in the acid-leached ash. This lowered the Van der Waals force and ionic force of attraction between the ashes and the heavy metal resulting in reduced and more specific heavy metal adsorption of iron and lead as can be seen in Fig. 12(d) to Fig. 12(f). With regard to coated ash, this specificity was less obvious due to a similar elemental content as the untreated ashes but the coating enabled a relatively specific adsorption profile. The percentage lead adsorption was slightly lowered upon coating for CFA, WFA and SSA, while the specificity of iron and lead adsorption increase drastically after coating (Fig. 12(g) to Fig. 12(i)). This could be due to the

enhanced effect of coating on SSA, which has a low silica content on its own. The composition of ash plays a role in functionalizing organosilane. The SSA may contain more hydroxy (-OH) group which favours the anchoring of more moieties of organosilane which leads to more adsorption. Core-shell ashes had superior adsorption capacity towards specific heavy metals, such as lead and iron. This was due to the functional groups (N-$(OH)_2$) present on the shell, which was from the organosilane coating. The coordination of the functional groups on the shell could form a strong chelating effect with the heavy metal with specific size and geometry. Further modification on the core-shell ashes may allow for highly selective adsorption towards either iron or lead ion, which would be more useful for valuable metal recovery process.

As can be seen from the cationic mixed solution (Fig. 13(b)), coated ash gave a more specific adsorption where iron and lead were adsorbed in greater amounts (20-30% higher) as compared to raw ash. In contrast, other cations (such as those of Al, Cd, Co and Zn) were significantly adsorbed in the untreated ash but not for the coated ash. As for the anionic adsorption profile (Fig. 13(a)), chromium was adsorbed the most by all the ashes (80% to 100%) with coated ashes adsorbing slightly lesser amounts than untreated or leached ashes. Arsenic and molybdenum were adsorbed in lower amounts (about 10%) with coated ashes adsorbing lesser amount as compared to the untreated ash, which indicates specificity with anions too.

The 4 majorly adsorbed elements (iron, lead, arsenic and zinc) for the 3 coated ashes, namely coal fly ash, wood fly ash and sewage sludge ash (see Fig. 12), were explored for time scale based adsorption (see Fig. 14), where they were found to saturate within 2 to 3 hours after which there was minimal change in the adsorption pattern.

The time scale multi-element adsorption profile (see Fig. 15) was similar to that of mono-element pattern (see Fig. 14) where saturation was observed within 2 to 3 hours for both the cations (iron and lead) and anions (chromium and molybdenum) for all 3 coated ashes. Thus, further adsorption experiments were carried out at 3 hours after this observation.

Table 3: Size Fractions of ashes used for coating

	Size Fraction		
CFA	< 50 um	50 -75 um	75 -100 um
WFA	< 100 um	100 -500 um	500- 1000 um
SSA	< 100 um	100 -500 um	500- 1000 um

The ashes were then sieved according to 3 different size fractions: CFA (< 50 µm, 50 to 75 µm and 75 to 100 µm) (b) C-WFA (< 100 µm, 100 to 500 µm and 500 to 1000um) (c) C-SSA (< 100 µm, 100 to 500 µm and 500 to 1000 µm) and then coated using the organosilane.

From Fig. 16, it can be seen that the smallest size fraction for the various ashes adsorbed the highest. In addition, the degree of adsorption decreased with increasing size fraction. Iron and lead adsorptions were tested for single-element adsorption, whilst chromium and molybdenum were also included for the multi-element testing. This pattern was also observed for multi-element adsorption (see Fig. 17) of cations and anions. This could be attributed to the fact that the smaller size fractions had a more uniform coating due to greater surface area as compared to larger sized particles, which would have relatively more of the untreated ash surface exposed, leading to lowered and non-specific adsorption as observed previously.

In Fig. 18, the tested cations, namely iron and lead were found to exhibit slightly lower adsorption when subject to adsorption in the presence of interfering anions such as nitrate, chloride, acetate and sulfates as compared to multi-element adsorption as shown in Fig. 13, which was due to the favoured specific cation adsorption that remained unaffected. The anions, namely chromium and molybdenum exhibited significantly lowered adsorption as compared to their multi-element adsorption profile (see Fig. 13), which could be due to the presence of multiple competing anions.

The Bis(2-hydroxyethyl)amino functional moiety present in the silane coating agent played a vital role in the adsorption of metal ions in the solution. The metal adsorption was due to the lone pair present in the nitrogen atom and the interaction of the two oxygen atoms present in the functional groups with the positive charge of the metal species. The -OH group in the functional moiety showed partial disassociation into $-O^-$ and H^+ and the presence of negative charge over oxygen species facilitated ionic interaction between the adsorbent and metal species in the solution. The designed adsorbent (i.e., the silane-coated ash) was mainly focused on the separation of cations (especially iron and lead) from the solution compared to anions due to the charge and structural arrangements of the functional moiety present in the silane coating agent.

The adsorbent showed specific adsorption of lead and iron species from the multi-ion solution. The specificity was due the distance between the nitrogen and oxygen atom in the functional moiety. Bis(2-hydroxyethyl)amino functional moiety had two carbon between the nitrogen and oxygen atoms, which formed a cavity with a specific size and can accommodate particular metal species with the same size. The ionic charge also favoured the interlocking into the cavity. In the solution, the metal ions were surrounded by ligands, like H_2O molecules, which formed the coordination sphere. The size of the each metal ion depended on its own coordination sphere and this could enhances the specificity towards lead and iron ions to fit in to the cavity of the Bis(2-hydroxyethyl)amino functional moiety. Further, the tertiary amine present in the

functional moiety had less negative charge due to the electron withdrawing effect of two neighbouring -OH groups. The weakened nitrogen group interacted with the H_2O ligand molecules of the lead and iron ions and the -OH group from the functional moiety interacted with the positive cloud of the metal species, which favoured the adsorption from the solution. The size and charge of the lead and iron favoured the chelation inside the cavity of the functional moiety. As compared to iron, lead showed even greater specificity and adsorption capacity due to the strong interaction with the one single moiety of the Bis(2-hydroxyethyl)amino groups. If the two moieties of Bis(2-hydroxyethyl)amino groups interacted with the metal ions, then there would be adsorption of different ions instead of specificity towards one single metal ion.

In anionic species, the adsorption was relatively much lower due to the electronic repulsion between the negative charge of the -OH group in the adsorbent and the negative charge over the anions, even though some anions, like arsenate and chromate, showed adsorption due to the delocalization of negative charge and induced dipole-dipole interaction between adsorbent and adsorbate. When compared to anions, the adsorbents showed high adsorption towards cationic species like lead and iron ions with more specificity in mixture of multi-ion solution.

After a cycle of adsorption, the ashes were regenerated using NaOH and subjected to multi-element adsorption similar to that as shown in Fig. 13. It was seen that there was a slight drop in adsorption with multiple cycles of adsorption and regeneration for both cations (Fe, Pb) and anions (Cr, Mo) tested, which could be due to unavailability of some free sites that had been occupied by previously adsorbed ions (not 100% regeneration).

INDUSTRIAL APPLICABILITY

In the present disclosure, the method may be used to treat ashes and convert them into materials including geopolymers and core-shell particles. The treated ashes may be applied in pollutant removal (such as wastewater treatment), construction industry (such as being substitute for cement), composite manufacturing (such as being used as additives), glass manufacturing, ceramics and chemical engineering (such as being support for catalyst).

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading this foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A method of treating an ash composition comprising the steps of:

a) mixing said ash composition, an acid catalyst, a solvent and optionally an organosilane to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture of step (a) to form a treated ash composition.

2. The method of claim 1, wherein the acid catalyst is methanesulfonic acid or acetic acid.

3. A method of forming a treated ash composition comprising geopolymers, the method comprising the steps of:

a) mixing an ash composition, an acid catalyst and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture of step (a) to form the treated ash composition comprising geopolymers.

4. The method of claim 3, wherein the acid catalyst is methanesulfonic acid.

5. The method of claim 3 or 4, further comprising a step of adding a co-catalyst to the mixture of step (a) and stirring the mixture after the mixing step (a) but before the heating step (b).

6. A method of forming a treated ash composition comprising a plurality of core-shell particles, the method comprising the steps of:

a) mixing an ash composition, an acid catalyst, an organosilane and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture of step (a) to form the treated ash composition comprising the plurality of core-shell particles.

7. The method of claim 6, wherein the acid catalyst is acetic acid.

8. The method of claim 6 or 7, wherein the solvent has a polarity index in the range of 12 to 5.

9. The method of any one of claims 6 to 8, further comprising a step of leaching the ash composition before the mixing step (a).

10. A treated ash composition comprising geopolymers formed according to the method of any one of claims 3 to 5.

11. A treated ash composition comprising a plurality of core-shell particles formed according to the method of any one of claims 6 to 9.

12. A method of preparing geopolymers from an ash composition, comprising the steps of:

a) mixing an ash composition, an acid catalyst and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture to form geopolymers.

13. The method of claim 12, wherein the acid catalyst is methanesulfonic acid.

14. The method of claim 12 or 13, further comprising a step of adding a co-catalyst to the mixture of step (a) and stirring the mixture after the mixing step (a) but before the heating step (b).

15. A method of preparing core-shell particles from an ash composition, comprising the steps of:

a) mixing an ash composition, an acid catalyst, an organosilane and a solvent to form a mixture, wherein the acid catalyst is an organic acid; and

b) heating the mixture to form core-shell particles.

16. The method of claim 15, wherein the acid catalyst is acetic acid.

17. The method of claim 15 or 16, wherein the solvent has a polarity index in the range of 12 to 5.

18. The method of any one of claims 15 to 17, further comprising a step of leaching the ash composition before the mixing step (a).

19. Geopolymers prepared according to the method of any one of claims 12 to 14.

20. Core-shell particles prepared according to the method of any one of claims 15 to 18.