

SORBENTS DERIVED FROM INCINERATION AND GASIFICATION ASHES FOR HIGH TEMPERATURE CARBON CAPTURE BY CALCIUM LOOPING

The present application claims priority from Singapore patent application no. 10202403010Q filed on 27 September 2024, the entire content of which is incorporated herein by reference.

Field of Invention

The present disclosure generally relates to method of producing CO₂ sorbents from calcium-containing incineration and gasification ashes. The present disclosure also relates to an ash-derived CO₂ sorbent prepared according to such a method as well as an ash-derived CO₂ sorbent comprising washed incineration bottom ash, agglomerated calcined gasification fly ash, or a combination thereof. The present disclosure also relates to a calcium looping apparatus for carbon dioxide capture comprising such ash-derived sorbents. Finally, the present disclosure relates to the use of an ash-derived CO₂ sorbent prepared according to the method provided herein or an ash-derived CO₂ sorbent in a calcium looping method or apparatus.

Background

The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

Carbon capture and storage (CCS) is a scheme involving the reduction of CO₂ emissions by emission-intensive industries, effectively contributing to the mitigation of climate change. Existing CO₂ capture technologies operate based on the principles of chemisorption, adsorption, membrane separation, and mineral carbonation. Research on carbon capture technologies is centred around reducing the cost of CO₂ capture, mainly consisting of the cost of manufacturing the CO₂ capture materials (e.g., sorbents), the cost associated with energy penalties and the capital cost of the CO₂ capture plant.

Currently, one of the most popular methods of capturing CO₂ on the commercial scale is the use of alkaline liquids, such as aqueous monoethanolamine (MEA) solutions in a gas scrubber, where the sorbent is then regenerated via a stripper. Even at its high technology readiness level, MEA regeneration induces high energy consumptions, costing an equivalent to about 48% of the operating expenditure in a typical power plant. Basicity and oxidative

decomposition will also bring about potential corrosion issues, contributing further to the cost in terms of maintenance and replacements.

The cheaper and promising method of using calcium looping (CaL) as a method of post-combustion capture features the use of dual fluidised bed reactor, comprising a carbonator and calciner. Through a similar concept as amine scrubbing, calcium oxide (CaO) performs a chemisorption reaction to form calcium carbonate in the carbonator, and with the reversible reaction in play, calcines calcium carbonate (CaCO_3) back into CaO. The biggest issue that calcium looping is currently facing is the problem of sorbent deactivation. Prolonged cycling of raw limestone induces a sintering process that lowers the capturing capacity of the sorbent material, thus requiring a constant makeup in the system, incurring operational costs of constantly purchasing and replacing the spent limestone when operating CaL.

In recent years, many researchers have attempted to find various means of lowering the cost of sorbent input. Regeneration of sintered limestone, engineering synthetic sorbents with higher stability and strength, and identifying isolated waste biomaterials such as eggshells have also been explored. Therefore, there is great interest in modifying the input sorbent to push the envelope that CaL is the preferred CCSU technique for demonstration, as well as for future commercialization prospects.

US 8052948 B2 describes the use of alkaline liquids such as aqueous monoethanolamine (MEA) solutions in a gas scrubber. The sorbent is regenerated in a stripper. The main disadvantage of this system is the energy consumption, primarily due to sorbent regeneration, which is equivalent to 48% of the operating expenditure in a typical power plant. The use of MEA also has corrosion issues owing to its strong basicity and its tendency to oxidatively decompose.

US20170267538 A1 describes an integrated process for capturing carbon dioxide using CO_2 separation membranes. Using membranes for flue gas treatment could also result in carbonate and sulphate formation in/on the membrane, creating scaling problems. Although scaling can be prevented by using antiscalants, the use of antiscalants gives rise to negative environmental impact associated with the waste discharge. In addition, high operating pressures and frequent maintenance requirement of membrane units are costly and disadvantageous.

US 8876953 B2 describes the use of metal organic frameworks (MOF) to adsorb carbon dioxide, utilizing its high specific surface area and microporosity. MOFs are synthesised using hydrothermal or solvothermal reactions between organic ligands and metal salt solutions. The synthesis of MOFs is highly sensitive to pH, temperature, concentration, and the type of

solvent used, where minute perturbations in the synthesis parameters would impact the physical and chemical properties of the products. Other disadvantages include the MOFs' low stability in moisture, low CO₂ uptake capacities at low partial pressures of CO₂, and difficulties in using MOFs for high temperature applications.

US 9651252 B2 describes the use of calcium looping, implemented with a carbonator and calciner, to extract carbon dioxide from combustion flue gases. The deactivation of Ca-based sorbents due to sintering means large amount of make-up sorbents are required at low cost to maintain the cost-effectiveness of the calcium looping process. Alternatively, the problem of sintering could be improved by using stabilizers such as aluminium oxide or magnesium oxide, at the expense of additional synthesis cost associated with the use of expensive alumina and magnesium precursors.

There is therefore a need for new sorbent materials that are low-cost and suitable for CaL based technologies.

Summary of Invention

Aspects and embodiments of the invention are provided in the following numbered clauses.

1. A method of producing CO₂ sorbents from Ca-containing incineration and gasification ashes, comprising:
 - a. removing any ferrous metals, non-ferrous metals, particles larger than a predetermined size, and glass from the ashes to provide a cleaned ash;
 - b. assessing the cleaned ash of step a, including
 - i. assessing the particle size distribution and elemental composition to categorize the cleaned ash into high Ca-containing ash having a Ca content of 15wt% or higher and low Ca-containing ash having a Ca content of less than 15wt%;
 - ii. assessing the CO₂ uptake capacity of the high Ca-containing ash and further categorizing the high Ca-containing ash into inactive Ca-containing ashes and active Ca-containing ashes;
 - iii. assessing the active Ca-containing ashes for their fluidization characteristics; and
 - c. either i) crushing the active Ca-containing ashes with particle sizes larger than a predetermined particle size to smaller sizes, or ii) agglomerating the active Ca-containing ashes with particle sizes smaller than a predetermined particle size into larger agglomerated particles, in order to obtain a processed ash.

2. The method according to Clause 1, wherein the method further comprises:
 - d. chemically and/or thermally treating the agglomerated particles to strengthen the agglomerated particles.
3. The method according to Clause 2, wherein thermally treating the agglomerated particles includes sintering the agglomerated particles, optionally via calcination, such as at around 650 to around 850°C, such as around 750°C, for 2 hours in air.
4. The method according to Clause 2 or Clause 3, wherein the strengthened agglomerated particles are sized to within a predetermined size range, optionally wherein the sizing includes grinding and sieving, further optionally wherein the method further comprises providing any particles which are outside the predetermined size range to either step b. or step c.
5. The method according to any preceding clause, wherein the method further comprises:
 - e. providing the processed ash to a chemical looping apparatus, such as a chemical looping process for carbon capture.
6. The method according to Clause 5, wherein the method further comprises contacting the processed ash with a fluid stream comprising carbon dioxide to remove at least a portion of the carbon dioxide from the fluid stream, optionally wherein the method comprises calcining the processed ash to liberate captured carbon dioxide.
7. A method of producing CO₂ sorbents according to any preceding clause, wherein the active calcium includes calcium oxide, calcium hydroxide, and calcium chloride hydroxide while the inactive calcium includes mayenite, calcium silicates, calcium ferrites and calcium sulfates.
8. A method of producing CO₂ sorbents according to any preceding clause, wherein the inactive Ca-containing ashes further undergo chemical treatment to convert to active Ca-containing ashes.
9. A method of producing CO₂ sorbents according to any preceding clause, wherein the ashes are further assessed for their suitability for CO₂ capture, including resistance to attrition and fluidisation behaviour over high temperature carbonation-calcination cycles in a fluidised bed reactor (FBR).

10. A method of producing CO₂ sorbents according to any preceding clause, wherein the method includes collecting Ca-containing incineration and gasification ashes from a thermochemical waste treatment plant, optionally wherein the thermochemical waste treatment plant is an incineration plant or a gasification plant
11. The method according to any preceding clause, wherein the ferrous metals are removed magnetically.
12. The method according to any preceding clause, wherein step a. includes removing particles with a particle size greater than 50 mm.
13. The method according to any preceding clause, wherein assessing the particle size distribution of the cleaned ash in step b.i. is conducted by mechanical sieving for particle sizes of 0.5 mm or higher, and by light scattering for particles sizes of less than 0.5 mm.
14. The method according to any preceding clause, wherein one or more of the following apply:
 - i) assessing the elemental composition of the cleaned ash in step b.i. is performed via one or both of inductively coupled plasma – optical emission spectrometry (ICP-OES) and inductively coupled plasma – mass spectrometry (ICP-MS) of a microwave acid digestion solution of the cleaned ash;
 - ii) assessing the CO₂ uptake capacity of the high Ca-containing ash in step b.ii. is performed thermogravimetrically;
 - iii) assessing the active Ca-containing ashes for their fluidization characteristics is performed without heating using a suitable fluidising gas, such as compressed air.
15. The method according to any preceding clause, wherein the predetermined particle size is from about 80 to about 975 µm, such as from about 130 to about 850 µm, such as about 95 to about 700 µm, such as about 86 to 650 µm, such as about 150 to 950 µm.
16. The method according to any preceding clause, wherein the active Ca-containing ashes have a minimum active Ca content of 2.9 wt%, such as a minimum content of 4.1wt% calcium oxide, optionally wherein the active Ca-containing ashes have an active Ca content of 29.7wt%.

17. The method according to any preceding clause, wherein the Ca-containing incineration and gasification ashes are selected from gasification fly ash, incineration bottom ash, and combinations thereof.
18. An ash-derived CO₂ sorbent comprising ash prepared according to any of Clauses 1 to 17.
19. An ash-derived CO₂ sorbent comprising washed incineration bottom ash, agglomerated calcined gasification fly ash, or a combination thereof.
20. A calcium looping apparatus for carbon dioxide capture, the apparatus comprising the ash-derived sorbent according to Clause 18 or 19.
21. Use of an ash-derived CO₂ sorbent prepared according to the method of any of Clauses 1 to 17 or the ash-derived CO₂ sorbent according to Clause 18 or 19 in a calcium looping method or apparatus.

As such, the present invention involves the concept of using ash as a sorbent to capture CO₂ using a calcium looping process. The invention focuses on three main aspects, namely the ash screening process, the pre-processing methods used on the ashes, and the methodologies of applying ash-derived sorbents in the calcium looping process.

In particular, in the screening process, an important factor to have ash viable for the carbon capture process is the active Ca content. With the use of elemental characterization, ashes used for this invention may be profiled to determine if the ash used is suitable. Ca% contained in this step may preferably be at least 2.9 wt%, such as 3wt% or greater assuming complete conversion of CaO. Thermogravimetric analysis (TGA) can be used to determine the carbon capture capacities of the ashes used in this invention. As mentioned, active Ca% contained in this step may be more than 3wt%, or 33 mg/g of CO₂ capture capacity.

Mineral analysis may be applied in tandem with the TGA to determine the species of active Ca in the ash, as well as the inactive Ca to account for the high Ca in elemental characterization with low capture capacities.

In the pre-treatment process, size control is a useful step in achieving fluidizable sorbents, where smaller variances in sizes can allow for smoother fluidization. For size reduction, the method applied may be through jaw crushing. Particles larger than, for example, 1mm may be

physically crushed into particles $<1\text{mm}$. For size increments, the method applied may be agglomeration, where fine particles are agglomerated into larger agglomerates with atomized solvents of more than 0.150 mm . Any particles formed may be calcined to sinter these particles.

During the preliminary testing phase, samples may be assessed with cold and hot fluidised bed tests to determine the fluidization characteristics and capture capacities in a controlled environment.

For cold fluidised bed testing, minimum fluidization velocity (U_{mf}) may be determined, and attrition rates may be assessed as a stress test to determine the viability of the ash for hot fluidised bed testing and eventually the carbonator.

For hot fluidised bed testing, like cold fluidised bed testing, stress tests may be conducted on the ash to assess its particle attrition rate under high temperature conditions with dry gas, followed by moisture, and acidity.

Indicative results are as follows for the following ash-derived sorbents.

Incineration bottom ash (IBA) is observed to display low attrition and low capture capacity, but is still a viable candidate for the present invention.

Washed IBA has similar attrition to IBA and stable capture capacity across multiple cycles compared to IBA, especially with higher amounts of CO_2 in gas stream.

Gasification fly ash (GFA) is observed to display minimal attrition, exceptionally high capture capacity but subject to higher losses due to calcination and entrainment.

Air pollution control (APC) unit ash has exceptionally high capture capacity in TGA results. APC unit ash benefits from further pre-treatment for viable assessment in a fluidized bed regime due to high attrition rates.

The products made in this invention can be used in a carbonator/calciner circulating calcium looping process.

Pre-calcined ash-derived sorbents used in this invention may be loaded into a carbonator.

In an embodiment of the present invention, clean flue gas (after removal of sour gas) may enter from the bottom of a carbonator and with a velocity of the system at, for example, 3-4 times the U_{mf} of the sorbent, and the desired size range can be applied based on the

parameters of the gas flowrate and carbonator design. The working range for the velocity of the ash sorbent may be between 495 and 13220 cm/min.

The aspect ratio of the fluidized bed may be maintained at 2 to 2.5 and maintained with reflux from a calciner.

The operating temperature of the system may be between 650°C and 850°C, such as around 750°C.

Elutriated sorbents may be conveyed into a calciner with an average residence time in the carbonator at 1 to 15 minutes, such as 3 to 12 minutes, such as 6 to 10 minutes.

The circulating fluidized bed conveys the carbonated ash-derived sorbents into a calciner. A 100% CO₂ gas stream is supplied into the calciner at a velocity of 4 times U_{mf} .

The aspect ratio of the fluidized bed may be maintained at 2 to 2.5 and maintained with sorbent makeup and reflux from the carbonator.

The operating temperature of the system may be between 750 to 900 °C, such as around 850°C. Spent sorbent may be upcycled as a construction material.

A carbonator gas outlet stream may be sent to a stack and vented to the atmosphere.

A calciner gas outlet stream may be sent to a CO₂ purification unit (CPU).

Drawings

Aspects of the present invention are described in the following figures.

FIG. 1 depicts an ash-processing protocol according to one embodiment of the present invention;

FIGS. 2a to d are photos of selected ash samples collected and utilized in this invention. (a) incinerator bottom ash (IBA), (b) air pollution control unit (APC), (c) gasification fly ash (GFA), and (d) electrostatic precipitator (ESP) ashes;

FIGS. 3A and 3B are photos of ash-derived sorbents according to the present invention derived from ashes. (a) IBA and (b) IFA, with size range of 0.150 – 0.315 mm;

FIG. 4 depicts the fluidization of IBA ash in a 2 cm ID quartz tube at room temperature with of 3.5 L/min of compressed air as the fluidising gas;

FIG. 5 depicts a reactor set-up for carbon capture by calcium looping in a hot fluidised bed;

FIG. 6 depicts a Geldart chart for the classification of fluidisation of particles. Geldart groups: A (aeratable), B (sand-like), C (cohesive), and D (spoutable);

FIGS. 7A and 7B depict the total elements content of ashes, major elements were detected with ICP-OES, and minor elements with ICP-MS, including washed-incinerator bottom ash (W-IBA);

FIG. 8 depicts XRD patterns of ashes. The diffraction peaks are indexed as 1. CaCO_3 , 2. CaSO_4 , 3. SiO_2 4. CaClOH , 5. KCl , 6. NaCl and 7. CaO ;

FIGS. 9A and 9B depict gravimetric CO_2 capture capacities of (a) fly ashes (b) bottom ashes, as measured in TGA using 60 vol% CO_2 and N_2 as the carbonation gas and calcination gas, respectively, over 20 isothermal carbonation-calcination cycles at 750 °C.

FIG. 10 depicts a comparison of CO_2 capture capacity of raw IBA, W-IBA, GFA at 15% CO_2 , in a fluidised bed reactor at 750 °C, fluidised by a total gas flow of 1000 mL/min (measured at 25°C, 1 atm pressure), over 100 carbonation-calcination cycles.

FIGS. 11A to 11F depict a comparison of CO_2 capture performance of raw IBA and W-IBA in a fluidized bed reactor at 750 °C, when the carbonation gas contains 15% and 60% CO_2 . a) CO_2 uptake of W-IBA in different CO_2 compositions, b) relative uptake of W-IBA in different gas conditions, c) CO_2 uptake of various ashes in 15% CO_2 d) relative of various ashes in 15% CO_2 , e) CO_2 uptake of various ashes in 60% CO_2 , f) relative of various ashes in 60% CO_2 .

Description

It has been found that it is possible to produce carbon dioxide sorbents from calcium-containing incineration and gasification ashes. In this way, ashes that are usually disposed of, e.g. by landfill, are upcycled as low-cost and regenerable sorbents for CO_2 capture, to economically reduce CO_2 emissions from all forms of combustion and industrial processes. Processes and techniques for pre-treating (or pre-processing) and converting the ashes to functional sorbents that are subsequently applied in high temperature fluidized bed reactor systems for CO_2 capture by calcium looping are provided. The present invention provides a comprehensive strategy for preparing regenerable Ca-based sorbents from incineration and

gasification ashes. The processed ashes are effective over 100 cycles of carbon capture and release, with potential for long-lasting performance beyond 100 cycles. The present invention provides a novel, low cost, and environmentally beneficial method developed to capture carbon dioxide (CO_2) from waste gas streams using ash-derived sorbents via a calcium looping process. The captured CO_2 can be subsequently sequestered in geological formations or utilised for the production of fuels and chemicals. This scheme involves the production of low-cost Ca-based sorbents from ashes, generated by incinerators, gasifiers or any thermochemical waste treatment or valorisation plants, and using the sorbents for the cyclic carbonation of CaO and thermal decomposition of CaCO_3 to capture CO_2 . The present invention covers a systematic protocol to handle various types of incineration and gasification ashes from waste treatment facilities, employing appropriate physical and chemical modifications, to convert Ca-containing ashes into Ca-based sorbent particles for CO_2 capture.

Thus, according to a first aspect of the present invention, there is provided a method of producing CO_2 sorbents from Ca-containing incineration and gasification ashes, comprising:

- a. removing any ferrous metals, non-ferrous metals, particles larger than a predetermined size, and glass from the ashes to provide a cleaned ash;
- b. assessing the cleaned ash of step a, including
 - i. assessing the particle size distribution and elemental composition to categorize the cleaned ash into high Ca-containing ash having a Ca content of 15wt% or higher and low Ca-containing ash having a Ca content of less than 15wt%;
 - ii. assessing the CO_2 uptake capacity of the high Ca-containing ash and further categorizing the high Ca-containing ash into inactive Ca-containing ashes and active Ca-containing ashes;
 - iii. assessing the active Ca-containing ashes for their fluidization characteristics; and
- c. either i) crushing the active Ca-containing ashes with particle sizes larger than a predetermined particle size to smaller sizes, or ii) agglomerating the active Ca-containing ashes with particle sizes smaller than a predetermined particle size into larger agglomerated particles, in order to obtain a processed ash.

In countries that incinerate waste to conserve space, such as Singapore, ash materials are generated in abundance, and at the end of the process, it is usually sent for landfilling. Various studies performed on the typical elemental composition of ash materials; it is observed that

most ash materials have exceptionally high calcium content. By upcycling the ash materials into ash-derived sorbents, we can further explore alternative materials to replace naturally mined limestone.

The present invention provides for preparation techniques to convert the various ashes, generated from the thermal treatment of waste materials, such as municipal solid waste (MSW), into highly functional and regenerable sorbents. Ashes with calcium-rich compositions are potential raw material for preparing CO₂ sorbents. However, unlike conventional natural and synthetic CO₂ sorbents, the ashes, having unique sintering behaviours, physical and chemical properties, require specific processing protocols before application in high temperature CO₂ capture cycles.

In the present invention, sorbents derived from ashes obtained from incineration and gasification of waste materials may be employed in fluidised bed carbonator and calciner to absorb CO₂, as an alternative to low temperature CO₂ capture by synthetic sorbents (e.g. MEA, MOFs and zeolites) or high temperature CO₂ sorbents derived from natural minerals such as lime, dolomite, etc.

The claimed procedure for preparing ash-derived sorbents ensures appropriate physical and chemical properties for carbon capture, including high surface area, cyclic stability and fluidisability. The claimed procedure may include a combination of crushing, agglomeration, and calcination steps. Additional steps (e.g. sieving) may be used to modulate and control the size of the sorbent particles for desirable fluidisation performance. In addition, the sorbent pre-processing may include steps to strengthen the particles' resistance to fragmentation and attrition in fluidised beds.

According to the present invention, several types of ashes may be treated through a series of pre-processing procedures to produce functional sorbents. For example, washed incineration bottom ash (W-IBA) and gasification fly ash (GFA) have different elemental composition, particle sizes and phase compositions. Depending on the properties of the raw ashes and the desired properties of the sorbent particles in specific reactor designs, application-driven pre-processing procedures can be appropriately devised and implemented for the preparation of ashes with high CO₂ uptake, low cost, high cyclic durability and low waste generation.

As mentioned, in the present invention, the ash-derived sorbent demonstrates high carbon capture capacity, comparable to commercially available pure CaO, and satisfactory stability of up to 100 carbonation-calcination cycles and possibly beyond.

It will be understood that active Ca-containing ashes are ashes which are able to react with carbon dioxide to produce carbonates. Inactive Ca-containing ashes are not able to react with carbon dioxide to form carbonates.

In addition, the sorbent materials produced according to the present invention demonstrate stable CO₂ capture performance in various CO₂ mole fractions, making them relevant to a wide range of CO₂ capture applications such as post-combustion capture, pre-combustion capture and natural gas processing.

Furthermore, the ash-derived sorbents show high resistance against fragmentation and attrition, thus reducing the burden of gas clean-up systems (e.g., cyclones) for particulate removal. Low attrition rates also contribute to lowering fresh sorbent makeup, thereby reducing the overall operational expenditure. The sorbent materials produced according to the present invention maintain satisfactory physical integrity when applied to capture CO₂ in the presence of moisture and acid gas (e.g. HCl).

The present invention uses ash as a replacement for natural minerals and synthetic chemicals for producing sorbents for carbon capture, with lower economic cost and environmental benefits. The innovative use of low-cost waste materials generated by waste management facilities (e.g., MSW incinerators) potentially curbs the depletion of natural minerals and costly material manufacturing. In addition, the economic and environmental impacts associated with ash landfilling can be potentially reduced.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure,

such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a composition” includes mixtures of two or more such compositions, reference to “an oxygen carrier” includes mixtures of two or more such oxygen carriers, reference to “a catalyst” includes mixtures of two or more such catalysts, and the like.

The method may further comprise:

- d. chemically and/or thermally treating the agglomerated particles to strengthen the agglomerated particles.

Thermally treating the agglomerated particles may include sintering the agglomerated particles. The sintering may be via calcination. The calcination may be conducted at any suitable temperature to effect sintering. For example, the calcination may be conducted at around 650 to around 850°C, such as around 750°C. The calcination may be conducted for any suitable period of time to effect sintering, such as, for example, from around 1 hour to around 5 hours, such as around 2 hours. The calcination may be conducted in air.

The strengthened agglomerated particles may be sized to within a predetermined size range. The sizing may include grinding and/or sieving. The method may comprise providing any particles which are outside the predetermined size range to either step b. or step c.

The method may further comprise: f) providing the processed ash to a chemical looping apparatus. Such a chemical looping apparatus may be a chemical looping process for carbon capture. As described herein, a chemical looping apparatus may be configured to contact the processed ash with carbon dioxide at a temperature and a duration sufficient to allow at least some of the carbon dioxide to react with the processed ash. The processed ash which has reacted with carbon dioxide may be subsequently heated to a temperature and for a sufficient time to release at least some of the carbon dioxide previously taken up by the processed ash in order to recover the processed ash and a carbon dioxide stream.

The method may further comprise contacting the processed ash with a fluid stream comprising carbon dioxide to remove at least a portion of the carbon dioxide from the fluid stream. The method may comprise calcining the processed ash to liberate captured carbon dioxide.

The active calcium may include calcium oxide, calcium hydroxide, and calcium chloride hydroxide. The inactive calcium may include mayenite, calcium silicates, calcium ferrites, and calcium sulfates.

The inactive Ca-containing ashes may further undergo chemical treatment to convert them to active Ca-containing ashes. The present invention is not particularly limited by the conversion method and any method by which the Ca-containing ashes may be converted to ones which are able to react with carbon dioxide may be used.

The ashes may be further assessed for their suitability for CO₂ capture, including resistance to attrition and fluidisation behaviour over high temperature carbonation-calcination cycles in a fluidised bed reactor (FBR). Resistance to attrition is desirable as high attrition rates lead to the need for high rates of sorbent makeup. Consequently, improved resistance to attrition reduces the need for sorbent makeup. The rate of attrition may be measured experimentally at the relevant operating conditions. As detailed below, the fines loss, attrition loss and total loss may be estimated. Fines loss is the fractional loss of bed mass due to elutriation. Attrition loss refers to the fraction of particles whose size fall below the lower limit of the size range suitable for bubbling fluidisation. The total loss is the sum of fines loss and attrition loss. A combined attrition and fines loss rate below 10% over a 200-minute period is indicative of a material being potentially suitable for CO₂ capture. If the combined attrition and fines loss rate is greater than 10% over a 200-minute period, the material may require strengthening, such as via calcination, before use in continuous CO₂ capture devices. For use in a fluidised bed reactor, the particles need to be fluidizable. Materials which are unable to be fluidised under the relevant operating conditions of a fluidised bed reactor undertaking high temperature carbonation-calcination cycles may be subject to further processing to control the particle size in order to improve the fluidisation characteristics of the material. For example, materials comprising particles too small for fluidisation may be subject to processing to increase the particle size, such as via agglomeration. Sieving may be utilised to separate particles into a desired size range.

The method may include collecting Ca-containing incineration and gasification ashes from a thermochemical waste treatment plant. The thermochemical waste treatment plant may be an incineration plant or a gasification plant.

The ferrous metals may be removed magnetically. Any suitable means for removal of unwanted components may be utilised.

Step a. may include removing particles with a particle size greater than 50 mm. By removing particles which a particle size greater than 50 mm, the resulting material has more appropriate dimensions for use as a carbon dioxide sorbent, particularly in a calcium looping process.

Assessing the particle size distribution of the cleaned ash in step b.i. may be conducted by mechanical sieving for particle sizes of 0.5 mm or higher, and by light scattering for particles sizes of less than 0.5 mm.

Assessing the elemental composition of the cleaned ash in step b.i. may be performed via one or both of inductively coupled plasma – optical emission spectrometry (ICP-OES) and inductively coupled plasma – mass spectrometry (ICP-MS) of a microwave acid digestion solution of the cleaned ash.

Assessing the CO₂ uptake capacity of the high Ca-containing ash in step b.ii. may be performed thermogravimetrically.

Assessing the active Ca-containing ashes for their fluidization characteristics may be performed without heating using a suitable fluidising gas, such as compressed air.

The predetermined particle size may be from about 80 to about 975 µm, such as from about 130 to about 850 µm, such as about 95 to about 700 µm, such as about 86 to 650 µm, such as about 150 to 950 µm.

The active Ca-containing ashes may have a minimum active Ca content of 2.9wt%, such as a minimum content of 4.1wt% calcium oxide. In an example, the active Ca-containing ashes may have an active Ca content of 29.7wt%. It will be appreciated that a greater active Ca content provides a higher potential for carbon dioxide take up.

The Ca-containing incineration and gasification ashes may be selected from gasification fly ash, incineration bottom ash, and combinations thereof.

According to a second aspect of the present invention, there is provided an ash-derived CO₂ sorbent comprising ash prepared according to the first aspect of the present invention. As described herein, such as has particularly desirable properties as a sorbent in a calcium looping process.

According to a third aspect of the present invention, there is provided an ash-derived CO₂ sorbent comprising washed incineration bottom ash, agglomerated calcined gasification fly ash, or a combination thereof.

According to a fourth aspect of the present invention, there is provided a calcium looping apparatus for carbon dioxide capture, the apparatus comprising the ash-derived sorbent according to the second or third aspects of the present disclosure.

According to a fifth aspect of the present disclosure, there is provided the Use of an ash-derived CO₂ sorbent prepared according to the method of the first aspect of the present disclosure or the ash-derived CO₂ sorbent according to the second or third aspects of the present disclosure in a calcium looping method or apparatus.

Further aspects and embodiments of the invention may relate to the following numbered clauses.

1. A method of producing CO₂ sorbents from Ca-containing incineration and gasification ashes, comprising:
 - a. Removing both ferrous and non-ferrous metals, bulky particles (with particle size >50mm), and glass from the ashes;
 - b. Assessing the ash of step a, including
 - i. Assessing particle size distribution and elemental composition to categorize the ash into high Ca-containing ash and low Ca-containing ash;
 - ii. Assessing their CO₂ uptake capacity and further categorized the ashes into Inactive Ca-containing ashes and Active Ca-containing ashes;
 - iii. Assessing the active Ca-containing ashes for their fluidization characteristics to determine the optimal particle size; and
 - c. Crushing ashes with particle sizes larger than the optimal particle size to smaller sizes while agglomerating ashes with particle sizes smaller than the optimal particle size into larger particles with a binder.
2. A method of producing CO₂ sorbents according to clause 1, wherein the active calcium includes calcium oxide, calcium hydroxide, and calcium chloride hydroxide while the inactive calcium includes mayenite, calcium silicates, calcium ferrites and calcium sulfates.
3. A method of producing CO₂ sorbents according to clauses 1 and 2, wherein the Inactive Ca-containing ashes further undergo chemical treatment to convert to Active Ca-containing ashes.
4. A method of producing CO₂ sorbents according to clause 1, wherein the agglomerated

ashes further undergo calcination at 750 °C for 2 hours.

5. A method of producing CO₂ sorbents according to clauses 1 to 4, wherein the ashes are further assessed for their suitability for CO₂ capture, including resistance to attrition and fluidisation behaviour over high temperature carbonation-calcination cycles in a fluidised bed reactor (FBR).

It will be appreciated that the features described in respect of one of the aspects or embodiments of the present invention may be combined with any of the other aspects or embodiments of the present invention other than when such combinations are technically incompatible. All such combinations are expressly considered and disclosed.

Examples

An exemplary ash processing method according to the present invention is illustrated in Figure 1. Step 1) comprises ash collection from thermal treatment plants. Ashes may be collected from incineration plants, gasification plants or any other thermochemical waste treatment plants. Step 2) includes materials recovery. This step is intended to remove contaminants from the ashes, such as ferrous metals, non-ferrous metals, glass and particles larger than a predetermined size. Ferrous metals may be removed by magnetic extraction. As such, bulky particles (with particle size > 50 mm), glass and non-ferrous metals are removed from the ash matrix. Step 3) is a pre-processing assessment in which ashes are assessed for their particle size distribution (PSD) by mechanical sieving. The ashes are assessed for their elemental compositions. This is performed by analysing solutions obtained from microwave acid digestion of the ash samples using inductively coupled plasma – optical emission spectrometry (ICP-OES) and inductively coupled plasma – mass spectrometry (ICP-MS). The ashes are also assessed for their potential to take up CO₂ in a thermogravimetric analyser (TGA). The gravimetric CO₂ uptake capacity is estimated based on the observed mass changes over carbonation and calcination cycles. The ashes are also assessed for their fluidisation characteristics at room temperature using compressed air as the fluidising gas. Step 4) includes pre-treatment and processing of ashes. In this step, large (>1 mm) treated ashes are crushed to smaller size ranges, whereas smaller (<0.065 mm) ashes are agglomerated into larger particles with the help of binders. The ashes are chemically and/or thermally strengthened after the agglomeration process, such as by sintering. Step 5) relates to assessment and optimisation. The suitability of the pre-processed ashes for CO₂ capture, including resistance to attrition and fluidisation behaviour over high temperature carbonation-calcination cycles is assessed in a fluidised bed reactor (FBR). Pre-processed sorbents that are deemed unsuitable for calcium looping operations in fluidised beds can be subjected to

further modification (e.g. size control and strengthening), as shown in **Fig. 1**. The formulation and treatment procedure of the ash-derived sorbent can be further modified, if necessary, depending on the application and performance requirements.

Materials

Ashes generated as by-products (or waste residues) of the thermal treatment of waste materials are applied as the raw materials. As shown in **Fig. 2**, samples of incinerator bottom ash (IBA) (Fig. 2a), ash from electrostatic precipitator (ESP) (Fig. 2d), gasification fly ash (Fig. 2c), and ash from air pollution control unit (APC) (Fig. 2b) were collected from commercial municipal solid waste (MSW) incineration plants. **IBA** is the main solid residue generated by the incineration of MSW, Washed IBA (**W-IBA**) was prepared using raw IBA with particle size less than 1 mm in size and washed with deionised water for 1 hour with liquid to solid ratio of 2:1. An electrostatic precipitator collects particulates from incineration flue gas; these particulates are denoted as **ESP** ash. The flue gas is subsequently treated in the air pollution control unit, where the flue gas treatment sorbent is introduced to capture acidic gases and other pollutants, followed by the retention of solid residues using bag filters to collect **APC** ash. Gasification fly ash (**GFA**) was collected from a waste-to-energy research facility (WTERF) at Nanyang Technological University, Singapore. GFA is a mixture of particulates and solid residues from the air pollution control unit. Reagent grade CaO is obtained from GCE Laboratory Chemicals and is used as a benchmark Ca-based sorbent (i.e., a base sorbent formulation) for comparison.

Methods

General characterisation and analytical techniques

The particle size distribution of ashes and ash-derived sorbents were determined by mechanical sieving (For particle size ranges >0.5 mm) and Mastersizer (for particle size ranges <0.5 mm). Mechanical sieving (HAVER EML digital plus) used sieve trays of the following sizes: 0.5 mm, 1 mm, 4 mm, 20 mm, and 50 mm. Mastersizer (Malvern MS 2000+, Hydro2000 SM dispersion unit) was carried out by dispersing 20 ppm of ashes in a suspension, which was subsequently analysed by light scattering. The total metal contents in the ash samples were determined by dissolving 0.1 g of ash sample in 65 % w/w nitric acid by microwave digestion (Milestone Ethos one) at 180 °C for 30 mins. The digested solution was filtered by 40 µm PTFE syringe filters. The samples were then diluted in a mixture of deionised (DI) water and 1.2% ultrapure nitric acid solution for quantification by ICP-OES (PerkinElmer Optima 8300) and ICP-MS (Thermo Scientific iCAP Q), using the APHA 3125B method for quantification. The crystalline phases of the ashes and the ash-derived sorbents were examined by X-ray diffraction (Bruker D8 Advance Powder XRD), operated with Cu-K α

radiation at 40 kV and 40 mA. In a typical XRD measurement, the ash sample was loaded onto a bulk powder sample holder. The diffraction pattern with 2θ range from 5° to 60° was measured with a step size of 0.02° and a scan rate of 0.06° per second.

Thermogravimetric analysis

The carbon capture performance of the ash samples was preliminarily screened by thermogravimetric analysis (TGA), using a thermogravimetric analyser (STA 449 Jupiter®, Netzsch), from which the carbon capture capacities of the ashes were determined. In each TGA experiment, 15 ± 5 mg of fly ash or 25 ± 5 mg of bottom ash sample was placed on an alumina crucible and heated from 30°C to 750°C with a heating rate of $20^\circ\text{C}/\text{min}$ in continuous purging of N_2 at 200 mL/min, followed by 20 h of dwelling at 750°C in N_2 , before calcium looping cycles started. Each calcium looping cycle comprises a carbonation step and a calcination step. The carbonation step was performed with 120 mL/min of CO_2 and 80 mL/min of N_2 for 40 min at 750°C , while the calcination step was performed with 200 mL/min of N_2 for 20 min at 750°C . 20 calcium looping cycles were performed for each sample. The changes in the mass of the samples were recorded to determine their gravimetric CO_2 uptake capacities. The mass of the sample at 750°C is defined as the calcined mass of the sorbent, after moisture, organic materials, and carbonates have been fully removed by calcination. The uptake capacity of the ash is estimated according to:

$$\text{Uptake capacity} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{[\text{carbonated mass} - \text{calcined mass}] (\text{mg})}{\text{calcined mass} (\text{g})} \quad \text{Eq. 1}$$

Pre-treatment and processing methods

The pre-treatment and pre-processing protocols, depicted in **Fig. 1**, were applied to produce the ash-derived sorbents, which are shown in **Fig. 3**. Fig. 3A depicts IBA derived ashes and Fig. 3B depicts IFA-derived ashes. The pre-treatments include size control and strengthening of the ash-derived sorbent, and are selectively applied to the ashes, as and when needed. Agglomeration was done to increase the particle size of ashes that are otherwise too small for fluidisation. Ashes were agglomerated by spraying DI water using an atomizer over layer by layer, with agitation coat each layer and to form larger particles. The ash aggregates were sieved to the desired size fraction for fluidization experiments. Collectively, crushing and agglomeration were used for size control to achieve desirable fluidization behaviour. The choice of size control methods depends on the particle density and particle size, both of which governs the fluidization of the sorbent particles. Calcination is applied to the agglomerated

products to increase the particles' physical strength through tempering and sintering. Calcination was conducted at 750 °C in a muffle furnace with a holding time of 2 h in air. Owing to potential particle size change during thermal treatment, the calcined ashes were ground and sieved again to the desired size ranges.

Fluidisation experiments

Fluidisation experiments was first performed in a quartz fluidised bed reactor (as shown in **Fig. 4**) to preliminarily evaluate the mechanical strength of the ash-derived sorbents at room temperature. Sorbent particles with high mechanical strengths correspond to high resistance against attrition, fragmentation, and the subsequent elutriation over continuous operation in fluidised beds. This preliminary fluidisation test excludes particle breakage arising from thermochemical effects, e.g., particles breakage due to thermal stress and mechanical strain induced by phase changes during chemical reactions. In a typical fluidisation experiment, a 15 ml batch of ash-derived sorbent was added into a clear quartz tube to form a loose random packing with 19 mm internal diameter and 500 mm depth. A stainless-steel wire mesh was fixed at 100 mm above the gas inlet to function as a distributor, which allows for unobstructed flow and uniform distribution of the fluidising gas. A plug of quartz wool was inserted into the top of the quartz tube to collect the elutriated fines. The entire bed was fluidised by air, the flowrate of which was controlled by a mass flow controller. The pressure below the fluidised bed was measured using a U-tube manometer. The minimum fluidisation velocity was determined by increasing the flowrate of the fluidising air at increments of 0.2 L/min, while measuring the pressure reading on the manometer. After the flowrate reaches 3.5 L/min, it was reduced with decrements of 0.2 L/min to zero. After measuring the minimum fluidisation velocity, the sample was continuously fluidised for up to 200 min at $U/U_{mf} = 2$ to assess the attrition and elutriation of the ash-derived sorbents. Attrition was determined after the end of the experiment by sieving the particles that remained in the bed and determining the mass fraction of the bed that fell below the lower size limit of 0.150 mm. Elutriation was determined by the mass fraction of fines leaving the fluidised bed and collected in the quartz wool plug over the duration of the experiment. The losses are calculated by:

$$Fines\ loss\ (\%) = \frac{[initial\ mass - final\ mass]\ (g)}{initial\ mass\ (g)} * 100\% \quad \text{Eq. 2}$$

$$Attrition\ loss\ (\%) = \frac{mass\ of\ ash\ below\ size\ range\ (g)}{Final\ mass\ (g)} * \frac{Final\ mass\ (g)}{Initial\ mass\ (g)} * 100\% \quad \text{Eq. 3}$$

$$Total\ loss\ (\%) = Fines\ loss + Attrition\ loss \quad \text{Eq. 4}$$

High temperature calcium looping for carbon capture in a hot fluidised bed

The performance of the ash-derived sorbent was further examined in a hot fluidised bed reactor system, as shown in **Fig. 5**. In each test, a batch of 15 ml (untapped volume) of ash-derived sorbent was dropped into an Inconel fluidised bed reactor with an internal diameter of 19 mm and a length of 1000 mm. A stainless-steel wire mesh was fixed at the axial centre of the reactor to function as the distributor that hold the ashes in place, to ensure unobstructed and uniformly distributed gas flow. Before heating the bed to 750 °C at a heating rate of 10 °C/min, the reactor chamber was purged with N₂ for 30 min. The calcium looping experiment was performed isothermally at 750 °C with cycles of alternating carbonation and calcination stages, each lasting 10 min. In the case of simulating post-combustion CO₂ capture, three carbonation environments denoted “Dry”, “Wet” and “Acidic” were employed during the carbonate stages. The “dry” flue gas was simulated by 15 vol% CO₂, N₂ balance. The “wet” flue gas, simulating the high moisture content in combustion effluents, was composed of 15 vol% CO₂, 20 vol% H₂O with N₂ balance. The “acidic” flue gas was simulated by 15 vol% CO₂, 20 vol% H₂O, 23 ppmv HCl with N₂ balance. The calcination stage employed gas flow of 100% N₂. The total flowrate of the fluidising gas was set constant at 1000 mL/min (as measured at 25 °C, at 1 atm pressure). Each sample was evaluated over 100 carbonation-calcination cycles with a total test duration of 2000 min. Both the inlet and outlet of the reactor were heated and maintained at 150 °C to prevent condensation of moisture. The gas composition leaving the reactor was sampled and measured continuously by an online gas analyser (SICK GMS 810). The pressure within the reactor was maintained at 1 atm.

To validate the application of the ash-derived sorbents in different CO₂ capture scenarios, the calcium looping experiments were conducted in 15%, 25% and 60% CO₂, which represent typical CO₂ mole fractions in the flue gas of solid fuel combustion, waste gases in hydrogen production plants and the CO₂-rich feedstock in natural gas processing plants, respectively.

Results

Pre-processing assessment of raw ash

Particle analysis

The densities of the ash particles were measured and shown in **Table 1**. Based on the Geldart classification of fluidisable particles, as shown in **Fig. 6**, particle sizes were selected so that the fluidisation behaviour falls under group B (sand-like). As shown in **Fig. 6**, the densities of raw IBA, GFA, and APC were found to be 1774 ± 262 , 2346 ± 262 and 2600 ± 262 kg/m³, respectively. Accordingly, the fluidisable particle size ranges were determined to be 130-850 µm for IBA, 95-700 µm for GFA and ESP, and 85-650 µm for APC and 150-950 µm for W-IBA.

Ash sample	Particle density (kg/m ³)		Particle size range from chart (μm)	
	Mean	SD	Minimum	Maximum
IBA	1774	262	130	850
GFA	2346	268	90	700
APC	2600	316	80	650
ESP	2326	317	90	700
W-IBA	1432	253	150	950

Table 1: Particle density of ash and ash-derived sorbent with minimum particle size required to fluidize under Geldart group B. Particle density was measured with assumption that all particles are spherical.

Next, the particle size distributions of the raw IBA and raw fly ashes (including ESP, APC and GFA) were assessed by mechanical sieving and mastersizer, respectively, as shown **Table 2** and **Table 3**, respectively. The purpose of the particle analysis is to determine the need for size control during the pre-treatment of the raw ashes to ensure good fluidisability. For raw IBA, the majority (41.4 wt%) of the ashes were in the 4-20 mm size range, followed by the 1-4 mm range (32.9 wt%), 0.5-1 mm (17.7 wt%), <0.5 mm (7.6 wt%), and 20-50 mm (0.4 wt%). Such a wide size range requires further mechanical sieving to extract particles in the size range of 63 μm – 560 μm for fluidisation. Meanwhile, 74.7% of the raw IBA above 1.0 mm is not suitable for fluidisation at its current state and would require size reduction, e.g., by jaw crushing. Particle size distribution for W-IBA was as received <1000μm. The majority (50.4 wt%) of the ashes were in the 560-1000 μm size range, followed by the 315-560 μm range (28 wt%), 150-315 μm (10.2 wt%), 63-150 μm (6.7 wt%), and the lowest size distribution to fines <63μm (4.73 wt%).

For raw fly ashes, the particle size distribution was calculated by the Mastersizer, reflecting the size at the 10th percentile (d(0.1)), 50th percentile (d(0.5), median), and 90th percentile (d(0.9)). The median particle sizes of ESP, APC and GFA are 38.2 μm, 20.6 μm and 17.2 μm, respectively, which are too small for fluidisation. Therefore, agglomeration is needed for ESP, APC and GFA prior to fluidisation experiments.

Size Fraction (mm)	20 – 50	4 – 20	1 – 4	0.5 – 1.0	< 0.5	0 – 50
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Mass of IBA (kg)	0.12	11.82	9.39	5.04	2.17	28.53
Distribution of IBA (%)	0.4	41.4	32.9	17.7	7.6	100

Size Fraction (μm)	560 – 1000	315-560	150-315	63-150	<63	0 – 1000
Mass of W-IBA (g)	248.69	137.95	50.15	32.98	23.31	492.97
Distribution of IBA (%)	50.44	27.98	10.17	6.69	4.73	100

Table 2: Particle size distribution of raw IBA and W-IBA obtained from mechanical sieving.

Size distribution (μm)	d (0.1)	d (0.5)	d (0.9)
ESP	9.0	38.2	129.3
APC	5.0	20.6	50.1
GFA	4.9	17.2	50.7

Table 3: Particle size distribution of raw fly ashes obtained from Mastersizer.

Compositional analysis

The crystalline phase compositions of the ashes were analysed by XRD, as shown in **Fig. 7A**, **7B**, and **8**. All ashes show the presence calcium oxide (CaO) calcium carbonate (CaCO_3), calcium sulphate (CaSO_4) and calcium chloride hydroxide (CaClOH) at varying extents. Other crystalline phases were also detected, e.g. silicon dioxide (SiO_2) was found in raw IBA and W-IBA, while chloride salts such as sodium chloride (NaCl) and potassium chloride (KCl) were detected in all the fly ash samples. Major metal elements that have been detected by ICP analysis but absent in XRD, e.g. Al, Zn and Fe, are considered to be present either in amorphous phases or as dopants or impurities in other compounds. In the Figures, the results for each element are provided for the five different ashes. The ordering of the ashes from the top bar in each group of five is ESP, GFA, APC, IBA, and W-IBA as the lowermost bar.

The total elemental contents of the raw IBA and fly ashes, as analysed by ICP-OES and ICP-MS, are shown in **Table 4** and **5**, respectively. APC was found to have the highest Ca content of 42.6 wt%, followed by IBA and GFA at 29.6 wt% and 28.9 wt%, respectively. Other elements detectable in the raw ashes include Mg (0.5 - 1.5%), Na (0.7 - 8.1%), Al (0.2 - 4.4%), Zn (0.2 – 4.6%).

Based on the XRD patterns and total elements analysis results, it can be concluded that all the ashes analysed exhibit considerable high Ca contents, suggesting potential for application in calcium looping.

Elements		Total metals content (mg/kg)								
		ESP			APC			GFA		
		Mean	SD	%RSD	Mean	SD	%RSD	Mean	SD	%RSD
Major	Ca	209600	6306	3	426541	5871	1	289004	19010	7
	Mg	15063	229	2	9566	82	1	5472	411	8
	Na	26040	629	2	9957	116	1	55035	3548	6
	Al	30695	269	1	2014	3	0.2	11871	987	8
	Zn	36469	244	1	6333	90	1	16656	1194	7
	Fe	24306	405	2	1900	5	0.3	6388	696	11
	K	43801	74	0.2	15968	948	6	45819	4485	10
Minor	As	132	1	0.4	37	0.5	1	33	3	10
	Ba	1258	14	1	150	1	1	413	55	13
	Cd	236	2	1	75	0.1	0.2	100	7	7
	Co	49	8	15	<10	-	-	8	3	32
	Cr	208	6	3	17	0.5	3	70	4	6
	Cu	1497	1	0.1	331	6	2	714	71	10
	Mn	771	5	1	151	3	2	336	23	7
	Mo	44	3	7	<10	-	-	<10	-	-
	Ni	326	0.4	0.1	15	3	21	29	4	13
	Pb	3313	7	0.2	1401	23	2	2981	145	5
	Sb	41	0.3	1	186	26	14	365	246	68
	Sn	55	2	3	210	3	2	883	67	8
	Sr	291	4	1	134	1	1	154	13	8
	Ti	753	0.3	0.04	861	5	1	1251	894	71
	V	75	1	1	18	0.4	2	<10	-	-

Ag, Be, Ge, Hg, Se, Tl are below detectable range of 10 mg/kg for all samples.

Table 4: Total elements content of ESP, APC, and GFA, major elements were detected with ICP-OES, and minor elements with ICP-MS.

Elements		Total metals content (mg/kg)					
		IBA			W-IBA		
		Mean	SD	%RSD	Mean	SD	%RSD
Major	Ca	296451	2190	1	262017	5307	2
	Mg	14603	236	2	13257	257	2
	Na	13551	296	2	6885	490	7
	Al	30085	1067	4	44395	1178	3
	Zn	3982	323	8	5102	284	6
	Fe	19369	4188	22	45170	4231	9
	K	15126	532	4	6859	1261	18
Minor	As	<10	-	-	10	2	20
	Ba	1637	407	25	2006	5	0.2
	Cd	16	1	8	12	1	6
	Co	33	1	3	123	81	66
	Cr	184	45	24	318	159	50
	Cu	1931	375	19	5410	5014	93
	Mn	581	51	9	733	94	13
	Mo	10	0.1	1	17	11	66
	Ni	88	13	15	319	65	20
	Pb	439	53	12	371	4	1
	Sb	<10	-	-	<10	-	-
	Sn	26	23	88	<10	-	-
	Sr	403	18	5	374	3	1
	Ti	566	53	9	653	27	4
	V	11	1	6	14	1	8

N.B. Ag, Be, HG, Se, Tl are below detectable range of 10 mg/kg for all samples.

Table 5: Total elements content of IBA, and W-IBA, major elements were detected with ICP-OES, and minor elements with ICP-MS.

Thermogravimetric analysis

Figs. 9A and **9B** show the gravimetric CO₂ capture capacity of the raw ash samples over 20 carbonation-calcination cycles in TGA. **Fig. 9A** shows that, amongst ashes evaluated, ESP exhibits the lowest capture capacity of 17 mg/g, whereas APC exhibits the highest capacity at 442 mg/g. In comparison, commercially obtained pure CaO captures CO₂ with an average cyclic capacity of 313 mg/g. Therefore, both raw GFA and APC showed higher CO₂ capture capacity than the commercial benchmark.

Amongst the IBA samples (**Fig. 9B**), W-IBA showed higher average capture capacity (71 mg/g) than raw IBA (34 mg/g), indicating an improvement in cyclic stability after washing.

ESP ashes, despite their high calcium contents according to total elemental analysis, have low capture capacity. This low CO₂ capture performance can be explained by the fact that much of the Ca content in ESP is in the form of CaSO₄ (as indexed by XRD in **Fig. 8**), which are unreactive in calcium looping cycles.

Active calcium and utilization analysis

Table 6 summarises the key results of compositional analyses and TGA, the latter is more indicative of the actually amount of Ca in the samples that is active for CO₂ uptake. Based on a prior techno-economic analysis of the calcium looping process, a minimum active Ca content of 2.9 wt% (4.1 wt% CaO, CO₂ capture rate of 32 mg/g) is required to make calcium looping cost-competitive compared to existing CO₂ capture technologies such as MEA scrubbing. Accordingly, ESP having 1.5 wt% of active Ca content, as shown by **Table 6**, may not be feasible for calcium looping, as they are lower than the minimum Ca content requirement of 2.9 wt%. Therefore, ESP is not pursued further in the present study. W-IBA shows an increased active Ca content of 6.5 wt%, making a more viable candidate sorbent for calcium looping as compared to raw IBA.

Table 6 also shows that both GFA and APC contain more active Ca (40.2 wt% and 29.7 wt%, respectively) than the commercial benchmark (28.5%), suggesting promising viability of utilising APC and GFA as cost effective Ca-rich sorbents for calcium looping.

Sample	Calcined mass ^a %	Ca content %		CO ₂ capture mg/g		Active Ca %
		Original	Calcined	Experimental ^b	Theoretical ^c	
Benchmark*	94.6	71.4	75.5	313	830	28.5
ESP	86.9	21.0	24.2	17	266	1.5
APC	81.3	42.7	52.5	442	578	40.2
GFA	56.8	28.9	50.9	327	560	29.7
IBA	73.2	29.6	40.4	34	445	3.1
W-IBA	76.7	26.2	34.2	71	376	6.5

*Commercial pure CaO powders as a benchmark (reagent grade).

a. Calcined mass determined from TGA testing.

b. Experimental CO₂ capture determined from TGA testing.

c. Theoretical CO₂ capture determined from total elements content (with 100% active ca)

Table 6: Summary of ash characteristics from TGA and total element analysis, as well as theoretical CO₂ capture capacities determined based on ICP analysis and TGA.

Pre-treatment and processing of ashes

Pre-treatment processes include agglomeration, calcination are denoted “A” and “C” respectively. For example, AC-GFA denotes GFA that had undergone agglomeration, followed by calcination. Ashes that did not go through any pre-treatment process are denoted as “raw”, e.g. raw-IBA. Based on the preliminary assessment discussed above, both raw GFA and raw APC were agglomerated and calcined, denoted at AC-GFA and AC-APC, respectively.

Fluidisation in ambient conditions

Raw and treated ash samples within the range of 0.063-1.000 mm were subjected to fluidisation tests using air as the fluidising gas in ambient conditions. The size range tested corresponds to Geldart group B particles. **Table 7** summarises the experimentally measured Umf of all the ash samples in various particle size fractions. It can be seen that, all ash-derived samples studied are fluidisable, except for AC-APC ash in the size range of 0.063-0.150 mm, which showed Geldart group C behaviour (cohesive). Thus, this size range of AC-APC is not recommended for fluidisation and requires further iterations of processing and assessments to improve their fluidisability.

Average Umf (m/s)				
Ash-derived sorbent	Particle Size Distribution (µm)			
	63-150	150 - 315	315-560	560-1000
Raw-IBA	0.0275	0.0552	0.1377	0.3673
W-IBA	0.0275	0.0827	0.2295	0.505
AC-GFA	0.0275	0.0643	0.2295	0.5508
AC-APC	N.A.	0.0458	0.1837	0.3978

Table 7 Minimum fluidising velocity of various ash particles at various size ranges, determined using air as the fluidising gas at room temperature.

Loss analysis

Resistance to attrition and elutriation is also critical to the application of the ash-derived sorbents in the calcium looping process. High attrition rates, and consequently high elutriation rates, correspond to the need for high rates of sorbent makeup to maintain stable operation of carbon capture.

Accordingly, the rates of attrition and elutriation of the ash samples were first assessed in bubbling fluidised beds operating in ambient conditions, using air as the fluidising gas. The

test results are summarised in **Table 8**. Here, the fines loss, attrition loss and total loss were calculated according to **Eqs. 2, 3 and 4**, respectively, as described in the Methods section.

All the ash-derived sorbents assessed show that the combined attrition and fines loss rates are below 10% over a 200-min period, except for AC-APC, which showed 48.13% and 26.62% total loss in the size ranges of 150-315 μm and 560 – 1000 μm , respectively. Therefore, APC in this size fraction requires further strengthening (e.g., calcination) before application in continuous CO_2 capture reactors. Comparing raw IBA and W-IBA, it is apparent that attrition and fines loss have significantly decreased across all size ranges after washing.

Ash-derived sorbent	Fines loss, attrition loss and total mass loss (%)											
	Particle Size Distribution (μm)											
	63 -150			150 - 315			315 - 560			560 - 1000		
	Fines	Attrition	Total	Fines	Attrition	Total	Fines	Attrition	Total	Fines	Attrition	Total
Raw IBA	4.04	4.96	8.80	0.17	6.56	6.72	1.23	5.86	7.02	0.35	5.89	6.23
W-IBA	0.65	0.92	1.56	0.41	2.21	2.61	0.019	0.79	0.79	0.02	1.30	1.31
AC-GFA	3.31	5.47	8.60	7.74	8.41	15.50	0.38	2.86	3.23	0.22	3.84	4.04
AC-APC	-	-	-*	2.96	46.55	48.13	0.20	9.57	9.75	8.08	20.18	26.62

*Sample did not fluidise.

Table 8 Fines loss, attrition loss, and total mass loss of particles measured by a fluidised bed with an aspect ratio (height: diameter) of 2.5, operating in ambient air for 200 minutes.

High temperature carbon capture by calcium looping

After the one round of pre-assessment and pre-processing protocols, W-IBA, and AC-GFA were found to be particularly suitable for further evaluation in the hot fluidised bed reactor. ESP and raw IBA showing low active calcium content, while AC-APC showing high attrition rates and would require further iterative treatment and assessments (as outlined in **Fig. 1**) before it can be further pursued as a sorbent for CO_2 capture by calcium looping.

Fig. 10 shows the carbon capture capacity of the ash derived sorbents, namely, W-IBA and AC-GFA over 100 cycles of calcium looping in simulated dry flue gas containing 15% CO_2 . The results demonstrate that W-IBA behaved similarly to raw IBA, and AC-GFA performed significantly better than both raw-IBA and W-IBA, showing good cyclic stability and high capture capacity of 67 mg/g by the 100th cycle. All samples showed decayed CO_2 uptake over cycles, mostly likely to be owing to sintering, which could be accelerated by cyclic phase changes at high temperatures.

Table 9 summarises the losses of the ash particles due to attrition and elutriation (as calculated using **Eqs. 2-4**) over the duration of the 20 carbonation-calculation cycles in hot fluidised beds (with a total duration of 2000 mins). Based on **Table 9**, it is apparent that W-IBA showed a notable improvement in attrition resistance over raw IBA in all test conditions, with a reduction of total losses at 11.7%, 8.49%, and 6.8% for dry, wet, and acidic flue gas experiments, respectively. For AC-GFA, the lowest total losses were seen in dry gas, followed by wet gas. The highest total loss was seen in acidic gas. Despite the high fines losses, AC-GFA exhibited lower attrition loss and total loss than raw IBA and W-IBA in the absence of HCl. Regrettably, the CO₂ capture performance in wet and acid conditions were not quantified owing to the gas analysis setup being incompatible to moisture and HCl.

Fines loss, Attrition loss and total mass loss (%)				
Ash	Condition	Attrition Loss	Fines Loss	Total
Raw IBA	Dry	31.2	6.1	37.3
	Wet	24.9	13.4	38.3
	Acidic	26.2	4.4	30.6
W-IBA	Dry	23.2	2.4	25.6
	Wet	27.6	2.2	29.8
	Acidic	23.7	0.05	23.8
AC-GFA	Dry	4.4	16.6	21.0
	Wet	12.8	10.5	23.3
	Acidic	5.2	27.5	32.7

Table 9 Fines loss, attrition loss, and total mass loss of particles in over 100 calcium looping cycles in fluidised bed experiments at 750 °C. The total flowrate of the fluidising gas was at 1000 l/min (measured at 25 °C, 1 atm pressure).

Fig. 11A and **11B** show that the W-IBA afforded satisfactory CO₂ capture performance in fluidised beds at 750 °C under low and high CO₂ concentrations (viz. 15 and 60 vol%) during carbonation. It can be seen that the gravimetric CO₂ uptake by W-IBA increases with the CO₂ concentration used during carbonation, increasing from 72.3 mg/g in 15% CO₂ to and 134.4 mg/g in 60% CO₂ in the first cycle. By the 20th cycle, the CO₂ uptake stabilised towards 33 and 126 mg/g in 15% and 60%, respectively. The cyclic stability of the sorbents can also be characterised by “relative uptake”, by defining the CO₂ uptake in the first cycle as having 100% relative uptake, as shown in **Fig. 11B**. By the 20th cycle, W-IBA maintained 38.7%, 58.3% and 81.6% relative uptake rates when carbonated in 15% CO₂, 25% CO₂ and 60% CO₂ in each cycle.

When capturing from simulated flue gases containing 15% and 60% CO₂, GFA showed exceptional retention in relative uptake of 75% and 97% after 20 cycles in their respective gas

compositions as seen in **Fig. 11D** and **Fig. 11F**. When compared between raw IBA and W-IBA, both ashes yielded similar relative uptake of about 38-40% by the 20th cycle, but in 60% CO₂ conditions, W-IBA exhibited better stability than raw-IBA, maintaining at 82.9% and 53.6% of their respective initial capture capacities, as shown in **Fig. 11F**. Therefore, the W-IBA samples prepared in this invention is capable of sustaining reasonable capture performance in applications involving a wide range of CO₂ partial pressures, such as capturing CO₂ from waste gases of chemical process, e.g., hydrogen production and natural gas processing.

In summary, the present invention provides for useful methods and materials for carbon dioxide capture. In particular, the present invention can be used for CO₂ capture for waste gases, such as, for example, flue gas. The present invention may be used in a variety of contexts, including, but not limited, to:

- 1) Decarbonization of industries with high CO₂ emission rates. The present invention is suitable for a wide range of gas clean up units.
- 2) Minimizing ash disposal rates on to landfills by reintroducing spent or waste materials back into the process loop.
- 3) CO₂ enriched ashes and collected CO₂ gases as a form of upcycling can be potentially sold back into the market.
- 4) Increased savings in terms of materials costs when compared to existing carbon capture storage and utilisation (CCSU) applications, such as, for example, conventional calcium looping with limestone and MEA scrubbers.

CLAIMS:

1. A method of producing CO₂ sorbents from Ca-containing incineration and gasification ashes, comprising:
 - a. removing any ferrous metals, non-ferrous metals, particles larger than a predetermined size, and glass from the ashes to provide a cleaned ash;
 - b. assessing the cleaned ash of step a, including
 - i. assessing the particle size distribution and elemental composition to categorize the cleaned ash into high Ca-containing ash having a Ca content of 15wt% or higher and low Ca-containing ash having a Ca content of less than 15wt%;
 - ii. assessing the CO₂ uptake capacity of the high Ca-containing ash and further categorizing the high Ca-containing ash into inactive Ca-containing ashes and active Ca-containing ashes;
 - iii. assessing the active Ca-containing ashes for their fluidization characteristics; and
 - c. either i) crushing the active Ca-containing ashes with particle sizes larger than a predetermined particle size to smaller sizes, or ii) agglomerating the active Ca-containing ashes with particle sizes smaller than a predetermined particle size into larger agglomerated particles, in order to obtain a processed ash.
2. The method according to Claim 1, wherein the method further comprises:
 - d. chemically and/or thermally treating the agglomerated particles to strengthen the agglomerated particles.
3. The method according to Claim 2, wherein thermally treating the agglomerated particles includes sintering the agglomerated particles, optionally via calcination, such as at around 650 to around 850°C, such as around 750°C, for 2 hours in air.
4. The method according to Claim 2 or Claim 3, wherein the strengthened agglomerated particles are sized to within a predetermined size range, optionally wherein the sizing includes grinding and sieving, further optionally wherein the method further comprises providing any particles which are outside the predetermined size range to either step b. or step c.

5. The method according to any preceding claim, wherein the method further comprises:
 - f. providing the processed ash to a chemical looping apparatus, such as a chemical looping process for carbon capture.
6. The method according to Claim 5, wherein the method further comprises contacting the processed ash with a fluid stream comprising carbon dioxide to remove at least a portion of the carbon dioxide from the fluid stream, optionally wherein the method comprises calcining the processed ash to liberate captured carbon dioxide.
7. A method of producing CO₂ sorbents according to any preceding claim, wherein the active calcium includes calcium oxide, calcium hydroxide, and calcium chloride hydroxide while the inactive calcium includes mayenite, calcium silicates, calcium ferrites and calcium sulfates.
8. A method of producing CO₂ sorbents according to any preceding claim, wherein the inactive Ca-containing ashes further undergo chemical treatment to convert to active Ca-containing ashes.
9. A method of producing CO₂ sorbents according to any preceding claim, wherein the ashes are further assessed for their suitability for CO₂ capture, including resistance to attrition and fluidisation behaviour over high temperature carbonation-calcination cycles in a fluidised bed reactor (FBR).
10. A method of producing CO₂ sorbents according to any preceding claim, wherein the method includes collecting Ca-containing incineration and gasification ashes from a thermochemical waste treatment plant, optionally wherein the thermochemical waste treatment plant is an incineration plant or a gasification plant.
11. The method according to any preceding claim, wherein the ferrous metals are removed magnetically.
12. The method according to any preceding claim, wherein step a. includes removing particles with a particle size greater than 50 mm.
13. The method according to any preceding claim, wherein assessing the particle size distribution of the cleaned ash in step b.i. is conducted by mechanical sieving for

particle sizes of 0.5 mm or higher, and by light scattering for particles sizes of less than 0.5 mm.

14. The method according to any preceding claim, wherein one or more of the following apply:
 - i) assessing the elemental composition of the cleaned ash in step b.i. is performed via one or both of inductively coupled plasma – optical emission spectrometry (ICP-OES) and inductively coupled plasma – mass spectrometry (ICP-MS) of a microwave acid digestion solution of the cleaned ash;
 - ii) assessing the CO₂ uptake capacity of the high Ca-containing ash in step b.ii. is performed thermogravimetrically;
 - iii) assessing the active Ca-containing ashes for their fluidization characteristics is performed without heating using a suitable fluidising gas, such as compressed air.
15. The method according to any preceding claim, wherein the predetermined particle size is from about 80 to about 975 µm, such as from about 130 to about 850 µm, such as about 95 to about 700 µm, such as about 86 to 650 µm, such as about 150 to 950 µm.
16. The method according to any preceding claim, wherein the active Ca-containing ashes have a minimum active Ca content of 2.9 wt%, such as a minimum content of 4.1wt% calcium oxide, optionally wherein the active Ca-containing ashes have an active Ca content of 29.7wt%.
17. The method according to any preceding claim, wherein the Ca-containing incineration and gasification ashes are selected from gasification fly ash, incineration bottom ash, and combinations thereof.
18. An ash-derived CO₂ sorbent comprising ash prepared according to any of Claims 1 to 17.
19. An ash-derived CO₂ sorbent comprising washed incineration bottom ash, agglomerated calcined gasification fly ash, or a combination thereof.
20. A calcium looping apparatus for carbon dioxide capture, the apparatus comprising the ash-derived sorbent according to Claim 18 or 19.

21. Use of an ash-derived CO₂ sorbent prepared according to the method of any of Claims 1 to 17 or the ash-derived CO₂ sorbent according to claim 18 or 19 in a calcium looping method or apparatus.