METHODS OF PRODUCING A BUILDING MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

Pursuant to 35 U.S.C. §119(e), this application claims priority to the filing date of the United States Provisional Patent Application Serial No. 63/291,767, filed December 20, 2021, the disclosure of which application is herein incorporated by reference.

INTRODUCTION

Concrete is the most widely used engineering material in the world, due to its ease of placement and high load bearing capacity. It is estimated that the present world consumption of concrete is over 11 billion metric tons per year. (Concrete, Microstructure, Properties and Materials (2006, McGraw-Hill)).

The main ingredients of concrete are cement, such as Portland cement, with the addition of coarse and fine aggregates, air and water. Aggregates in conventional concretes include sand, natural gravel and crushed stone. Artificial aggregates may also be used, especially in lightweight concretes. Once the component materials are mixed together, the mixture sets or hardens due to the chemical process of hydration in which the water reacts with the cement which bonds the aggregates together to form a stone-like material. The proportions of the component materials affect the physical properties of the resultant concrete and, as such, the proportions of mixture components are selected to meet the requirements of a particular application.

Portland cement is made primarily from limestone, certain clay minerals, and gypsum, in a high temperature process that drives off carbon dioxide and chemically combines the primary ingredients into new compounds. The energy required to fire the mixture consumes about 4 GJ per ton of cement produced.

Because carbon dioxide is generated by both the cement production process itself, as well as by energy plants that generate power to run the production process, cement production is a leading source of current carbon

dioxide atmospheric emissions. It is estimated that cement plants account for 5% of global emissions of carbon dioxide. As global warming and ocean acidification become an increasing problem and the desire to reduce carbon dioxide gas emissions (a principal cause of global warming) continues, the cement production industry will fall under increased scrutiny.

Fossil fuels that are employed in cement plants include coal, natural gas, oil, used tires, municipal waste, petroleum coke and biofuels. Fuels are also derived from tar sands, oil shale, coal liquids, and coal gasification and biofuels that are made via syngas. Cement plants are a major source of CO_2 emissions, from both the burning of fossil fuels and the CO_2 released from the calcination which changes the limestone, shale and other ingredients to Portland cement. Cement plants also produce waste heat. Additionally, cement plants produce other pollutants like NOx, SOx, VOCs, particulates and mercury. Cement plants also produce cement kiln dust (CKD), which must sometimes be land filled, often in hazardous materials landfill sites.

CO_2 emissions have been identified as a major contributor to the phenomenon of global warming and ocean acidification. CO_2 is a by-product of combustion and it creates operational, economic, and environmental problems. It is expected that elevated atmospheric concentrations of CO_2 and other greenhouse gases will facilitate greater storage of heat within the atmosphere leading to enhanced surface temperatures and rapid climate change. CO_2 has also been interacting with the oceans driving down the pH toward 8.0. CO_2 monitoring has shown atmospheric CO_2 has risen from approximately 280 parts per million (ppm) in the 1950s to approximately 400 ppm today. The impact of climate change will likely be economically expensive and environmentally hazardous. Reducing potential risks of climate change will require sequestration of CO_2.

SUMMARY

Aspects of the invention include methods of producing a building material. Methods of interest include preparing a carbonate precipitate, which may be a

carbonate slurry, having an undifferentiated pluripotent polymorph precursor (also referred to herein as a polymorph precursor), and processing the carbonate precipitate, which may be a carbonate slurry, under conditions sufficient to produce the building material. Methods of interest also include preparing a calcium carbonate material comprised of any of, or a combination of, pluripotent polymorph precursor, polymorph precursor, ACC, vaterite, and/or aragonite, and processing the carbonate material via seeding and/or bicarbonate washing in a manner sufficient to produce a building material. In some versions, the carbonate slurry is a slurry of metal carbonate particles (e.g., alkaline earth metal carbonate particles). For example, in some versions, the metal carbonate particles are calcium carbonate particles or calcium magnesium carbonate particles. The polymorph precursors described herein exist in a state between an amorphous state and an ordered state (e.g., amorphous calcium carbonate (ACC) and a polymorph). As such, in some cases, polymorph precursors include vaterite precursor, calcite precursor, aragonite precursor and/or dolomite precursor. In some embodiments, methods also include evaluating the carbonate slurry for the presence of the polymorph precursor. Techniques for evaluating a carbonate slurry include, for example, scanning electron microscopy (SEM), X-ray diffraction (XRD), obtaining an infrared (IR) spectrum of the carbonate slurry, and obtaining a Ca:C ratio.

Embodiments of the invention further include contacting the carbonate precipitate, e.g., a carbonate slurry, (in the form of any of, or a combination of, pluripotent polymorph precursor, polymorph precursor, ACC, vaterite, calcite, and/or aragonite, or for calcium magnesium carbonate polymorph precursor, dolomite) with a curing liquid (e.g., carbonate curing liquid, a bicarbonate curing liquid, a phosphate curing liquid, a divalent alkali earth metal curing liquid or water) sufficient to produce a cured building material. Embodiments of the invention further include incorporating ‘seeds’ of the desired final product with the metal carbonate (any of, or a combination of, pluripotent polymorph precursor, polymorph precursor, ACC, vaterite, calcite, and/or aragonite, or for calcium magnesium carbonate polymorph precursor, dolomite), and then ‘curing’ with

moisture. Embodiments of these 'seeds' include aragonite, calcite or for calcium magnesium carbonate polymorph precursor, dolomite, or any crystalline metal carbonate particle with a desired final structure. Building materials produced via the subject methods include, for example, aggregates.

In some embodiments, preparing the carbonate precipitate, e.g., a carbonate slurry, comprises a CO_2 sequestering process. For example, in certain embodiments, the CO_2 sequestering process comprises contacting an aqueous capture liquid with a gaseous source of CO_2 under conditions sufficient to produce an aqueous carbonate. The method may additionally include combining a cation source and the aqueous carbonate under conditions sufficient to produce a CO_2 sequestering carbonate. In some cases, the aqueous capture liquid is an aqueous ammonia capture liquid. Aspects of the invention also include building materials (e.g., aggregates) as well as compositions (e.g., concrete dry composites, settable compositions and built structures) produced via the subject methods.

BRIEF DESCRIPTION OF THE FIGURES

The invention may be best understood from the following detailed description when read in conjunction with the accompanying drawings. Included in the drawings is the following figure:

FIG. 1 presents a flowchart depicting the production of a building material with a carbonate slurry having an undifferentiated pluripotent polymorph precursor, according to certain embodiments.

FIG. 2 presents a scanning electron microscope (SEM) image of an undifferentiated pluripotent polymorph precursor prepared from a CO_2 sequestering process. Note the globular nature of the material in the image.

FIG. 3 presents a scanning electron microscope (SEM) image of a building material processed from an evaluated carbonate slurry. Note the ordered crystal nature of the material in the image.

FIG. 4 presents the use of infrared (IR) spectroscopy to evaluate materials for the presence of polymorph precursors produced from carbonate slurries

prepared via a CO_2 sequestering process. Also included in the figure are IR spectra of building materials produced from processing carbonate slurries containing desirable differentiated polymorph precursors, as well as spectra of building materials produced from processing undesirable differentiated polymorph precursors. Note the phenomenon of an undifferentiated pluripotent polymorph (UPP) precursor in the carbonate slurries differentiating to specific polymorphs of calcium carbonate, namely, to calcite, in the building materials.

FIG. 5 presents the use of X-ray diffraction (XRD) as a means to evaluate materials for the presence of polymorph precursors produced from carbonate slurries prepared via a CO_2 sequestering process. The weight percent of different polymorphs present in the materials are based on Rietveld refinement results from XRD data. The phenomenon of an undifferentiated pluripotent polymorph precursor in the carbonate slurries differentiating to specific polymorphs of calcium carbonate, namely, from amorphous calcium carbonate (ACC) polymorphs to vaterite to calcite, in the building materials, is obviated by the mineralogical analyses from the XRD data refinement.

FIG. 6 presents a flowchart depicting the production of a building material, in one embodiment, by seeding an undesirable differentiated polymorph precursor produced from a carbonate slurry. By seeding the undesirable differentiated polymorph precursor with calcite polymorph, and processing the seeded polymorph precursor with heat and moisture, a continuous phase calcite polymorph suitable to be used as a building material may be produced.

FIG. 7 demonstrates the use of Scanning Electron Microscopy (SEM) to identify ‘polymorph precursors’ from a CO_2 sequestering process.

FIG. 8 demonstrates the use of XRD to identify polymorph precursors by broad peaks.

FIG. 9 presents data showing production of an aragonite final product using aragonite seeds, as was determined from XRD.

FIG. 10 demonstrates the improvement in strength from the same calcium carbonate precipitate when processed in a typical manner as compared to when seeds are added to the precipitate.

FIG. 11 presents a demonstration of the presence of different crystal systems of $CaCO_3$, including two different crystal systems of vaterite, using methods of X-ray diffraction (XRD).

DETAILED DESCRIPTION

Methods of producing a building material are provided. Methods of interest include preparing a carbonate precipitate, e.g., a carbonate slurry, comprising an undifferentiated pluripotent polymorph precursor (also referred to herein as a polymorph precursor) and processing the carbonate slurry under conditions sufficient to produce the building material. The polymorph precursors exist in an intermediate state between an amorphous state (e.g., amorphous calcium carbonate (ACC)) and an ordered state (e.g., a polymorph of calcium carbonate). Aspects of the invention also include building materials (e.g., aggregates) as well as compositions (e.g., concrete dry composites, settable compositions and built structures) that include building materials produced via the subject methods.

Before the present invention is described in greater detail, it is to be understood that this invention is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present invention will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the invention.

The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the invention.

Certain ranges are presented herein with numerical values being preceded by the term "about." The term "about" is used herein to provide literal support for the exact number that it precedes, as well as a number that is near to or approximately the number that the term precedes. In determining whether a number is near to or approximately a specifically recited number, the near or approximating un-recited number may be a number which, in the context in which it is presented, provides the substantial equivalent of the specifically recited number.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present invention, representative illustrative methods and materials are now described.

All publications and patents cited in this specification are herein incorporated by reference as if each individual publication or patent were specifically and individually indicated to be incorporated by reference and are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided may be different from the actual publication dates which may need to be independently confirmed.

It is noted that, as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise. It is further noted that the claims may be drafted to exclude any optional element. As such, this statement is intended to serve as antecedent basis for use of such exclusive terminology as “solely,” “only” and the like in connection with the recitation of claim elements, or use of a “negative” limitation.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present invention. Any recited method can be carried out in the order of events recited or in any other order which is logically possible.

METHODS OF PRODUCING A BUILDING MATERIAL

As discussed above, aspects of the invention include methods of producing a building material. Methods of interest include preparing a carbonate precipitate (e.g., in the form of a slurry) comprising an undifferentiated pluripotent polymorph precursor (i.e., a polymorph precursor), and processing the carbonate precipitate, e.g., a carbonate slurry, under conditions sufficient to produce the building material. As discussed herein, an "undifferentiated pluripotent polymorph precursor" or “polymorph precursor” refers to a carbonate compound that exists in a state between an amorphous state and an ordered state.

The preparation of a carbonate slurry via a CO_2 sequestering process (Box 101, FIG. 1) results in the production of an undifferentiated pluripotent polymorph precursor (Box 102, FIG. 1). That precursor can be manipulated/controlled to create a desirable differentiated polymorph precursor that is destined to form a specific polymorph such as calcite (or whatever polymorph is desirable) (Box 103, FIG. 1). There may be instances, however, where an undesirable differentiated polymorph precursor is created and is destined to form an undesirable polymorph such as aragonite (or whatever polymorph is undesirable) (Box 104, FIG. 1). In this case, an additional process might be employed to manipulate/control the undesirable polymorph back into a desirable differentiated polymorph precursor destined to form the specific polymorph of choice (Box 105, FIG. 1). In either case, the resulting produced building material, e.g., aggregate for concrete, is used to construct a built structure (Box 106, FIG. 1).

For example, an undifferentiated pluripotent polymorph precursor slurry may be produced in a carbon sequestration process, and then be differentiated to transform to a specific polymorph precursor or differentiated to prevent the formation of a specific polymorph precursor. If the differentiated polymorph precursor is not desirable for a building material, then a second method/system (rinsing, curing, chemical additives, seeding, etc.) can be applied to differentiate the polymorph precursor to a desirable final polymorph. An embodiment of the methods includes contacting the polymorph precursor with magnesium to differentiate the undifferentiated pluripotent polymorph precursor to an amorphous polymorph precursor to prevent the formation of calcite as the final polymorph. In alternative embodiments, methods include contacting the polymorph precursor with strontium to differentiate the undifferentiated pluripotent polymorph precursor to an amorphous polymorph precursor to prevent the formation of aragonite as the final polymorph.

Undifferentiated Pluripotent Polymorph Precursors

Undifferentiated pluripotent polymorph precursors (i.e., polymorph precursors) employed in embodiments of the invention may include any suitable carbonate compound or compounds. Cations of different valances can form solid carbonate compositions (e.g., in the form of carbonate minerals). In some instances, monovalent cations, such as sodium and potassium cations, may be present in carbonate compounds of the polymorph precursors. In other instances, divalent cations, such as alkaline earth metal cations, e.g., calcium and magnesium cations, may be present. Carbonate compounds of polymorph precursors may be compounds having a molecular formulation $X_m(CO_3)_n$ where X is any element or combination of elements that can chemically bond with a carbonate group or its multiple, wherein X is in certain embodiments an alkaline earth metal and not an alkali metal; wherein m and n are stoichiometric positive integers. These carbonate compounds may have a molecular formula of $X_m(CO_3)_n \bullet H_2O$, where there are one or more structural waters in the molecular formula. In certain cases, the carbonic salt is calcium carbonate ($CaCO_3$).

In embodiments of the invention where the carbonate compound is calcium carbonate, the amorphous state may be amorphous calcium carbonate (ACC) and the ordered state may be a polymorph of calcium carbonate. As is understood in the art, ACC describes a state of calcium carbonate lacking a crystalline structure. ACC is a generally transient form of calcium carbonate that will transform into a polymorph under certain conditions (e.g., in the presence of water and/or heat). ACC may include different levels of hydration. In some embodiments, ACC is hydrated (i.e., includes one or more structural waters) In certain cases, hydrated ACC can include approximately 1.6 mol of water per mol of calcium carbonate. In other cases, ACC may be anhydrous.

As discussed herein, a "polymorph" refers to one of a series of crystalline forms that may be derived from an amorphous substance. In other words, polymorphs are compounds that have the same empirical formula but different crystal structures. Polymorphs of interest may include anhydrous polymorphs as well as hydrated polymorphs. For example, anhydrous phases of calcium carbonate include calcite ($CaCO_3$), aragonite ($CaCO_3$), and vaterite ($CaCO_3$). Hydrated phases of calcium carbonate include monohydrocalcite ($CaCO_3 \bullet H_2O$) and ikaite ($CaCO_3 \bullet 6H_2O$). Calcite, aragonite, and vaterite are polymorphs of calcium carbonate ($CaCO_3$) since they all have the same empirical formula of $CaCO_3$, but they differ from each other in crystal structure, e.g., the crystal structure space groups of calcite and aragonite are R3c and Pmcn, respectively. ACC and calcium carbonate polymorphs are discussed in, for example, Bots et al. *Cryst. Growth Des*. (2012) 12:1306-1384; and Radha et al. *PNAS*. (2010) 107:16438-16443, the disclosures of which are herein incorporated by reference in their entirety. In additional cases, the polymorph includes calcium magnesium carbonate. In such cases, the polymorph may be dolomite or proto-dolomite.

Accordingly, in some instances, the polymorph precursor of the present invention is a calcium carbonate compound existing in an intermediate state between ACC and a calcium carbonate polymorph, as shown below:

ACC → polymorph precursor → polymorph (differentiated)

Polymorph precursors of interest may include, for example, vaterite precursor, calcite precursor, aragonite precursor, monohydrocalcite precursor and ikaite precursor. In certain cases, the polymorph precursor is selected from the group consisting of: vaterite precursor, calcite precursor, and aragonite precursor. In one embodiment, the polymorph precursor includes vaterite precursor. In another embodiment, the polymorph precursor includes calcite precursor. In yet another embodiment, the polymorph precursor includes aragonite precursor. Other embodiments of the invention may involve a combination of polymorph precursors (e.g., a combination of vaterite precursor, calcite precursor and aragonite precursor). Another polymorph precursor of the present invention is a calcium magnesium carbonate compound existing in an intermediate state between ACC and a calcium magnesium carbonate polymorph. Polymorph precursors of interest may include, for example, dolomite precursor or proto-dolomite precursor.

The undifferentiated pluripotent polymorph precursor may comprise different polymorph precursors of calcium carbonate, such as amorphous calcium carbonate (ACC) precursor, vaterite precursor, aragonite precursor or calcite precursor, as well as additional components, e.g., UCA/waste sludge. In some embodiments wherein the polymorph precursor is comprised of a vaterite precursor, the crystal system of the vaterite precursor may exist in any of the crystal systems of hexagonal, triclinic, monoclinic, or orthorhombic. For example, in some embodiments the polymorph precursor is comprised of 16% ACC precursor, 79% vaterite precursor and 5% calcite precursor, wherein the 79% vaterite precursor is comprised of 30% hexagonal vaterite precursor and 49% triclinic vaterite precursor as is determined by XRD (FIG. 11).

The polymorph precursor discussed herein may be described as being predestined with respect to the polymorph into which it will eventually transform. By “predestined”, it is meant that the composition and/or structure of the polymorph precursor is such that the polymorph into which said precursor will transform is already determined. For example, where ACC gives rise to vaterite

precursor, said vaterite precursor is predestined to form vaterite, and only vaterite. In other words, absent some other intervention, the vaterite precursor will not become, for example, aragonite or calcite. The same is true for the other polymorph precursors: aragonite precursor is predestined to become aragonite and calcite is predestined to become calcite.

In some instances, the polymorph precursors discussed herein are amorphous. By “amorphous” it is meant that the polymorph precursor is non-crystalline in nature. The amorphous character of the polymorph precursor may be observed by multiple suitable techniques. For example, polymorph precursors may appear as small globular structures when viewed via scanning electron microscopy (SEM), e.g., as is shown in FIG. 2, as opposed to the more ordered structures of a polymorph or crystal. In addition, when analyzed via infrared (IR) spectroscopy and/or X-ray diffraction (XRD), polymorph precursors exhibit broad peaks. Further, in some cases, a calcium to carbon ratio (Ca:C) taken of the carbonate slurry may exhibit a calcium deficiency (i.e., as compared to a carbonate slurry in which polymorph precursor is not present). Suitable SEM, IR, XRD, and Ca:C protocols are described in detail below.

In one embodiment where a carbonate slurry is prepared, e.g., via a CO_2 sequestering process, the carbonate slurry includes metal carbonate particles, specifically, of calcium carbonate particles. The carbonate slurry including calcium carbonate particles is evaluated for the presence of an undifferentiated pluripotent polymorph precursor by several techniques. FIG. 2 exemplifies the use of one such technique: scanning electron microscopy (SEM), whereby an image was taken immediately after dewatering the carbonate slurry of metal carbonate particles, specifically, of calcium carbonate particles. The globular characteristics of the material shown in the SEM image in FIG. 2 suggest the presence of an undifferentiated pluripotent polymorph precursor that is amorphous in nature. The evaluated carbonate slurry of metal carbonate particles, specifically of calcium carbonate particles, was further processed under conditions sufficient to produce a building material, e.g., an aggregate for concrete. Here, the evaluated carbonate slurry, which showed evidence of an

undifferentiated pluripotent polymorph precursor, was rinsed with water and with a solution of bicarbonate, was then agglomerated into large particles several millimeters in diameter, e.g., to form an aggregate building material suitable for concrete, and was finally cured in a bicarbonate solution for ten (10) days to produce a cured building material, e.g., an aggregate for concrete. An SEM image of the cured building material produced in this embodiment is shown in FIG. 3; note the ordered calcite crystal structures observed in this image. This provides one example of the invention whereby the presence of the undifferentiated pluripotent polymorph precursor in the carbonate slurry was processed in such a way so as to create a differentiated polymorph precursor destined to form the calcite polymorph in the final building material used to construct a built structure.

In other embodiments where a carbonate slurry is prepared, e.g., via a CO_2 sequestering process, the carbonate slurry, including metal carbonate particles and specifically, of calcium carbonate particles, is evaluated for the presence of an undifferentiated pluripotent polymorph precursor by infrared spectroscopy (IR), e.g., as is shown in the IR spectra in FIG. 4. The IR spectra help to illustrate the transitions that occur from an undifferentiated pluripotent polymorph precursor to a differentiated calcite polymorph by processing a carbonate slurry with washing and curing steps, ultimately producing a building material, e.g., aggregate for concrete. As shown in FIG. 4, representative IR spectra of calcium carbonate at different points during processing are presented. From top to bottom, the IR spectra show a fresh carbonate slurry, a carbonate slurry washed with water, a slurry washed with $NaHCO_3$, a fresh aggregate, an aggregate 7 days following production without treatment, an aggregate 3 days after curing, and a completed washed/cured aggregate after 7 days.

In some embodiments, where a carbonate slurry is prepared, e.g., via a CO_2 sequestering process, the carbonate slurry, including metal carbonate particles and specifically, of calcium carbonate particles, is evaluated for the presence of an undifferentiated pluripotent polymorph precursor by X-ray diffraction (XRD). In this embodiment of the method, the refinement of the XRD

data help to illustrate the transitions that occur from an undifferentiated pluripotent polymorph precursor to a differentiated calcite polymorph by processing a carbonate slurry with washing and curing steps, ultimately producing a specific polymorph suitable to be used as a building material, e.g., aggregate comprised of calcite polymorph that is suitable for concrete.

In FIG. 5, the weight percent of different polymorphs present in the materials analyzed are based on Rietveld refinement results from XRD data. The phenomenon of an undifferentiated pluripotent polymorph precursor in the carbonate slurries differentiating to specific polymorphs of calcium carbonate, namely, from amorphous calcium carbonate (ACC) polymorphs to vaterite to calcite, in the building materials, is shown by the mineralogical analyses from the XRD data refinement. FIG. 5 depicts, from left to right: fresh carbonate slurry, carbonate slurry washed with water, carbonate slurry washed with $NaHCO_3$, fresh agglomerated aggregate, and aggregate after curing.

As discussed above, the polymorph precursors may be described as existing in an intermediate state between ACC and a calcium carbonate polymorph. In other words, the polymorph precursor may adopt characteristics of both ACC and the polymorph to which the polymorph precursor is predestined to become. For example, a polymorph precursor may exist as a polymorph-specific lattice within a mass (e.g., globule) of ACC. In certain cases, the polymorph precursor may appear amorphous under analytical methods, but nonetheless contain a semi-ordered structure therein.

Carbonate precipitates of the invention may or may not have an impurity, where “impurity” is defined as a material or substance that is not an intended product. In some cases where the impurity is present, said impurity is a carbonate impurity. In other words, the impurity is a polymorph that is other than the desired polymorph. In an example where the desired polymorph is vaterite or aragonite, an impurity that may be present in the composition is calcite. In additional cases, the impurity may be a sludge waste (e.g., a sludge waste from another industry). However, the impurity may be considered inconsequential in some cases where the precipitated carbonate includes one of the following: a

pluripotent polymorph precursor, an undesirable polymorph precursor, a desirable polymorph precursor, an amorphous $CaCO_3$, vaterite, and/or aragonite.

Preparation of Undifferentiated Pluripotent Polymorph Precursor Composition

As discussed above, methods of the invention include preparing a carbonate precipitate, e.g., a carbonate slurry, comprising a polymorph precursor (also referred to herein as a "polymorph precursor composition"). The polymorph precursor composition produced in methods of the invention may include metal carbonates, such alkaline earth metal carbonates, e.g., calcium carbonates, magnesium carbonates, etc., such as described in greater detail below, where the carbonates are not crystalline. In some instances, the polymorph precursor composition is comprised in a slurry. In other words, the composition is a liquid composition comprising the precipitate.

In other embodiments, the carbonate precipitate is dewatered, e.g., mechanical water of the composition is removed. Put another way, the undifferentiated pluripotent polymorph precursor may exist in a dried composition (e.g., for storage, etc.). In such instances, dewatering may not result in remove of structural waters that may be part of the precipitate. In select cases, the dewatered carbonate precipitate may be rewatered at a later time. In some such cases, methods include producing a carbonate slurry (e.g., via methods described below), and drying the carbonate slurry to create a dewatered carbonate precipitate. The carbonate slurry may be dewatered via any convenient protocol, including but not limited to centrifugation, heating (e.g., via rotary dryers), and the like. The dwatered carbonate precipitate may be considered a storage stable format of calcium carbonate that may include polymorph precursor and/or polymorph, depending on how the precipitate has been treated. Methods of the invention may subsequently include rewatering the dewatered carbonate precipitate at a later time (e.g., at a point of use).

Polymorph precursor compositions may be produced using any convenient protocol. In some instances, the polymorph precursor compositions are produced using a CO_2 sequestering process. By CO_2 sequestering process is

meant a process that converts an amount of gaseous CO_2 into a carbonate solution, thereby sequestering CO_2. A variety of difference CO_2 sequestering processes may be employed to produce a polymorph precursor composition.

In some instances, an ammonia mediated CO_2 sequestering process is employed to produce the polymorph precursor composition. Embodiments of such methods include multistep or single step protocols, as desired. For example, in some embodiments, combination of a CO_2 capture liquid and gaseous source of CO_2 results in production of an aqueous carbonate, which aqueous carbonate is then subsequently contacted with a divalent cation source, e.g., a Ca^{2+} and/or Mg^{2+} source, to produce the polymorph precursor composition. In yet other embodiments, a one-step CO_2 gas absorption carbonate precipitation protocol is employed.

The CO_2 containing gas may be pure CO_2 or be combined with one or more other gasses and/or particulate components, depending upon the source, e.g., it may be a multi-component gas (i.e., a multi-component gaseous stream). In certain embodiments, the CO_2 containing gas is obtained from an industrial plant, e.g., where the CO_2 containing gas is a waste feed from an industrial plant. Industrial plants from which the CO_2 containing gas may be obtained, e.g., as a waste feed from the industrial plant, may vary. Industrial plants of interest include, but are not limited to, power plants and industrial product manufacturing plants, such as, but not limited to, chemical and mechanical processing plants, refineries, cement plants, steel plants, etc., as well as other industrial plants that produce CO_2 as a byproduct of fuel combustion or other processing step (such as calcination by a cement plant). Waste feeds of interest include gaseous streams that are produced by an industrial plant, for example as a secondary or incidental product, of a process carried out by the industrial plant.

Of interest in certain embodiments are waste streams produced by industrial plants that combust fossil fuels, e.g., coal, oil, natural gas, as well as man-made fuel products of naturally occurring organic fuel deposits, such as but not limited to tar sands, heavy oil, oil shale, etc. In certain embodiments, power plants are pulverized coal power plants, supercritical coal power plants, mass

burn coal power plants, fluidized bed coal power plants, gas or oil-fired boiler and steam turbine power plants, gas or oil-fired boiler simple cycle gas turbine power plants, and gas or oil-fired boiler combined cycle gas turbine power plants. Of interest in certain embodiments are waste streams produced by power plants that combust syngas, i.e., gas that is produced by the gasification of organic matter, e.g., coal, biomass, etc., where in certain embodiments such plants are integrated gasification combined cycle (IGCC) plants. Of interest in certain embodiments are waste streams produced by Heat Recovery Steam Generator (HRSG) plants. Waste streams of interest also include waste streams produced by cement plants. Cement plants whose waste streams may be employed in methods of the invention include both wet process and dry process plants, which plants may employ shaft kilns or rotary kilns, and may include pre-calciners. Each of these types of industrial plants may burn a single fuel, or may burn two or more fuels sequentially or simultaneously. A waste stream of interest is industrial plant exhaust gas, e.g., a flue gas. By "flue gas" is meant a gas that is obtained from the products of combustion from burning a fossil or biomass fuel that are then directed to the smokestack, also known as the flue of an industrial plant. These industrial plants may each burn a single fuel or may burn two or more fuels sequentially or simultaneously. Other industrial plants such as smelters and refineries are also useful sources of waste streams that include carbon dioxide.

Industrial waste gas streams may contain carbon dioxide as the primary non-air derived component, or may, especially in the case of coal-fired power plants, contain additional components (which may be collectively referred to as non-CO_2 pollutants) such as nitrogen oxides (NOx), sulfur oxides (SOx), and one or more additional gases. Additional gases and other components may include CO, mercury and other heavy metals, and dust particles (e.g., from calcining and combustion processes). Additional non-CO_2 pollutant components in the gas stream may also include halides such as hydrogen chloride and hydrogen fluoride; particulate matter such as fly ash, dusts, and metals including arsenic, beryllium, boron, cadmium, chromium, chromium VI, cobalt, lead, manganese,

mercury, molybdenum, selenium, strontium, thallium, and vanadium; and organics such as hydrocarbons, dioxins, and PAH compounds. Suitable gaseous waste streams that may be treated have, in some embodiments, CO_2 present in amounts of 200 ppm to 1,000,000 ppm; or 200 ppm to 500,000 ppm; or 200 ppm to 100,000 ppm; or 200 ppm to 10,000; or 200 ppm to 5,000 ppm; or 200 ppm to 2000 ppm; or 200 ppm to 1000 ppm; or 200 to 500 ppm; or 500 ppm to 1,000,000 ppm; or 500 ppm to 500,000 ppm; or 500 ppm to 100,000 ppm; or 500 ppm to 10,000; or 500 ppm to 5,000 ppm; or 500 ppm to 2000 ppm; or 500 ppm to 1000 ppm; or 1000 ppm to 1,000,000 ppm; or 1000 ppm to 500,000 ppm; or 1000 ppm to 100,000 ppm; or 1000 ppm to 10,000; or 1000 ppm to 5,000 ppm; or 1000 ppm to 2000 ppm; or 2000 ppm to 1,000,000 ppm; or 2000 ppm to 500,000 ppm; or 2000 ppm to 100,000 ppm; or 2000 ppm to 10,000; or 2000 ppm to 5,000 ppm; or 2000 ppm to 3000 ppm; or 5000 ppm to 1,000,000 ppm; or 5000 ppm to 500,000 ppm; or 5000 ppm to 100,000 ppm; or 5000 ppm to 10,000; or 10,000 ppm to 1,000,000 ppm; or 10,00 ppm to 500,000 ppm; or 10,000 ppm to 100,000 ppm; or 50,000 ppm to 1,000,000 ppm; or 50,000 ppm to 500,000 ppm; or 50,000 ppm to 100,000 ppm; or 100,000 ppm to 1,000,000 ppm; or 100,000 ppm to 500,000 ppm; or 200,000 ppm to 1000 ppm, including 200,000 ppm to 2000 ppm, for example 180,000 ppm to 2000 ppm, or 180,000 ppm to 5000 ppm, also including 180,000 ppm to 10,000 ppm.

The waste streams, particularly various waste streams of combustion gas, may include one or more additional non-CO_2 components, for example only, water, NOx (mononitrogen oxides: NO and NO_2), SOx (monosulfur oxides: SO, SO_2 and SO_3), VOC (volatile organic compounds), heavy metals such as, but not limited to, mercury, and particulate matter (particles of solid or liquid suspended in a gas). Flue gas temperature may also vary. In some embodiments, the temperature of the flue gas comprising CO_2 is from 0 ºC to 2000 ºC, or 0 ºC to 1000 ºC, or 0 ºC to 500 ºC, or 0 ºC to 100 ºC, or 0 ºC to 50 ºC, or 10 ºC to 2000 ºC, or 10 ºC to 1000 ºC, or 10 ºC to 500 ºC, or 10 ºC to 100 ºC, or 10 ºC to 50 ºC, or 50 ºC to 2000 ºC, or 50 ºC to 1000 ºC, or 50 ºC to 500 ºC, or 50 ºC to 100 ºC, or 100 ºC to 2000 ºC, or 100 ºC to 1000 ºC, or 100 ºC to 500 ºC, or 500 ºC to

2000 ºC, or 500 ºC to 1000 ºC, or 500 ºC to 800 ºC, or such as from 60 ºC to 700 ºC, and including 100 ºC to 400 ºC.

Another gaseous source of CO_2 is a direct air capture (DAC) generated gaseous source of CO_2. The DAC generated gaseous source of CO_2 is a product gas produced by a direct air capture (DAC) system. DAC systems are a class of technologies capable of separating carbon dioxide CO_2 directly from ambient air. A DAC system is any system that captures CO_2 directly from air and generates a product gas that includes CO_2 at a higher concentration than that of the air that is input into the DAC system. While the concentration of CO_2 in the DAC generated gaseous source of CO_2 may vary, in some instances the concentration 1,000 ppm or greater, such as 10,000 ppm or greater, including 100,000 ppm or greater, where the product gas may not be pure CO_2, such that in some instances the product gas is 3% or more non-CO_2 constituents, such as 5% or more non-CO_2 constituents, including 10% or more non-CO_2 constituents. Non-CO_2 constituents that may be present in the product stream may be constituents that originate in the input air and/or from the DAC system. In some instances, the concentration of CO_2 in the DAC product gas ranges from 1,000 to 999,000 ppm, such as 1,000 to 10,000 ppm, or 10,000 to 100,000 ppm or 100,000 to 999,000 ppm. DAC generated gaseous streams have, in some embodiments, CO_2 present in amounts of 200 ppm to 1,000,000 ppm; or 200 ppm to 500,000 ppm; or 200 ppm to 100,000 ppm; or 200 ppm to 10,000; or 200 ppm to 5,000 ppm; or 200 ppm to 2000 ppm; or 200 ppm to 1000 ppm; or 200 to 500 ppm; or 500 ppm to 1,000,000 ppm; or 500 ppm to 500,000 ppm; or 500 ppm to 100,000 ppm; or 500 ppm to 10,000; or 500 ppm to 5,000 ppm; or 500 ppm to 2000 ppm; or 500 ppm to 1000 ppm; or 1000 ppm to 1,000,000 ppm; or 1000 ppm to 500,000 ppm; or 1000 ppm to 100,000 ppm; or 1000 ppm to 10,000; or 1000 ppm to 5,000 ppm; or 1000 ppm to 2000 ppm; or 2000 ppm to 1,000,000 ppm; or 2000 ppm to 500,000 ppm; or 2000 ppm to 100,000 ppm; or 2000 ppm to 10,000; or 2000 ppm to 5,000 ppm; or 2000 ppm to 3000 ppm; or 5000 ppm to 1,000,000 ppm; or 5000 ppm to 500,000 ppm; or 5000 ppm to 100,000 ppm; or 5000 ppm to 10,000; or 10,000 ppm to 1,000,000 ppm; or 10,00 ppm to 500,000 ppm; or 10,000 ppm

to 100,000 ppm; or 50,000 ppm to 1,000,000 ppm; or 50,000 ppm to 500,000 ppm; or 50,000 ppm to 100,000 ppm; or 100,000 ppm to 1,000,000 ppm; or 100,000 ppm to 500,000 ppm; or 200,000 ppm to 1000 ppm, including 200,000 ppm to 2000 ppm, for example 180,000 ppm to 2000 ppm, or 180,000 ppm to 5000 ppm, also including 180,000 ppm to 10,000 ppm.

The DAC product gas that is contacted with the aqueous capture liquid may be produced by any convenient DAC system. DAC systems are systems that extract CO_2 from the air using media that binds to CO_2 but not to other atmospheric chemicals (such as nitrogen and oxygen). As air passes over the CO_2 binding medium, CO_2 "sticks" to the binding medium. In response to a stimulus, e.g., heat, humidity, etc., the bound CO_2 may then be released from the binding medium resulting the production of a gaseous CO_2 containing product. DAC systems of interest include, but are not limited to: hydroxide based systems; CO_2 sorbent/temperature swing based systems, and CO_2 sorbent/temperature swing based systems. In some instances, the DAC system is a hydroxide based system, in which CO_2 is separated from air by contacting the air with is an aqueous hydroxide liquid. Examples of hydroxide based DAC systems include, but are not limited to, those described in PCT published application Nos. WO/2009/155539; WO/2010/022339; WO/2013/036859; and WO/2013/120024; the disclosures of which are herein incorporated by reference. In some instances, the DAC system is a CO_2 sorbent based system, in which CO_2 is separated from air by contacting the air with sorbent, such as an amine sorbent, followed by release of the sorbent captured CO_2 by subjecting the sorbent to one or more stimuli, e.g., change in temperature, change in humidity, etc. Examples of such DAC systems include, but are not limited to, those described in PCT published application Nos. WO/2005/108297; WO/2006/009600; WO/2006/023743; WO/2006/036396; WO/2006/084008; WO/2007/016271; WO/2007/114991; WO/2008/042919; WO/2008/061210; WO/2008/131132; WO/2008/144708; WO/2009/061836; WO/2009/067625; WO/2009/105566; WO/2009/149292; WO/2010/019600; WO/2010/022399 ; WO/2010/107942; WO/2011/011740; WO/2011/137398; WO/2012/106703; WO/2013/028688; WO/2013/075981;

WO/2013/166432; WO/2014/170184; WO/2015/103401; WO/2015/185434; WO/2016/005226; WO/2016/037668; WO/2016/162022; WO/2016/164563; WO/2016/161998; WO/2017/184652; and WO/2017/009241; the disclosures of which are herein incorporated by reference.

Further details regarding DAC generated gaseous sources of CO_2 and their use in producing polymorph precursor compositions may be found in PCT application serial no. PCT/US2018/020527 published as WO 2018/160888, the disclosure of which is herein incorporated by reference.

As summarized above, an aqueous capture liquid is contacted with the gaseous source of CO_2 under conditions sufficient to produce an aqueous carbonate. The aqueous capture liquid may vary. Examples of aqueous capture liquids include, but are not limited to fresh water to bicarbonate buffered aqueous media. Bicarbonate buffered aqueous media employed in embodiments of the invention include liquid media in which a bicarbonate buffer is present. The bicarbonate buffered aqueous medium may be a naturally occurring or man-made medium, as desired. Naturally occurring bicarbonate buffered aqueous media include, but are not limited to, waters obtained from seas, oceans, lakes, swamps, estuaries, lagoons, brines, alkaline lakes, inland seas, etc. Man-made sources of bicarbonate buffered aqueous media may also vary, and may include brines produced by water desalination plants, and the like. Further details regarding such capture liquids are provided in PCT published application Nos. WO2014/039578; WO 2015/134408; and WO 2016/057709; the disclosures of which applications are herein incorporated by reference.

In some embodiments, an aqueous capture ammonia is contacted with the gaseous source of CO_2 under conditions sufficient to produce an aqueous ammonium carbonate. The concentration of ammonia in the aqueous capture ammonia may vary, where in some instances the aqueous capture ammonia includes ammonia (NH_3) at a concentration ranging from 10 ppm to 350,000 ppm NH_3, such as 10 to 10,000 ppm, or 10 to 1,000 ppm, or 10 to 5,000 ppm, or 10 to 8,000 ppm, or 10 to 10,000 ppm, or 100 to 100,000 ppm, or 100 to 10,000 ppm, or 100 to 50,000 ppm, or 100 to 80,000 ppm, or 100 to 100,000 ppm, or 1,000 to

350,000 ppm, or 1,000 to 50,000 ppm, or 1,000 to 80,000 ppm, or 1,000 to 100,000 ppm, or 1,000 to 200,000 ppm, or 1,000 to 350,000 ppm, or such as from 6,000 to 85,000 ppm, and including 8,000 to 50,000 ppm. The aqueous capture ammonia may include any convenient water. Waters of interest from which the aqueous capture ammonia may be produced include, but are not limited to, freshwaters, seawaters, brine waters, reclaimed or recycled waters, produced waters and waste waters. The pH of the aqueous capture ammonia may vary, ranging in some instances from 9.0 to 13.5, such as 9.0 to 13.0, including 10.5 to 12.5. Further details regarding aqueous capture ammonias of interest are provided in PCT published application No. WO 2017/165849; the disclosure of which is herein incorporated by reference.

The CO_2 containing gas, e.g., as described above, may be contacted with the aqueous capture liquid, e.g., aqueous capture ammonia, using any convenient protocol. For example, contact protocols of interest include, but are not limited to: direct contacting protocols, e.g., bubbling the gas through a volume of the aqueous medium, concurrent contacting protocols, i.e., contact between unidirectionally flowing gaseous and liquid phase streams, countercurrent protocols, i.e., contact between oppositely flowing gaseous and liquid phase streams, and the like. Contact may be accomplished through use of infusers, bubblers, fluidic Venturi reactors, spargers, gas filters, sprays, trays, scrubbers, absorbers or packed column reactors, and the like, as may be convenient. In some instances, the contacting protocol may use a conventional absorber or an absorber froth column, such as those described in U.S. Patent Nos. 7,854,791; 6,872,240; and 6,616,733; and in United States Patent Application Publication US-2012-0237420-A1; the disclosures of which are herein incorporated by reference. The process may be a batch or continuous process. In some instances, a regenerative froth contactor (RFC) may be employed to contact the CO_2 containing gas with the aqueous capture liquid, e.g., aqueous capture ammonia. In some such instances, the RFC may use a catalyst (such as described elsewhere), e.g., a catalyst that is immobilized on/to the internals of

the RFC. Further details regarding a suitable RFC are found in U.S. Patent No. 9,545,598, the disclosure of which is herein incorporated by reference.

In some instances, the gaseous source of CO_2 is contacted with the liquid using a microporous membrane contactor. Microporous membrane contactors of interest include a microporous membrane present in a suitable housing, where the housing includes a gas inlet and a liquid inlet, as well a gas outlet and a liquid outlet. The contactor is configured so that the gas and liquid contact opposite sides of the membrane in a manner such that molecule may dissolve into the liquid from the gas via the pores of the microporous membrane. The membrane may be configured in any convenient format, where in some instances the membrane is configured in a hollow fiber format. Hollow fiber membrane reactor formats which may be employed include, but are not limited to, those described in U.S. Patent Nos. 7,264,725; 6,872,240 and 5,695,545; the disclosures of which are herein incorporated by reference. In some instances, the microporous hollow fiber membrane contactor that is employed is a hollow fiber membrane contactor, which membrane contactors include polypropylene membrane contactors and polyolefin membrane contactors.

Contact between the capture liquid and the CO_2-containing gas occurs under conditions such that a substantial portion of the CO_2 present in the CO_2-containing gas goes into solution, e.g., to produce bicarbonate ions. By substantial portion is meant 10 % or more, such as 50% or more, including 80% or more.

The temperature of the capture liquid that is contacted with the CO_2-containing gas may vary. In some instances, the temperature ranges from -1.4 to 100°C, such as 20 to 80°C and including 40 to 70°C. In some instances, the temperature may range from -1.4 to 50 °C or higher, such as from -1.1 to 45 °C or higher. In some instances, cooler temperatures are employed, where such temperatures may range from -1.4 to 4°C, such as -1.1 to 0 °C. In some instances, warmer temperatures are employed. For example, the temperature of the capture liquid in some instances may be 25°C or higher, such as 30°C or

higher, and may in some embodiments range from 25 to 50°C, such as 30 to 40°C.

The CO_2-containing gas and the capture liquid are contacted at a pressure suitable for production of a desired CO_2 charged liquid. In some instances, the pressure of the contact conditions is selected to provide for optimal CO_2 absorption, where such pressures may range from 1 ATM to 100 ATM, such as 1 to 50 ATM, e.g., 20-30 ATM or 1 ATM to 10 ATM. Where contact occurs at a location that is naturally at 1 ATM, the pressure may be increased to the desired pressure using any convenient protocol. In some instances, contact occurs where the optimal pressure is present, e.g., at a location under the surface of a body of water, such as an ocean or sea.

In those embodiments where the gaseous source of CO_2 is contacted with an aqueous capture ammonia, contact is carried out in manner sufficient to produce an aqueous ammonium carbonate. The aqueous ammonium carbonate may vary, where in some instances the aqueous ammonium carbonate comprises at least one of ammonium carbonate and ammonium bicarbonate and in some instances comprises both ammonium carbonate and ammonium bicarbonate. The aqueous ammonium bicarbonate may be viewed as a DIC containing liquid. As such, in charging the aqueous capture ammonia with CO_2, a CO_2 containing gas may be contacted with CO_2 capture liquid under conditions sufficient to produce dissolved inorganic carbon (DIC) in the CO_2 capture liquid, i.e., to produce a DIC containing liquid. The DIC is the sum of the concentrations of inorganic carbon species in a solution, represented by the equation: $DIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$, where $[CO_2^*]$ is the sum of carbon dioxide ($[CO_2]$) and carbonic acid ($[H_2CO_3]$) concentrations, $[HCO_3^-]$ is the bicarbonate concentration (which includes ammonium bicarbonate) and $[CO_3^{2-}]$ is the carbonate concentration (which includes ammonium carbonate) in the solution. The DIC of the aqueous media may vary, and in some instances may be 3 ppm to 168,000 ppm carbon (C), such as 3 to 1,000 ppm, or 3 to 100 ppm, or 3 to 500 ppm, or 3 to 800 ppm, or 3 to 1,000 ppm, or 100 to 10,000 ppm, or 100 to 1,000 ppm, or 100 to 5,000 ppm, or 100 to 8,000 ppm, or 100 to 10,000 ppm, or 1,000 to

50,000 ppm, or 1,000 to 8,000 ppm, or 1,000 to 15,000 ppm, or 1,000 to 30,000 ppm, or 5,000 to 168,000 ppm, or 5,000 to 25,000 ppm, or such as from 6,000 to 65,000 ppm, and including 8,000 to 95,000 ppm carbon (C). The amount of CO_2 dissolved in the liquid may vary, and in some instances ranges from 0.05 to 40 mM, such as 1 to 35 mM, including 25 to 30 mM. The pH of the resultant DIC containing liquid may vary, ranging in some instances from 4 to 12, such as 6 to 11 and including 7 to 11, e.g., 8 to 9.5.

Where desired, the CO_2 containing gas is contacted with the capture liquid in the presence of a catalyst (i.e., an absorption catalyst, either hetero- or homogeneous in nature) that mediates the conversion of CO_2 to bicarbonate. Of interest as absorption catalysts are catalysts that, at pH levels ranging from 8 to 10, increase the rate of production of bicarbonate ions from dissolved CO_2. The magnitude of the rate increase (e.g., as compared to control in which the catalyst is not present) may vary, and in some instances is 2-fold or greater, such as 5-fold or greater, e.g., 10-fold or greater, as compared to a suitable control. Further details regarding examples of suitable catalysts for such embodiments are found in U.S. Patent No. 9,707,513, the disclosure of which is herein incorporated by reference.

In some embodiments, the resultant aqueous carbonate is a two-phase liquid which includes droplets of a liquid condensed phase (LCP) in a bulk liquid, e.g., bulk solution. By “liquid condensed phase” or “LCP” is meant a phase of a liquid solution which includes bicarbonate ions wherein the concentration of bicarbonate ions is higher in the LCP phase than in the surrounding, bulk liquid. LCP droplets are characterized by the presence of a meta-stable bicarbonate-rich liquid precursor phase in which bicarbonate ions associate into condensed concentrations exceeding that of the bulk solution and are present in a non-crystalline solution state. The LCP contains all of the components found in the bulk solution that is outside of the interface. However, the concentration of the bicarbonate ions is higher than in the bulk solution. In those situations where LCP droplets are present, the LCP and bulk solution may each contain ion-pairs and pre-nucleation clusters (PNCs). When present, the ions remain in their

respective phases for long periods of time, as compared to ion-pairs and PNCs in solution. Further details regarding LCP containing liquids are provided in U.S. Patent Application Serial No. 14/636,043, the disclosure of which is herein incorporated by reference.

As summarized above, both multistep and single step protocols may be employed to produce the polymorph precursor composition from the CO_2 containing gas the aqueous capture ammonia. For example, in some embodiments the product aqueous ammonium carbonate is forwarded to a CO_2 sequestering polymorph precursor composition production module, where divalent cations, e.g., Ca^{2+} and/or Mg^{2+}, are combined with the aqueous ammonium carbonate to produce the CO_2 sequestering polymorph precursor composition. In yet other instances, aqueous capture ammonia includes a source of divalent cations, e.g., Ca^{2+} and/or Mg^{2+}, such that aqueous ammonium carbonate combines with the divalent cations as it is produced to result in production of a CO_2 sequestering polymorph precursor composition.

Accordingly, in some embodiments, following production of an aqueous carbonate, such as an aqueous ammonium carbonate, e.g., as described above, the aqueous carbonate is subsequently combined with a cation source under conditions sufficient to produce a solid CO_2 sequestering carbonate. Cations of different valances can form solid carbonate compositions (e.g., in the form of carbonate minerals). In some instances, monovalent cations, such as sodium and potassium cations, may be employed. In other instances, divalent cations, such as alkaline earth metal cations, e.g., calcium (Ca^{2+}) and magnesium (Mg^{2+}) cations, may be employed. When cations are added to the aqueous carbonate, precipitation of carbonate solids, such as amorphous calcium carbonate ($CaCO_3$) when the divalent cations include Ca^{2+}, may be produced with a stoichiometric ratio of one carbonate-species ion per cation.

Any convenient cation source may be employed in such instances. Cation sources of interest include, but are not limited to, the brine from water processing facilities such as sea water desalination plants, brackish water desalination plants, groundwater recovery facilities, wastewater facilities, blowdown water

from facilities with cooling towers, and the like, which produce a concentrated stream of solution high in cation contents. Also of interest as cation sources are naturally occurring sources, such as but not limited to native seawater and geological brines, which may have varying cation concentrations and may also provide a ready source of cations to trigger the production of carbonate solids from the aqueous ammonium carbonate. In some instances, the cation source may be a waste product of another step of the process, e.g., a calcium salt (such as $CaCl_2$) produced during regeneration of ammonia from the aqueous ammonium salt.

In yet other embodiments, the aqueous capture ammonia includes cations, e.g., as described above. The cations may be provided in the aqueous capture ammonia using any convenient protocol. In some instances, the cations present in the aqueous capture ammonia are derived from a geomass (e.g., recycled concrete aggregate (RCA)) used in regeneration of the aqueous capture ammonia from an aqueous ammonium salt. In addition, and/or alternatively, the cations may be provided by combining an aqueous capture ammonia with a cation source, e.g., as described above.

Following production of an aqueous carbonate, such as an aqueous ammonium carbonate, e.g., as described above, the aqueous carbonate is combined with a cation source under conditions sufficient to produce a solid CO_2 sequestering carbonate. Cations of different valances can form solid carbonate compositions (e.g., in the form of carbonate minerals). In some instances, monovalent cations, such as sodium and potassium cations, may be employed. In other instances, divalent cations, such as alkaline earth metal cations, e.g., calcium and magnesium cations, may be employed. Transition metals may also be employed, e.g., Fe, Mn, Cu, etc. When cations are added to the aqueous carbonate, precipitation of carbonate solids, such as amorphous calcium carbonate when the divalent cations include Ca^{2+}, may be produced with a stoichiometric ratio of one carbonate-species ion per cation.

As summarized above, production of CO_2 sequestering carbonate from the aqueous ammonia capture liquid and the gaseous source of CO_2 yields an

aqueous ammonium salt. The produced aqueous ammonium salt may vary with respect to the nature of the anion of the ammonium salt, where specific ammonium salts that may be present in the aqueous ammonium salt include, but are not limited to, ammonium chloride, ammonium acetate, ammonium sulfate, ammonium nitrate, etc.

Some aspects of the invention further include regenerating an aqueous capture ammonia, e.g., as described above, from the aqueous ammonium salt. By regenerating an aqueous capture ammonium is meant processing the aqueous ammonium salt in a manner sufficient to generate an amount of ammonium from the aqueous ammonium salt. The percentage of input ammonium salt that is converted to ammonia during this regeneration step may vary, ranging in some instances from 5 to 80%, such as 15 to 55%, and in some instances 20 to 80%, e.g., 35 to 55%.

Ammonia may be regenerated from an aqueous ammonium salt in this regeneration step using any convenient regeneration protocol. In some instances, a distillation protocol is employed. While any convenient distillation protocol may be employed, in some embodiments the employed distillation protocol includes heating the aqueous ammonium salt in the presence of an alkalinity source, e.g., geomass, to produce a gaseous ammonia/water product, which may then be condensed to produce a liquid aqueous capture ammonia. In some instances, the protocol happens continuously in a stepwise process wherein heating the aqueous ammonium salt in the present of an alkalinity source happens before the distillation and condensation of liquid aqueous capture ammonia.

The alkalinity source may vary, so long as it is sufficient to convert ammonium in the aqueous ammonium salt to ammonia. Any convenient alkalinity source may be employed. Alkalinity sources that may be employed in this regeneration step include chemical agents. Chemical agents that may be employed as alkalinity sources include, but are not limited to, hydroxides, organic bases, super bases, oxides, and carbonates. Hydroxides include chemical species that provide hydroxide anions in solution, including, for example, sodium

hydroxide (NaOH), potassium hydroxide (KOH), calcium hydroxide ($Ca(OH)_2$), or magnesium hydroxide ($Mg(OH)_2$). Organic bases are carbon-containing molecules that are generally nitrogenous bases including primary amines such as methyl amine, secondary amines such as diisopropylamine, tertiary such as diisopropylethylamine, aromatic amines such as aniline, heteroaromatics such as pyridine, imidazole, and benzimidazole, and various forms thereof. Super bases suitable for use as proton-removing agents include sodium ethoxide, sodium amide ($NaNH_2$), sodium hydride (NaH), butyl lithium, lithium diisopropylamide, lithium diethylamide, and lithium bis(trimethylsilyl)amide. Oxides including, for example, calcium oxide (CaO), magnesium oxide (MgO), strontium oxide (SrO), beryllium oxide (BeO), and barium oxide (BaO) are also suitable proton-removing agents that may be used.

Also of interest as alkalinity sources are silica sources. The source of silica may be pure silica or a composition that includes silica in combination with other compounds, e.g., minerals, so long as the source of silica is sufficient to impart desired alkalinity. In some instances, the source of silica is a naturally occurring source of silica. Naturally occurring sources of silica include silica containing rocks, which may be in the form of sands or larger rocks. Where the source is larger rocks, in some instances the rocks have been broken down to reduce their size and increase their surface area. Of interest are silica sources made up of components having a longest dimension ranging from 0.01 mm to 1 meter, such as 0.1 mm to 500 cm, including 1 mm to 100 cm, e.g., 1 mm to 50 cm. The silica sources may be surface treated, where desired, to increase the surface area of the sources. A variety of different naturally occurring silica sources may be employed. Naturally occurring silica sources of interest include, but are not limited to, igneous rocks, which rocks include: ultramafic rocks, such as Komatiite, Picrite basalt, Kimberlite, Lamproite, Peridotite; mafic rocks, such as Basalt, Diabase (Dolerite) and Gabbro; intermediate rocks, such as Andesite and Diorite; intermediate felsic rocks, such as Dacite and Granodiorite; and Felsic rocks, such as Rhyolite, Aplite—Pegmatite and Granite. Also of interest are man-made sources of silica. Man-made sources of silica include, but are not

limited to, waste streams such as: mining wastes; fossil fuel burning ash; slag, e.g. iron and steel slags, phosphorous slag; cement kiln waste; oil refinery/petrochemical refinery waste, e.g. oil field and methane seam brines; coal seam wastes, e.g. gas production brines and coal seam brine; paper processing waste; water softening, e.g. ion exchange waste brine; silicon processing wastes; agricultural waste; metal finishing waste; high pH textile waste; and caustic sludge. Mining wastes include any wastes from the extraction of metal or another precious or useful mineral from the earth. Wastes of interest include wastes from mining to be used to raise pH, including: red mud from the Bayer aluminum extraction process; the waste from magnesium extraction for sea water, e.g., at Moss Landing, Calif.; and the wastes from other mining processes involving leaching. Ash from processes burning fossil fuels, such as coal fired power plants, create ash that is often rich in silica. In some embodiments, ashes resulting from burning fossil fuels, e.g., coal fired power plants, are provided as silica sources, including fly ash, e.g., ash that exits out the smokestack, and bottom ash. Additional details regarding silica sources and their use are described in U.S. patent No. 9,714,406; the disclosure of which is herein incorporated by reference.

In embodiments of the invention, ash is employed as an alkalinity source. Of interest in certain embodiments is use of a coal ash as the ash. The coal ash as employed in this invention refers to the residue produced in power plant boilers or coal burning furnaces, for example, chain grate boilers, cyclone boilers and fluidized bed boilers, from burning pulverized anthracite, lignite, bituminous or sub-bituminous coal. Such coal ash includes fly ash which is the finely divided coal ash carried from the furnace by exhaust or flue gases; and bottom ash which collects at the base of the furnace as agglomerates.

Fly ashes are generally highly heterogeneous, and include of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite, and various iron oxides. Fly ashes of interest include Type F and Type C fly ash. The Type F and Type C fly ashes referred to above are defined by CSA Standard A23.5 and ASTM C618 as mentioned above. The chief difference

between these classes is the amount of calcium, silica, alumina, and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite). Fly ashes of interest include substantial amounts of silica (silicon dioxide, SiO_2) (both amorphous and crystalline) and lime (calcium oxide, CaO, magnesium oxide, MgO).

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. Class F fly ash is pozzolanic in nature, and contains less than 10% lime (CaO). Fly ash produced from the burning of younger lignite or subbituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20% lime (CaO). Alkali and sulfate (SO_4^{2-}) contents are generally higher in Class C fly ashes. In some embodiments it is of interest to use Class C fly ash to regenerate ammonia from an aqueous ammonium salt, e.g., as mentioned above, with the intention of extracting quantities of constituents present in Class C fly ash so as to generate a fly ash closer in characteristics to Class F fly ash, e.g., extracting 95% of the CaO in Class C fly ash that has 20% CaO, thus resulting in a remediated fly ash material that has 1% CaO.

Fly ash material solidifies while suspended in exhaust gases and is collected using various approaches, e.g., by electrostatic precipitators or filter bags. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape and range in size from 0.5 µm to 100 µm. Fly ashes of interest include those in which at least about 80%, by weight comprises particles of less than 45 microns. Also of interest in certain embodiments of the invention is the use of highly alkaline fluidized bed combustor (FBC) fly ash.

Also of interest in embodiments of the invention is the use of bottom ash. Bottom ash is formed as agglomerates in coal combustion boilers from the combustion of coal. Such combustion boilers may be wet bottom boilers or dry bottom boilers. When produced in a wet or dry bottom boiler, the bottom ash is

quenched in water. The quenching results in agglomerates having a size in which 90% fall within the particle size range of 0.1 mm to 20 mm, where the bottom ash agglomerates have a wide distribution of agglomerate size within this range. The main chemical components of a bottom ash are silica and alumina with lesser amounts of oxides of Fe, Ca, Mg, Mn, Na and K, as well as sulphur and carbon.

Also of interest in certain embodiments is the use of volcanic ash as the ash. Volcanic ash is made up of small tephra, i.e., bits of pulverized rock and glass created by volcanic eruptions, less than 2 millimeters in diameter.

In one embodiment of the invention, cement kiln dust (CKD) is employed as an alkalinity source. The nature of the fuel from which the ash and/or CKD were produced, and the means of combustion of said fuel, will influence the chemical composition of the resultant ash and/or CKD. Thus ash and/or CKD may be used as a portion of the means for adjusting pH, or the sole means, and a variety of other components may be utilized with specific ashes and/or CKDs, based on chemical composition of the ash and/or CKD.

In certain embodiments of the invention, slag is employed as an alkalinity source. The slag may be used as a as the sole pH modifier or in conjunction with one or more additional pH modifiers, e.g., ashes, etc. Slag is generated from the processing of metals, and may contain calcium and magnesium oxides as well as iron, silicon and aluminum compounds. In certain embodiments, the use of slag as a pH modifying material provides additional benefits via the introduction of reactive silicon and alumina to the precipitated product. Slags of interest include, but are not limited to, blast furnace slag from iron smelting, slag from electric-arc or blast furnace processing of iron and/or steel, copper slag, nickel slag and phosphorus slag.

As indicated above, ash (or slag in certain embodiments) is employed in certain embodiments as the sole way to modify the pH of the water to the desired level. In yet other embodiments, one or more additional pH modifying protocols is employed in conjunction with the use of ash.

Also of interest in certain embodiments is the use of other waste materials, e.g., crushed or demolished or recycled or returned concretes or mortars, as an

alkalinity source. When employed, the concrete dissolves releasing sand and aggregate which, where desired, may be recycled to the carbonate production portion of the process. Use of demolished and/or recycled concretes or mortars is further described below.

Of interest in certain embodiments are mineral alkalinity sources. The mineral alkalinity source that is contacted with the aqueous ammonium salt in such instances may vary, where mineral alkalinity sources of interest include, but are not limited to: silicates, carbonates, fly ashes, slags, limes, cement kiln dusts, etc., e.g., as described above. In some instances, the mineral alkalinity source comprises a rock, e.g., as described above.

While the temperature to which the aqueous ammonium salt is heated in these embodiments may vary, in some instances the temperature ranges from 25 to 200 ºC, such as 25 to 185 ºC. The heat employed to provide the desired temperature may be obtained from any convenient source, including steam, a waste heat source, such as flue gas waste heat, etc.

Distillation may be carried out at any pressure. Where distillation is carried out at atmospheric pressure, the temperature at which distillation is carried out may vary, ranging in some instances from 50 to 120 ºC, such as 60 to 100 ºC, e.g., from 70 to 90 ºC. In some instances, distillation is carried out at a sub-atmospheric pressure. While the pressure in such embodiments may vary, in some instances the sub-atmospheric pressure ranges from 1 to 14 psig, such as from 2 to 6 psig. Where distillation is carried out at sub-atmospheric pressure, the distillation may be carried out at a reduced temperature as compared to embodiments that are performed at atmospheric pressure. While the temperature may vary in such instances as desired, in some embodiments where a sub-atmospheric pressure is employed, the temperature ranges from 15 to 60 ºC, such as 25 to 50 ºC. Of interest in sub-atmospheric pressure embodiments is the use of a waste heat for some, if not all, of the heat employed during distillation. Waste heat sources of that may be employed in such instances include, but are not limited to: flue gas, process steam condensate, heat of absorption generated by CO_2 capture and resultant ammonium carbonate production; and a cooling

liquid (such as from a co-located source of CO_2 containing gas, such as a power plant, factory etc., e.g., as described above), and combinations thereof.

Aqueous capture ammonia regeneration may also be achieved using an electrolysis mediated protocol, in which a direct electric current is introduced into the aqueous ammonium salt to regenerate ammonia. Any convenient electrolysis protocol may be employed. Examples of electrolysis protocols that may be adapted for regeneration of ammonia from an aqueous ammonium salt may employed one or more elements from the electrolysis systems described in U.S. Patent Nos. 7,727,374 and 8,227,127, as well as published PCT Application Publication No. WO/2008/018928; the disclosures of which are hereby incorporated by reference.

In some instances, the aqueous capture ammonia is regenerated from the aqueous ammonium salt without the input of energy, e.g., in the form of heat and/or electric current, such as described above. In such instances, the aqueous ammonium salt is combined with an alkaline source in a manner sufficient to produce a regenerated aqueous capture ammonia. The resultant aqueous capture ammonia is then not purified, e.g., by input of energy, such as via stripping protocol, etc.

The resultant regenerated aqueous capture ammonia may vary, e.g., depending on the particular regeneration protocol that is employed. In some instances, the regenerated aqueous capture ammonia includes ammonia (NH_3) at a concentration ranging from 0.1 to 25 moles per liter (M), such as from 4 to 20 M, including from 12.0 to 16.0 M, as well as any of the ranges provided for the aqueous capture ammonia provided above. The pH of the aqueous capture ammonia may vary, ranging in some instances from 10.0 to 13.0, such as 10.0 to 12.5. In some instances, e.g., where the aqueous capture ammonia is regenerated in a geomass mediated protocol that does not include input of energy, e.g., as described above, the regenerated aqueous capture ammonia may further include cations, e.g., divalent cations, such as Ca^{2+}. In addition, the regenerated aqueous capture ammonia may further include an amount of ammonium salt. In some instances, ammonia (NH_3) is present at a concentration

ranging from 0.05 to 4 moles per liter (M), such as from 0.05 to 1 M, including from 0.1 to 2 M. The pH of the aqueous capture ammonia may vary, ranging in some instances from 8.0 to 11.0, such as from 8.0 to 10.0. The aqueous capture ammonia may further include ions, e.g., monovalent cations, such as ammonium (NH_4^+) at a concentration ranging from 0.1 to 5 moles per liter (M), such as from 0.1 to 2 M, including from 0.5 to 3 M, divalent cations, such as calcium (Ca^{2+}) at a concentration ranging from 0.05 to 2 moles per liter (M), such as from 0.1 to 1 M, including from 0.2 to 1 M, divalent cations, such as magnesium (Mg^{2+}) at a concentration ranging from 0.005 to 1 moles per liter (M), such as from 0.005 to 0.1 M, including from 0.01 to 0.5 M, divalent anions, such as sulfate (SO_4^{2-}) at a concentration ranging from 0.005 to 1 moles per liter (M), such as from 0.005 to 0.1 M, including from 0.01 to 0.5 M.

Aspects of the methods further include contacting the regenerated aqueous capture ammonia with a gaseous source of CO_2, e.g., as described above, under conditions sufficient to produce a CO_2 sequestering carbonate, e.g., as described above. In other words, the methods include recycling the regenerated ammonia into the process. In such instances, the regenerated aqueous capture ammonia may be used as the sole capture liquid, or combined with another liquid, e.g., make up water, to produce an aqueous capture ammonia suitable for use as a CO_2 capture liquid. Where the regenerated aqueous ammonia is combined with additional water, any convenient water may be employed. Waters of interest from which the aqueous capture ammonia may be produced include, but are not limited to, freshwaters, seawaters, brine waters, produced waters and waste waters.

In some embodiments an additive is present in the cation source and/or in the aqueous ammonia capture liquid regenerated from the aqueous ammonium salt. Additives may include, e.g., ionic species such as magnesium (Mg^{2+}), strontium (Sr^{2+}), barium (Ba^{2+}), radium (Ra^{2+}), ammonium (NH_4^+), sulfate (SO_4^{2-}), phosphates (PO_4^{3-}, HPO_4^{2-}, or $H_2PO_4^-$), carboxylate groups such as, e.g., oxylate, carbamate groups such as, e.g., H_2NCOO^-, transition metal cations such as, e.g., manganese (Mn), copper (Cu), nickel (Ni), zinc (Zn), cadmium (Cd),

chromium (Cr). In some instances, the additives are intentionally added to the cation source and/or to the aqueous ammonia capture liquid regenerated from the aqueous ammonium salt. In other instances, the additives are extracted from an alkalinity source during some embodiments of the method.

Evaluation of Polymorph Precursor Composition

In some embodiments, methods also involve evaluating the carbonate precipitate (e.g., carbonate slurry) for the presence of the polymorph precursor. By “evaluating” the carbonate slurry, it is meant assessing whether an amount of polymorph precursor (e.g., calcite precursor, aragonite precursor, vaterite precursor) is present within a given carbonate slurry. Any suitable technique may be employed for evaluating the carbonate slurry for the presence of the polymorph precursor. In some instances, evaluating the carbonate slurry for the presence of the polymorph precursor comprises assaying the carbonate slurry by SEM. As is known in the art, SEM produces an image of a sample by scanning the surface of the sample with a beam of electrons. These electrons interact with the sample and produce signals that may be analyzed. For example, electrons emitted by the sample after being scanned by the electron beam may be detected to produce the image and derive information regarding sample topography. In some instances, evaluating the carbonate slurry for the presence of polymorph precursor includes assessing whether the carbonate slurry comprises smooth globular structures. By “smooth”, it is meant that the polymorph precursor structures have a continuous and even surface (i.e., they do not possess a varied surface topography). By “globular”, it is meant that the polymorph precursor structures are substantially (i.e., to a greater or lesser degree) spherical. The smooth globular structures identified via SEM may range in diameter, for example, from 0.001 μm to 50 μm. Any suitable scanning electron microscope may be employed to evaluate the carbonate slurry (see, e.g., FIG. 2 and corresponding description above). In some cases, benchtop scanning electron microscopes may be employed. Exemplary benchtop scanning electron microscopes are produced by Hitachi, such as the Hitatchi TM-3030 and

Hitatchi TM-4000II benchtop models. Any suitable scanning electron microscopy protocol may be employed. For example, obtaining SEM images from calcium carbonate particles is described in Kirboga and Oner. *Chemical Engineering Transactions*. (2013) 32:2119-2124, herein incorporated by reference in its entirety. In some embodiments, where carbonate slurries include smooth globular structures, it may reasonably be concluded that one or more types of polymorph precursor are present within said slurries.

FIG. 7 demonstrates the use of Scanning Electron Microscopy (SEM) to identify polymorph precursors from a CO_2 sequestering process. The spherical morphology of the material in the image indicates the presence of polymorph precursor.

In additional instances, evaluating the carbonate slurry for the presence of polymorph precursor includes obtaining an IR spectrum of the carbonate slurry. As is known in the art, infrared spectroscopy involves the irradiation of a sample with infrared light and is used to identify samples as well as their constituent functional groups. In some instances, evaluating the carbonate slurry for the presence of polymorph precursor involves Fourier-transform infrared spectroscopy (FTIR). FTIR collects spectral data over a wide spectral range, as opposed to dispersive spectrometers that collect data from a narrow range of wavelengths at a given time. IR spectra plot infrared light absorbance on the vertical axis against frequency or wavelength on the horizontal axis. Peaks characteristic of the polymorph precursor may appear on the obtained IR spectrum at, approximately, 700 cm^{-1}, 710 cm^{-1}, 745 cm^{-1}, and 875 cm^{-1}. In some embodiments, aspects of the invention may also involve assessing whether the IR spectrum exhibits wide peaks. By “wide peaks”, it is meant that the bands at approximately 700 cm^{-1}, 710 cm^{-1}, 745 cm^{-1}, and 875 cm^{-1} are broad. Where polymorph precursor compositions include wide peaks in an IR spectrum, it may reasonably be concluded that one or more types of polymorph precursor are present within said slurries. The IR spectrum described herein may be produced via any suitable protocol. Obtaining IR spectra of calcium carbonate compositions is described in, for example, United States Patent Application

Publication 2020/0129916 as well as Andersen and Brecevic. *Acta Chemica Standinavica*. (1991) 45:1018-1024; the disclosures of which are herein incorporated by reference.

In further embodiments, evaluating the carbonate slurry for the presence of polymorph precursor includes obtaining an XRD spectrum. As is known in the art, X-ray diffraction operates by directing a beam of X-rays towards a sample and measuring the resultant diffraction pattern as a function of outgoing direction. The diffraction pattern contains information about how atoms are arranged within the substance. Amorphous materials do not have a long-range atomic order. Therefore, X-ray diffraction conducted with respect to carbonate slurries having polymorph precursors are expected to possess one or more wide (i.e., broad) scattering peaks. As such, if an XRD spectrum obtained for a carbonate slurry possesses wide peaks, it may reasonably be concluded that the carbonate slurry includes a polymorph precursor. Any suitable XRD protocol for analyzing calcium carbonate compounds may be employed. For example, obtaining XRD spectra is described in Ni and Ratner. *Surf Interface Anal.* (2008) 40(10):1356-1361, herein incorporated by reference in its entirety.

FIG. 8 depicts the use of XRD to identify polymorph precursors comprising a carbonate slurry, as is evidenced by the broad peaks. The figure presents an XRD pattern of a sample of which the major phase present in a carbonate slurry is a vaterite polymorph precursor. Here, peaks match the 2 theta reference pattern of vaterite, and the peaks seen are broad compared to peaks from crystalline materials, indicating a vaterite-polymorph-precursor. The vaterite polymorph precursor is in a state between an amorphous state and a crystalline vaterite state.

In still further instances, evaluating the carbonate slurry for the presence of polymorph precursor comprises obtaining a Ca:C ratio of the carbonate slurry or a component thereof. Any suitable method for determining the ratio of calcium to carbon may be employed. In some embodiments, mass spectrometry is applied for determining the ratio of calcium to carbon. Any suitable mass spectrometry protocol may be used. For example, in certain instances, time-of-

flight secondary ion mass spectrometry (ToF-SIMS) is employed. As is known in the art, ToF-SIMS is an analytical method that uses a pulsed ion beam to remove molecules from a sample. Mass is determined by measuring the time it takes for the dislodged molecules to reach a detector. ToF-SIMS protocols for analyzing calcium carbonate compounds are described in, for example, Ni and Ratner. *Surf Interface Anal.* (2008) 40(10):1356-1361, herein incorporated by reference in its entirety. In some instances, evaluating the carbonate slurry for the presence of polymorph precursor comprises assessing whether the Ca:C ratio indicates a Ca deficiency. Where components of the carbonate slurry include a Ca deficiency, it may reasonably be concluded that those components include one or more types of polymorph precursor. In other embodiments, evaluating the carbonate slurry for the presence of undifferentiated pluripotent polymorph precursor comprises using a combination of methods, one for analysis of calcium (Ca^{2+}) by, e.g., ion chromatography, and one for analysis of inorganic carbon by, e.g., CO_2 coulometer. The Ca:C ratio can then be determined from the molar ratio as measured from each method. The implications of the Ca:C ratio are such that with an undifferentiated pluripotent polymorph precursor the ratio should be less than one, e.g., every Ca^{2+} ion is surrounded by two HCO_3^- ions yielding a Ca:C ratio of 0.5. As the transition to a desirable differentiated polymorph precursor occurs, eventually leading to a specific $CaCO_3$ polymorph suitable to be used as a building material, the Ca:C ratio will be 1, e.g., as is an embodiment that produces calcite polymorph. The ranges of precursor phases are: amorphous $CaCO_3$ (ACC) 0-100%, vaterite 0-100%. Ca-deficiency can happen when Ca is less than 40 wt% of the total $CaCO_3$. In terms of Ca:C ratio, calcium less than 1:1 ratio may be considered “Ca-deficient”.

FIG. 5 exemplifies the amount of undifferentiated pluripotent polymorph precursor that exists in the carbonate slurry, as was determined by refinement of XRD data. In this instance, the carbonate slurry contains between 60 and 70 wt% amorphous calcium carbonate (ACC) polymorph precursor and between 30 and 40 wt% vaterite polymorph precursor. After washing the same carbonate slurry with water, the ratios of polymorph precursors change to roughly the same wt%

of both ACC and vaterite polymorph precursors. Washing the same carbonate slurry a second time with bicarbonate solution results in a shift to 30 to 40 wt% ACC polymorph precursor and 60 to 70 wt% vaterite polymorph precursor. This processing step of washing with water and then with bicarbonate solution, e.g., as is exemplified in Box 103 in FIG. 1, leads to production of a desirable differentiated polymorph precursor that is destined to form a specific polymorph. In this embodiment the specific polymorph is calcite, as is indicated by the Building Material Cured point in FIG. 5, whereby the wt% of the building material is >95 wt% calcite polymorph and <5 wt% vaterite polymorph precursor.

In some embodiments, evaluating the carbonate slurry includes determining which crystal system(s) is/are present in the carbonate slurry. As discussed above, where the polymorph precursor is comprised of a vaterite precursor, the crystal system of the vaterite precursor may exist in any of the crystal systems of hexagonal, triclinic, monoclinic, or orthorhombic. Some methods of the invention accordingly include determining whether a carbonate precipitate (e.g., in the form of a calcium carbonate slurry) includes hexagonal, triclinic, monoclinic, or orthorhombic crystal systems, or some combination thereof. Any suitable determination method may be employed. In some cases, methods include using X-ray diffraction to determine the structure of the vaterite precursor. For example, FIG. 11 illustrates how a calcium carbonate composition can include different crystal systems of the vaterite precursor and of other precursors. As shown in FIG. 11, a given composition of $CaCO_3$ can involve several crystal systems (e.g., vaterite - hexagonal, vaterite - triclinic).

Production of Building Materials

As discussed above, methods of the invention include producing a building material. As discussed herein, a “building material” refers to a material that may be employed in the construction of a built structure. Building materials of interest include, for example, aggregates. In certain cases, methods include mineralizing carbon from the polymorph precursor composition to produce the building material. By “mineralization” it is meant that carbon (e.g., in the form of

CO_2) becomes embodied in solid composition (e.g., a CO_2 embodied cement or a CO_2 embodied aggregate, etc.).

In certain cases, the building material is, or includes, an aggregate. The term "aggregate" is used in its conventional sense to refer to a granular material, i.e., a material made up of grains or particles. As the aggregate is a carbonate aggregate, the particles of the granular material include one or more carbonate compounds, where the carbonate compound(s) component may be combined with other substances (e.g., substrates) or make up the entire particles, as desired. In certain cases, methods of the invention include producing carbonate coated aggregates, e.g., for use in concretes and other applications. The carbonate coated aggregates may be conventional or lightweight aggregates. The CO_2 sequestering aggregate compositions include aggregate particles having a core and a CO_2 sequestering carbonate coating on at least a portion of a surface of the core. The CO_2 sequestering carbonate coating is made up of a CO_2 sequestering carbonate material.

In some embodiments, production of the building material involves the use of an aggregate substrate. The aggregate substrate can be coated with CO_2 sequestering metal carbonate to form a coated aggregate. When employed, any convenient aggregate substrate may be used. Examples of suitable aggregate substrates include, but are not limited to: natural mineral aggregate materials, e.g., rocks, sand (e.g., natural silica sand), sandstone, gravel, granite, diorite, gabbro, basalt, etc.; and synthetic aggregate materials, such as industrial byproduct aggregate materials, e.g., blast-furnace slag, fly ash, municipal waste, and recycled concrete, etc. In these instances, the aggregate substrate includes a material that is different from the particles of the polymorph precursor composition.

In other instances, the substrate may be the aggregate formed from the process described herein from an earlier production. In some cases, that substrate may be an agglomeration of non-carbonate particles agglomerated together with the carbonate slurry in the earlier production cycle, especially when finer core substrate grains are employed. Such agglomerated composite

substrates may have certain benefits, such as having a light weight characteristic, bestowing the final aggregate with properties suitable for light weight concrete, or have a greater proportion of the aggregate comprising CO_2-sequestered carbonate, increase the CO_2 sequestration potential of the aggregate when deployed in concrete, thus lowering the embodied CO_2 of the concrete in a lifecycle analysis.

Where the precipitated calcium carbonate is mixed with an aggregate substrate in a revolving drum, the resultant carbonate aggregate is a carbonate coated aggregate, where the particulate members of the aggregate include a core material at least partially, if not completely, coated by a carbonate material. In some cases, especially with finer core grains, the carbonate slurry binds more than one particle of core material together into an agglomerated composite.

In some embodiments, a carbonate slurry comprising a polymorph precursor is introduced into a revolving drum and subjected to rotational action (e.g., mixed) in the revolving drum under conditions sufficient to produce a carbonate aggregate. Methods of producing an aggregate involving subjecting a carbonate slurry to rotational action are described in, for example, U.S. Patent Application Serial No. 17/297,278 published as US 2021-0403336 A1, the disclosure of which is incorporated by reference herein. In some instances, the polymorph precursor composition is introduced into the revolving drum with an aggregate substrate and then mixed in the revolving drum to produce a carbonate coated aggregate. In some instances, the slurry (and substrate) is introduced into the revolving drum and mixing is commenced shortly after production of the polymorph precursor composition, such as within 12 hours, such as within 6 hours and including within 4 hours of preparing the polymorph precursor composition. In some instances, the entire process (i.e., from commencement of polymorph precursor composition preparation to obtainment of carbonate aggregate product) is performed in 15 hours or less, such as 10 hours or less, including 5 hours or less, e.g., 3 hours or less, including 1 hour less. The polymorph precursor composition, and aggregate substrate when present, is mixed in the revolving drum for a period of time sufficient to produce

the desired carbonate aggregate. While the period of time may vary, in some instances the period of time ranges from 10 min to 5 hours, such as 15 min to 3 hours or more.

During and/or following mixing, the resultant carbonate aggregate may be dried. Where desired, drying may be achieved using any convenient protocol. In some instances, drying the resultant carbonate aggregate may occur during production, e.g., by application of heat during mixing. Such protocols include, e.g., direct heating of the mixing vessel, e.g., using waste energy to supply the heat, or, e.g., heating the inside of the mixing vessel with, e.g., hot flue gas from a fossil fuel combustion process, so that the temperature of the internal atmosphere where the carbonate aggregate is being produced is between 15 ºC and 260 ºC, or between 15 ºC and 30 ºC, or 15 ºC and 50 ºC, or 15 ºC and 200 ºC, or between or 20 ºC and 200 ºC, such as 20 ºC and 60 ºC, or 25 ºC and 75 ºC, or 25 ºC and 150 ºC, or between 30 ºC and 250 ºC, such as 30 ºC and 150 ºC, or 30 ºC and 200 ºC, and including between 40 ºC and 250 ºC, to dry the carbonate aggregate. In other instances, drying the resultant carbonate aggregate may occur after production, e.g., after the aggregate has exited the mixing and/or aggregate production vessel. Convenient protocols include drying the resultant carbonate aggregate in open atmosphere under ambient conditions, e.g., outside in an aggregate storage bay and/or silo at a production plant or, e.g., in a covered dome or enclosed container away from outside elements. In some instances of the embodiment, the method of drying may include curing the resultant aggregate, e.g., as described below.

In some instances, methods include combining the carbonate precipitate with a seed structure. A seed structure may be employed in certain cases where it is desirable to influence the structure of the carbonate precipitate in order to obtain a particular result. For example, precipitated $CaCO_3$ can be mixed with seeds of a desirable structure of $CaCO_3$ to form a suitable final product including an aggregate and/or building product. In other words, the carbonate precipitate may adopt the structure of the seed. The seed structure may be a crystalline seed structure. In such cases, the carbonate precipitate may adopt crystal

structure and/or nano/microstructure of said crystalline seed structure. In some cases, the crystalline seed structure may be any desirable crystalline form of $CaCO_3$. Crystalline seed structures may include, but are not limited to, calcite, aragonite, and vaterite.

In one aspect of the invention, the carbonate precipitate and seeds are combined and then cured (or hardened) to create a strong building product. In such cases, the calcium carbonate precipitate must contain at least one of the following: amorphous calcium carbonate, pluripotent polymorph precursor, desirable polymorph precursor, undesirable polymorph precursor, pre-vaterite polymorph precursor, vaterite, and/or aragonite. The calcium carbonate precipitate may be any combination or mixture of the above, and may include calcite if it also contains at least one of the above. The seeds may be crystalline calcium carbonate, of the crystal structure and/or nano/microstructure which is desired. The calcium carbonate precipitate and seeds are then formed into aggregates, in one example by agglomerating. The agglomerates are then cured to strengthen them into the strong building material final product.

The seeds may be added at any stage before curing. For example, the seeds may be added to the aqueous capture liquid before or after the calcium carbonate precipitate is formed or precipitated, to the precipitate-liquid mixture, to the filtration, during filtration, after filtration, to the slurry, to the agglomeration drum or mold. The seeds may be mixed in or not mixed in. The seeds may be sprinkled into a liquid or slurry or powder or solid. For example, if a calcite building product is desired, calcite seeds would be used. If aragonite building product is desired, aragonite containing seeds would be used. If vaterite is desired, aragonite seeds would be used.

The seeds may vary in particle size, e.g., from 10nm to 5cm; with a typical size range being from 5 um to 5000 um. In some cases, the seeds may be a finished produced building product described elsewhere herein, which are pulverized to the desired particle size and incorporated at the desired percentage as seeds back into the liquid before calcium carbonate precipitation, or into the calcium carbonate precipitate. This circular process of incorporating produced

products to act as seeds enables an additive-free process, which can have beneficial cost, supply chain, and CO_2 footprint impacts. In one embodiment of the invention, the seeds may be naturally occurring carbonates (see below).

The calcium carbonate and seeds are then formed into the desired shape and particle size, as described in, e.g., U.S. Patent Application Publication Nos. 2015/0246314; 2016/0121298; 2021/0403336; 2021/0262320; 2020/0129916; and International Publication No. WO 2022/140260; the disclosures of which are incorporated by reference herein in their entirety. After the aggregates are formed to the desired shape and particle size, the aggregates (calcium carbonate precipitate and seeds) are cured to harden them into a strong building material until they reach their maximum strength. In embodiments, curing involves maintaining a level of moisture in the carbonate precipitate composition. Some embodiments of curing include keeping the composition in a sealed or moist environment such as a bag, bucket, pile of moist product, or humidity chamber. Curing can also include spraying with curing liquid (including water), steaming, or submerging the product in curing liquid (including water). Optionally, the temperature can be controlled during curing. The temperature can optionally be chosen based on the desired end product polymorph.

In some instances, the seed structure may be aragonite, and/or calcite. In some instances, the seed structure may be vaterite if vaterite is a desired product. In some instances, e.g., wherein the carbonate slurry comprises calcium magnesium carbonate particles, the seed structure may be dolomite. In some instances, the seed is strong rock which has been pulverized into a smaller particle size. In some instances, the seed structure can be recycled product from the process (“circular” process). In other words, a product or by-product of the subject methods may be employed as the subject seed structure.

In some instances, the seed structure may be or include naturally occurring rocks or minerals. Examples include, but are not limited to: natural mineral aggregate materials, e.g., rocks, sand (e.g., natural silica sand), dolomite, sandstone, gravel, granite, diorite, gabbro, basalt, etc.; and synthetic aggregate materials, such as industrial byproduct aggregate materials, e.g.,

blast-furnace slag, fly ash, municipal waste, and recycled concrete, etc. In some cases, the rocks or minerals are selected from aggregate, waste concrete, tropical sands, limestone and fine waste dust comprising $CaCO_3$. In select instances, the seed structures include aggregate, e.g., a recycled aggregate or an aggregate produced via the subject methods. In addition or alternatively, embodiments of the seed structures include waste concrete (e.g., from a demolished built structure). In addition or alternatively, embodiments of the seed structures include tropical sands. Any metal carbonate containing rock could be used, such as but not limited to limestone, marble, and coral rock. In some instances, the seed structure may be coarse aggregates, such as friable Pleistocene coral rock, e.g., as may be obtained from tropical areas (e.g., Florida) that are too weak to serve as aggregate for concrete. In this case, the friable coral rock can be used as a seed, and the solid CO_2 sequestering carbonate mineral may be deposited in the internal pores, making the coarse aggregate suitable for use in concrete, allowing it to pass the Standard Test Method for Resistance to Degradation of Large-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine (ASTM C535). In some instances, where a lightweight aggregate is desired, the outer surface will only be penetrated by the solution of deposition, leaving the inner core relatively ‘hollow’ making a lightweight aggregate for use in light weight concrete.

Seed structures may range from singular objects or particulate compositions, as desired. The seed structure may have a variety of different shapes, which may be regular or irregular, and a variety of different dimensions. The seed structure may have any suitable size (e.g., diameter), where sizes of interest range from 2 nm to 20 cm, such as 3 nm to 15 cm, such as 4 nm to 10 cm, and including 5 nm to 5 cm. In some instances, the seeds are of a fine particle size e.g., granular composition, made up of a plurality of particles. Where the seed structure is a particulate composition, the dimensions of particles making up the seed structure may vary, ranging in some instances from 0.01 to 1,000,000 µm, such as 0.1 to 100,000 µm. The percentage of seeds in the carbonate precipitate-seed composition may also vary, ranging in some

instances from 0.1% to 90% w/w dry, such as 1% to 20% w/w dry basis.

In some embodiments, the seed structures may be introduced prior to precipitation of the metal carbonate. In some such embodiments, the seed structures may be included in an aqueous solution containing cations and/or dissolved inorganic carbon. In other embodiments, the seeds may be introduced to the carbonate after precipitation. In some instances, the seeds may be added to the carbonate precipitate in its aqueous suspension form, during filtration, after filtration, or to the slurry before, during, or after agglomeration.

The carbonate composition, and seeds when present, may be mixed in a revolving drum for a period of time sufficient to produce the desired carbonate aggregate. While the period of time may vary, in some instances the period of time ranges from 10 min to 5 hours, such as 15 min to 3 hours or more. In other embodiments, the method may not involve drying the resultant carbonate aggregate. Such embodiments may involve curing the building product in its residual moisture/water, or residual curing liquid present in the product from the production process. They can also include subjecting the produced building product to a curing step in a humid environment or steam environment. In some cases, combining the carbonate precipitate with the seed structure comprises coating the seed structure with the carbonate precipitate. For example, where the seed structure is porous, carbonate precipitate may occupy space within the pores. In other cases, combining the carbonate precipitate with the seed structure comprises coating the carbonate precipitate with the seed structure.

As discussed above, the methods may include curing the resultant carbonate building material (e.g., aggregate). As used herein, “curing” means a transformation to a hardened state, altering the crystal structure and/or morphological nano/micro-structure of a compound. In some cases, curing includes changing a compound in an initial CO_2 sequestering solid composition (e.g., a precipitate or aggregate composition) from a first polymorph to a second polymorph. Methods of curing an aggregate product are described in, for example, U.S. Patent Application Publication No. 2021/0403336, the disclosure of which is incorporated by reference in its entirety. Accordingly, embodiments of

the invention include contacting the building material (e.g., aggregate) with a curing liquid sufficient to produce a cured building material, or curing via residual moisture in the produced product (i.e., curing liquid is present in the produced product but it was not added to the building material). The curing liquid is a composition that can be contacted with the initial CO_2 sequestering composition, thereby curing it and producing a cured CO_2 sequestering solid. The term “liquid” in “curing liquid” means that the curing composition includes a compound in a liquid state of matter, e.g., water. For example, the curing liquid can be an aqueous liquid wherein water is the most abundant compound present in the curing liquid. In certain cases, the curing liquid may be chosen from a carbonate curing liquid, a bicarbonate curing liquid, a phosphate curing liquid, a divalent alkali earth metal curing liquid water, or a combination thereof. In some versions, the curing liquid is substantially free or completely free of any compounds dissolved in the water of the aqueous curing liquid. In other embodiments, the curing liquid includes water and compounds dissolved in the water, i.e., the curing liquid is a solution that includes solutes dissolved in a solvent. In some cases, the curing liquid also includes a compound in a solid state of matter, i.e., a solid compound that is not dissolved in the liquid. In some embodiments the curing liquid is an emulsion, i.e., it is a mixture of two or more liquids that normally form two immiscible layers, but wherein addition of an emulsifier causes the two layers to merge and form a single layer.

Some embodiments of the method include keeping the precipitated carbonate (and optionally seeds) moist (i.e., containing water) until the composition achieves the desired properties of the building material. Any protocol for keeping the composition moist may be employed. For example, in some cases, methods include keeping an already moist mixture wet by: preventing moisture from evaporating (e.g., in a bag or pile), humidity, steam, and spraying with water. In some embodiments, curing includes placing the carbonate building material in a humid area (e.g., a humidity chamber). The humidity in the humidity chamber may vary, and can in some instances range from 40% to 100% such as 50% to 75%. In certain instances, the humidity chamber may be a bag, such as a

plastic bag. In certain instances, the humidity chamber may be a pile, such as a covered pile.

In some cases, the curing step includes changing a compound of the initial CO_2 sequestering composition from a first crystal structure to a second crystal structure, wherein the curing compound permits or increases the rate of this change. In some instances, the curing liquid allows for the temporary dissolution of solid compounds into the curing liquid, followed by a transition of these compounds back into a solid state, but in a second crystal structure. In some cases, the curing liquid favors the formation of the second crystal structure over formation of the first crystal structure. In some embodiments, the curing liquid includes an ion, e.g., carbonate, that is also present in the initial CO_2 sequestering composition. Due to limitation on solubility, the presence of this ion in the curing liquid can help prevent an undesirably high amount of the initial CO_2 sequestering composition from dissolving in the curing liquid and remaining in the curing liquid. In other words, the presence of this common ion can favor the transition of the compound back into a solid state, but in the second crystal structure. In other cases, the curing compound can directly interact with the solid in the first crystal structure and cause it to change into the second crystal structure without dissolving into the curing liquid.

In other embodiments, the curing happens because the curing compound changes the pH of the initial CO_2 sequestering solid composition. In other words, the curing liquid can have a pH that causes the protonation or deprotonation of compounds within the initial CO_2 sequestering solid composition. In some cases, the curing process happens because some solid compounds of the initial CO_2 sequestering solid composition become dissolved in the curing liquid, thereby separating them from the sequestering solid. The curing liquid can also contain compounds that transition from dissolved in the curing liquid to the solid state, thereby becoming part of the sequestering solid.

In some cases, the curing liquid has a dissolved inorganic carbon concentration sufficient to produce the desired cured composition. Dissolved inorganic carbon (DIC) refers to carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_3),

and CO_2 dissolved in a liquid. In some instances, the curing liquid has a DIC ranging from 0.01 M to 10 M, such as from 0.05 M to 5 M, 0.1 M to 4 M, or 0.5 M to 3 M. For example, if the curing liquid includes 1 M of carbonate ions, 0.2 M of bicarbonate ions, and 0.1 M of dissolved CO_2, then the dissolved inorganic carbon concentration will be 1.3 M. In some cases, the curing liquid has concentration of positive ions ranging from 0.01 M to 10 M, such as from 0.05 M to 5 M, 0.1 M to 4 M, or 0.5 M to 3 M, e.g., wherein the positive ion is selected from the group consisting of Na^+, K^+, and NH_4^+. For example, in some cases the curing liquid has a concentration of Na^+ ions ranging from 0.5 M to 5 M.

In some cases, the curing liquid comprises a carbonate curing liquid, i.e., the liquid includes a carbonate compound including the carbonate ion (CO_3^{2-}), a bicarbonate compound including the bicarbonate ion (HCO_3^{2-}), or both. In some cases, the carbonate compound has the formula M_2CO_3, wherein M is a monovalent positive ion, e.g., an alkali metal cation. For example, the carbonate compound can be sodium carbonate (Na_2CO_3), ammonium carbonate ($(NH_4)_2CO_3$), or potassium carbonate (K_2CO_3). In some cases, the curing liquid includes a bicarbonate compound, e.g., of the formula $MHCO_3$, wherein M is a monovalent position ion, e.g., an alkali metal cation. Exemplary bicarbonate compounds include sodium bicarbonate ($NaHCO_3$), ammonium bicarbonate (NH_4HCO_3), and potassium bicarbonate (K_2HCO_3).

In some instances, the curing liquid is a phosphate curing liquid, i.e., it can include a phosphate compound. As used herein, “phosphate” refers to a compound that includes four oxygen atoms bonded to a phosphorous atom, i.e., a compound that includes a phosphate group. In some cases, the phosphate compound has the formula $PO_4R^1R^2R^3$, wherein R^1, R^2, and R^3 are each independently hydrogen or a negative charge. When R^1, R^2, and R^3 are all a hydrogen atom then the compound is H_3PO_4, which is referred to as phosphoric acid herein. When R^1 and R^2 are hydrogen and R^3 is a negative charge, the resulting compound is $H_2PO_4^-$, which is referred to herein as the dihydrogen phosphate ion, and the curing liquid has a corresponding positive ion, such as an alkali metal cation, e.g., Na^+ or K^+. When R^1 is hydrogen and R^2 and R^3 are

negative charges, the resulting compound is HPO_4^{2-}, which is referred to herein as the hydrogen phosphate ion, and the curing liquid has corresponding positive ion or ions. When R^1, R^2, and R^3 are all negative charges then the compound is PO_4^{3-}, which is referred to herein as the phosphate ion, and the curing liquid has corresponding positive ion or ions. The phosphate curing liquid can also include a polyphosphate group, i.e., a group having two or more phosphorous atoms which are each bonded to four oxygen atoms, wherein one of the oxygen atoms is bonded to two phosphorous atoms. An exemplary polyphosphate compound is polyphosphoric acid, which has the formula $HO-(PO_3H)_n-H$, wherein n is an integer of 2 or more, such as from 2 to 10,000. In some cases, the polyphosphate is deprotonated, i.e., wherein one or more of the hydrogen atoms are replaced with negative charges, and the curing liquid includes corresponding positive ions, e.g., alkali metal cations such as Na^+ and K^+. In some cases, the phosphate compound is an organophosphate compound, i.e., has the formula $PO_4R^1R^2R^3$, wherein R^1, R^2, and R^3 are each independently hydrogen, a hydrocarbon group, or negative charge, wherein at least one of R^1, R^2, and R^3 is a hydrocarbon group.

In some cases, the curing liquid is a divalent alkali earth metal, e.g., calcium, magnesium, etc., curing liquid, such as a calcium curing liquid, i.e., it can include divalent alkali earth metal ions, e.g., calcium ions (Ca^{2+}) magnesium ions (Mg^{2+}), etc. In some instances, the divalent alkali earth metal, e.g., calcium, curing liquid has a divalent alkali earth metal, e.g., calcium ion concentration ranging from 0.01 M to 1.0 M, such as from 0.02 M to 0.2 M, or 0.09 M to 0.9 M. Such curing liquids may vary, as desired, so long as they provide a source of divalent alkali earth ion, where examples of such curing liquids include, but are not limited to, $CaCl_2$, $MgCl_2$, etc. In some cases where the curing liquid is a calcium curing liquid, the calcium curing liquid is supersaturated with Ca^{2+} and DIC, wherein additional CO_2 sequestering solid is formed. For example, if the curing liquid is the filtrate from preparing the initial CO_2 sequestering solid composition from a method that comprises contacting an aqueous capture liquid

comprising a cation source with a gaseous source of CO_2 under conditions sufficient to produce the initial CO_2 sequestering solid.

In some cases, the curing liquid includes water, i.e., the curing liquid includes water. The water may be from any convenient source, In some instances, the water is obtained from a municipal water supply. The term “municipal water supply” refers to potable water (i.e., drinking water) that is regarded as safe for humans to drink and that is delivered by pipes to two or more businesses or homes, such as 100 or more businesses or homes. In some instances, the water may be recycled water, which may or may not be potable. In some cases, the curing liquid comprises a combination of any of the abovementioned curing liquids, i.e., a composite curing liquid comprised of bicarbonate curing liquid, carbonate curing liquid, phosphate curing liquid, alkali earth metal, e.g., calcium, curing liquid and water, or any composite combination thereof.

Where the carbonate coating is produced using a CO_2 sequestering process, e.g., as described above, the resultant aggregate compositions may be considered to be CO_2 sequestering aggregate compositions. In some instances, the CO_2 sequestering aggregate compositions include aggregate particles having a core and a CO_2 sequestering carbonate coating on at least a portion of a surface of the core. The CO_2 sequestering carbonate coating is made up of a CO_2 sequestering carbonate material. By "CO_2 sequestering carbonate material" is meant a material that stores a significant amount of CO_2 in a storage-stable format, such that CO_2 gas is not readily produced from the material and released into the atmosphere. In certain embodiments, the CO_2-sequestering material includes 5% or more, such as 10% or more, including 25% or more, for instance 50% or more, such as 75% or more, including 90% or more of CO_2, e.g., present as one or more carbonate compounds. In additional embodiments, the CO_2-sequestering material may form independent particles without a substrate particle. The CO_2-sequestering materials present in coatings in accordance with the invention may include one or more carbonate compounds. The amount of carbonate in the CO_2-sequestering material, e.g., as determined by coulometry,

may be 10% or higher, 20% or higher 40% or higher, such as 70% or higher, including 80% or higher, such as 100% when the particle form without a core substrate, or the core substrate is a particle that formed without a core substrate.

FIG. 9, discussed in greater detail below in the Experimental section, shows the effect of seeding to transform ACC and vaterite polymorphs into a desired aragonite polymorph. As shown in FIG. 9, the proportion of different calcium carbonate polymorphs changes throughout the production, seeding and curing steps, to produce a building material final product from precipitated calcium carbonate. Use of seeding may be employed to synthesize metal carbonates of a desired crystal structure and morphology, ranging from nm to m in scale. While described herein in terms of building materials, seeding in embodiments of the invention has utility to additional fields outside of building materials and CO_2 sequestration.

In some instances, the undifferentiated pluripotent polymorph precursor present in the carbonate slurry may produce an undesirable differentiated polymorph precursor not suitable to be used as a building material (Box 104 in FIG. 1). By “undesirable” differentiated polymorph precursor, it is meant that the differentiated polymorph precursor in question is not useful for generating a building material of interest. However, as discussed above, the undesirable differentiated polymorph precursor may be processed under conditions sufficient to form a specific polymorph suitable to be used as a building material (Box 105, FIG. 1), such as by adding a seed structure or by curing.

In a certain embodiment, methods begin with a calcium carbonate containing at least one of the following: a pluripotent polymorph precursor, an amorphous calcium carbonate, a desirable polymorph precursor, an undesirable polymorph precursor, a vaterite polymorph precursor, and vaterite. Optionally, this calcium carbonate is freshly precipitated and in a carbonate slurry form containing an aqueous solution or water.

Methods may subsequently include the addition of a desired polymorph and mixing until homogenous. In such cases, calcium carbonate seeds of the desired polymorph are added to the slurry. The seeds may be added from 0.01%

to 90% w/w (dry basis), including 1% to 20% w/w (dry basis). Alternatively, the calcium carbonate seeds could be added to the aqueous solution before precipitation (creation) of the calcium carbonate.

In some embodiments, before aggregation, water/aqueous solution is added to or taken away from the calcium carbonate, until a slurry consistency containing 15% to 50% water is achieved, including 18% to 25% water. The calcium carbonate (precipitate - seed mixture) is formed into the desired particle shape and size. In one example, these are coarse aggregates (gravel), in another example the desired size is sand. In one example, the precipitate-seed-water mixture is rolled inside a rotating drum. In another example, the precipitate-seed-water mixture is placed into molds.

Methods may then include placing the carbonate product in an environment where moisture is retained (i.e., “curing” the product). The humid environment can include, for example a humidity chamber or a sealed container which does not allow evaporation. In additional cases, the carbonate product is exposed to steam. Optionally, this environment can be temperature controlled. When carbonate aggregate/building material reaches maximum strength (e.g., compressive strength, tensile strength, etc.), it may then be removed from the humid environment.

In one embodiment of this protocol, an undesirable differentiated polymorph precursor may be seeded with aragonite polymorph crystals to produce a suitable building material. One example of this embodiment is described in the following steps below:

1. A calcium-alkalinity solution is prepared, either by dissolving recycled concrete aggregate in ammonium chloride, or by preparing the solution from commercial chemicals. In this embodiment, solution contains:
    a. 0.38 M Ca^{2+}
    b. 0.29 M NH_4^+
    c. 0.34 M NH_3
    d. 5 mM Mg^{2+}
    e. 8 mM $(SO_4)^{2-}$

2. Gaseous CO_2 at 7% (range during experiment 6-9%) w/w in air is contacted with the calcium-alkalinity solution using a bubbling stone. pH is monitored and the reaction is stopped when alkalinity is reacted / the pH reaches 7
3. The solid phase is allowed to fall out of the liquid by settling for 30-45 minutes
4. The liquid phase is decanted
5. The solid phase is filtered using a Büchner funnel and 1.5um filter paper
6. The solid phase is rinsed four times with water
7. The solid phase is filtered using a Büchner funnel until moisture content of the slurry/solid phase is 30-38% water
8. Powdered aragonite (a crystalline form of calcium carbonate) is mixed in at 10% w/w of the total (final product) calcium carbonate, using a stand mixer, until the precipitate-water-aragonite mixture is homogenous, about 2 minutes at low speed.
    a. Powdered aragonite preparation:
        i. Aragonite was crushed using a jaw crusher
        ii. In this example, the crushed aragonite was sieved to be mesh size #50x#100 (0.15-0.30mm)
9. The precipitate-aragonite-water mixture is transferred to a rotating drum, with low temp heated air flowing into the drum (85F)
10. The mixture is tumbled in the drum for about 20 minutes, until desired (gravel) sized aggregates are formed
11. The aggregates are transferred to a curing chamber: a high humidity (70-80% RH) chamber at 75C
12. The aggregates are kept in the curing chamber for 2 days
13. The aggregates are removed from the curing chamber and dried at ambient condition.

In another embodiment of this protocol, an undesirable differentiated polymorph precursor may be seeded with calcite polymorph crystals to produce a suitable building material, for example, as is illustrated in FIG. 6. FIG. 6 presents

a flowchart showing the steps of creating a desired $CaCO_3$ product by seeding. $CaCO_3$ is precipitated (601) and contains at least one of: pluripotent polymorph precursor, undesirable polymorph precursor, desirable polymorph precursor, amorphous $CaCO_3$, vaterite, and/or aragonite. This precipitated $CaCO_3$ containing at least one of the polymorphs listed is combined with the desired crystalline $CaCO_3$ seeds (602). The seeds may be added either before or after precipitating $CaCO_3$. Then, the mixture (603) of precipitated $CaCO_3$ and seeds are cured with moisture/water (604). The moisture can come from any convenient source. Optionally, the temperature may be controlled while curing with moisture, for example, by warming. After the product is cured, it is in the form of a product, for example a building product or aggregate (605).

In some embodiments, methods of the invention include the following steps below:

1. A calcium-alkalinity solution is prepared, either by dissolving recycled concrete aggregate in ammonium chloride, or by preparing the solution from commercial chemicals In this embodiment, the solution contains:
    a. 0.38 M Ca^{2+}
    b. 0.29 M NH_4^+
    c. 0.34 M NH_3
    d. 5 mM Mg^{2+}
    e. 8 mM $(SO_4)^{2-}$
2. Gaseous CO_2 at 7% (range during experiment 6-9%) w/w in air is contacted with the calcium-alkalinity solution using a bubbling stone. pH is monitored and the reaction is stopped when alkalinity is reacted / the pH reaches 7
3. The solid phase is allowed to fall out of the liquid by settling for 30-45 minutes
4. The liquid phase is decanted
5. The solid phase is filtered using a Büchner funnel and 1.5um filter paper
6. The solid phase is rinsed four times with water

7. The solid phase is filtered using a Büchner funnel until moisture content of the slurry/solid phase is 30-38% water
8. Powdered calcite (a crystalline form of calcium carbonate) is mixed in at 10% w/w of the total (final product) calcium carbonate, using a stand mixer, until the precipitate-water-aragonite mixture is homogenous, about 2 minutes at low speed.
    a. Powdered calcite preparation:
        i. Calcite is crushed by hand
        ii. In this example, the crushed calcite is sieved to be <0.15mm
9. The precipitate-calcite-water mixture is transferred to a rotating drum, with low temp heated air flowing into the drum (85F)
10. The mixture is tumbled in the drum for about 20 minutes, until desired (gravel) sized aggregates are formed
11. The aggregates are transferred to a curing chamber: a high humidity (70-80% RH) chamber at 75C
12. The aggregates are kept in the curing chamber for 5 days
13. The aggregates are removed from the curing chamber and dried at ambient condition.

METHODS OF PRODUCING COMPOSITIONS INCLUDING BUILDING MATERIALS

Aspects of the invention further include the production of compositions including building materials (e.g., aggregates) of the invention. In some embodiments, the subject compositions are settable compositions. Settable compositions of the invention, such as concretes and mortars, are produced by combining a hydraulic cement with an amount of aggregate (e.g., such as those produced as described above) and water, either at the same time or by pre-combining the cement with aggregate, and then combining the resultant dry components with water. The liquid phase, e.g., aqueous fluid, with which the dry component (i.e., concrete dry composite) is combined to produce the settable composition, e.g., concrete, may vary, from pure water to water that includes one or more solutes, additives, co-solvents, etc., as desired. The ratio of dry

component to liquid phase that is combined in preparing the settable composition may vary, and in certain embodiments ranges from 2:10 to 7:10, such as 3:10 to 6:10 and including 4:10 to 6:10.

The term "cement" as used herein refers to a particulate composition that sets and hardens after being combined with a setting fluid, e.g., an aqueous solution, such as water. The particulate composition that makes up a given cement may include particles of various sizes. In some instances, a given cement may be made up of particles having a longest cross-sectional length (e.g., diameter in a spherical particle) that ranges from 1 nm to 100 μm, such as 10 nm to 20 μm and including 15 nm to 10 μm. Cements of interest include hydraulic cements. The term “hydraulic cement” as used herein refers to a cement that, when mixed with a setting fluid, hardens due to one or more chemical reactions that are independent of the water content of the mixture and are stable in aqueous environments. As such, hydraulic cements can harden underwater or when constantly exposed to wet weather conditions. Hydraulic cements of interest include, but are not limited to Portland cements, modified Portland cements, and blended hydraulic cements.

Following the combination of the components to produce settable compositions (e.g., concrete), the settable compositions are in some instances initially flowable compositions, and then set after a given period of time. The setting time may vary, and in certain embodiments ranges from 30 minutes to 48 hours, such as 30 minutes to 24 hours and including from 1 hour to 4 hours.

The components of the settable composition can be combined using any convenient protocol. Each material may be mixed at the time of work, or part of or all of the materials may be mixed in advance. Alternatively, some of the materials are mixed with water with or without admixtures, such as high-range water-reducing admixtures, and then the remaining materials may be mixed therewith. As a mixing apparatus, any conventional apparatus can be used. For example, Hobart mixer, slant cylinder mixer, Omni Mixer, Henschel mixer, V-type mixer, and Nauta mixer can be employed.

In some embodiments, the production of the subject settable compositions includes the addition of admixtures. “Admixtures” are referred to in their conventional sense to describe substances other than cement, water and aggregate that are added to produce a settable composition (e.g., concrete). Admixtures may, in some cases, be added to confer a desired property to the settable composition (e.g., corrosion resistance, hydration control, etc.).

Admixtures of interest include finely divided mineral admixtures such as cementitious materials; pozzolans; pozzolanic and cementitious materials; and nominally inert materials. Pozzolans include diatomaceous earth, opaline cherts, clays, shales, fly ash, silica fume, volcanic tuffs and pumicites are some of the known pozzolans. Certain ground granulated blast-furnace slags and high calcium fly ashes possess both pozzolanic and cementitious properties. Nominally inert materials can also include finely divided raw quartz, dolomites, limestone, marble, granite, and others. Fly ash is defined in ASTM C618. Other types of admixture of interest include plasticizers, accelerators, retarders, air-entrainers, foaming agents, water reducers, corrosion inhibitors, and pigments. As such, admixtures of interest include, but are not limited to: set accelerators, set retarders, air-entraining agents, defoamers, alkali-reactivity reducers, bonding admixtures, dispersants, coloring admixtures, corrosion inhibitors, dampproofing admixtures, gas formers, permeability reducers, pumping aids, shrinkage compensation admixtures, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, rheology modifying agents, finely divided mineral admixtures, pozzolans, aggregates, wetting agents, strength enhancing agents, water repellents, and any other concrete or mortar admixture or additive. Admixtures are well-known in the art and any suitable admixture of the above type or any other desired type may be used; see, e.g., United States Patent No. 7,735,274, incorporated herein by reference in its entirety.

Methods of interest may additionally include producing concrete dry composites that, upon combination with a suitable setting liquid, produce a settable composition that sets and hardens into a concrete or a mortar. Concrete dry composites as described herein include an amount of an aggregate (e.g.,

CO_2 sequestering aggregate, produced as described above), and a cement, such as a hydraulic cement. The setting and hardening of the product produced by combination of the concrete dry composites of the invention with an aqueous liquid are a result of the production of hydrates that are formed from the cement upon reaction with water, where the hydrates are essentially insoluble in water.

Also of interest are formed building materials. Formed building materials of interest include a building material (e.g., an aggregate) of the invention. The formed building materials of the invention may vary greatly. By "formed" is meant shaped, e.g., molded, cast, cut or otherwise produced, into a man-made structure defined physical shape, i.e., configuration. Formed building materials are distinct from amorphous building materials, e.g., particulate (such as powder) compositions that do not have a defined and stable shape, but instead conform to the container in which they are held, e.g., a bag or other container. Illustrative formed building materials include, but are not limited to: bricks; boards; conduits; beams; basins; columns; drywalls etc. Further examples and details regarding formed building materials include those described in United States Patent No. 8,431,100; the disclosure of which is herein incorporated by reference.

In some embodiments, the formed building material may include one or more different carbonate compounds, such as two or more different carbonate compounds, e.g., three or more different carbonate compounds, five or more different carbonate compounds, etc., including non-distinct, amorphous carbonate compounds. Carbonate compounds may be compounds having a molecular formulation $X_m(CO_3)_n$ where X is any element or combination of elements that can chemically bond with a carbonate group or its multiple, wherein X is in certain embodiments an alkaline earth metal and not an alkali metal; wherein m and n are stoichiometric positive integers. These carbonate compounds may have a molecular formula of $X_m(CO_3)_n \bullet H_2O$, where there are one or more structural waters in the molecular formula. The amount of carbonate in the formed building material, e.g., as determined by coulometry using the protocol described as coulometric titration, may be 10% or more, such as 25% or more, 50% or more, including 60% or more.

Methods of the invention may additionally include constructing a built structure using the building materials described herein. The built structure may be any structure in which a building material may be used, such as a building, dam, levee, roadway or any other manmade structure that incorporates an aggregate, rock, or settable composition. The built structure may be constructed via any suitable method using techniques that are known to those of skill in the art of construction.

BUILDING MATERIALS PRODUCED BY THE METHODS

As reviewed above, the methods of the invention may be employed to produce building materials such as metal carbonate aggregates (synthetic rocks or sand, depending on particle size), or metal carbonate coated aggregates, e.g., for use in concretes and other applications. The carbonate containing aggregates may be conventional or lightweight aggregates. Aspects of the invention include CO_2 sequestering aggregate compositions. The CO_2 sequestering aggregate compositions include aggregate particles having a core and a CO_2 sequestering carbonate coating on at least a portion of a surface of the core. The CO_2 sequestering carbonate aggregate or aggregate coating is made up of a CO_2 sequestering carbonate material, e.g., as described above.

The CO_2 sequestering carbonate material that is present in carbonate aggregates or coatings of the carbonate-coated particles of the subject aggregate compositions may vary. In some instances, the carbonate material is a highly reflective microcrystalline/amorphous carbonate material. As the materials may be highly reflective, the coatings that include the same may have a high total surface reflectance (TSR) value. TSR may be determined using any convenient protocol, such as ASTM E1918 Standard Test Method for Measuring Solar Reflectance of Horizontal and Low-Sloped Surfaces in the Field (see also R. Levinson, H. Akbari, P. Berdahl, Measuring solar reflectance – Part II: review of practical methods, LBNL 2010).

In some instances, the carbonate aggregates or coatings of the carbonate-coated aggregates that include the carbonate materials are highly

reflective of near infra-red (NIR) light, ranging in some instances from 10 to 99%, such as 50 to 99%. By NIR light is meant light having a wavelength ranging from 700 nanometers (nm) to 2.5mm. NIR reflectance may be determined using any convenient protocol, such as ASTM C1371 - 04a(2010)e1 Standard Test Method for Determination of Emittance of Materials Near Room Temperature Using Portable Emissometers (http://www(dot)astm(dot)org/Standards/ C1371(dot)htm) or ASTM G173 - 03(2012) Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface (http://rredc(dot)nrel(dot)gov/solar/spectra/am1(dot)5/ASTMG173/ASTMG173(dot)html). In some instances, the coatings exhibit a NIR reflectance value ranging from Rg;0 = 0.0 to Rg;0 = 1.0, such as Rg;0 = 0.25 to Rg;0 = 0.99, including Rg;0 = 0.40 to Rg;0 = 0.98, e.g., as measured using the protocol referenced above.

In some instances, the carbonate aggregates or coatings of the carbonate-coated aggregates are highly reflective of ultra-violet (UV) light, ranging in some instances from 10 to 99%, such as 50 to 99%. By UV light is meant light having a wavelength ranging from 400 nm and 10 nm. UV reflectance may be determined using any convenient protocol, such as ASTM G173 - 03(2012) Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface. In some instances, the materials exhibit a UV value ranging from Rg;0 = 0.0 to Rg;0 = 1.0, such as Rg;0 = 0.25 to Rg;0 = 0.99, including Rg;0 = 0.4 to Rg;0 = 0.98, e.g., as measured using the protocol referenced above.

In some instances, the carbonate aggregates or coatings of the carbonate-coated aggregates are reflective of visible light, e.g., where reflectivity of visible light may vary, ranging in some instances from 10 to 99%, such as 10 to 90%. By visible light is meant light having a wavelength ranging from 380 nm to 740 nm. Visible light reflectance properties may be determined using any convenient protocol, such as ASTM G173 - 03(2012) Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface. In some instances, the carbonate aggregates or coatings of the carbonate-coated aggregates exhibit a visible light reflectance value ranging from

Rg;0 = 0.0 to Rg;0 = 1.0, such as Rg;0 = 0.25 to Rg;0 = 0.99, including Rg;0 = 0.4 to Rg;0 = 0.98, e.g., as measured using the protocol referenced above.

The materials making up the carbonate components are, in some instances, amorphous or microcrystalline. Where the materials are nano- or micro-crystalline, the crystal size, e.g., as determined using the Scherrer equation applied to the FWHM of X-ray diffraction pattern, is small, and in some instances is 1000 microns or less in diameter, such as 100 microns or less in diameter, and including 10 microns or less in diameter or 100 nanometers or less in diameter. In some instances, the crystal size ranges in diameter from 1000µm to 0.001µm, such as 10 to 0.001µm, including 1 to 0.001µm. In some instances, the crystal size is chosen in view of the wavelength(s) of light that are to be reflected. For example, where light in the visible spectrum is to be reflected, the crystal size range of the materials may be selected to be less than one-half the "to be reflected" range, so as to give rise to photonic band gap. For example, where the to be reflected wavelength range of light is 100 to 1000 nm, the crystal size of the material may be selected to be 50 nm or less, such as ranging from 1 to 50 nm, e.g., 5 to 25 nm. In some embodiments, the materials produced by methods of the invention may include rod-shaped crystals and amorphous solids. The rod-shaped crystals may vary in structure, and in certain embodiments have length to diameter ratio ranging from 500 to 1, such as 10 to 1. In certain embodiments, the length of the crystals ranges from 0.5µm to 500µm, such as from 5µm to 100µm. In yet other embodiments, substantially completely amorphous solids are produced.

The density, porosity, and permeability of the carbonate aggregates or carbonate-coated aggregates may vary according to the application. With respect to density, while the density of the material may vary, in some instances the density ranges from 5 g/cm^3 to 0.01 g/cm^3, such as 3 g/cm^3 to 0.3 g/cm^{3}and including 2.7 g/cm^{3}to 0.4 g/cm^3. With respect to porosity, as determined by Gas Surface Adsorption as determined by the BET method (Brown Emmett Teller (e.g., as described in E. Teller, *J. Am. Chem. Soc.*, 1938, 60, 309. doi:10.1021/ja01269a023) the porosity may range in some instances from 100

m^2/g to 0.1 m^2/g, such as 60 m^2/g to 1 m^2/g and including 40 m^2/g to 1.5 m^2/g. With respect to permeability, in some instances the permeability of the material may range from 0.1 to 100 darcies, such as 1 to 10 darcies, including 1 to 5 darcies (e.g., as determined using the protocol described in H. Darcy, Les Fontaines Publiques de la Ville de Dijon, Dalmont, Paris (1856).). Permeability may also be characterized by evaluating water absorption of the material. As determined by water absorption protocol, e.g., the water absorption of the material ranges, in some embodiments, from 0 to 25%, such as 1 to 15% and including from 2 to 9 %.

The hardness of the materials may also vary. In some instances, the materials exhibit a Mohs hardness of 3 or greater, such as 5 or greater, including 6 or greater, where the hardness ranges in some instances from 3 to 8, such as 4 to 7and including 5 to 6 Mohs (e.g., as determined using the protocol described in American Federation of Mineralogical Societies. "Mohs Scale of Mineral Hardness"). Hardness may also be represented in terms of tensile strength, e.g., as determined using the protocol described in ASTM C1167. In some such instances, the material may exhibit a compressive strength of 100 to 3000 N, such as 400 to 2000 N, including 500 to 1800 N.

In some embodiments, the carbonate material includes one or more contaminants predicted not to leach into the environment by one or more tests selected from the group consisting of Toxicity Characteristic Leaching Procedure, Extraction Procedure Toxicity Test, Synthetic Precipitation Leaching Procedure, California Waste Extraction Test, Soluble Threshold Limit Concentration, American Society for Testing and Materials Extraction Test, and Multiple Extraction Procedure. Tests and combinations of tests may be chosen depending upon likely contaminants and storage conditions of the composition. For example, in some embodiments, the composition may include As, Cd, Cr, Hg, and Pb (or products thereof), each of which might be found in a waste gas stream of a coal-fired power plant. Since TCLP tests for As, Ba, Cd, Cr, Pb, Hg, Se, and Ag, TCLP may be an appropriate test for aggregates described herein. In some embodiments, a carbonate composition of the invention includes

As, wherein the composition is predicted not to leach As into the environment. For example, a TCLP extract of the composition may provide less than 5.0 mg/L As indicating that the composition is not hazardous with respect to As. In some embodiments, a carbonate composition of the invention includes Cd, wherein the composition is predicted not to leach Cd into the environment. For example, a TCLP extract of the composition may provide less than 1.0 mg/L Cd indicating that the composition is not hazardous with respect to Cd. In some embodiments, a carbonate composition of the invention includes Cr, wherein the composition is predicted not to leach Cr into the environment. For example, a TCLP extract of the composition may provide less than 5.0 mg/L Cr indicating that the composition is not hazardous with respect to Cr. In some embodiments, a carbonate composition of the invention includes Hg, wherein the composition is predicted not to leach Hg into the environment. For example, a TCLP extract of the composition may provide less than 0.2 mg/L Hg indicating that the composition is not hazardous with respect to Hg. In some embodiments, a carbonate composition of the invention includes Pb, wherein the composition is predicted not to leach Pb into the environment. For example, a TCLP extract of the composition may provide less than 5.0 mg/L Pb indicating that the composition is not hazardous with respect to Pb. In some embodiments, a carbonate composition and aggregate that includes of the same of the invention may be non-hazardous with respect to a combination of different contaminants in a given test. For example, the carbonate composition may be non-hazardous with respect to all metal contaminants in a given test. A TCLP extract of a composition, for instance, may be less than 5.0 mg/L in As, 100.0 mg/L in Ba, 1.0 mg/L in Cd, 5.0 mg/mL in Cr, 5.0 mg/L in Pb, 0.2 mg/L in Hg, 1.0 mg/L in Se, and 5.0 mg/L in Ag. Indeed, a majority if not all of the metals tested in a TCLP analysis on a composition of the invention may be below detection limits. In some embodiments, a carbonate composition of the invention may be non-hazardous with respect to all (e.g., inorganic, organic, etc.) contaminants in a given test. In some embodiments, a carbonate composition of the invention may be non-hazardous with respect to all contaminants in any combination of tests selected

from the group consisting of Toxicity Characteristic Leaching Procedure, Extraction Procedure Toxicity Test, Synthetic Precipitation Leaching Procedure, California Waste Extraction Test, Soluble Threshold Limit Concentration, American Society for Testing and Materials Extraction Test, and Multiple Extraction Procedure. As such, carbonate compositions and aggregates including the same of the invention may effectively sequester CO_2 (e.g., as carbonates, bicarbonates, or a combination thereof) along with various chemical species (or co-products thereof) from waste gas streams, industrial waste sources of divalent cations, industrial waste sources of proton-removing agents, or combinations thereof that might be considered contaminants if released into the environment. Compositions of the invention incorporate environmental contaminants (e.g., metals and co-products of metals such as Hg, Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, or combinations thereof) in a non-leachable form.

The aggregate compositions of the invention include particles having a core region and a CO_2 sequestering carbonate coating on at least a portion of a surface of the core, also called “carbonate coated aggregates.” The coating may cover 10% or more, 20% or more, 30% or more, 40% or more, 50% or more, 60% or more, 70% or more, 80% or more, 90% or more, including 95% or more of the surface of the core. The thickness of the carbonate layer may vary, as desired. In some instances, the thickness may range from 0.1µm to 10mm, such as 1µm to 1000 µm, including 10 µm to 500 µm.

The core of the coated particles of the aggregate compositions described herein may vary widely. The core may be made up of any convenient aggregate material. Examples of suitable aggregate materials include, but are not limited to: natural mineral aggregate materials, e.g., carbonate rocks, sand (e.g., natural silica sand), sandstone, gravel, granite, diorite, gabbro, basalt, etc.; and synthetic aggregate materials, such as industrial byproduct aggregate materials, e.g., blast-furnace slag, fly ash, municipal waste, and recycled concrete, etc. In some instances, the core comprises a material that is different from the carbonate coating.

In some instances, the aggregates are lightweight aggregates. In such instances, the core of the coated particles of the aggregate compositions described herein may vary widely, so long as when it is coated it provides for the desired lightweight aggregate composition. The core may be made up of any convenient material. Examples of suitable aggregate materials include, but are not limited to: conventional lightweight aggregate materials, e.g., naturally occurring lightweight aggregate materials, such as crushed volcanic rocks, e.g., pumice, scoria or tuff, and synthetic materials, such as thermally treated clays, shale, slate, diatomite, perlite, vermiculite, blast-furnace slag and fly ash; as well as unconventional porous materials, e.g., crushed corals, synthetic materials like polymers and low density polymeric materials, recycled wastes such as wood, fibrous materials, cement kiln dust residual materials, recycled glass, various volcanic minerals, granite, silica bearing minerals, mine tailings and the like.

The physical properties of the coated particles of the aggregate compositions may vary. Aggregates of the invention have a density that may vary so long as the aggregate provides the desired properties for the use for which it will be employed, e.g., for the building material in which it is employed. In certain instances, the density of the aggregate particles ranges from 1.1 to 5 gm/cc, such as 1.3 gm/cc to 3.15 gm/cc, and including 1.8 gm/cc to 2.7 gm/cc. Other particle densities in embodiments of the invention, e.g., for lightweight aggregates, may range from 1.1 to 2.2 gm/cc, e.g., 1.2 to 2.0 g/cc or 1.4 to 1.8 g/cc. In some embodiments the invention provides aggregates that range in bulk density (unit weight) from 50 lb/ lb/ft^3 to 200 lb/ft^3, or 75 lb/ft^3 to 175 lb/ft^3, or 50 lb/ft^3 to 100 lb/ft^3, or 75 lb/ft^3 to 125 lb/ft^3, or lb/ft^3 to 115 lb/ft^3, or 100 lb/ft^3 to 200 lb/ft^3, or 125 lb/ft^3 to lb/ft^3, or 140 lb/ft^3 to 160 lb/ft^3, or 50 lb/ft^3 to 200 lb/ft^3. Some embodiments of the invention provide lightweight aggregate, e.g., aggregate that has a bulk density (unit weight) of 75 lb/ft^3 to 125 lb/ft^3, such as 90 lb/ft^3 to 115 lb/ft^3. In some instances, the lightweight aggregates have a weight ranging from 50 to 1200 kg/m^3, such as 80 to 11 kg/m^3.

The hardness of the aggregate particles making up the aggregate compositions of the invention may also vary, and in certain instances the

hardness, expressed on the Mohs scale, ranges from 1.0 to 9, such as 1 to 7, including 1 to 6 or 1 to 5. In some embodiments, the Mohr's hardness of aggregates of the invention ranges from 2-5, or 2-4. In some embodiments, the Mohs hardness ranges from 2-6. Other hardness scales may also be used to characterize the aggregate, such as the Rockwell, Vickers, or Brinell scales, and equivalent values to those of the Mohs scale may be used to characterize the aggregates of the invention; e.g., a Vickers hardness rating of 250 corresponds to a Mohs rating of 3; conversions between the scales are known in the art.

The abrasion resistance of an aggregate may also be important, e.g., for use in a roadway surface, where aggregates of high abrasion resistance are useful to keep surfaces from polishing. Abrasion resistance (i.e., abrasion value) is related to hardness but is not the same. Aggregates of the invention include aggregates that have an abrasion resistance similar to that of natural limestone, or aggregates that have an abrasion resistance superior to natural limestone, as well as aggregates having an abrasion resistance lower than natural limestone, as measured by art accepted methods, such as ASTM C131-03, the Los Angeles Abrasion Test, and the Micro Deval Test. In some embodiments aggregates of the invention have an abrasion resistance of less than 50%, or less than 40%, or less than 35%, or less than 30%, or less than 25%, or less than 20%, or less than 15%, or less than 10%, when measured by ASTM C131-03. In some embodiments aggregates of the invention have an abrasion value of less than 40%, or less than 35%, or less than 30%, or less than 25%, or less than 20%, or less than 15%, or less than 10%, when measured by the Los Angeles Abrasion Test. In some embodiments aggregates of the invention have an abrasion value of less than 25%, or less than 20%, or less than 15%, or less than 10%, when measured by the Micro Deval Test.

Aggregates of the invention may also have a porosity within particular ranges. As will be appreciated by those of skill in the art, in some cases a highly porous aggregate is desired, in others an aggregate of moderate porosity is desired, while in other cases aggregates of low porosity, or no porosity, are desired. Porosities of aggregates of some embodiments of the invention, as

measured by water uptake after oven drying followed by full immersion for 60 minutes, expressed as % dry weight, can be in the range of 1-40%, such as 2-20%, or 2-15%, including 2-10% or even 3-9%.

The dimensions of the aggregate particles may vary. Aggregate compositions of the invention are particulate compositions that may in some embodiments be classified as fine or coarse. Fine aggregates according to embodiments of the invention are particulate compositions that almost entirely pass through a Number 4 sieve (ASTM C 125 and ASTM C 33). Fine aggregate compositions according to embodiments of the invention have an average particle size ranging from 10 µm to 4.75mm, such as 50 µm to 3.0 mm and including 75 µm to 2.0 mm. Coarse aggregates of the invention are compositions that are predominantly retained on a Number 4 sieve (ASTM C 125 and ASTM C 33). Coarse aggregate compositions according to embodiments of the invention are compositions that have an average particle size ranging from 4.75 mm to 200 mm, such as 4.75 to 150 mm in and including 5 to 100 mm. As used herein, "aggregate" may also in some embodiments encompass larger sizes, such as 3 in to 12 in or even 3 in to 24 in, or larger, such as 12 in to 48 in, or larger than 48 in.

COMPOSITIONS INCLUDING BUILDING MATERIALS

Aspects of the invention also include compositions that include building materials (e.g., aggregates) of the invention. Compositions of interest include, for example, concrete dry composites, settable compositions, and built structures.

Concrete Dry Composites

Provided herein are concrete dry composites including a building material (e.g., aggregate) of the invention, upon combination with a suitable setting liquid (such as described below), produce a settable composition that sets and hardens into a concrete or a mortar. Concrete dry composites as described herein include an amount of an aggregate, e.g., as described above, and a cement, such as a hydraulic cement. The term "hydraulic cement" is employed in its conventional

sense to refer to a composition which sets and hardens after combining with water or a solution where the solvent is water, e.g., an admixture solution. The setting and hardening of the product produced by combination of the concrete dry composites of the invention with an aqueous liquid results from the production of hydrates that are formed from the cement upon reaction with water, where the hydrates are essentially insoluble in water.

Aggregates of the invention find use in place of conventional natural rock aggregates used in conventional concrete when combined with pure Portland cement. Other hydraulic cements of interest in certain embodiments are Portland cement blends. The phrase "Portland cement blend" includes a hydraulic cement composition that includes a Portland cement component and significant amount of a non-Portland cement component. As the cements of the invention are Portland cement blends, the cements include a Portland cement component. The Portland cement component may be any convenient Portland cement. As is known in the art, Portland cements are powder compositions produced by grinding Portland cement clinker (more than 90%), a limited amount of calcium sulfate which controls the set time, and up to 5% minor constituents (as allowed by various standards). When the exhaust gases used to provide carbon dioxide for the reaction contain SOx, then sufficient sulphate may be present as calcium sulfate in the precipitated material, either as a cement or aggregate to offset the need for additional calcium sulfate. As defined by the European Standard EN197.1, "Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates ($3CaO.SiO_2$ and $2CaO.SiO_2$), the remainder consisting of aluminum- and iron-containing clinker phases and other compounds. The ratio of CaO to SiO_2 shall not be less than 2.0. The magnesium content (MgO) shall not exceed 5.0% by mass." The concern about MgO is that later in the setting reaction, magnesium hydroxide, brucite, may form, leading to the deformation and weakening and cracking of the cement. In the case of magnesium carbonate containing cements, brucite will not form as it may with MgO. In certain embodiments, the Portland cement constituent of the present invention is any Portland cement that satisfies the ASTM Standards and

Specifications of C150 (Types I-VIII) of the American Society for Testing of Materials (ASTM C50-Standard Specification for Portland Cement). ASTM C150 covers eight types of Portland cement, each possessing different properties, and used specifically for those properties.

Also of interest as hydraulic cements are carbonate-containing hydraulic cements. Such carbonate-containing hydraulic cements, methods for their manufacture and use are described in U.S. Patent No. 7,735,274; the disclosure of which applications are herein incorporated by reference.

In certain embodiments, the hydraulic cement may be a blend of two or more different kinds of hydraulic cements, such as Portland cement and a carbonate containing hydraulic cement. In certain embodiments, the amount of a first cement, e.g., Portland cement in the blend ranges from 10 to 90% (w/w), such as 30 to 70% (w/w) and including 40 to 60% (w/w), e.g., a blend of 80% OPC and 20% carbonate hydraulic cement.

In some instances, the concrete dry composite compositions, as well as concretes produced therefrom, have a CarbonStar Rating (CSR) that is less than the CSR of the control composition that does not include an aggregate of the invention. The Carbon Star Rating (CSR) is a value that characterizes the embodied carbon (in the form of $CaCO_3$) for any product, in comparison to how carbon intensive production of the product itself is (i.e., in terms of the production CO_2). The CSR is a metric based on the embodied mass of CO_2 in a unit of concrete. Of the three components in concrete – water, cement and aggregate – cement is by far the most significant contributor to CO_2 emissions, roughly 1:1 by mass (1 ton cement produces roughly 1 ton CO_2). So, if a cubic yard of concrete uses 600 lb cement, then its CSR is 600. A cubic yard of concrete according to embodiments of the present invention which include 600 lb cement and in which at least a portion of the aggregate is carbonate coated aggregate, e.g., as described above, will have a CSR that is less than 600, e.g., where the CSR may be 550 or less, such as 500 or less, including 400 or less, e.g., 250 or less, such as 100 or less, where in some instances the CSR may be a negative value, e.g., -100 or less, such as -500 or less including -1000 or less, where in some

instances the CSR of a cubic yard of concrete having 600 lbs cement may range from 500 to -5000, such as -100 to - 4000, including -500 to -3000. To determine the CSR of a given cubic yard of concrete that includes carbonate coated aggregate of the invention, an initial value of CO_2 generated for the production of the cement component of the concrete cubic yard is determined. For example, where the yard includes 600 lbs of cement, the initial value of 600 is assigned to the yard. Next, the amount of carbonate coating in the yard is determined. Since the molecular weight of carbonate is 100 a.u., and 44% of carbonate is CO_2, the amount of carbonate coating is present in the yard is then multiplied by .44 and the resultant value subtracted from the initial value in order to obtain the CSR for the yard. For example, where a given yard of concrete mix is made up of 600lbs of cement, 300lbs of water, 1429 lbs of fine aggregate and 1739lbs of coarse aggregate, the weight of a yard of concrete is 4068lbs and the CSR is 600. If 10% of the total mass of aggregate in this mix is replaced by carbonate coating, e.g., as described above, the amount of carbonate present in the revised yard of concrete is 317 lbs. Multiplying this value by .44 yields 139.5. Subtracting this number from 600 provides a CSR of 460.5.

Settable Compositions

Settable compositions of the invention, such as concretes and mortars, are produced by combining a hydraulic cement with an amount of an aggregate of the invention and an aqueous liquid, e.g., water, either at the same time or by pre-combining the cement with aggregate, and then combining the resultant dry components with water. The choice of coarse aggregate material for concrete mixes using cement compositions of the invention may have a minimum size of about 3/8 inch and can vary in size from that minimum up to one inch or larger, including in gradations between these limits. Finely divided aggregate is smaller than 3/8 inch in size and again may be graduated in much finer sizes down to 200-sieve size or so. Fine aggregates may be present in both mortars and concretes of the invention. The weight ratio of cement to aggregate in the dry

components of the cement may vary, and in certain embodiments ranges from 1:10 to 4:10, such as 2:10 to 5:10 and including from 55:1000 to 70:100.

The liquid phase, e.g., aqueous fluid, with which the dry component is combined to produce the settable composition, e.g., concrete, may vary, from pure water to water that includes one or more solutes, additives, co-solvents, etc., as desired. The ratio of dry component to liquid phase that is combined in preparing the settable composition may vary, and in certain embodiments ranges from 2:10 to 7:10, such as 3:10 to 6:10 and including 4:10 to 6:10.

In certain embodiments, the cements may be employed with one or more admixtures. Admixtures are compositions added to concrete to provide it with desirable characteristics that are not obtainable with basic concrete mixtures or to modify properties of the concrete to make it more readily useable or more suitable for a particular purpose or for cost reduction. As is known in the art, an admixture is any material or composition, other than the hydraulic cement, aggregate and water, that is used as a component of the concrete or mortar to enhance some characteristic, or lower the cost, thereof. The amount of admixture that is employed may vary depending on the nature of the admixture. In certain embodiments the amounts of these components range from 1 to 50% w/w, such as 2 to 10% w/w.

Admixtures of interest include finely divided mineral admixtures such as cementitious materials; pozzolans; pozzolanic and cementitious materials; and nominally inert materials. Pozzolans include diatomaceous earth, opaline cherts, clays, shales, fly ash, silica fume, volcanic tuffs and pumicites are some of the known pozzolans. Certain ground granulated blast-furnace slags and high calcium fly ashes possess both pozzolanic and cementitious properties. Nominally inert materials can also include finely divided raw quartz, dolomites, limestone, marble, granite, and others. Fly ash is defined in ASTM C618. Other types of admixture of interest include plasticizers, accelerators, retarders, air-entrainers, foaming agents, water reducers, corrosion inhibitors, and pigments.

As such, admixtures of interest include, but are not limited to: set accelerators, set retarders, air-entraining agents, defoamers, alkali-reactivity

reducers, bonding admixtures, dispersants, coloring admixtures, corrosion inhibitors, dampproofing admixtures, gas formers, permeability reducers, pumping aids, shrinkage compensation admixtures, fungicidal admixtures, germicidal admixtures, insecticidal admixtures, rheology modifying agents, finely divided mineral admixtures, pozzolans, aggregates, wetting agents, strength enhancing agents, water repellents, and any other concrete or mortar admixture or additive. Admixtures are well-known in the art and any suitable admixture of the above type or any other desired type may be used; see, e.g., U.S. Patent No. 7,735,274, incorporated herein by reference in its entirety.

In certain embodiments, settable compositions of the invention include a cement employed with fibers, e.g., where one desires fiber-reinforced concrete. Fibers can be made of zirconia containing materials, steel, carbon, fiberglass, or synthetic materials, e.g., polypropylene, nylon, polyethylene, polyester, rayon, high-strength aramid, (i.e., Kevlar®), or mixtures thereof.

The components of the settable composition can be combined using any convenient protocol. Each material may be mixed at the time of work, or part of or all of the materials may be mixed in advance. Alternatively, some of the materials are mixed with water with or without admixtures, such as high-range water-reducing admixtures, and then the remaining materials may be mixed therewith. As a mixing apparatus, any conventional apparatus can be used. For example, Hobart mixer, slant cylinder mixer, Omni Mixer, Henschel mixer, V-type mixer, and Nauta mixer can be employed.

Following the combination of the components to produce a settable composition (e.g., concrete), the settable compositions are in some instances initially flowable compositions, and then set after a given period of time. The setting time may vary, and in certain embodiments ranges from 30 minutes to 48 hours, such as 30 minutes to 24 hours and including from 1 hour to 4 hours.

The strength of the set product may also vary. In certain embodiments, the strength of the set cement may range from 5 Mpa to 70 MPa, such as 10 MPa to 50 MPa and including from 20 MPa to 40 MPa. In certain embodiments, set

products produced from cements of the invention are extremely durable. e.g., as determined using the test method described at ASTM C1157.

Built Structures

Aspects of the invention further include structures produced from the aggregates and settable compositions of the invention. As such, further embodiments include manmade structures that contain the aggregates of the invention and methods of their manufacture. Thus, in some embodiments the invention provides a manmade structure that includes one or more aggregates as described herein. The manmade structure may be any structure in which an aggregate may be used, such as a building, dam, levee, roadway or any other manmade structure that incorporates an aggregate or rock. In some embodiments, the invention provides a manmade structure, e.g., a building, a dam, or a roadway, that includes an aggregate of the invention, where the aggregate may be produced from a polymorph precursor composition, e.g., as described above. In some embodiments the invention provides a method of manufacturing a structure, comprising providing an aggregate of the invention.

UTILITY

The subject aggregate compositions and settable compositions that include the same, find use in a variety of different applications, such as above ground stable CO_2 sequestration products, as well as building or construction materials. Specific structures in which the building materials of the invention find use include, but are not limited to: pavements, architectural structures, e.g., buildings, foundations, motorways/roads, overpasses, parking structures, brick/block walls and footings for gates, fences and poles. Mortars of the invention find use in binding construction blocks, e.g., bricks, together and filling gaps between construction blocks. Mortars can also be used to fix existing structure, e.g., to replace sections where the original mortar has become compromised or eroded, among other uses.

Methods of invention, e.g., as described above, also find use in the sequestration of CO_2, i.e., CO_2 sequestration. By "CO_2 sequestration" is meant the removal or segregation of an amount of CO_2 from CO_2 containing gas, e.g., a gaseous waste stream produced by an industrial plant, so that at least a portion of the CO_2 is no longer present in the CO_2 containing gas from which it has been removed. CO_2 sequestering methods of the invention sequester CO_2, and in some instances produce a storage stable CO_2 sequestering product from an amount of CO_2, such that the CO_2 from which the product is produced is then sequestered in that product. The storage stable CO_2 sequestering product is a storage stable composition that incorporates an amount of CO_2 into a storage stable form, such as an above-ground storage or underwater storage stable form, so that the CO_2 is no longer present as, or available to be, a gas in the atmosphere. As such, sequestering of CO_2 according to methods of the invention results in prevention of CO_2 gas from entering the atmosphere and allows for long term storage of CO_2 in a manner such that CO_2 does not become part of the atmosphere.

Notwithstanding the appended claims, the invention may be defined by the following clauses:

1. A method of producing a building material, the method comprising:

preparing a carbonate precipitate comprising an undifferentiated pluripotent polymorph precursor; and

processing the carbonate precipitate under conditions sufficient to produce the building material.

2. The method according to Clause 1, wherein the carbonate precipitate is dwatered.

3. The method according to Clause 1, wherein the carbonate precipitate is comprised in a carbonate slurry.

4. The method according to Clause 3, further comprising drying the carbonate slurry.

5. The method according to Clause 4, wherein processing the carbonate precipitate under conditions sufficient to produce the building material comprises rehydrating the dried carbonate slurry.

6. The method according to any of the preceding clauses, wherein the carbonate precipitate is comprised of metal carbonate particles.

7. The method according to Clause 6, wherein the metal carbonate particles are alkaline earth metal carbonate particles.

8. The method according to Clause 7, wherein the metal carbonate particles are calcium carbonate particles.

9. The method according to Clause 8, wherein the metal carbonate particles are calcium magnesium carbonate particles.

10. The method according to any of the preceding clauses, wherein the polymorph precursor is an amorphous polymorph precursor.

11. The method according to any of the preceding clauses, wherein the polymorph precursor is selected from the group consisting of: vaterite precursor, calcite precursor, aragonite precursor, dolomite precursor and proto-dolomite precursor.

12. The method according to Clause 11, wherein the polymorph precursor comprises vaterite precursor.

13. The method according to Clause 11, wherein the polymorph precursor comprises calcite precursor.

14. The method according to Clause 11, wherein the polymorph precursor comprises aragonite precursor.

15. The method according to Clause 11, wherein the polymorph precursor comprises dolomite precursor.

16. The method according to Clause 11, wherein the polymorph precursor comprises proto-dolomite precursor.

17. The method according to any of the preceding clauses, further comprising combining the carbonate precipitate with a seed structure.

18. The method according to Clause 17, wherein the seed structure is crystalized.

19. The method according to Clause 18, wherein the seed structure is selected from calcite, aragonite, vaterite, and dolomite.

20. The method according to any of Clauses 17 to 19, wherein the seed structure ranges in size from 5 nm to 5 cm.

21. The method according to Clause 19, wherein the carbonate precipitate comprises an impurity.

22. The method according to Clause 21, wherein the impurity is selected from a sludge waste and calcite.

23. The method according to any of Clauses 17 to 22, wherein the seed structure comprises rocks or minerals.

24. The method according to Clause 23, wherein the rocks or minerals are selected from aggregate, waste concrete, tropical sands, limestone and fine waste dust comprising $CaCO_3$.

25. The method according to any of Clauses 17 to 24, wherein combining the carbonate precipitate with the seed structure comprises mixing.

26. The method according to any of Clauses 17 to 24, wherein combining the carbonate precipitate with the seed structure comprises coating the seed structure with the carbonate precipitate.

27. The method according to any of Clauses 17 to 24, wherein combining the carbonate precipitate with the seed structure comprises coating the carbonate precipitate with the seed structure.

28. The method according to any of Clauses 17 to 27, wherein the combining occurs prior to the precipitation of the carbonate precipitate.

29. The method according to any of the preceding clauses, wherein processing the carbonate precipitate under conditions sufficient to produce the building material comprises maintaining a moisture level of the carbonate precipitate.

30. The method according to Clause 29, wherein maintaining the moisture level comprises preventing evaporation.

31. The method according to Clause 29, wherein maintaining the moisture level comprises adding water.

32. The method according to Clause 31, wherein maintaining the moisture level comprises cycling drying and adding water.

33. The method according to any of the preceding clauses, further comprising evaluating the carbonate precipitate for the presence of the polymorph precursor.

34. The method according to Clause 33, wherein evaluating the carbonate precipitate for the presence of the polymorph precursor comprises assaying the carbonate precipitate by scanning electron microscopy (SEM).

35. The method according to Clause 33, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises assessing whether the carbonate precipitate comprises smooth globular structures.

36. The method according to Clause 33, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises obtaining an infrared (IR) spectrum of the carbonate precipitate.

37. The method according to Clause 33, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises collecting a powder X-ray diffraction (XRD) pattern of the carbonate precipitate.

38. The method according to Clause 37, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises detecting the presence of one or more crystal systems in the carbonate precipitate.

39. The method according to Clauses 36 or 37, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises assessing whether the pattern exhibits broad peaks.

40. The method according to Clause 38, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises assessing whether the pattern exhibits a peak at 39 degrees 2 theta.

41. The method according to Clause 33, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises obtaining a Ca:C ratio.

42. The method according to Clause 41, wherein evaluating the carbonate precipitate for the presence of polymorph precursor comprises assessing whether the Ca:C ratio indicates a Ca deficiency.

43. The method according to any of the preceding clauses, further comprising contacting the building material with a curing liquid sufficient to produce a cured building material.

44. The method according to Clause 43, wherein the method comprises contacting the carbonate precipitate with the curing liquid.

45. The method according to Clause 43 or 44, wherein the curing liquid comprises a carbonate curing liquid, a bicarbonate curing liquid, a phosphate curing liquid, a divalent alkali earth metal curing liquid or water.

46. The method according to any of Clauses 43 to 45, further comprising controlling the temperature of the building material during the contacting the building material with a curing liquid.

47. The method according to any of the preceding clauses, wherein the building material comprises an aggregate.

48. The method according to Clause 47, wherein processing the carbonate precipitate comprises combining the carbonate precipitate with an aggregate substrate.

49. The method according to Clauses 47 or 48, wherein processing the carbonate precipitate comprises subjecting the carbonate precipitate to rotational action.

50. The method according to any of Clauses 47 to 49, further comprising:

combining:

(a) a cement; and

(b) the aggregate;

to produce a concrete dry composite.

51. The method according to Clause 50, wherein the cement comprises a hydraulic cement.

52. The method according to Clause 51, wherein the hydraulic cement comprises a Portland cement.

53. The method according to any of Clauses 50 to 52, further comprising producing a settable composition by combining the concrete dry composition with a liquid.

54. The method according to any of the preceding clauses, wherein preparing the carbonate precipitate comprises a CO_2 sequestering process.

55. The method according to Clause 54, wherein the CO_2 sequestering process comprises contacting an aqueous capture liquid with a gaseous source of CO_2 under conditions sufficient to produce an aqueous carbonate.

56. The method according to Clause 55, further comprising combining a cation source and the aqueous carbonate under conditions sufficient to produce a CO_2 sequestering carbonate.

57. The method according to Clause 55 or 56, wherein the aqueous capture liquid is an aqueous ammonia capture liquid.

58. An aggregate produced according to any of Clauses 47 to 49.

59. A concrete dry composite produced according to any of Clauses 50 to 52.

60. The concrete dry composite according to Clause 59, wherein the concrete dry composite has a compressive strength of 4,000 psi or greater.

61. A settable composition produced according to the method of Clause 53.

62. A method of constructing a built structure, the method comprising employing the building material produced according to any of Clauses 1 to 57 to construct the built structure.

The following is presented by way of example and not by way of limitation

EXPERIMENTAL

Example 1:

10% (dry w/w basis) aragonite seeds were added to freshly precipitated calcium carbonate. The mixture was cured at high humidity and warmed in a temperature controlled chamber. The final product was obtained when the polymorph was completely transformed to the desired polymorph structure and reached its final strength. FIG. 9 presents data showing production of the aragonite final product using aragonite seeds. It also demonstrates use of XRD (X-ray Diffraction) to characterize polymorphs in a seeded sample.

Example 2:

Seed structures were combined with a calcium carbonate precipitate which was already in solid form. The seed - precipitate mixture was then agglomerated to form the desired particle size and shape, and cured in a temperature controlled (warmed at 75C) humidity chamber. This was compared to a sample which was treated the same way, except seeds were not added. In other words, the precipitate was agglomerated to the desired particle size and shape, and then cured in a temperature controlled (warmed at 75C) humidity chamber ('negative control' sample). Both samples were subsequently subjected to a durability test, the results of which are presented in FIG. 10. As shown in FIG. 10, an improvement in strength is observable for a calcium carbonate sample in which seed structures have been added as compared to the same calcium carbonate sample lacking the seed structures.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it is readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

Accordingly, the preceding merely illustrates the principles of the invention. It will be appreciated that those skilled in the art will be able to devise various arrangements which, although not explicitly described or shown herein, embody the principles of the invention and are included within its spirit and scope. Furthermore, all examples and conditional language recited herein are principally intended to aid the reader in understanding the principles of the invention and the concepts contributed by the inventors to furthering the art, and are to be construed as being without limitation to such specifically recited examples and conditions. Moreover, all statements herein reciting principles, aspects, and embodiments of the invention as well as specific examples thereof, are intended to encompass both structural and functional equivalents thereof.

Additionally, it is intended that such equivalents include both currently

known equivalents and equivalents developed in the future, i.e., any elements developed that perform the same function, regardless of structure. The scope of the present invention, therefore, is not intended to be limited to the exemplary embodiments shown and described herein. Rather, the scope and spirit of present invention is embodied by the appended claims.

WHAT IS CLAIMED IS:

1. A method of producing a building material, the method comprising:

preparing a carbonate precipitate comprising an undifferentiated pluripotent polymorph precursor; and

processing the carbonate precipitate under conditions sufficient to produce the building material.

2. The method according to Claim 1, wherein the carbonate precipitate is comprised of metal carbonate particles.

3. The method according to Claim 2, wherein the metal carbonate particles are alkaline earth metal carbonate particles.

4. The method according to any of the preceding claims, wherein the polymorph precursor is an amorphous polymorph precursor.

5. The method according to any of the preceding claims, further comprising combining the carbonate precipitate with a seed structure.

6. The method according to any of the preceding claims, wherein processing the carbonate precipitate under conditions sufficient to produce the building material comprises maintaining a moisture level of the carbonate precipitate.

7. The method according to any of the preceding claims, further comprising evaluating the carbonate precipitate for the presence of the polymorph precursor.

8. The method according to any of the preceding claims, further comprising contacting the building material with a curing liquid sufficient to produce a cured building material.

9. The method according to any of the preceding claims, wherein the building material comprises an aggregate.

10. The method according to any of the preceding claims, wherein preparing the carbonate precipitate comprises a CO_2 sequestering process.

11. An aggregate produced according to the method of Claims 9 or 10.

12. A concrete dry composite comprising

(a) a cement; and

(b) the aggregate according to Claim 11.

13. A settable composition produced by combining the concrete dry composite of Claim 12 with a setting liquid.

14. A method of constructing a built structure, the method comprising employing the building material produced according to any of Claims 1 to 10 to construct the built structure.