METHODS AND SYSTEMS FOR TREATMENT OF LIME TO FORM VATERITE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of US Provisional Application No. 62/981,266, filed February 25, 2020, which is incorporated herein by reference in its entirety in the present disclosure.

BACKGROUND

[0002] Carbon dioxide (CO_2) emissions have been identified as a major contributor to the phenomenon of global warming. CO_2 is a by-product of combustion and it creates operational, economic, and environmental problems. It may be expected that elevated atmospheric concentrations of CO_2 and other greenhouse gases can facilitate greater storage of heat within the atmosphere leading to enhanced surface temperatures and rapid climate change. In addition, elevated levels of CO_2 in the atmosphere may also further acidify the world's oceans due to the dissolution of CO_2 and formation of carbonic acid. The impact of climate change and ocean acidification may likely be economically expensive and environmentally hazardous if not timely handled. Reducing potential risks of climate change requires sequestration and avoidance of CO_2 from various anthropogenic processes.

SUMMARY

[0002a] In an aspect of the present disclosure, there is provided a method to form calcium carbonate comprising vaterite, comprising:

(i) calcining limestone to form lime wherein the lime comprises dead burnt lime, soft burnt lime, or combination thereof, and a gaseous stream comprising carbon dioxide;

(ii) dissolving the lime in an aqueous solution comprising N-containing inorganic salt, N-containing organic salt, or combination thereof, to produce an aqueous solution comprising calcium salt; and

(iii) treating the aqueous solution comprising calcium salt with the gaseous stream comprising carbon dioxide to form a precipitation material comprising calcium carbonate, wherein the calcium carbonate comprises vaterite.

[0002b] In another aspect of the present disclosure, there is provided a system to form calcium carbonate comprising vaterite, comprising:

(i) a calcining reactor configured to calcine limestone to form lime wherein the lime comprises dead burnt lime, soft burnt lime, or combination thereof, and a gaseous stream comprising carbon dioxide;

(ii) a dissolution reactor configured for dissolving the lime in an aqueous N-containing salt solution to produce an aqueous solution comprising calcium salt; and

(iii) a treatment reactor configured for treating the aqueous solution comprising calcium salt with the gaseous stream comprising carbon dioxide to form a precipitation material comprising calcium carbonate, wherein the calcium carbonate comprises vaterite.

[0003] In one example, there are provided methods to form calcium carbonate comprising vaterite, comprising:

(i) calcining limestone to form lime and a gaseous stream comprising carbon dioxide;

(ii) dissolving the lime in an aqueous N-containing inorganic salt solution under one or more dissolution conditions to produce a first aqueous solution comprising calcium salt, and a gaseous stream comprising ammonia;

(iii) recovering the gaseous stream comprising carbon dioxide and the gaseous stream comprising ammonia and subjecting the gaseous streams to a cooling process under one or more cooling conditions to condense a second aqueous solution comprising ammonium bicarbonate, ammonium carbonate, ammonia, or combinations thereof; and

(iv) treating the first aqueous solution comprising calcium salt with the second aqueous solution comprising ammonium bicarbonate, ammonium carbonate, ammonia, or combinations thereof under one or more precipitation conditions to form a precipitation material comprising calcium carbonate and a supernatant solution, wherein the calcium carbonate comprises vaterite.

[0004] In some examples of the foregoing example, the calcination is carried out in shaft kiln, rotary kiln, or electric kiln.

[0005] In some examples of the foregoing example and examples, the lime is underburnt lime, soft burnt lime, dead burnt lime, or combinations thereof.

[0006] In some examples of the foregoing example and examples, the N-containing inorganic salt is selected from the group consisting of ammonium halide, ammonium sulfate, ammonium sulfite, ammonium nitrate, ammonium nitrite, and combinations thereof. In some examples of the foregoing example and examples, the ammonium halide is ammonium chloride.

[0007] In some examples of the foregoing example and examples, the first aqueous solution further comprises ammonia and/or N-containing inorganic salt.

[0008] In some examples of the foregoing example and examples, molar ratio of the N-containing inorganic salt : lime is between about 0.5:1-2:1.

[0009] In some examples of the foregoing example and examples, the one or more dissolution conditions are selected from the group consisting of temperature between about 30-200°C; pressure between about 0.1-10 atm; N-containing salt wt% in water between about 0.5-50%; and combinations thereof.

[0010] In some examples of the foregoing example and examples, no external source of carbon dioxide and/or ammonia is used and the process is a closed loop process.

[0011] In some examples of the foregoing example and examples, the gaseous stream comprising ammonia further comprises water vapor.

[0012] In some examples of the foregoing example and examples, the gaseous stream further comprises between about 20-90% water vapor.

[0013] In some examples of the foregoing example and examples, no external water is added to the cooling process.

[0014] In some examples of the foregoing example and examples, the one or more cooling conditions comprise temperature between about 0-100°C; pressure between about 0.5-50 atm; pH of the aqueous solution between about 8-12; flow rate of the CO_2; ratio of CO_2:NH_3 between about 0.1:1-20:1; or combinations thereof.

[0015] In some examples of the foregoing example and examples, the second aqueous solution further comprises ammonium carbamate.

[0016] In some examples of the foregoing example and examples, the second aqueous solution is formed by the condensation of the gases.

[0017] In some examples of the foregoing example and examples, the one or more precipitation conditions are selected from the group consisting of pH of the first aqueous solution

of between 7-9, temperature of the solution between 20-60°C, residence time of between 5-60 minutes, or combinations thereof.

[0018] In some examples of the foregoing example and examples, the first aqueous solution further comprises solids.

[0019] In some examples of the foregoing example and examples, the method further comprises separating the solids from the first aqueous solution before the treatment step by filtration and/or centrifugation.

[0020] In some examples of the foregoing example and examples, the separated solids are added to the precipitation material as filler.

[0021] In some examples of the foregoing example and examples, the separated solids further comprise residual ammonium halide when the N-containing inorganic salt is the ammonium halide.

[0022] In some examples of the foregoing example and examples, the method further comprises recovering the residual ammonium halide from the solids using a recovery process selected from the group consisting of rinsing, thermal decomposition, pH adjustment, and combinations thereof.

[0023] In some examples of the foregoing example and examples, the solids are not separated from the first aqueous solution and the first aqueous solution is subjected to the treatment step to produce the precipitation material further comprising the solids. In some examples of the foregoing example and examples, the solids comprise silicates, iron oxides, alumina, or combinations thereof. In some examples of the foregoing example and examples, the solids are between 1-40 wt% in the aqueous solution, in the precipitation material, or combinations thereof.

[0024] In some examples of the foregoing example and examples, the method further comprises dewatering the precipitation material to separate the precipitation material from the supernatant solution.

[0025] In some examples of the foregoing example and examples, the precipitation material and the supernatant solution comprise residual N-containing inorganic salt.

[0026] In some examples of the foregoing example and examples, the residual N-containing inorganic salt comprises ammonium halide, ammonium sulfate, ammonium sulfite, ammonium hydrosulfide, ammonium thiosulfate, ammonium nitrate, ammonium nitrite, or combinations thereof.

[0027] In some examples of the foregoing example and examples, the method further comprises removing and optionally recovering ammonia and/or N-containing inorganic salt from the residual N-containing inorganic salt comprising removing and optionally recovering

the residual N-containing inorganic salt from the supernatant aqueous solution and/or removing and optionally recovering the residual N-containing inorganic salt from the precipitation material.

[0028] In some examples of the foregoing example and examples, the method further comprises recovering the residual N-containing inorganic salt from the supernatant aqueous solution using recovery process selected from the group consisting of thermal decomposition, pH adjustment, reverse osmosis, multi-stage flash, multi-effect distillation, vapor recompression, distillation, and combinations thereof.

[0029] In some examples of the foregoing example and examples, the step of removing and optionally recovering the residual N-containing inorganic salt from the precipitation material comprises heating the precipitation material between about 300-360°C to evaporate the N-containing inorganic salt from the precipitation material with optional recovery by condensation of the N-containing inorganic salt.

[0030] In some examples of the foregoing example and examples, the N-containing inorganic salt is ammonium chloride which evaporates from the precipitation material in a form comprising ammonia gas, hydrogen chloride gas, chlorine gas, or combinations thereof.

[0031] In some examples of the foregoing example and examples, the method further comprises recycling the recovered residual ammonia and/or N-containing inorganic salt back to the dissolving and/or treating step of the process.

[0032] In some examples of the foregoing example and examples, the vaterite is stable vaterite or reactive vaterite.

[0033] In some examples of the foregoing example and examples, the method further comprises adding water to the precipitation material comprising reactive vaterite and transforming the vaterite to aragonite wherein the aragonite sets and hardens to form cement or cementitious product.

[0034] In some examples of the foregoing example and examples, the cementitious product is a formed building material selected from masonry unit, construction panel, conduit, basin, beam, column, slab, acoustic barrier, insulation material, and combinations thereof.

[0035] In some examples of the foregoing example and examples, the method further comprises adding water to the precipitation material comprising reactive vaterite and transforming the vaterite to aragonite wherein the aragonite sets and hardens to form non-cementitious product.

[0036] In one example, there is provided a product formed by the method according to the aforementioned example and the examples.

[0037] In one example, there is provided a system to form calcium carbonate comprising vaterite, comprising:

(i) a calcining reactor configured to calcine limestone to form lime and a gaseous stream comprising carbon dioxide;

(ii) a dissolution reactor configured for dissolving the lime in an aqueous N-containing inorganic salt solution under one or more dissolution conditions to produce a first aqueous solution comprising calcium salt, and a gaseous stream comprising ammonia;

(iii) a cooling reactor configured for recovering the gaseous stream comprising carbon dioxide and the gaseous stream comprising ammonia and subjecting the gaseous streams to a cooling process under one or more cooling conditions to condense a second aqueous solution comprising ammonium bicarbonate, ammonium carbonate, ammonia, or combinations thereof; and

(iv) a treatment reactor configured for treating the first aqueous solution comprising calcium salt with the second aqueous solution comprising ammonium bicarbonate, ammonium carbonate, ammonia, or combinations thereof under one or more precipitation conditions to form a precipitation material comprising calcium carbonate and a supernatant solution, wherein the calcium carbonate comprises vaterite.

[0038] In some examples of the foregoing example, the dissolution reactor is integrated with the cooling reactor.

DRAWINGS

[0039] The features of the invention are set forth with particularity in the appended claims. A better understanding of the features and advantages of the invention will be obtained by reference to the following detailed description that sets forth illustrative embodiments, in which the principles of the invention are utilized, and the accompanying drawings of which:

[0040] **Fig. 1** illustrates some embodiments of the methods and systems provided herein.

[0041] **Fig. 2** illustrates some embodiments of the methods and systems provided herein.

[0042] **Fig. 3** illustrates some embodiments of the methods and systems provided herein.

[0043] **Fig. 4** illustrates some embodiments of the methods and systems comprising an integrated reactor provided herein.

[0044] **Fig. 5** illustrates some embodiments of the methods and systems comprising an integrated reactor provided herein.

[0045] **Fig. 6** illustrates some embodiments of the methods and systems comprising an integrated reactor provided herein.

[0046] **Fig. 7** illustrates some embodiments of the methods and systems comprising an integrated reactor provided herein.

[0047] **Fig. 8** illustrates a Gibbs free energy diagram of the transition from vaterite to aragonite.

WHAT IS CLAIMED IS:

1. A method to form calcium carbonate comprising vaterite, comprising:

(i) calcining limestone to form lime wherein the lime comprises dead burnt lime, soft burnt lime, or combination thereof, and a gaseous stream comprising carbon dioxide;

(ii) dissolving the lime in an aqueous solution comprising N-containing inorganic salt, N-containing organic salt, or combination thereof, to produce an aqueous solution comprising calcium salt; and

(iii) treating the aqueous solution comprising calcium salt with the gaseous stream comprising carbon dioxide to form a precipitation material comprising calcium carbonate, wherein the calcium carbonate comprises vaterite.

2. The method of claim 1, wherein the N-containing inorganic salt is selected from the group consisting of ammonium halide, ammonium sulfate, ammonium sulfite, ammonium nitrate, ammonium nitrite, and combination thereof.

3. The method of claim 2, wherein the ammonium halide is ammonium chloride.

4. The method of any one of the preceding claims, wherein the N-containing organic salt is salt of N-containing organic compound selected from the group consisting of aliphatic amine, alicyclic amine, heterocyclic amine, and combination thereof.

5. The method of any one of the preceding claims, wherein the aqueous solution further comprises ammonia; and/or molar ratio of the N-containing inorganic salt or N-containing organic salt : lime is between about 0.5:1-2:1 or 2.5:1.

6. The method of any one of the preceding claims, wherein the dissolving step is under one or more dissolution conditions selected from the group consisting of temperature between about 30-200°C; pressure between about 0.1-10 atm; N-containing salt wt% in water between about 0.5-50%; and combination thereof.

7. The method of any one of the preceding claims, wherein the dissolving step further produces a gaseous stream comprising ammonia and the method further comprises (iv) recovering the gaseous stream comprising carbon dioxide and the gaseous stream comprising ammonia and subjecting the gaseous streams to a cooling process to condense a second aqueous solution comprising ammonium bicarbonate, ammonium carbonate, ammonia, ammonium carbamate, or combination thereof; and (v) treating the aqueous solution comprising calcium salt with the second aqueous solution comprising ammonium bicarbonate, ammonium carbonate, ammonia, ammonium carbamate, or combination thereof to form the precipitation material.

8. The method of claim 7, wherein the gaseous stream comprising ammonia further comprises water vapor and/or further comprises between about 20-90% water vapor.

9. The method of claim 7 or 8, wherein the cooling process is under one or more cooling conditions comprising temperature between about 0-100°C; pressure between about 0.5-50 atm; pH of the aqueous solution between about 8-12; ratio of CO_2:NH_3 between about 0.1:1-20:1; or combination thereof.

10. The method of any one of the preceding claims, wherein the treating step is under one or more precipitation conditions selected from the group consisting of pH of the aqueous solution of between 7-9, temperature of the solution between 20-60°C, residence time of between 5-60 minutes, and combination thereof.

11. The method of any one of the preceding claims, wherein the aqueous solution further comprises solid.

12. The method of claim 11, further comprising separating the solid from the aqueous solution before the treatment step by filtration and/or centrifugation.

13. The method of claim 12, further comprising adding the solid back to the precipitation material as filler.

14. The method of claim 11, wherein the solid is not separated from the aqueous solution and the aqueous solution is subjected to the treatment step to produce the precipitation material further comprising the solid.

15. The method of any one of the claims 11-14, wherein the solid comprises silicate, iron oxide, alumina, or combination thereof.

16. The method of claim 14 or 15, wherein the solid is between 1-40 wt% in the precipitation material.

17. The method of any one of the preceding claims, further comprising removing and optionally recovering residual N-containing salt from supernatant aqueous solution and/or removing and optionally recovering residual N-containing salt from the precipitation material.

18. The method of claim 17, further comprising recovering the residual N-containing salt from the supernatant aqueous solution using recovery process selected from the group consisting of thermal decomposition, pH adjustment, reverse osmosis, multi-stage flash, multi-effect distillation, vapor recompression, distillation, and combination thereof.

19. The method of claim 17, further comprising heating the precipitation material between about 300-360°C to evaporate the residual N-containing salt from the precipitation material with optional recovery by condensation of the N-containing salt.

20. The method of any one of the preceding claims, wherein the vaterite is stable vaterite or reactive vaterite.

21. The method of any one of the preceding claims, wherein the precipitation material comprises reactive vaterite and the method further comprises adding water to the precipitation material comprising reactive vaterite and transforming the reactive vaterite to aragonite wherein the aragonite sets and hardens to form cement, cementitious product, or non-cementitious product.

22. The method of any one of the preceding claims, further comprising adding an additive to the aqueous solution or to the precipitation material, wherein the additive is selected from the group consisting of fatty acid ester, sodium decyl sulfate, lauric acid, sodium salt of lauric acid, urea, citric acid, sodium salt of citric acid, phthalic acid, sodium salt of phthalic acid, taurine, creatine, dextrose, poly(n-vinyl-1-pyrrolidone), aspartic acid, sodium salt of aspartic acid, magnesium chloride, acetic acid, sodium salt of acetic acid, glutamic acid, sodium salt of glutamic acid, strontium chloride, gypsum, lithium chloride, sodium chloride, glycine, sodium citrate dehydrate, sodium bicarbonate, magnesium sulfate, magnesium acetate, sodium polystyrene, sodium dodecylsulfonate, poly-vinyl alcohol, and combination thereof.

23. The method of any one of the preceding claims, wherein the vaterite is unimodal, bimodal, or multimodal distribution of a particulate composition with an average particle size of between 0.1-100 micron.

24. The method of any one of the preceding claims, further comprising blending the precipitation material with Ordinary Portland Cement (OPC), aggregate, or combination thereof.

25. The method of any one of the preceding claims, further comprising mixing the precipitation material with an admixture selected from the group consisting of set accelerator, set retarder, air-entraining agent, foaming agent, defoamer, alkali-reactivity reducer, bonding admixture, dispersant, coloring admixture, corrosion inhibitor, damp-proofing admixture, gas former, permeability reducer, pumping aid, shrinkage compensation admixture, fungicidal admixture, germicidal admixture, insecticidal admixture, rheology modifying agent, finely divided mineral admixture, pozzolan, aggregate, wetting agent, strength enhancing agent, water repellent, reinforced material, and combination thereof.

26. The method of claim 25, wherein the reinforced material is a fiber made of zirconia, aluminum, glass, steel, carbon, ceramic, grass, bamboo, wood, fiberglass, synthetic material, or combination thereof.

27. A system to form calcium carbonate comprising vaterite, comprising:

(i) a calcining reactor configured to calcine limestone to form lime wherein the lime comprises dead burnt lime, soft burnt lime, or combination thereof, and a gaseous stream comprising carbon dioxide;

(ii) a dissolution reactor configured for dissolving the lime in an aqueous N-containing salt solution to produce an aqueous solution comprising calcium salt; and

(iii) a treatment reactor configured for treating the aqueous solution comprising calcium salt with the gaseous stream comprising carbon dioxide to form a precipitation material comprising calcium carbonate, wherein the calcium carbonate comprises vaterite.