

METHODS AND COMPOSITIONS FOR TREATMENT OF CONCRETE RECLAIMED WATER

CROSS-REFERENCE

[0001] This application is related to PCT Application No. PCT/CA2018/050750, filed
5 June 20, 2018, PCT Application No. PCT/CA2017/050445, filed April 11, 2017, U.S.
Provisional Patent Application No. 62/321,013, filed April 11, 2016, U.S. Provisional Patent
Application No. 62/522,510 filed June 20, 2017, U.S. Provisional Patent Application No.
62/554,830 filed September 6, 2017, U.S. Provisional Patent Application No. 62/558,173
filed September 13, 2017, U.S. Provisional Patent Application No. 62/559,771 filed
10 September 18, 2017, U.S. Provisional Patent Application No. 62/560,311 filed September 19,
2017, U.S. Provisional Patent Application No. 62/570,452 filed October 10, 2017, U.S.
Provisional Patent Application No. 62/675,615 filed May 23, 2018, U.S. Provisional Patent
Application No. 62/652,385 filed April 4, 2018, and to U.S. Provisional Patent Application
No. 62/573,109 filed October 16, 2017 all of which are incorporated herein by reference in
15 their entirety. This application also claims priority to U.S. Provisional Patent Application No.
62/911,871 filed October 7, 2019, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] Wash water, produced in the making of concrete, poses a significant problem in
20 terms of use and/or disposal. Methods and compositions to better manage concrete wash
water are needed.

SUMMARY OF THE INVENTION

[0003] In one aspect, provided herein are compositions.
25 [0004] In certain embodiments, provided herein is an apparatus for introducing a gas into
concrete reclaimed water comprising (i) a first conduit operably connected to a source of
concrete reclaimed water at a proximal end of the first conduit, wherein the first conduit
allows the reclaimed water to flow through it from the proximal end and out of it at a distal
end; and (ii) a second conduit situated inside the first conduit, wherein the second conduit is
30 operably connected to a source of a gas and is configured to allow the gas to flow into it and
to flow out of it into the reclaimed water in the first conduit. In certain embodiments, the gas
comprises carbon dioxide. In certain embodiments, the diameter of the first conduit is 0.5-5
inches and the diameter of the second conduit is 0.3-3 inches. In certain embodiments, the

first conduit is operably connected to the source of concrete reclaimed water at its proximal end by a third conduit, wherein the diameter of the first conduit is greater than the diameter of the third conduit. In certain embodiments, the first conduit is operably connected at its distal end to a reclaimer by a fourth conduit, wherein the diameter of the first conduit is greater than the diameter of the fourth conduit. In certain embodiments, the apparatus further comprises a control system comprising (iii) a sensor to sense the specific gravity of the reclaimed water and transmit information regarding the specific gravity to (iv) a controller that processes the information from the sensor. The control system can further comprise (v) an actuator that receives a signal from the controller based, at least in part, on the processed information from the sensor. In certain embodiments, the actuator comprises a valve that can modulate the flow of the gas into the second conduit. In certain embodiments, the second conduit comprises perforations that are configured to allow the gas to pass from the second conduit to the reclaimed water in the first conduit when the gas exceeds a threshold pressure in the second conduit, but that do not allow reclaimed water from the first conduit into the second conduit. In certain embodiments, the apparatus further comprises at least one of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, wherein the sensor, device or timer is configured to send information to the controller, which processes the information. In certain embodiments, the apparatus further comprises at least two of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, wherein the sensor, device or timer is configured to send information to the controller, which processes the information. In certain embodiments, the apparatus further comprises at least three of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, wherein the sensor, device or timer is configured to send information to the controller, which processes the information. In certain embodiments, the

apparatus further comprises at least four of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, wherein the sensor, device or timer is configured to send information to the controller, which processes the information. In certain embodiments, the controller further receives information about the composition of the reclaimed water, wherein the information includes a proportion of the reclaimed water that is cementitious material.

10 [0005] In another aspect, provided herein are methods

[0006] In certain embodiments, provided herein is a method of treating concrete reclaimed water with a gas comprising (i) flowing the reclaimed water from a source of the reclaimed water into a first conduit at a proximal end of the first conduit and out of the first conduit at a distal end of the first conduit; (ii) flowing a gas from a source of the gas into a second conduit situated inside the first conduit; and (iii) flowing the gas out of the second conduit into the reclaimed water in the first conduit. In certain embodiments, the gas comprises carbon dioxide. In certain embodiments, the diameter of the first conduit is 0.5-5 inches and the diameter of the second conduit is 0.3-3 inches. In certain embodiments, the reclaimed water is flowed into the first conduit from the source of concrete reclaimed water via a third conduit operably connected to the source of concrete reclaimed water and connected to the first conduit at the proximal end of the first conduit, wherein the diameter of the first conduit is greater than the diameter of the third conduit. In certain embodiments, the reclaimed water is flowed out of the first conduit into a fourth conduit operably connected to the distal end of the first conduit, wherein the diameter of the first conduit is greater than the diameter of the fourth conduit. In certain embodiments, the method further comprises determining the specific gravity of the reclaimed water and transmitting information regarding the specific gravity to a controller that processes the information. In certain embodiments, the method further comprises sending a signal to from the controller to an actuator wherein the signal is based, at least in part on the processed information. In certain embodiments, the actuator comprises a valve that modulates the flow of the gas into the second conduit based, at least in part, on the signal received from the controller. In certain embodiments, the gas moves from the second conduit into the reclaimed water in the first conduit via perforations that are configured to allow the gas to pass from the second conduit to the reclaimed water in the first conduit when the gas exceeds a threshold pressure in the

second conduit, but that do not allow reclaimed water from the first conduit into the second conduit. In certain embodiments, the method further comprises sending information to the controller from at least one of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, and processing the information at the controller. In certain embodiments, the method further comprises sending information to the controller from at least two of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, and processing the information at the controller. In certain embodiments, the method further comprises sending information to the controller from at least three of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, and processing the information at the controller. In certain embodiments, the method further comprises sending information to the controller from at least four of a sensor to sense a level of reclaimed water in a reclaimed water holding tank, a sensor to sense a temperature of the reclaimed water, a sensor to sense rate of flow of the gas into the second conduit, a sensor to sense whether and/or how much admixture is added to the reclaimed water, a device that indicates whether a pump to pump reclaimed water through the first conduit is activated, or a timer, and processing the information at the controller. In certain embodiments, the controller further receives information about the composition of the reclaimed water, wherein the information includes a proportion of the reclaimed water that is cementitious material.

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INCORPORATION BY REFERENCE

[0007] All publications, patents, and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication,

patent, or patent application was specifically and individually indicated to be incorporated by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

- [0008] The novel features of the invention are set forth with particularity in the appended claims. A better understanding of the features and advantages of the present 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:
- 5 [0009] **Figure 1** shows slump for concrete mixes produced with 10% w/w dried carbonated washwater solids, 20% w/w dried carbonated washwater solids, or control (no dried carbonated washwater solids).
- [0010] **Figure 2** shows compressive strength for concrete mixes produced with 10% w/w dried carbonated washwater solids, 20% w/w dried carbonated washwater solids, or control (no dried carbonated washwater solids), at 1, 7, and 28 days.
- 15 [0011] **Figure 3** shows calorimetry, as power vs. time, for concrete mixes produced with 10% w/w dried carbonated washwater solids, 20% w/w dried carbonated washwater solids, or control (no dried carbonated washwater solids).
- [0012] **Figure 4** shows compositions of various concrete mixes produced with 10% w/w dried carbonated washwater solids, 20% w/w dried carbonated washwater solids, or control
- 20 (no dried carbonated washwater solids).
- [0013] **Figure 5** shows slump for concrete mixes produced with washwater exposed to carbon dioxide by exposure to simulated flue gas and various levels of cement, or cement and water reduction, compared to control.
- [0014] **Figure 6** shows compressive strength for concrete mixes produced with
- 25 washwater exposed to carbon dioxide by exposure to simulated flue gas and various levels of cement, or cement and water reduction, compared to control, at 1, 7, and 28 days.
- [0015] **Figure 7** shows calorimetry, as power vs. time, for concrete mixes produced with washwater exposed to carbon dioxide by exposure to simulated flue gas and various levels of cement, or cement and water reduction, compared to control.
- 30 [0016] **Figure 8** shows compositions of various concrete mixes produced with washwater exposed to carbon dioxide by exposure to simulated flue gas and various levels of cement, or cement and water reduction, compared to control.

[0017] **Figure 9** shows slump for a control concrete made with no washwater; concrete batch made with 1.10 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; a concrete batch made with 1.075 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; and a concrete batch made with 1.05 specific gravity treated washwater batch with full washwater replacement and 1.5% sodium gluconate.

[0018] **Figure 10** shows compressive strength for a control concrete made with no washwater; concrete batch made with 1.10 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; a concrete batch made with 1.075 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; and a concrete batch made with 1.05 specific gravity treated washwater batch with full washwater replacement and 1.5% sodium gluconate, at 1, 7, and 28 days.

[0019] **Figure 11** shows calorimetry, as power vs. time, for a control concrete made with no washwater; concrete batch made with 1.10 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; a concrete batch made with 1.075 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; and a concrete batch made with 1.05 specific gravity treated washwater batch with full washwater replacement and 1.5% sodium gluconate.

[0020] **Figure 12** shows compositions of various concrete mixes produced as a control concrete made with no washwater; concrete batch made with 1.10 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; a concrete batch made with 1.075 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; and a concrete batch made with 1.05 specific gravity treated washwater batch with full washwater replacement and 1.5% sodium gluconate.

[0021] **Figure 13** shows slump for various concrete mixes, including a control mix (no washwater), and mixes made with untreated washwater comprising no gluconate; untreated washwater comprising gluconate which was added after 3 hours of hydration; untreated washwater comprising gluconate which was added after 24 hours of hydration and immediately before concrete batching; treated washwater comprising no gluconate; treated washwater comprising gluconate which was added before treatment and after 3 hours of hydration; and treated washwater comprising gluconate which was added after 24 hours and immediately before concrete batching.

[0022] **Figure 14** shows compressive strength for various concrete mixes, including a control mix (no washwater), and mixes made with untreated washwater comprising no

gluconate; untreated washwater comprising gluconate which was added after 3 hours of hydration; untreated washwater comprising gluconate which was added after 24 hours of hydration and immediately before concrete batching; treated washwater comprising no gluconate; treated washwater comprising gluconate which was added before treatment and after 3 hours of hydration; and treated washwater comprising gluconate which was added after 24 hours and immediately before concrete batching, at 7 days and 28 days.

[0023] **Figure 15** shows calorimetry, as power vs. time, for various concrete mixes, including a control mix (no washwater), and mixes made with untreated washwater comprising no gluconate; untreated washwater comprising gluconate which was added after 3 hours of hydration; untreated washwater comprising gluconate which was added after 24 hours of hydration and immediately before concrete batching; treated washwater comprising no gluconate; treated washwater comprising gluconate which was added before treatment and after 3 hours of hydration; and treated washwater comprising gluconate which was added after 24 hours and immediately before concrete batching.

[0024] **Figure 16** shows compositions of various concrete mixes, including a control mix (no washwater), and mixes made with untreated washwater comprising no gluconate; untreated washwater comprising gluconate which was added after 3 hours of hydration; untreated washwater comprising gluconate which was added after 24 hours of hydration and immediately before concrete batching; treated washwater comprising no gluconate; treated washwater comprising gluconate which was added before treatment and after 3 hours of hydration; and treated washwater comprising gluconate which was added after 24 hours and immediately before concrete batching.

[0025] **Figure 17** shows slump for a control concrete batch made with no washwater; a concrete batch made with untreated washwater with 0.6% sodium gluconate, with full washwater replacement; a concrete batch made with untreated washwater with 1.2% sodium gluconate with full washwater replacement; a concrete batch made with treated washwater batch with 3% sodium gluconate and 5% cement reduction, and full washwater replacement; and a concrete batch made with treated washwater with 3% sodium gluconate and 10% cement reduction, with full washwater replacement.

[0026] **Figure 18** shows compressive strength for a control concrete batch made with no washwater; a concrete batch made with untreated washwater with 0.6% sodium gluconate, with full washwater replacement; a concrete batch made with untreated washwater with 1.2% sodium gluconate with full washwater replacement; a concrete batch made with treated washwater batch with 3% sodium gluconate and 5% cement reduction, and full washwater

replacement; and a concrete batch made with treated washwater with 3% sodium gluconate and 10% cement reduction, with full washwater replacement.

[0027] **Figure 19** shows calorimetry, as power vs. time, for a control concrete batch made with no washwater; a concrete batch made with untreated washwater with 0.6% sodium gluconate, with full washwater replacement; a concrete batch made with untreated washwater with 1.2% sodium gluconate with full washwater replacement; a concrete batch made with treated washwater batch with 3% sodium gluconate and 5% cement reduction, and full washwater replacement; and a concrete batch made with treated washwater with 3% sodium gluconate and 10% cement reduction, with full washwater replacement.

[0028] **Figure 20** shows the composition of concrete batches made a control concrete batch made with no washwater; a concrete batch made with untreated washwater with 0.6% sodium gluconate, with full washwater replacement; a concrete batch made with untreated washwater with 1.2% sodium gluconate with full washwater replacement; a concrete batch made with treated washwater batch with 3% sodium gluconate and 5% cement reduction, and full washwater replacement; and a concrete batch made with treated washwater with 3% sodium gluconate and 10% cement reduction, with full washwater replacement.

[0029] **Figure 21** shows slump for a control concrete batch made with no washwater; a concrete batch made with aged treated washwater with no sodium gluconate and full washwater replacement; a concrete batch made with aged treated washwater comprising 2.4% sodium gluconate with full washwater replacement; and a concrete batch made with aged treated washwater comprising 4.8% sodium gluconate with full washwater replacement.

[0030] **Figure 22** shows compressive strength for a control concrete batch made with no washwater; a concrete batch made with aged treated washwater with no sodium gluconate and full washwater replacement; a concrete batch made with aged treated washwater comprising 2.4% sodium gluconate with full washwater replacement; and a concrete batch made with aged treated washwater comprising 4.8% sodium gluconate with full washwater replacement, at 1, 7, and 28 days.

[0031] **Figure 23** shows compositions for a control concrete batch made with no washwater; a concrete batch made with aged treated washwater with no sodium gluconate and full washwater replacement; a concrete batch made with aged treated washwater comprising 2.4% sodium gluconate with full washwater replacement; and a concrete batch made with aged treated washwater comprising 4.8% sodium gluconate with full washwater replacement.

[0032] **Figure 24** shows slump for concrete batches made as follows: Control (no washwater); Untreated washwater control (2.7% gluconate immediately before batching); Treated washwater (no gluconate); Treated washwater (2.7% gluconate added immediately before batching); Treated washwater control (8.1% lignosulfonate added immediately before batching).

[0033] **Figure 25** shows compressive strength for concrete batches made as follows: Control (no washwater); Untreated washwater control (2.7% gluconate immediately before batching); Treated washwater (no gluconate); Treated washwater (2.7% gluconate added immediately before batching); Treated washwater control (8.1% lignosulfonate added immediately before batching), at 3, 7, and 28 days.

[0034] **Figure 26** shows calorimetry, as power v. time, for concrete batches made as follows: Control (no washwater); Untreated washwater control (2.7% gluconate immediately before batching); Treated washwater (no gluconate); Treated washwater (2.7% gluconate added immediately before batching); Treated washwater control (8.1% lignosulfonate added immediately before batching)

[0035] **Figure 27** shows compositions for concrete batches made as follows: Control (no washwater); Untreated washwater control (2.7% gluconate immediately before batching); Treated washwater (no gluconate); Treated washwater (2.7% gluconate added immediately before batching); Treated washwater control (8.1% lignosulfonate added immediately before batching).

[0036] **Figure 28** shows slump for concrete batches made as follows: Control (no washwater); Treated washwater batch, full washwater replacement, 1.4% sodium gluconate; Treated washwater batch, full washwater replacement, 1.4% sodium gluconate before carbonation and 0.7% sodium gluconate after carbonation; Treated washwater batch with 5% cementitious reduction, full washwater replacement, 1.4% sodium gluconate.

[0037] **Figure 29** shows compressive strength for concrete batches made as follows: Control (no washwater); Treated washwater batch, full washwater replacement, 1.4% sodium gluconate; Treated washwater batch, full washwater replacement, 1.4% sodium gluconate before carbonation and 0.7% sodium gluconate after carbonation; Treated washwater batch with 5% cementitious reduction, full washwater replacement, 1.4% sodium gluconate, at 1, 7, and 28 days.

[0038] **Figure 30** shows calorimetry, as power vs. time, for concrete batches made as follows: Control (no washwater); Treated washwater batch, full washwater replacement, 1.4% sodium gluconate; Treated washwater batch, full washwater replacement, 1.4% sodium

gluconate before carbonation and 0.7% sodium gluconate after carbonation; Treated washwater batch with 5% cementitious reduction, full washwater replacement, 1.4% sodium gluconate.

5 [0039] **Figure 31** shows compositions of concrete batches made as follows: Control (no washwater); Treated washwater batch, full washwater replacement, 1.4% sodium gluconate; Treated washwater batch, full washwater replacement, 1.4% sodium gluconate before carbonation and 0.7% sodium gluconate after carbonation; Treated washwater batch with 5% cementitious reduction, full washwater replacement, 1.4% sodium gluconate.

10 [0040] **Figure 32** shows slump over time (minutes) for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.4% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids.

15 [0041] **Figure 33** shows compressive strength for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.4% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids.

20 [0042] **Figure 34** shows calorimetry, as power vs. time, for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.4% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids.

[0043] **Figure 35** shows compositions for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.4% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids.

25 [0044] **Figure 36** shows slump for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, no gluconate; Treated washwater, full replacement, 1.6% gluconate by weight of washwater solids.

30 [0045] **Figure 37** shows compressive strength for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, no gluconate; Treated washwater, full replacement, 1.6% gluconate by weight of washwater solids, at 1, 7, and 28 days.

[0046] **Figure 38** shows calorimetry, as power vs. time, for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, no gluconate; Treated washwater, full replacement, 1.6% gluconate by weight of washwater solids.

[0047] **Figure 39** shows the composition for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, no gluconate; Treated washwater, full replacement, 1.6% gluconate by weight of washwater solids.

5 [0048] **Figure 40** shows slump for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids; Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids with a 5% cementitious reduction.

[0049] **Figure 41** shows compressive strength for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids; Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids with a 5% cementitious reduction, at 1 day and 28 days.

[0050] **Figure 42** shows calorimetry, as power vs. time, for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids; Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids with a 5% cementitious reduction.

[0051] **Figure 43** shows compositions for concrete batches made as follows: Control (no washwater); Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids; Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids with a 5% cementitious reduction.

20 [0052] **Figure 44** shows slump for concrete batches made as follows: Control (no washwater); Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater mixed with potable water and added upfront; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater added upfront with the potable water added later; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, potable added upfront with the washwater added later.

[0053] **Figure 45** shows compressive strength for concrete batches made as follows: Control (no washwater); Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater mixed with potable water and added upfront; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater added upfront with the potable water added later; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, potable added upfront with the washwater added later.

[0054] **Figure 46** shows calorimetry as power vs time for concrete batches made as follows: Control (no washwater); Treated washwater, half replacement, 2% gluconate by

weight of washwater solids, washwater mixed with potable water and added upfront; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater added upfront with the potable water added later; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, potable added upfront with the washwater added later.

[0055] **Figure 47** shows compositions for concrete batches made as follows: Control (no washwater); Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater mixed with potable water and added upfront; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater added upfront with the potable water added later; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, potable added upfront with the washwater added later.

[0056] **Figure 48** shows slump for concrete batches made as follows: Control (no washwater). Treated washwater, full replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 75% replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2.5% gluconate by weight of washwater solids.

[0057] **Figure 49** shows compressive strength for concrete batches made as follows: Control (no washwater). Treated washwater, full replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 75% replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2.5% gluconate by weight of washwater solids, at 7 and 28 days.

[0058] **Figure 50** shows calorimetry, as power vs. time, for concrete batches made as follows: Control (no washwater). Treated washwater, full replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 75% replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2.5% gluconate by weight of washwater solids.

[0059] **Figure 51** shows compositions for concrete batches made as follows: Control (no washwater). Treated washwater, full replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 75% replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2.5% gluconate by weight of washwater solids.

[0060] **Figure 52** shows slump for concrete batches made as follows: Control (no washwater); Untreated washwater, full replacement, 2% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids; Untreated washwater, 50% replacement, 2% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2% gluconate by weight of washwater solids.

- [0061] **Figure 53** shows compressive strength for concrete batches made as follows: Control (no washwater; Untreated washwater, full replacement, 2% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids; Untreated washwater, 50% replacement, 2% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2% gluconate by weight of washwater solids.
- [0062] **Figure 54** shows calorimetry as power vs. time for concrete batches made as follows: Control (no washwater; Untreated washwater, full replacement, 2% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids; Untreated washwater, 50% replacement, 2% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2% gluconate by weight of washwater solids.
- [0063] **Figure 55** shows compositions for concrete batches made as follows: Control (no washwater; Untreated washwater, full replacement, 2% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids; Untreated washwater, 50% replacement, 2% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2% gluconate by weight of washwater solids.
- [0064] **Figure 56** shows carbon dioxide uptake for washwater treated with carbon dioxide at low, medium, and high flow rates.
- [0065] **Figure 57** shows 7-day compressive strength, compared to control, for mortar batches made as follows (test was repeated for each flow rate): Control ; Untreated washwater, full replacement, no CO₂; Treated washwater, full replacement, 7-8% CO₂; Treated washwater, full replacement, 10-13% CO₂; Treated washwater, full replacement, 14-15% CO₂; Treated washwater, full replacement, 16-17% CO₂; Treated washwater, full replacement, 19-21% CO₂.
- [0066] **Figure 58** shows slump, compared to control, for mortar batches made as follows (test was repeated for each flow rate): Control ; Untreated washwater, full replacement, no CO₂; Treated washwater, full replacement, 7-8% CO₂; Treated washwater, full replacement, 10-13% CO₂; Treated washwater, full replacement, 14-15% CO₂; Treated washwater, full replacement, 16-17% CO₂; Treated washwater, full replacement, 19-21% CO₂.
- [0067] **Figure 59** shows calorimeter setting time relative to control for mortar batches made as follows (test was repeated for each flow rate): Control ; Untreated washwater, full replacement, no CO₂; Treated washwater, full replacement, 7-8% CO₂; Treated washwater,

full replacement, 10-13% CO₂; Treated washwater, full replacement, 14-15% CO₂; Treated washwater, full replacement, 16-17% CO₂; Treated washwater, full replacement, 19-21% CO₂.

[0068] **Figure 60** shows calorimeter peak energy output relative to control for mortar batches made as follows (test was repeated for each flow rate): Control ; Untreated

- 5 washwater, full replacement, no CO₂; Treated washwater, full replacement, 7-8% CO₂; Treated washwater, full replacement, 10-13% CO₂; Treated washwater, full replacement, 14-15% CO₂; Treated washwater, full replacement, 16-17% CO₂; Treated washwater, full replacement, 19-21% CO₂.

- [0069]** **Figure 61** shows washwater temperature for mortar batches made as follows (test was repeated for each flow rate): Control ; Untreated washwater, full replacement, no CO₂; Treated washwater, full replacement, 7-8% CO₂; Treated washwater, full replacement, 10-13% CO₂; Treated washwater, full replacement, 14-15% CO₂; Treated washwater, full replacement, 16-17% CO₂; Treated washwater, full replacement, 19-21% CO₂.

- [0070]** **Figure 62** shows washwater pH for mortar batches made as follows (test was repeated for each flow rate): Control ; Untreated washwater, full replacement, no CO₂; Treated washwater, full replacement, 7-8% CO₂; Treated washwater, full replacement, 10-13% CO₂; Treated washwater, full replacement, 14-15% CO₂; Treated washwater, full replacement, 16-17% CO₂; Treated washwater, full replacement, 19-21% CO₂.

- [0071]** **Figure 63** shows carbon dioxide uptake vs. time for washwaters of various specific gravities treated with carbon dioxide.

[0072] **Figure 64** shows temperature vs. time for washwaters of various specific gravities treated with carbon dioxide.

- [0073]** **Figure 65** shows compressive strengths of mortar that contained a blend of 70% cement and 30% class C fly ash. The class C fly ash was all in prepared wash waters, treated with 1.2, 2.2, 2.4, 3.2, or 3.5% carbon dioxide.

[0074] **Figure 66** shows calorimetry, as power vs. time, of mortar that contained a blend of 70% cement and 30% class C fly ash. The class C fly ash was all in prepared wash waters, treated with 1.2, 2.2, 2.4, 3.2, or 3.5% carbon dioxide.

- [0075]** **Figure 67** shows the compositions of mortars made with mortar that contained a blend of 70% cement and 30% class C fly ash. The class C fly ash was all in prepared wash waters, treated with 1.2, 2.2, 2.4, 3.2, or 3.5% carbon dioxide.

[0076] **Figure 68** shows slump in concrete mixes made as follows: Control, no washwater; Untreated washwater, full replacement; Treated washwater, 20 minutes of CO₂ injection; Treated washwater, 40 minutes of CO₂ injection.

[0077] **Figure 69** shows compressive strength in concrete mixes made as follows:

Control, no washwater; Untreated washwater, full replacement; Treated washwater, 20 minutes of CO₂ injection; Treated washwater, 40 minutes of CO₂ injection.

[0078] **Figure 70** shows calorimetry as power vs. time in concrete mixes made as

- 5 follows: Control, no washwater; Untreated washwater, full replacement; Treated washwater, 20 minutes of CO₂ injection; Treated washwater, 40 minutes of CO₂ injection.

[0079] **Figure 71** shows the compositions of concrete mixes made as follows: Control, no washwater; Untreated washwater, full replacement; Treated washwater, 20 minutes of CO₂ injection; Treated washwater, 40 minutes of CO₂ injection.

- 10 [0080] **Figure 72** shows slump for concrete mixes made as follows: Control, no washwater, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture, sodium gluconate added 2% by weight of washwater solids.

[0081] **Figure 73** shows air entrained for concrete mixes made as follows: Control, no washwater, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture, sodium gluconate added 2% by weight of washwater solids.

- 15 [0082] **Figure 74** shows compressive strength at 1, 7, and 28 days for concrete mixes made as follows: Control, no washwater, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture, sodium gluconate added 2% by weight of washwater solids.

[0083] **Figure 75** shows calorimetry as power vs. time for concrete mixes made as follows: Control, no washwater, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture, sodium gluconate added 2% by weight of washwater solids.

- 25 [0084] **Figure 76** shows compositions for concrete mixes made as follows: Control, no washwater, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture, sodium gluconate added 2% by weight of washwater solids.

- 30 [0085] **Figure 77** shows slump for concrete mixes made as follows: Control, no washwater; Treated washwater, full replacement, added assuming 12% of the washwater was unavailable for concrete hydration; Treated washwater, full replacement, added assuming 17% of the washwater was unavailable for concrete hydration.

- [0086] **Figure 78** shows compressive strength at 1, 7, and 28 days for concrete mixes made as follows: Control, no washwater; Treated washwater, full replacement, added assuming 12% of the washwater was unavailable for concrete hydration; Treated washwater, full replacement, added assuming 17% of the washwater was unavailable for concrete hydration.
- [0087] **Figure 79** shows calorimetry as power vs. time for concrete mixes made as follows: Control, no washwater; Treated washwater, full replacement, added assuming 12% of the washwater was unavailable for concrete hydration; Treated washwater, full replacement, added assuming 17% of the washwater was unavailable for concrete hydration.
- [0088] **Figure 80** shows compositions for concrete mixes made as follows: Control, no washwater; Treated washwater, full replacement, added assuming 12% of the washwater was unavailable for concrete hydration; Treated washwater, full replacement, added assuming 17% of the washwater was unavailable for concrete hydration.
- [0089] **Figure 81** shows slump for concrete mixes produced as follows: Control, no washwater; Treated washwater, full replacement, sodium gluconate added 1% by weight of washwater solids; Treated washwater, full replacement, Daratard 17 added 5% by weight of washwater solids; Treated washwater, full replacement, Recover added 5% by weight of washwater solids.
- [0090] **Figure 82** shows compressive strength at 1, 7, and 28 days for concrete mixes produced as follows: Control, no washwater; Treated washwater, full replacement, sodium gluconate added 1% by weight of washwater solids; Treated washwater, full replacement, Daratard 17 added 5% by weight of washwater solids; Treated washwater, full replacement, Recover added 5% by weight of washwater solids.
- [0091] **Figure 83** shows calorimetry as power vs. time for concrete mixes produced as follows: Control, no washwater; Treated washwater, full replacement, sodium gluconate added 1% by weight of washwater solids; Treated washwater, full replacement, Daratard 17 added 5% by weight of washwater solids; Treated washwater, full replacement, Recover added 5% by weight of washwater solids.
- [0092] **Figure 84** shows compositions for concrete mixes produced as follows: Control, no washwater; Treated washwater, full replacement, sodium gluconate added 1% by weight of washwater solids; Treated washwater, full replacement, Daratard 17 added 5% by weight of washwater solids; Treated washwater, full replacement, Recover added 5% by weight of washwater solids.

- [0093] **Figure 85** shows slump for concrete mixes made as follows: Control, no washwater; Treated washwater, full replacement, washwater from pump system; Treated washwater, full replacement, washwater from drill system.
- [0094] **Figure 86** shows compressive strength for concrete mixes made as follows:
- 5 Control, no washwater; Treated washwater, full replacement, washwater from pump system; Treated washwater, full replacement, washwater from drill system.
- [0095] **Figure 87** shows calorimetry as power vs. time for concrete mixes made as follows: Control, no washwater; Treated washwater, full replacement, washwater from pump system; Treated washwater, full replacement, washwater from drill system.
- 10 [0096] **Figure 88** shows compositions for concrete mixes made as follows: Control, no washwater; Treated washwater, full replacement, washwater from pump system; Treated washwater, full replacement, washwater from drill system.
- [0097] **Figure 89** shows carbon dioxide uptake and efficiency of uptake for different flowrates and total carbon dioxide added to a slurry.
- 15 [0098] **Figure 90** shows carbon dioxide uptake and efficiency of uptake for inline vs. no inline mixing as carbon dioxide is added.
- [0099] **Figure 91** shows carbon dioxide uptake and efficiency of uptake for 1 vs. 2 carbon dioxide injection points.
- [0100] **Figure 92** shows an apparatus for adding carbon dioxide to a wash water slurry.
- 20 [0101] **Figure 93** shows workability (slump) for concrete prepared with washwater at high specific gravity (1.15) and low replacement levels (10, 20, and 30%).
- [0102] **Figure 94** shows calorimetry (power v time) for concrete prepared with washwater at high specific gravity (1.15) and low replacement levels (10, 20, and 30%).
- [0103] **Figure 95** shows compressive strength at 1, 7, and 28 days for concrete prepared
- 25 with washwater at high specific gravity (1.15) and low replacement levels (10, 20, and 30%).
- [0104] **Figure 96** shows mix designs for concrete prepared with washwater at high specific gravity (1.15) and low replacement levels (10, 20, and 30%).
- [0105] **Figure 97** shows workability (slump) for concrete prepared with two different batches of washwater, at specific gravities of 1.10 and 1.05, respectively.
- 30 [0106] **Figure 98** shows calorimetry (power v time) for concrete prepared with two different batches of washwater, at specific gravities of 1.10 and 1.05, respectively.
- [0107] **Figure 99** shows compressive strength at 1, 7, and 28 days for concrete prepared with two different batches of washwater, at specific gravities of 1.10 and 1.05, respectively.

- [0108] **Figure 100** shows mix designs for concrete prepared with two different batches of washwater, at specific gravities of 1.10 and 1.05, respectively.
- [0109] **Figure 101** shows x-ray diffraction analysis for washwater at a specific gravity of 1.10 and treated with CO₂ to 0, 5, 10, 15, 20 and 25% by weight of cement, at 0 hours.
- 5 [0110] **Figure 102** shows x-ray diffraction analysis for washwater at a specific gravity of 1.10 and treated with CO₂ to 0, 5, 10, 15, 20 and 25% by weight of cement, at 3 hours.
- [0111] **Figure 103** shows x-ray diffraction analysis for washwater at a specific gravity of 1.10 and treated with CO₂ to 0, 5, 10, 15, 20 and 25% by weight of cement, at 6 hours.
- [0112] **Figure 104** shows x-ray diffraction analysis for washwater at a specific gravity of 1.10 and treated with CO₂ to 0, 5, 10, 15, 20 and 25% by weight of cement, at 24 hours.
- 10 [0113] **Figure 105** shows x-ray diffraction analysis for washwater at a specific gravity of 1.10 and treated with CO₂ to 0, 5, 10, 15, 20 and 25% by weight of cement, at 72 hours.
- [0114] **Figure 106** shows slump for concrete made with treated washwater at two different treatment levels (5, 25%) and compared to potable water reference and an untreated washwater reference. All conditions were made with and without a 3% reduction in cement.
- 15 [0115] **Figure 107** shows calorimetry (power v time) for concrete prepared with treated washwater at two different treatment levels (5, 25%) and compared to potable water reference and an untreated washwater reference. All conditions were made with and without a 3% reduction in cement.
- 20 [0116] **Figure 108** shows compressive strength at 1, 7, and 28 days for concrete prepared with treated washwater at two different treatment levels (5, 25%) and compared to potable water reference and an untreated washwater reference. All conditions were made with and without a 3% reduction in cement.
- [0117] **Figure 109** shows mix designs for concrete prepared with treated washwater at two different treatment levels (5, 25%) and compared to potable water reference and an untreated washwater reference. All conditions were made with and without a 3% reduction in cement.
- 25 [0118] **Figure 110** shows slump for concrete made with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes.
- 30 [0119] **Figure 111** shows calorimetry (power v time) for concrete prepared with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a

large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes.

5 [0120] **Figure 112** shows compressive strength at 1, 7, and 28 days for concrete prepared with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes.

10 [0121] **Figure 113** shows mix designs for concrete prepared with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes.

15 [0122] **Figure 114** shows slump for concrete made with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes, then allowed to age for 24 hours after treatment.

20 [0123] **Figure 115** shows calorimetry (power v time) for concrete prepared with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes, then allowed to age for 24 hours after treatment.

25 [0124] **Figure 116** shows compressive strength at 1, 7, and 28 days for concrete prepared with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes, then allowed to age for 24 hours after treatment.

30 [0125] **Figure 117** shows mix designs for concrete prepared with washwater treated with 0, 3, 6, and 9% CO₂ by weight solids; washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer--washwater was

transferred from one tank to another with CO₂ being injected in the transfer line. The washwater was transferred/treated every 30 minutes, then allowed to age for 24 hours after treatment.

5 [0126] **Figure 118** shows slump of mortar made with 100% water replacement with washwater treated with CO₂ to an uptake of 8% CO₂ by weight washwater solids, either as is or treated with two different concentrations of a commercial set retarding admixture.

[0127] **Figure 119** shows calorimetry (power v time) of mortar made with 100% water replacement with washwater treated with CO₂ to an uptake of 8% CO₂ by weight washwater solids, either as is or treated with two different concentrations of a commercial set retarding
10 admixture.

[0128] **Figure 120** shows compressive strength at 1, 7, and 28 days of mortar made with 100% water replacement with washwater treated with CO₂ to an uptake of 8% CO₂ by weight washwater solids, either as is or treated with two different concentrations of a commercial set retarding admixture.

15 [0129] **Figure 121** shows mix designs of mortar made with 100% water replacement with washwater treated with CO₂ to an uptake of 8% CO₂ by weight washwater solids, either as is or treated with two different concentrations of a commercial set retarding admixture.

[0130] **Figure 122** shows X-ray diffraction for washwater prepared with 100% cement treated with 0, 5, 10, 15, 20, and 25% CO₂ by weight of cement at 0 hours.

20 [0131] **Figure 123** shows X-ray diffraction for washwater prepared with 100% cement treated with 0, 5, 10, 15, 20, and 25% CO₂ by weight of cement at 24 hours.

[0132] **Figure 124** shows X-ray diffraction for washwater prepared with 75% cement and 25% slag treated with 0, 5, 10, 15, 20, and 25% CO₂ by weight of cement at 0 hours.

[0133] **Figure 125** shows X-ray diffraction for washwater prepared with 75% cement and
25 25% slag treated with 0, 5, 10, 15, 20, and 25% CO₂ by weight of cement at 24 hours.

[0134] **Figure 126** shows X-ray diffraction for washwater prepared with 100% cement and treated with CO₂ at a flow rate of 5 LPM for 0, 5, 10, 15, 20, and 25% CO₂ by weight cement solids at 0 hours.

[0135] **Figure 127** shows X-ray diffraction for washwater prepared with 100% cement
30 and treated with CO₂ at a flow rate of 5 LPM for 0, 5, 10, 15, 20, and 25% CO₂ by weight cement solids at 24 hours.

[0136] **Figure 128** shows X-ray diffraction for washwater prepared with 100% cement and treated with CO₂ at a flow rate of 10 LPM for 0, 5, 10, 15, 20, and 25% CO₂ by weight cement solids at 0 hours.

[0137] **Figure 129** shows X-ray diffraction for washwater prepared with 100% cement and treated with CO₂ at a flow rate of 10 LPM for 0, 5, 10, 15, 20, and 25% CO₂ by weight cement solids at 24 hours.

5 [0138] **Figure 130** shows X-ray diffraction for washwater prepared with 100% cement to a specific gravity of 1.05, treated with CO₂ for 0, 5, 10, 15, 20, 25 and 30% CO₂ by weight of cement solids at 0 hours.

[0139] **Figure 131** shows X-ray diffraction for washwater prepared with 100% cement to a specific gravity of 1.05, treated with CO₂ for 0, 5, 10, 15, 20, 25 and 30% CO₂ by weight of cement solids at 24 hours.

10 [0140] **Figure 132** shows X-ray diffraction for washwater prepared with 100% cement to a specific gravity of 1.05, treated with CO₂ for 0, 5, 10, 15, 20, 25 and 30% CO₂ by weight of cement solids at 48 hours.

[0141] **Figure 133** shows X-ray diffraction for washwater prepared with 100% cement to a specific gravity of 1.15, treated with CO₂ for 0, 5, 10, 15, 20, 25 and 30% CO₂ by weight
15 of cement solids at 0 hours.

[0142] **Figure 134** shows X-ray diffraction for washwater prepared with 100% cement to a specific gravity of 1.15, treated with CO₂ for 0, 5, 10, 15, 20, 25 and 30% CO₂ by weight of cement solids at 24 hours.

[0143] **Figure 135** shows X-ray diffraction for washwater prepared with 100% cement to
20 a specific gravity of 1.15, treated with CO₂ for 0, 5, 10, 15, 20, 25 and 30% CO₂ by weight of cement solids at 48 hours.

DETAILED DESCRIPTION OF THE INVENTION

[0144] Wash water, also called grey water or reclaimed water herein, is produced as a
25 byproduct of the concrete industry. This water, which may contain suspended solids in the form of sand, aggregate and/or cementitious materials, is generated through various steps in the cycle of producing concrete structures. Generally a large volume of concrete wash water (reclaimed water) is produced by the washing-out of concrete mixer trucks following the delivery of concrete. This water is alkaline in nature and requires specialized treatment,
30 handling and disposal. As used herein, “wash water” includes waters that are primarily composed of concrete drum wash water; such water may contain water from other parts of the concrete production process, rain runoff water, etc., as is known in the art. As will be clear from context, “wash water” includes water used to clean the drum of a ready-mix truck

and/or other mixers, which contains cement and aggregate, as well as such water after aggregate has been removed, e.g., in a reclaimer, but still containing solids, such as cementitious solids. Typically at least a portion of such solids are retained in the wash water for re-use in subsequent concrete batches.

- 5 [0145] While this water can be suitable for reuse in the production of concrete, it has been documented that the wash water can result in negative impacts on the properties of concrete, for example, set acceleration and loss of workability. Wash water is mainly a mixture of cement and, in many cases, supplementary cementitious materials (SCMs) in water. It becomes problematic as a mix water because as the cement hydrates it changes the chemistry of the water. These changes in chemistry, along with the hydration products, cause a host of issues when the water is used as mix water, such as acceleration, increased water demand, reduced 7-day strength, and the like. These issues generally worsen as the amount of cement in the water increases, and/or the water ages.

- 10 [0146] The methods and compositions of the invention utilize the application of CO₂ to concrete wash water to improve its properties for reuse in the production of concrete. Thus, wash water that has a cement content (e.g., specific gravity) and/or that has aged to a degree that would normally not allow its use as mix water can, after application of carbon dioxide, be so used.

- 15 [0147] Without being bound by theory, it is thought that by carbonating wash water, several results may be achieved that are beneficial in terms of using the water as part or all of mix water for subsequent batches of concrete:

- [0148] 1) Maintain a pH of ~7: This effectively dissolves the cement due to the acidity of CO₂. This helps deliver a grey water of consistent chemistry and removes the "ageing effects". In certain embodiments, a pH of less than or greater than 7 may be maintained, as described elsewhere herein.

- 25 [0149] 2) Precipitate any insoluble carbonates: CO₂ actively forms carbonate reaction products with many ions. This removes certain species from solution, such as calcium, aluminum, magnesium and others. This is another step that helps provide a grey water of consistent chemistry.

- 30 [0150] 3) Change solubility of cement ions: The solubilities of many ions depend on pH. By maintaining the pH at ~7 with CO₂ the nature of the water chemistry is changed, potentially in a favorable direction. In certain embodiments, a pH of less than or greater than 7 may be maintained, as described elsewhere herein.

[0151] 4) Shut down pozzolanic reactions: By maintaining the pH around 7 no $\text{Ca}(\text{OH})_2$ is available to react with slag and/or fly ash in the grey water. This can mean that these SCMs are unaltered through the treatment and reuse of the grey water, thus reducing the impact of the grey water substantially. In certain embodiments, a pH of less than or greater than 7 may be maintained, as described elsewhere herein.

[0152] 5) Reduce amount of anions left behind: The formation of carbonate precipitates using CO_2 is advantageous over other common acids, like HCl or H_2SO_4 , whose anions, if left soluble in the treated water, can adversely impact the chemistry of the grey water for concrete batching.

10 [0153] 6) Cause retardation: By saturating the grey water with $\text{CO}_2/\text{HCO}_3^-$ retardation can be achieved when used as batch water.

[0154] 7) Nature of precipitates: The process may potentially be altered to form precipitates that have less effects on the water demand of concrete prepared with grey water. In particular, conditions of carbonation may be used that produce nanocrystalline carbonates, such as nanocrystalline calcium carbonate, that are known to be beneficial when used in concrete products.

[0155] In certain embodiments, the invention provides a method of providing a mix water for a batch of concrete, where the mix water comprises wash water from one or more previous batches of concrete that has been exposed to carbon dioxide in an amount above atmospheric concentrations of carbon dioxide, to carbonate the wash water ("carbonated wash water"). The mix water may contain at least 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 99, or 99.5% carbonated wash water. Alternatively or additionally, the mix water may contain no more than 20, 30, 40, 50, 60, 70, 80, 90, 95, 99, 99.5, or 100% carbonated wash water. In certain embodiments, the mix water is 100% carbonated wash water. In certain
25 embodiments, the mix water is 1-100% carbonated wash water. In certain embodiments, the mix water is 1-80% carbonated wash water. In certain embodiments, the mix water is 1-50% carbonated wash water. In certain embodiments, the mix water is 1-30% carbonated wash water. In certain embodiments, the mix water is 10-100% carbonated wash water. In certain
30 embodiments, the mix water is 20-100% carbonated wash water. In certain embodiments, the mix water is 50-100% carbonated wash water. In certain embodiments, the mix water is 70-100% carbonated wash water. In certain embodiments, the mix water is 90-100% carbonated wash water.

[0156] In certain embodiments, a first portion of mix water that is plain water, e.g., not wash or other water that has been carbonated, such as plain water as normally used in concrete mixes, is mixed with concrete materials, such as cement, aggregate, and the like, and then a second portion of mix water that comprises carbonated water, which can be carbonated plain water or, e.g., carbonated wash water is added. The first portion of water may be such that an acceptable level of mixing is achieved, e.g., mixing without clumps or without substantial amounts of clumps. For example, the first portion of mix water that is plain water may be more than 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, or 90%, and/or less than 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 or 95%, such as % 1-90%, or 1-80%, or 1-75%, or 1-70%, or 1-65%, or 1-60%, or 1-55%, or 1-50%, or 1-45%, or 1-40%, or 1-30%, or 1-20%, or 1-10% of the total mix water used in the concrete mix, while the remainder of the mix water used in the concrete mix is the second portion, i.e., carbonated mix water. The first portion of water may be added at one location and the second portion at a second location. For example, in a ready mix operation, the first portion may be added to concrete materials which are mixed, then the mixed materials are transferred to a drum of a ready-mix truck, where the second portion of water is added to the concrete in the drum of the ready-mix truck. However, it is also possible that both the first and the second locations are the same location, e.g., a mixer prior to deposit into a ready-mix truck, or the drum of the ready-mix truck. The second portion of water may be added at any suitable time after the addition of the first portion. In general, the second portion of water is added at least after the first portion and the concrete materials have mixed sufficiently to achieve mixing without clumps or without substantial amounts of clumps. In certain embodiments, the second portion of water is added at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 40, 50, or 60 minutes after the first portion of water, and/or not more than 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 40, 50, or 60 minutes, or 1, 2, 3, 4, 5, or 6 hours after the first portion of water.

[0157] The wash water may be carbonated at any suitable time, for example, right after its production, at some time after production, or just before use in the concrete, or any combination thereof. Without being bound by theory, it is probable that at time 0 (immediately after formation of the wash water), added carbon dioxide will react with unhydrated cement phases (C3S, C2S, C3A, etc.) while at later ages added carbon dioxide will react with hydrated cement phases (CSH, ettringite, etc.). Providing dosage later can result in different properties than when the dosage is applied earlier, potentially leading to different properties when the wash water is reused in concrete production. In addition, the phases reacting in wash water at later ages can be generally more thermodynamically stable

and thus have lower heats of reaction when reacting with carbon dioxide; the inventors have observed that the exothermic heat rise (e.g., as measured by temperature) can be greater when treating fresh wash water with carbon dioxide than when treating aged wash water. It can be advantageous to have a lower heat rise because a treated water that becomes heated may have to be cooled before it can be used as a mix water. Hence, certain embodiments provide methods and apparatus that cause a cooling of the wash water due to production of gaseous carbon dioxide for treatment of the wash water from liquid carbon dioxide, e.g., piping or conduits that contact the wash water and absorb heat necessary to convert liquid to gaseous carbon dioxide and thus cooling the wash water. These are described in more detail elsewhere herein. In addition, when treating an aged wash water with carbon dioxide, it can be possible that less carbon dioxide is required to achieve a stable wash water than with wash water that is fresh. The amount of carbon dioxide to create a stable wash water (e.g., properties are relatively unchanged after further aging) can depend on the relative contributions of $\text{Ca}(\text{OH})_2$, ettringite, CSH, and/or unreacted cement (e.g., unreacted Ordinary Portland Cement, OPC) to the undesirable properties of wash water. In addition, different phases can have different carbon dioxide reaction kinetics, which in turn can influence choices of carbon dioxide delivery settings, approaches (e.g., type of delivery system or adjustments to delivery system), and the like.

[0158] Thus, for example, in certain embodiments, carbonation of wash water can commence no later than 1, 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180, 240, 300, 360, 420, or 480 minutes, or 7, 8, 9, 10, 11, 12, 14, 16, 18, or 24 hours, or 1.5, 2, 3, 4, or 5 days after formation of the wash water, and/or no sooner than 0, 0.5, 1, 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180, 240, 300, 360, 420, 480, or 540 minutes or 8, 9, 10, 11, 12, 14, 16, 18, or 24 hours, or 1.5, 2, 3, 4, 5, or 6 days after formation of the wash water. The carbonation can continue for any suitable period of time, for example, in certain embodiments wash water is continuously exposed to carbon dioxide for a period of time after carbonation commences. Alternatively or additionally, wash water can be carbonated just before its use as mix water, for example, no more than 1, 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180, 240, 300, 360, 420, or 480 minutes before its use as mix water (e.g., before contacting the concrete mixture), and/or no sooner than 0, 0.5, 1, 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180, 240, 300, 360, 420, 480, or 540 minutes before its use as mix water. Additionally or alternatively, the wash water may be aged for some amount of time after addition of carbon dioxide before it is used as wash water, for example, carbonated wash water can be used as mix water no later than 1, 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180, 240, 300, 360, 420, or 480 minutes, or,

7, 8, 9, 10, 12, 18, or 24 hours, or 1.5, 2, 3, 4, 5, or six days after carbonation of the wash water, and/or no sooner than 0, 0.5, 1, 2, 5, 10, 20, 30, 40, 60, 80, 100, 120, 150, 180, 240, 300, 360, 420, 480, or 540 minutes or 8, 10, 12, 18, 24 hours, or 1.5, 2, 3, 4, 5, 6, 7, 8, 10, 12, or 14 days after carbonation of the wash water; for example, at least 3 hours, at least 6 hours, at least 12 hours, at least one day, at least 3 days, or at least 5 days after carbonation of the wash water.

[0159] The water used for washing may be clean water or recycled wash water. In certain embodiments, the water that is used to wash out trucks may be carbonated before and/or during the wash process, i.e., before the wash water enters a reclamation tank. Concrete trucks typically have 10-15 min of mixing when washing out. Carbon dioxide can be, e.g., injected into the water pump line on its way to the truck (fresh water input), or from the settlement pond/reclamation system pump (recycled water input).

[0160] Additionally or alternatively, after a truck is emptied and water is added to the truck for washing, carbon dioxide can be added to the truck. The carbon dioxide reacts with the slurry, and the carbon dioxide can “put the cement to sleep” (e.g., halt or retard most or all deleterious reactions, and react with most or all deleterious materials, as outlined herein). In certain embodiments, the slurry can be reused in a new batch. In certain embodiments, the slurry need not even leave the truck. Carbon dioxide can be added as a solid, liquid, or gas, or combination thereof. For example, carbon dioxide may be added as a solid. In certain embodiments, carbon dioxide is added as a mixture of solid and gas, produced when liquid carbon dioxide is released to atmospheric pressure. A conduit carries liquid carbon dioxide from a container to an injector, which is configured so as to cause a desired conversion to gas and solid. The mixture of gaseous and solid carbon dioxide is directed into the drum of a ready mix truck. The amount of carbon dioxide added may be a predetermined amount, based, e.g., on typical residual amounts of concrete left in the truck. The amount of carbon dioxide added may also be regulated according to the condition of the wash water, e.g., according to pH as the carbon dioxide mixes and reacts with components of the wash water. Using this method, it is possible to eliminate the need to discharge wash water from the mixer. This allows the wash water to be used as mix water in the next batch of concrete produced and prevents the residual plastic concrete from hardening. In certain embodiments, the treatment allows stabilization of the wash water, so that it can be used as mix water for the next batch, after at least 0.5, 1, 2, 3, 4, 5, 6, 12, 18, 24, 30, 36, 42, 48, 54, 60, 66, 72, 78, 86, or 92 hours and/or not more than 12, 18, 24, 30, 36, 42, 48, 54, 60, 66, 72, 78, 86, 92, or 104 hours. The carbon dioxide treatment may be used alone or used with other treatments

that are designed to stabilize wash water and allow reuse, such as Recover, GCP Applied Technologies, Inc., Cambridge, Mass., or similar admixture.

[0161] In certain embodiments, the wash water is circulated before its use as a mix water.

For example, part or all of the wash water that is carbonated may be circulated (e.g., run
5 through one or more loops to, e.g., aid in mixing and/or reactions, or agitated, or stirred, or the like). This circulation may occur continuously or intermittently as the water is held prior to use. In certain embodiments the wash water is circulated for at least 5, 10, 20, 50, 70, 80, 90, 95, or 99% and/or not more than 10, 20, 50, 70, 80, 90, 95, 99 or 100% of the time it is held prior to use as mix water.

10 [0162] It will be appreciated that many different wash waters are typically combined and held, for example, in a holding tank, until use or disposal. Carbonation of wash water may occur before, during, or after its placement in a holding tank, or any combination thereof. Some or all of the wash water from a given operation may be carbonated. It is also possible that wash water from one batch of concrete may be carbonated then used directly in a
15 subsequent batch, without storage. In general, the tank will be outfitted or retrofitted to allow circulation of the water in such a way that sedimentation does not occur, to allow reuse of materials in the wash water as it is carbonated.

[0163] Any suitable method or combination of methods may be used to carbonate the wash water. For example, the wash water may be held in a container and exposed to a carbon
20 dioxide atmosphere while mixing. Carbon dioxide may be bubbled through mix water by any suitable method; for example, by use of bubbling mats, or alternatively or additionally, by introduction of carbon dioxide via one or more conduits with one or a plurality of openings beneath the surface of the wash water. The conduit may be positioned to be above the sludge that settles in the tank and, in certain embodiments, regulated so as to not significantly
25 impede settling. Catalysts may also be used to accelerate one or more reactions in the carbonating wash water. In certain embodiments, liquid carbon dioxide injection is used. A vaporizer can be set inside the tank and converts liquid carbon dioxide to gas, drawing heat from the water to do so, and thereby cooling the water. For example, a series of metal tubes may be submerged in the water that are configured to ensure gas rises to the top and is pushed
30 out of a nozzle. Pipes run vertically, but with the heat capacity and transfer rate in water being so much higher than air, fins that are normally be present in a cryogenic carbon dioxide heat exchanger that operates in air may not be needed.

Impeller blades

[0164] In certain embodiments, carbon dioxide is added to a slurry tank by injecting it through a specially designed agitator blade. As known in the water treatment industry, a flash mixing style blade can be used that is designed to create turbulence, vortices, vacuum pockets and high shear behind the mixer blades to promote rapid mixing action. See, e.g., blades
5 supplied by Dynamix Inc., 14480 River Road, Unit 150, Richmond, British Columbia, Canada V6V 1L4, such as the P4 Pitch Impeller Blade. This is merely exemplary and those of skill in the art will recognize that various types, such as pitch-blade impellers or airfoil impellers may be used.

[0165] Injection of carbon dioxide at a particular location along the blade edge can increase
10 mixing action and contact time. The blade action forces the carbon dioxide bubbles to undergo more mixing rather than being buoyantly forced towards the surface. Fine dispersed bubbles can be assured through selecting the proper hole size. It is important to ensure that the holes remain unplugged. Whereas a perforated hose in the bottom of a tank with have solids settle upon it when the slurry is unagitated, the agitator blade holes will not be at the
15 bottom of a tank and get covered by the settling solids. Further the holes can be placed on the sides or bottom of the agitator element to avoid vertical settlement buildup.

Augur

[0166] In a pond where an auger is used for mixing, injection can be through the central axis of the auger shaft. In certain embodiments, to ensure serviceability and possibly to reduce
20 the occurrence of buildup, a retractable injection pipe with a gas distribution nozzle at the end can be routed through the central axis of the mixing auger shaft. The carbon dioxide can be injected, e.g., when a control system calls for it and then the injector can retract out of the water when the system has determined that the amount of carbon dioxide is sufficient. Alternately, a retractable injector is not routed through the shaft, but the shaft is simply
25 hollow. Carbon dioxide can be injected down the center of the mixing auger shaft. An orifice at the injection point can promote the formation of finely dispersed bubbles. Either way, the injector nozzle positioning, direction, and injection speed are such that they do not interfere with normal mixing, so that sedimentation does not occur.

Submersible pump

30 [0167] A suitably efficient or powerful pump can both circulate the slurry and also, in some cases, send the slurry to the concrete batching process. Carbon dioxide can be integrated with the pump via, for example, injection into the impeller housing at a location chosen to maximize mixing, or, for example, just under the intake to allow the suction to bring the gas into the housing. The impeller blades mix up and pressurize the carbon dioxide/wastewater

mix, providing better uptake of carbon dioxide, and pump the slurry through a long hose. The transport in the hose provides additional time to promote uptake. The slurry can be directed back into the tank or pumped directly into the batch process.

- 5 [0168] The CO₂ injection rate can be tied to the flow rate/density of the slurry. If one cycle through the loop is insufficient to provide the desired degree of carbon dioxide uptake, then it can be recirculated through the same loop or through another loop, e.g., via a secondary, smaller pump, until the desired amount of CO₂ has been absorbed.

- 10 [0169] Carbon dioxide injection can take place near an impeller. Carbon dioxide injection can also take place in a discharge pipe line, near the pump itself or at any point in the pipe line. Carbon dioxide injection can be achieved with single or multiple injection points and carbon dioxide can be injected at 90 degrees or any suitable angle relative to the direction of flow. Directing the carbon dioxide exit parallel to the rising liquid flow will increase liquid flow as the buoyancy of the carbon dioxide displaces the wash water upwards.

Eductor nozzles

- 15 [0170] In certain embodiments, one or more eductor nozzles are used. Eductor nozzles are well-known in the art. An eductor nozzle mixes and agitates, and increases overall water flow, thus allowing a smaller pump to move sufficient water to ensure adequate mixing to prevent sedimentation. The nozzle allows high pressure into a first stage nozzle to increase velocity, then the eductor provides a venturi effect of high velocity flow which creates low
20 pressure, pulling added liquid into the stream of flow, and allowing higher volume lower velocity output. Such nozzles are supplied by, e.g., Bete Ltd., P.O. Box 2748, Lewes, East Sussex, United Kingdom. Such a nozzle can incorporate carbon dioxide injection into its operation. If carbon dioxide is injected as nanobubbles in solution (supersaturated carbon dioxide water, see elsewhere in this application, e.g., systems supplied by Gaia USA Inc.,
25 Scottsdale, Arizona) then the buoyancy that acts upon coarse bubbles may be avoided. Pumps can be used for mixing, provided they are placed strategically and provide sufficient flow.

- 30 [0171] In certain embodiments, a combination of mixing blades and sump pump with eductor may be used, so long as the pump or pumps is in a non-intrusive location and does not impede the mixing action required. The discharge of water and carbon dioxide (eductor) is in a location that does not disturb the blade mixing action. Most reclaimer blades push material downward so it is preferred to discharge the pump water/carbon dioxide near the axis of the blades to help promote mixing. In certain embodiments, an integrated mixing and injection process is used: Strategically placed eductor nozzles can be used to carbonate water

and maintain sufficient fluid flow. The eductors are fed by a pump or pumps which can incorporate carbon dioxide in several ways, as described herein. For retrofitting of existing wash water settlement ponds, a series of eductors can be configured to mix the pond. It is important to ensure the eductor configuration keeps the water flow throughout the tank above the settlement velocity of suspended solids.

Head space integration

[0172] If the treatment vessel is a closed container then increased efficiency can be had by recycling gas from the headspace into the injection hardware. As bubbles rise through the liquid to join the headspace such an approach allows the carbon dioxide molecules another chance to dissolve and react. The process can monitor the headspace gas for carbon dioxide and pressure. For a given fixed mass of carbon dioxide injected the carbon dioxide content and pressure will initially increase. As reaction proceeds the carbon dioxide concentration and pressure will decrease. This can be a signal that causes another dose of carbon dioxide. The dosing efficiency of the dose is in direct response to the absorption.

Super-saturated carbon dioxide

[0173] In certain cases, mix water, e.g., wash water may be treated with carbon dioxide in such a manner that the carbon dioxide content of the water increases beyond normal saturation, for example, at least 10, 20, 30, 40, 50, 70, 100, 150, 200, or 300% , or not more than 10, 20, 30, 40, 50, 70, 100, 150, 200, 300, 400, or 500% beyond normal saturation, compared to the same water under the same conditions that is normally saturated with carbon dioxide. Normal saturation is, e.g., the saturation achieved by, e.g., bubbling carbon dioxide through the water, e.g., wash water, until saturation is achieved, without using manipulation of the water beyond the contact with the carbon dioxide gas. For methods of treating water to increase carbon dioxide concentration beyond normal saturation levels, see, e.g., U.S. Patent Application Publication No. 2015/0202579.

[0174] In certain embodiments, washwater is exposed to carbon dioxide in a conduit, where wash water is pulled from a source of washwater, such as a slurry pond, through an input into the conduit, and moved through the conduit to an output. In certain embodiments, the treated washwater is conducted from the output to a concrete mixing operation; that is, exposure to carbon dioxide occurs outside the source of washwater, and the system can operate as an on-demand washwater carbonation system. The water thus carbonated can be used in a concrete mix, disposed of, or used in any other appropriate manner. This type of system can be easily retrofitted into virtually any existing washwater system, since most or all of the injection system stands alone from the source of washwater, e.g., slurry pond. The conduit is operably

connected to a source of carbon dioxide at one or more injection points for carbon dioxide, such as at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, or 20 injection points, and/or not more than 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, or 30 injection points. At each injection point, carbon dioxide is injected into a flowing stream of washwater slurry. If more than one injection point is used, the injection points are sufficiently spaced from one another that, with the appropriate flow rate for the slurry and injection rate for the carbon dioxide, together with the diameter of the conduit, and cement content of the washwater, carbon dioxide is injected as bubbles at the injection point, with each bubble separated from each other (or at least 50, 60, 70, 80, or 90% of the bubbles separated from each other), and by the end of the conduit section the carbon dioxide from the injection is at least 20, 30, 40, 50, 60, 70, 80, 90, 95, or 99% absorbed and/or reacted by the slurry, and/or not more than 30, 40, 50, 60, 70, 80, 90, 95, 99, or 100% absorbed and/or reacted by the slurry. See Figure 92 for an illustration of one section of an injector system. The conduit can comprise any suitable number of injection points, as described, thus allowing for carbon dioxide to be added in each section and a desired carbon dioxide uptake to be achieved. Thus, merely as an example, a single section may allow for, e.g., 2% carbon dioxide uptake and a desired carbon dioxide uptake may be 10%, so the conduit would have 5 sections/injection points. In certain embodiments, the sections are contiguous; however, it is also possible to have one or more sections separated from the others, with non-contiguous sections operably connected by a conduit; this may help to utilize available space, e.g., allow for multiple sections to be used with minimal height requirement, compared to a contiguous system. Additionally or alternatively, to increase carbon dioxide uptake, washwater may be recirculated through the system, so that with each pass the washwater more carbon dioxide is taken up; thus in certain embodiments, the washwater is recirculated at least 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 times and/or not more than 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, or 20 times. Any suitable orientation of the system may be used. In certain embodiment, the conduit (or conduit sections, if sections are non-contiguous) is positioned to be vertical, such as within 1, 2, 5, 10, 15, 20, 30, 40, or 50% of vertical. In certain embodiments, one or more of the sections is configured to mix the washwater as it moves through. Sample calculations for system parameters and additional description are given in Example 27.

[0175] In certain embodiments, the invention allows the use of wash water substantially “as is,” that is, without settling to remove solids. Carbonation of the wash water permits its use as mix water, even at high specific gravities.

[0176] This technology can allow the use of grey (wash) water as mix water, where the grey (wash) water is at specific gravities of at least 1.01, 1.02, 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.09, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19, 1.20, 1.22, 1.25, 1.30, 1.35, 1.40, or 1.50, and/or not more than 1.02, 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.09, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19, 1.20, 1.22, 1.25, 1.30, 1.35, 1.40, 1.50 or 1.60; e.g., 1.0-1.2, or 1.0 to 1.3, or 1.0 to 1.18, or 1.0 to 1.16, or 1.0 to 1.15, or 1.0 to 1.14, or 1.0 to 1.13, or 1.0 to 1.12, or 1.0 to 1.10, or 1.0 to 1.09, or 1.0 to 1.08, or 1.0 to 1.07, or 1.0 to 1.06, or 1.0 to 1.05, or 1.0 to 1.04, or 1.0 to 1.03, or 1.0 to 1.02, 1.01-1.2, or 1.01 to 1.3, or 1.01 to 1.18, or 1.01 to 1.16, or 1.01 to 1.15, or 1.01 to 1.14, or 1.01 to 1.13, or 1.01 to 1.12, or 1.01 to 1.10, or 1.01 to 1.09, or 1.01 to 1.08, or 1.01 to 1.07, or 1.01 to 1.06, or 1.01 to 1.05, or 1.01 to 1.04, or 1.01 to 1.03, or 1.01 to 1.02, or 1.02-1.2, or 1.02 to 1.3, or 1.02 to 1.18, or 1.02 to 1.16, or 1.02 to 1.15, or 1.02 to 1.14, or 1.02 to 1.13, or 1.02 to 1.12, or 1.02 to 1.10, or 1.02 to 1.09, or 1.02 to 1.08, or 1.02 to 1.07, or 1.02 to 1.06, or 1.02 to 1.05, or 1.02 to 1.04, or 1.02 to 1.03, or 1.03-1.2, or 1.03 to 1.3, or 1.03 to 1.18, or 1.03 to 1.16, or 1.03 to 1.15, or 1.03 to 1.14, or 1.03 to 1.13, or 1.03 to 1.12, or 1.03 to 1.10, or 1.03 to 1.09, or 1.03 to 1.08, or 1.03 to 1.07, or 1.03 to 1.06, or 1.03 to 1.05, or 1.03 to 1.04, or 1.05-1.2, or 1.05 to 1.3, or 1.05 to 1.18, or 1.05 to 1.16, or 1.05 to 1.15, or 1.05 to 1.14, or 1.05 to 1.13, or 1.05 to 1.12, or 1.05 to 1.10, or 1.05 to 1.09, or 1.05 to 1.08, or 1.05 to 1.07, or 1.05 to 1.06. In certain embodiments the methods and compositions of the invention allow the use of grey (wash) water as mix water, where the grey water has a specific gravity of at least 1.01, 1.02, 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.09, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19, or 1.20. The methods and compositions of the invention can reduce or even eliminate the need to further treat wash water, beyond carbonation, for the wash water to be suitable for use as mix water in a subsequent batch. In certain embodiments, after grey (wash) water is carbonated, it is used in subsequent batches of concrete with no more than 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, or 95% of remaining solids removed. In certain embodiments, none of the remain solids are removed. The carbonated wash water may be combined with non-wash water, e.g., normal mix water, before or during use in a subsequent concrete batch, to provide a total amount of water used in the batch; in certain embodiments, the carbonated wash water comprises at least 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 95, or 99% of the total amount of water used in the batch; in certain embodiments, 100% of the total amount of water used in the batch is carbonated wash water, excluding water used to wash down equipment and, in some cases, excluding water added at the job before or during pouring of the concrete mix.

- [0177] The use of wash water in a concrete mix, especially carbonated wash water, often results in enhanced strength of the resulting concrete composition at one or more times after pouring, for example, an increase in compressive strength, when compared to the same concrete mix without carbonated wash water, of at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, or 25% at 1-day, 7-days, and/or 28-days. This increase in early strength, as well as additionally or alternatively the presence of cementitious materials in the carbonated wash water that can replace some of the cementitious materials in a subsequent mix, often allows the use of less cement in a mix that incorporates carbonated wash water than would be used in the same mix that did not incorporate carbonated wash water; for example, the use of at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 20, 22, 25, 30, 35, or 40% less cement in the mix where the mix retains a compressive strength at a time after pouring, e.g., at 1, 7, and/or 28-days, that is within 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 30, 40, or 50% of the compressive strength of the mix that did not incorporate carbonated wash water, e.g., within 5%, or within 7%, or within 10%.
- [0178] In addition, the carbonation of wash water can allow the use of wash water at certain ages that would otherwise not be feasible, e.g., wash water that has aged at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, or 15 days. Wash water that has been carbonated may be used in concrete at an age where it would otherwise produce a concrete mix without sufficient workability to be used.
- [0179] The CO₂ treatment produces carbonate reaction products that likely contain some amount of nano-structured material. Of the carbonated products in the wash water, e.g., calcium carbonate, at least 1, 2, 5, 7, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, or 90% may be present as nano-structured materials, and/or not more than 5, 7, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 95, or 100% may be present as nano-structured material. A “nano-structured material,” as that term used herein, includes a solid product of reaction of a wash water component with carbon dioxide whose longest dimension is no more than 500 nm, in certain embodiments no more than 400 nm, in certain embodiment no more than 300 nm, and in certain embodiments no more than 100 nm.
- [0180] Carbon dioxide treatment of wash water can result in a solid material that is distinct from untreated wash water in terms of the coordination environment of aluminum and silicon crosslinking, e.g., as measured by NMR. Without being bound by theory, it is thought that carbon dioxide treatment of the wash water can create a carbonate shell around the particle, and that this shell can have an inhibiting effect on the phases contained therein, perhaps physically inhibiting dissolution.

[0181] The CO₂ treatment has the further benefit of sequestering carbon dioxide, as the carbon dioxide reacts with components of the wash water (typically cement or supplementary cementitious material), as well as being present as dissolved carbon dioxide/carbonic acid/bicarbonate which, when the wash water is added to a fresh concrete mix, further reacts with the cement in the mix to produce further carbon dioxide-sequestering products. In certain embodiments, the carbon dioxide added to the wash water results in products in the wash water that account for at least 1, 2, 5, 7, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, or 90% carbon dioxide by weight cement (bwc) in the wash water, and/or not more than 2, 5, 7, 10, 12, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 95, or 100% carbon dioxide by weight cement (bwc) in the wash water.

[0182] Embodiments include applying CO₂ immediately after the wash water is generated, in a tank, and/or as the grey water is being loaded for batching.

[0183] Alternatively or additionally, carbonation of grey (wash) water can allow use of aged wash water as mix water, for example, wash water that has aged at least 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 days.

[0184] The source of the carbon dioxide can be any suitable source. In certain embodiments, some or all of the carbon dioxide is recovered from a cement kiln operation, for example, one or more cement kiln operations in proximity to the concrete production facility, e.g., one or more cement kiln operations that produce cement used in the concrete production facility. In certain embodiments, wash water is transported from a concrete wash station or similar facility where concrete wash water is produced, to a cement kiln, or a power plant and flue gas from the cement kiln or power plant is used to carbonate the wash water. Carbon dioxide concentrations in cement kiln flue gas or power plant flue gas may be sufficient that no additional carbon dioxide is needed to carbonate the wash water; it is also possible that the flue gas need not be completely treated before exposure to wash water; i.e., it will be appreciated that cement kiln and power plant flue gas, in addition to containing carbon dioxide, may also contain SO_x, NO_x, mercury, volatile organics, and other substances required to be removed, or brought to an acceptable level, before the flue gas is released to the atmosphere. In certain embodiments, the flue gas is treated to remove one or more of these substances, or bring them to acceptable levels, before it is exposed to the wash water. In certain embodiments, one or more of these substances is left in the flue gas as it contacts the wash water, and after contacting the wash water the amount of the substance in the flue gas is reduced, so that further treatment for that substance is decreased or eliminated. For example, in certain embodiments, the flue gas comprises SO_x, and treatment of the wash

- water with the flue gas decreases the amount of SO_x in the flue gas (e.g., by formation of insoluble sulfates) so that the flue gas after wash water treatment requires decreased treatment to remove SO_x, or no treatment. Additionally or alternatively, one or more of NO_x, volatile organics, acids, and/or mercury may be decreased in the flue gas by contact
- 5 with wash water so that the need for treatment of the flue gas for the substance is reduced or eliminated. After treatment with the flue gas, the carbonated wash water may be transported to a concrete production facility, either the same one where it was produced and/or a different one, and used in producing concrete at the facility, e.g., used as an admixture, e.g., to reduce cement requirements in the concrete due to the cement in the wash water.
- 10 **[0185]** The wash water may be monitored, e.g., as it is being carbonated. Any suitable characteristic, as described herein, may be used to determine whether to modify carbon dioxide delivery to the wash water. One convenient measurement is pH. For example, in certain embodiments, a carbonated wash water of pH less than 8.0, 7.9, 7.8, 7.7, 7.6, 7.5, 7.4, 7.3, 7.2, 7.1, or 7.0 is desired, e.g., to be used as a mix water. The pH may be monitored and
- 15 brought to a suitable pH or within a suitable range of pHs before, e.g., its use as a mix water. For example, the pH can be at least 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, or 8.5, and/or not more than 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, 8.5, 8.7, 9.0, 9.3, 9.5, 9.7, 10, 10.3, 10.5, 10.7, 11.0, 12.0, or 13.0.
- 20 **[0186]** In addition, it is desirable that gas flow in a wash water, e.g., in a holding tank, not be increased to a level high enough that the rate of supply exceeds the rate of absorption/reaction; if this occurs, typically, bubbles will be observed at the surface of the wash water. If the rate of supply is equal to or less than the rate of absorption/reaction, then no bubbles are observed at the surface of the wash water. The rate of absorption and reaction
- 25 may change with time, for example, decreasing as more of particles react or become coated with reaction products. Thus, appearance of bubbles may be used as an indicator to adjust carbon dioxide flow rate, and an appropriate sensor or sensors may be used to determine whether or not bubbles are appearing. Alternatively, or additionally, carbon dioxide content of the air above the surface of the wash water may be monitored using appropriate sensor or
- 30 sensors and be used as a signal to modulate delivery of carbon dioxide to the wash water, e.g., slow or stop delivery when a certain threshold concentration of carbon dioxide in the air above the surface is reached. Rate of change of concentration can also be used as an indicator to modulate flow rate of carbon dioxide.

[0187] Bubble formation, in particular, is to be minimized or avoided, because in a tank where water is agitated to prevent settling of solids, it is desired to use the minimum amount of energy to cause the water to move in a pattern with sufficient motion that solids remain suspended; bubbles, which automatically rise to the surface no matter where they are in the overall flow pattern of the tank, can disrupt the flow, and cause more energy to be required for sufficient agitation. In a holding tank in which, e.g., an auger is used for agitation, systems of the invention may pull water from the tank into a recirculation loop where carbon dioxide is introduced. The rate of introduction, length of the loop, and other relevant factors are manipulated so that carbon dioxide is absorbed into the water and/or reacts with constituents of the water before it's released back into the tank. The carbon dioxide can be input into the loop near or at the start of the loop, so that there is maximum distance for the carbon dioxide to be absorbed and/or react. It is also advantageous to inject the carbonated water at a downward location in the tank.

[0188] Additional characteristics that can be useful to monitor include temperature of the wash water (reaction of carbon dioxide with cement products is typically exothermic), ionic concentration of the wash water, electrical conductivity of the wash water, and/or optical properties of the wash water (e.g., it has been observed that carbon dioxide can change the color of the wash water). Appropriate sensors for one or more of these characteristics may be included in an apparatus of the invention. Other characteristics and sensors are also appropriate as described herein.

[0189] Compositions include an apparatus for carbonating concrete wash water in a wash water operation that includes a source of carbon dioxide operably connected to a conduit that runs to a wash water container containing wash water from a concrete production site, where one or more openings of the conduit are positioned to deliver carbon dioxide at or under the surface of wash water in the container, or both, and a system to transport the carbonated wash water to a concrete mix operation where the carbonated wash water is used as mix water in a concrete mix, e.g. a second conduit that can be positioned to remove carbonated wash water from the wash water container and transport it to a concrete mix operation, where the carbonated wash water is used as part or all of mix water for concrete batches. Generally, the carbon dioxide will be delivered directly to the wash water tank as described elsewhere herein, though in some embodiments carbonation may occur outside the tank and the carbonated water returned to the tank. The apparatus may further include a controller that determines whether or not to modify the delivery of carbon dioxide based at least in part on one or more characteristics of the wash water or wash water operation. The characteristics

may include one or more of pH of the wash water, rate of delivery of carbon dioxide to the wash water, total amount of wash water in the wash water container, temperature of the wash water, specific gravity of the wash water, concentration of one or more ions in the wash water, age of the wash water, circulation rate of the wash water, timing of circulation of the wash water, bubbles on surface, carbon dioxide concentration of air above surface, optical properties, electrical properties, e.g., conductivity, or any combination thereof. One or more sensors may be used for monitoring one or more characteristics of the wash water; additionally, or alternatively, manual measurements may be made periodically, e.g., manual measurements of specific gravity, pH, or the like. The apparatus may further comprise one or more actuators operably connected to the controller to modify delivery of carbon dioxide to the wash water, or another characteristic of the wash water, or both. The apparatus may include a system for moving the wash water, such as by circulating or agitating the wash water, either continuously or intermittently. The composition may further include a delivery system for delivering carbon dioxide to the source of carbon dioxide, where some or all of the carbon dioxide is derived from a cement kiln operation in proximity to the concrete production site, for example, a cement kiln operation that produces some or all of cement used in the concrete production site.

[0190] In certain embodiments, solids are removed from the carbonated wash water, for example, by filtration. These solids, which mostly comprise carbonated cement particles, can be further treated, e.g., dried. The dried solids can then be, e.g., re-used in new concrete batches.

Carbonation of wash water in ready-mix truck, reclaimer, and/or lines.

[0191] In certain embodiments, concrete wash water is carbonated directly in the drum of a ready-mix truck and/or before it reaches a holding tank, e.g., during cycling in a reclaimer, or in the line between a reclaimer and a holding tank.

[0192] In a typical operation, a ready-mix truck is loaded at a batching facility; the load may be a partial load or a full load. A full load may be several cubic meters, e.g., 8 m³, depending on the size of the truck. However, regardless of the size of the load, a large portion, in some cases virtually all, of the drum and interior components of the drum (e.g., fins, etc.), come in contact with the wet cement. The load is then released at the job site and the truck returns to a wash facility, usually at the batching facility, where it is cleaned prior to further batching. After the load is released at the job site, a certain amount of water that is carried in containers on the truck (typically called saddlebags) can be released into the truck and mixed in the truck at the site and during the trip back to the wash station, to prevent the wet concrete from

hardening during the time before the truck is cleaned at the wash station. Additional water is then introduced into the drum at the wash station, with spraying and mixing to thoroughly clean the interior of the drum, and the resultant wash water is then either dumped, or, more commonly, sent to one or more tanks to be treated prior to disposal and/or reuse.

5 [0193] Typically, around 100-160 (e.g., 120) L wash water/m³ of concrete is used to wash the truck; however, as stated, since partial loads result in a coating of the empty truck that is a greater part of the truck than the proportion of the load to a full load, and in some cases result in a completely coated empty truck drum, in some cases in which there has been a partial load a more realistic estimate of the amount of water needed is larger than the 120L/m³ of
10 concrete. For example, if the total capacity of the truck is 8 m³ and a 4 m³ load is delivered, it is possible that the amount of wash water will be greater than 4 x 120 L, perhaps as much as that used for a full load, e.g., 8 x 120 L or 960 L. For any particular operation, the amount of water needed for a particular size load and mix type is generally known and can be used in any calculations required.

15 [0194] In some facilities, a reclaimer is used to separate out aggregate (e.g., sand and gravel) from the wash water, generally for reuse in further concrete batches. The remainder of the wash water is generally sent to a settlement pond to settle out further solids, or, alternatively, it is pumped into a slurry tank where it is kept suspended with paddles and diluted to a specific gravity and otherwise treated so that at least some of the water may be used again in
20 concrete production. In a conventional reclaimer process, not all of the treated wash water produced can be reused, e.g. in concrete, and the overflow is sent to a holding pond, where it is disposed of in the conventional manner.

[0195] In certain embodiments, provided herein are methods and compositions for carbonating wash water in a system that includes a reclaimer, i.e., a system that includes a
25 mechanism for removing aggregate from wash water. The methods and compositions can be used to create a de novo system, but are advantageously also used in retrofits of existing systems. Generally, in a reclaimer system, wash water is passed through an apparatus to remove a portion of the aggregate and other solids in the wash water; an exemplary system is a rotating perforated drum from which treated wash water, with a lower proportion of solids,
30 is sent to a holding tank. As a new truck comes in to be cleaned, water can be provided to wash the truck drum and/or other components, for example, with a portion or all of the water coming from the holding tank. The drum and/or other components are washed, the washwater moves through a system to remove a portion of solids, then is sent back to the tank. In many systems, a recirculation loop is provided back from the tank to the system for

removing solids, so that water can have a plurality of passes through the solid-removing system. In certain embodiments, a portion of this recirculation line is used to carbonate the wash water. For example, a section of the line can be replaced with a system that comprises two conduits. The first is a conduit for the wash water and the second is a conduit, within the first conduit, to supply carbon dioxide to the wash water. In order to keep flow unimpeded, the first conduit can be of a larger diameter than the conduit leading up to and away from the carbonation section, i.e., the conduit used in the system before carbonation. For example, if the system uses a 2 inch-diameter conduit, the first conduit of the carbonation section may be more than 2 inch-diameter, for example, 3 inches. This is merely exemplary, and the diameter of the first conduit relative to the portion of conduit that is not in the carbonation section can be any suitable multiple of non-carbonation conduit, so long as flow through the first conduit is not impeded or not substantially impeded, e.g., so long as flow through the first conduit is sufficient for the purposes of the system. In general, unless otherwise indicated, diameters are outside diameters. For example, the diameter of the first conduit of the carbonation section can be at least 1.01, 1.02, 1.05, 1.07, 1.1, 1.12, 1.15, 1.17, 1.2, 1.25, 1.3, 1.35, 1.4, 1.45, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.2, 2.5, 3.0, 3.5, 4, 5, 6, 7, 8, or 9 times the diameter of the non-carbonation portion of conduit, e.g., the diameter of the recirculation conduit leading up to the carbonation section, and/or not more than 1.02, 1.05, 1.07, 1.1, 1.12, 1.15, 1.17, 1.2, 1.25, 1.3, 1.35, 1.4, 1.45, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.2, 2.5, 3.0, 3.5, 4, 5, 6, 7, 8 9, or 10 times the diameter of the non-carbonation portion of conduit, e.g., the diameter of the recirculation conduit leading up to the carbonation section, for example, 1.1-3x, or 1.2-2x, or 1.3-2x the diameter. In certain embodiments, the first conduit is 0.5-10 inches, or 1-8 inches, or 1.5-7 inches, or 1.5-5 inches, or 2-5 inches, or 2-4 inches in diameter. The first conduit may join the non-carbonation sections of the recirculation loop by any suitable fixture; in some embodiments, the first conduit is fitted to the non-carbonation conduit at its proximal and/or distal ends so that the low point (bottom) of the first conduit is even with, or not substantially offset from, the low point (bottom) of the non-carbonation conduit. Without being bound by theory it is thought that this arrangement wherein the centers of the conduits are offset but the low points are even or substantially even prevents settling or trapping of solids as the non-carbonation conduit expands into the first conduit. However, any suitable configuration that prevents or limits solid accumulation in the first conduit may be used.

[0196] The second conduit in the carbonation section is situated inside the first conduit, and supplies carbon dioxide gas to carbonate the wash water flowing through the first conduit. The second conduit is configured to allow carbon dioxide gas supplied in the second conduit

- to flow into the first conduit but not to allow wash water from the first conduit to flow into the second conduit. For example, the second conduit may be made of pliable material that comprises perforations that essentially act as one-way valves, closing off and not allowing water into the second conduit but allowing gas from the second conduit through into the first conduit when gas is supplied to the second conduit. A suitable number, diameter, and density of perforations may be used to allow carbonation of the wash water. The second conduit has a smaller diameter than the first conduit; any suitable diameter relative to the first conduit may be used so long as it is sufficient to allow transfer of carbon dioxide to the wash water flowing through the first conduit. Thus, in certain embodiments, the diameter of the second conduit is less than 0.99, 0.95, 0.9, 0.85, 0.8, 0.75, 0.7, 0.65, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, 0.3, 0.25, 0.2, 0.15, or 0.1 times the diameter of the first conduit, and/or more than 0.95, 0.9, 0.85, 0.8, 0.75, 0.7, 0.65, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, 0.3, 0.25, 0.2, 0.15, 0.1, or 0.05 times the diameter of the first conduit, for example, 0.1-0.9x, or 0.2-0.8x, or 0.3-0.7x the diameter of the first conduit. In certain embodiments the second conduit has a diameter of 0.2-5 inches, or 0.5-2 inches, or 0.5-1.5 inches. Appropriate fittings can be used to connect the second conduit to the first conduit, and to connect to further conduits that lead to a source of carbon dioxide gas; in some cases, a conduit leading from the second conduit leads to waste and in some cases a conduit can lead back to the source of carbon dioxide gas in order to recycle gas that is not taken up in a first pass.
- [0197] In embodiments in which a reclaimer system is retrofitted, a section of the recirculation line in the current system is removed and replaced with the first and second conduits, as described, appropriate fittings, a source of carbon dioxide, generally, appropriate sensors as described below, and, generally, a control system that receives information from the sensors and/or from sensors already present in the system, and that modulate delivery of carbon dioxide according to the information received. In retrofitted or de novo systems, the length of carbonation conduit section is any suitable length, such as at least 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 20, 25, 30, 40, or 50 feet, and/or not more than 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 15, 20, 25, 30, 40, 50, or 100 feet, such as 0.5-50 feet, or 1-20 feet, or 2-15 feet, or 5-15 feet.
- [0198] Thus the carbonation section of the recirculation loop between reclaimer and holding tank allows for carbonation of wash water without a large amount of additional apparatus, but merely by replacing a section of conduit with a carbonation section and installing appropriate sensors, control system, and source of carbon dioxide.

[0199] Generally, the system is configured to provide information regarding relevant parameters. Such information may be determined by sensors, human input, or any other suitable method. In certain embodiments, at least one, two, three, four, five, six, or all of the 1) operation of the pump for the recirculation loop (e.g., on/off and/or circulation rate); 2) the level of washwater in the holding tank; 3) temperature; 4) specific gravity, e.g., of wash water in the holding tank or other relevant area; 5) composition of solids in holding tank (e.g., cement vs. aggregate); 6) amount of new wash water received from incoming trucks or other sources; 7) carbon dioxide content of washwater in the carbonation section or in other areas (which can be monitored directly and/or indirectly); 8) flow rate of carbon dioxide sent to second conduit; 9) time of carbon dioxide flow; 10) type, amount, and/or timing of admixture addition, and any other suitable characteristics. Some or all of this information can be sent to a controller, which can process the information, compare it to pre-determined parameters, and send output to appropriate actuators to modulate the process. Actuators can include one, two, three or more of 1) one or more valves to regulate carbon dioxide flow, 2) one or more pumps to regulate washwater flow through recirculation section; 3) one or more systems to add admixture to the system; and any other suitable actuators. The control system can be tied into the overall control system for the reclaimer.

[0200] In operation, the system monitors appropriate characteristics of the wash water and adjusts carbon dioxide delivery accordingly, in order to carbonate the wash water to a desired level; generally, the desired level will be such that allows a higher specific gravity of treated wash water to be used in concrete production operations than could otherwise be used; in certain embodiment, it also allows less new cement to be used in subsequent batches of concrete because batches made with the carbonated washwater can have higher compressive strength than those made without carbonated wash water and, thus, less cement is needed to provide the same compressive strength. Thus, in a typical reclaimer system, wash water is produced that, with dilution with city water, is at a specific gravity of, e.g., 1.03 or less and can then be used in concrete. The present methods and compositions can produce wash water that requires less dilution before use in concrete production, for example, wash water that can be used in concrete production at a specific gravity of at least 1.02, 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.09, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19, or 1.2 and/or not more than 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.09, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19, 1.2, 1.25, 1.3, 1.4, or 1.5, for example, 1.03-1.25, or 1.04-1.2, or 1.05-1.15. In addition or alternatively, the present methods and compositions can produce wash water that, when used in subsequent batches of cement, allows the use of at least 0.5, 1, 1.5, 2, 2.5,

3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 20, 25, 30, 35, or 40%, and/or not more than 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 20, 25, 30, 35, 40, or 50% less cement than would be used without the use of carbonated wash water to produce concrete with the same or substantially the same compressive strength at, e.g., 1, 2, 7, 14, or 28 days, or at any other suitable time point. In addition, the use of carbonated wash water produced by the system can also allow less and/or different admixture to be used than would be required if non-carbonated wash water were used in a concrete batch.

[0201] Carbon dioxide can be introduced into the carbonation section at suitable time intervals, and at suitable flow rates and times, depending on conditions in the system. It is desirable that the rate of flow of carbon dioxide is such that little or no carbon dioxide is wasted, but any suitable flow rate may be used and/or time interval may be used to achieve the desired carbonation. In systems in which the carbonation section is new, or has not been used for a significant time, carbon dioxide can be added to bring the wash water currently present to the desired level of carbonation. Typically, so long as new wash water is not added, the wash water in the system will retain carbonation and require little or no “touch-up” carbon dioxide. In certain cases, admixture, such as one or more set retarders, for example a carbohydrate set retarder such as sodium gluconate, is added to the wash water. In these cases, not only is the amount of set retarder monitored, but the time interval from last addition may also be monitored; unlike carbonation, set retarders may require additional amounts to be added over time. For both carbon dioxide and admixture (if used), when additional, new, wash water is added, an appropriate amount of carbon dioxide and admixture (if used) is added. The amount of carbon dioxide to be added can depend on, e.g., specific gravity of the new wash water (directly measured and/or calculated from change in SG of wash water in system, e.g., in holding tank, or determined by any other suitable method), volume of wash water added (directly measured and/or calculated from change in level of wash water in system, e.g., in holding tank, or determined by any other suitable method), in some cases also determined by composition of wash water (e.g., percent solids as cementitious material vs. inert material such as aggregates; and by any other parameters. Addition of carbon dioxide is commenced and is halted at a suitable time, e.g., when the amount of carbon dioxide added reaches a predetermined amount, when one or more characteristics of the wash water indicate desired level of carbonation has been achieved, and/or by any other suitable method. The amount of admixture to be added can be determined by similar characteristics and can also be modified based on time from last

addition of admixture; in some cases additional admixture is added even if new wash water has not been added, based on time from previous addition.

[0202] A further advantage of the carbonation system is that it can allow the use of smaller holding tanks; in some cases, holding tanks can be eliminated altogether. In the latter case, in current setups trucks come in at the end of the day and the water must be held until the next day, to be treated and released and/or to be reused in additional batches. With carbonation, the wash water can be treated with carbon dioxide and/or admixture so that is ready to be batched, and stored, e.g., in the drums of the trucks themselves. In addition or alternatively, a smaller holding tank can be used and, in some retrofit embodiments, replacement of the current holding tank with a smaller one can be included in the retrofit.

[0203] An exemplary wash water control system is as follows:

Quantity of Cementitious Solids

CO₂ treatment targets are dependent on the quantity of cementitious solids contained within a reclaimer tank. This is a function of: Tank volume; Tank specific gravity (SG), or solids content; Solids characterization (fraction cement, fraction fly ash, fraction non-cementitious e.g. sand). Exemplary control protocols for determining quantity of cementitious solids contained in reclaimer tank are as follows:

1. Continuous measurement of reclaimer tank volume;
2. Semi-continuous measurement of reclaimer tank SG; and/or
3. Monitor all tank inflows and outflows (current sensors on all pumps providing infeed / drawing from reclaimer tank)

[0204] OPTION 1 assumes all material inflows can be monitored and measured. OPTION 2 assumes that this is not possible due to equipment limitations. Both options assume continuous monitoring of tank level.

[0205] OPTION 1: total volume and SG of all inflows are measured

4. For tank outflows: $TANK_SG(n) = TANK_SG(n-1)$

[0206] Where n is Tank SG following tank outflow, and $TANK_SG(n-1)$ is Tank SG prior to tank outflow. Previous SG setpoint is maintained in control logic.

5. For tank inflows: $TANK_SG(n) = VOL_TANK(n-1)*TANK_SG(n-1)/[VOL-TANK(n-1)*VOL_INFLOW] + VOL_INFLOW*INFLOW_SG/[VOL-TANK(n-1)*VOL_INFLOW]$

[0207] SG of inflows can be setpoints or measured. For example: If inflow is city water, SG setpoint would be 1; If inflow is a washout inflow, SG can be measured OR can be established as a setpoint.

[0208] New SG setpoint is established based on total volume and SG of inflow.

6. For both inflows and outflows:

$$\text{QUANTITY_SOLIDS}(n) = \text{TANK_SG}(n) * \text{VOL_TANK}(n)$$

$$\text{QUANTITY_CEMENTITIOUS_SOLIDS}(n) =$$

$$5 \quad \text{QUANTITY_SOLIDS}(n) * \%_CEMENTITIOUS_SOLIDS$$

[0209] Where $\%_CEMENTITIOUS_SOLIDS$ is a setpoint or continuously revised setpoint based on historical batch records or quantitative washout solids data. This can be further characterized as $\%_CEMENT$, $\%_FLYASH$, and $\%_SLAG$ depending on characterization requirements. $\%_CACO3$ will be discussed below.

10 [0210] OPTION 2: volume and SG of inflows not measured

[0211] Some systems do not allow for measurement of all material inflows (use gravity drainage or overflow from preceding unit operations to manage material flows).

7. For tank outflows: Same as (4) above.

8. For tank inflows: Tank SG is measured semi-continuously.

15 9. For both inflows and outflows: Same as (6) above.

[0212] **CO2 Treatment** Knowing quantity of cementitious solids within reclaimer tank, quantity of CO2 injected is determined based on the established setpoint. The setpoint will be described as **MASS_CACO3_CAO/MASS_CEMENT_CAO ratio** in the reclaimer system, which is described below.

20 [0213] **STARTUP SCENARIO:** Consider that, for a given reclaimer tank system, there is a known characterization of tank solids. For example:

- TANK_SG = 1.1
- VOL_TANK = 100,000 L

25 10. With Solids characterized (as pre-defined setpoint) as follows:

- MASS%_CEMENT (of solids fraction) = 80% → SG_CEMENT = 3.15
- MASS%_FLYASH (of solids fraction) = 10% → SG_FLYASH = 2.2
- MASS%_SLAG (of solids fraction) = 5% → SG_SLAG = 2.9
- MASS%_SAND (of solids fraction) = 5% → SG_SAND = 1.6
- 30 • MASS%_CACO3 (of solids fraction) = 0% → SG_CACO3 = 2.6

11. Conversion to vol% is required for TANK_SG conversion to solids content:

- $\text{VOL\%_CEMENT (of solids fraction)} = [0.8/3.15] / [0.8/3.15 + 0.1/2.2 + 0.05/2.9 + 0.05/1.6 + 0/2.6] = 72.6\%$
- 35 • $\text{VOL\%_FLYASH (of solids fraction)} = [0.1/2.2] / [0.8/3.15 + 0.1/2.2 + 0.05/2.9 + 0.05/1.6 + 0/2.6] = 13\%$

- VOL%_SLAG (of solids fraction) = 5%
- VOL%_SAND (of solids fraction) = 9%
- VOL%_CACO3 (of solids fraction) = 0%

- 5 12. Determine solids fraction of slurry in reclaimer tank using TANK_SG and %VOL_consituents:
- $SG_SOLIDS = [VOL\%_CEMENT*SG_CEMENT + VOL\%_FLYASH*SG_FLYASH + VOL\%_SLAG*SG_SLAG + VOL\%_SAND*SG_SAND + + VOL\%_CACO3*SG_CACO3]$
 - $SG_SOLIDS = [0.73*3.15 + 2.2*0.13 + 2.9*0.05 + 1.6*0.05 + 0*0] = 2.87$

10

13. Therefore,

- $MASS\%SOLIDS_TANK = [SG_SOLIDS*[TANK_SG -1]/[SG_SOLIDS -1]]/TANK_SG$
- $MASS\%SOLIDS_TANK = [2.87*[1.1-1]/[2.87-1]]/1.1 = 0.1395 = 13.95\%$

15

14. Therefore,

- $MASS\%_CEMENT = 0.8*0.1395 = 11.2\%$
- $KG_SLURRY = TANK_SG*VOL_TANK = 1.1*100,000 = 110,000\text{ KG}$
- $KG_CEMENT = 0.112*110,000 = 12,320\text{ KG}$

Other constituents:

- 20 • $KG_FLYASH = 1,534.5\text{ kg}$
- $KG_SLAG = 767.25\text{ kg}$
 - $KG_SAND = 767.25\text{ kg}$
 - $KG_WATER = 94,611$

[0214] With a known amount of cement in the system, the quantity of CO₂ injection required can be determined based on the stoichiometric reaction of CaO with CaCO₃.

25

[0215] Consider, using the above example, that the known quantity of cement has a known fraction of CaO.

[0216] The treatment system would then establish a target treatment level based on the target MASS_CACO3_CAO/MASS_CEMENT_CAO setpoint for the system.

30

[0217] Consider, using the above example, that the MASS_CACO3_CAO/MASS_CEMENT_CAO setpoint is 0.4.

16. Therefore, using above example:

- 35 • $KG_CAO = KG_CEMENT_CAO + KG_CACO3_CAO$
- $8,008 = KG_CEMENT_CAO + 0.4*KG_CEMENT_CAO$
 - $KG_CEMENT_CAO = 8,008/1.4 = 5,720\text{ KG}$
 - $KG_CACO3_CAO = 0.4*5,720 = 2,288\text{ KG}$
 - $KMOL_CACO3_CAO = 2,288/56.08 = 40.8\text{ KMOL}$

17. Therefore, using stoichiometry of reaction $\text{CO}_2 + \text{CaO} = \text{CaCO}_3$ and molar mass of CO_2 (44.01):

- Where $\text{KMOL}_{\text{CO}_2} = \text{KMOL}_{\text{CAO}}$
- 5 • $\text{KG}_{\text{CO}_2} = \text{KMOL}_{\text{CO}_2} * 44.01 = 40.8 * 44.01 = 1,795.6 \text{ KG}$

[0218] In this example, 1,795.6 CO_2 is required to treat to desired level.

18. Resulting solids characterization:

Resulting solids characterization is as follows for this example, where (n) is post-treatment, n-1 is pre-treatment with CO_2 .

- 10 • $\text{KG}_{\text{CEMENT}}(n) = \text{KG}_{\text{CEMENT}}(n-1) - \text{KG}_{\text{CACO}_3\text{CAO}}(n) = 12,320 - 2,288 = 10,032 \text{ KG}$
- $\text{KG}_{\text{FLYASH}}(n) = \text{KG}_{\text{FLYASH}}(n-1) = 1,534.5 \text{ KG}$
- $\text{KG}_{\text{SLAG}}(n) = \text{KG}_{\text{SLAG}}(n-1) = 767.25 \text{ KG}$
- 15 • $\text{KG}_{\text{SAND}}(n) = \text{KG}_{\text{SAND}}(n-1) = 767.25 \text{ KG}$
- $\text{KG}_{\text{CACO}_3}(n) = \text{KG}_{\text{CACO}_3}(n-1) + \text{KG}_{\text{CO}_2} + \text{KG}_{\text{CACO}_3\text{CAO}}(n) = 0 + 1795.6 + 2,288 = 4,083 \text{ KG}$

19. Resulting $\text{MASS\%}_{\text{XX}}$ (of solids fraction) is determined:

- 20 • $\text{MASS\%}_{\text{CEMENT}}(n) = 58.4\%$
- $\text{MASS\%}_{\text{FLYASH}}(n) = 9\%$
- $\text{MASS\%}_{\text{SLAG}}(n) = 4.4\%$
- $\text{MASS\%}_{\text{SAND}}(n) = 4.4\%$
- 25 • $\text{MASS\%}_{\text{CACO}_3}(n) = 23.8\%$

AND solids% =

- $\% \text{SOLIDS}_{\text{TANK}} = (10,032 + 1534.5 + 767.25 + 767.25 + 4,083) / [(10,032 + 1534.5 + 767.25 + 767.25 + 4,083) + 94,611] = 15.4\%$

30 STEADY-STATE SCENARIO:

[0219] Consider the above example, now comprising a fraction of solids as CaCO_3 , with known inflow material characterization from truck washouts as follows:

- $\text{MASS\%}_{\text{CEMENT}}$ (of solids fraction) = 80% → $\text{SG}_{\text{CEMENT}} = 3.15$
- $\text{MASS\%}_{\text{FLYASH}}$ (of solids fraction) = 10% → $\text{SG}_{\text{FLYASH}} = 2.2$
- 35 • $\text{MASS\%}_{\text{SLAG}}$ (of solids fraction) = 5% → $\text{SG}_{\text{SLAG}} = 2.9$
- $\text{MASS\%}_{\text{SAND}}$ (of solids fraction) = 5% → $\text{SG}_{\text{SAND}} = 1.6$
- $\text{MASS\%}_{\text{CACO}_3}$ (of solids fraction) = 0% → $\text{SG}_{\text{CACO}_3} = 2.6$

And consider a scenario for which the following daily operating parameters are known

/measured:

- TANK_SG (end of day) = 1.12
- VOL_TANK = 98,000 L
- 5 • VOL_SLURRY_OUTFLOW = 20,000 L (measured and monitored through batching of concrete)
- VOL_WATER_INFLOW = 10,000 L (monitoring of city / fresh water inflows to reclaimer tank)

Assuming steady-state material balance in reclaimer tank at beginning of operating day as

10 established in previous example:

- MASS%_CEMENT(n) (of solids fraction) = 58.4%
- MASS%_FLYASH (n) (of solids fraction) = 9%
- MASS%_SLAG (n) (of solids fraction) = 4.4%
- MASS%_SAND (n) (of solids fraction) = 4.4%
- 15 • MASS%_CACO3 (n) (of solids fraction) = 23.8%

20. Therefore, using SG_SOLIDS calculations as above:

- SG_SOLIDS_TANK ($n-1$) = 2.85

20 Where $n-1$ is SG_SOLIDS_TANK and beginning of operating day

21. Therefore, using Volume balance and SG_SOLIDS calculations as above:

- VOL_SLURRY_INFLOW = VOL_TANK(n) - [VOL_TANK($n-1$) + VOL_WATER_INFLOW - VOL_SLURRY_OUTFLOW]
- 25 = 98,000 - [100,000 + 10,000 - 20,000] = 8,000 L

22. From Steps (10) to (12) above:

- SG_SOLIDS_SLURRY_INFLOW = 2.87
- 30 • SG_SOLIDS_TANK ($n-1$) = 2.85
- SG_WATER_INFLOW = 1

Therefore, Volume of original slurry from beginning of day with SG 1.1 is:

- VOL_SLURRY($n-1$) = 100,000 - 20,000 = 80,000 L → SG 1.1

Including inflows:

- 35 • VOL_WATER_INFLOW = 10,000 L → SG 1
- VOL_SLURRY INFLOW = 8,000 L → SG UNKNOWN

23. With SG measurement of 1.12, it follows:

- $SG_TANK(n) = [VOL_SLURRY(n-1)*SG_SLURRY(n-1) + VOL_WATER_INFLOW*SG_WATER + VOL_SLURRY_INFLOW*[SG_SLURRY_INFLOW]/[VOL_TANK(n)]$
- $1.12 = [80,000*1.1 + 10,000*1 + 8,000*SG_SLURRY_INFLOW]/98,000$
- 5 • $SG_SLURRY_INFLOW = 1.47$

24. With SG of slurry inflows calculated at 1.47, it follows from (13) above:

- $MASS\%_SOLIDS_SLURRY_INFLOW = [2.87*[1.47-1]/[2.87-1]]/1.47 = 0.49 = 49\%$

10 25. Therefore, from (14) above:

- $MASS\%_CEMENT = 0.8*0.49 = 39.2\%$
- $KG_SLURRY = SG_SLURRY_INFLOW*VOL_SLURRY_INFLOW = 1.47*8,000 = 11,760 \text{ KG}$
- $KG_CEMENT = 0.392*11,760 = 4,609.9 \text{ KG}$

15 Other constituents:

- $KG_FLYASH = 576.24 \text{ kg}$
- $KG_SLAG = 288.1 \text{ kg}$
- $KG_SAND = 288.1 \text{ kg}$

20 26. From 15 above, CEMENT_CAO_IN is determined as follows:

- $KG_CEMENT_CAO = KG_CEMENT*0.65 = 4,609.9*0.65 = 2,996.4 \text{ KG}$

25 27. New material balance is then determined at end of operating day, prior to treatment of reclaimer tank with CO₂ using balance of inflows and outflows. For this example, resulting balance is as follows:

- OUT

- 30 • $KG_CEMENT = 10,032 - (20,000 \text{ L})*(1.1 \text{ KG/L})*0.154*0.584 = 8,053 \text{ KG}$
- $KG_FLYASH = 1,534.5 - (20,000 \text{ L})*(1.1 \text{ KG/L})*0.154*0.09 = 1,229.6 \text{ KG}$
- $KG_SLAG = 614.8 \text{ KG}$
- $KG_SAND = 614.8 \text{ KG}$
- $KG_CACO3 = 4,083 \text{ KG} - 806.34 = 3,276.7 \text{ KG}$
- $KG_WATER = 94,611 - (20,000 \text{ L})*(1.1 \text{ KG/L})*(1-0.154) = 75,999 \text{ KG}$

35

+IN

- $KG_CEMENT = 8,053 + 4,609.9 = 12,692.9 \text{ KG}$
- $KG_FLYASH = 1,229.6 + 576.24 = 1,805.84 \text{ KG}$

- $\text{KG_SLAG} = 614.8 \text{ KG} + 288.1 \text{ KG} = 902.9 \text{ KG}$
- $\text{KG_SAND} = 614.8 \text{ KG} + 288.1 \text{ KG} = 902.9 \text{ KG}$
- $\text{KG_CACO}_3 = 3,276.7 + 0 \text{ KG} = 3,276.7 \text{ KG}$
- $\text{KG_WATER} = 75,999 + 10,000 + (8,000 \text{ L}) * (1.47 \text{ KG/L}) * (1-0.49) = 91,996 \text{ KG}$

5

28. $\text{MASS_CACO}_3\text{_CAO}/\text{MASS_CEMENT_CAO}$:

Using molar mass of CaO (56.08) and CaCO₃ (100.9), it follows:

- 10
- $\text{MASS_CACO}_3\text{_CAO} = 3,276.7 \text{ KG} * (56.08/100.9) = 1,821.2 \text{ KG}$

Using CAO_fraction (Cement) for cement as a constant = 65% (as (15) above):

- $\text{MASS_CEMENT_CAO} = 12,692.9 \text{ KG} * 0.65 = 8,250.4 \text{ KG}$

Therefore ratio is:

15 $\text{MASS_CACO}_3\text{_CAO}/\text{MASS_CEMENT_CAO} = 1821.2/8250.4 = 0.22$

$\text{TOTAL_CAO} = 1821.2 + 8250.4 = 10,071.6$

29. If desired ratio is **0.4** it follows from (16) above that the amount of KG_CACO₃_CAO is 2,877.4. With 1,821.2 KG CAO already present as CACO₃_CAO, the net amount of CAO required for reaction is $2,877.4 - 1,821.2 = 1,056.2 \text{ KG} = 18.83 \text{ KMOL}$.

20

30. Using stoichiometry as in (17) and (18) above, the required amount of CO₂ for reaction to the desired setpoint is:

- 25
- Where $\text{KMOL CO}_2 = \text{KMOL CAO}$
 - $\text{KG_CO}_2 = \text{KMOL_CO}_2 * 44.01 = 18.83 * 44.01 = 828.7 \text{ KG}$

In this example, 828.7 KG of CO₂ is required to treat to desired level.

31. Resulting solids characterization:

Resulting solids characterization is as follows for this example, where (n) is post-treatment,

30 n-1 is pre-treatment with CO₂.

- 35
- $\text{KG_CEMENT}(n) = \text{KG_CEMENT}(n-1) - \text{KG_CACO}_3\text{_CAO_NET}(n) = 12,692.9 - 1,056.2 = 11,636.7 \text{ KG}$
 - $\text{KG_FLYASH}(n) = \text{KG_FLYASH}(n-1) = 1,805.84$
 - $\text{KG_SLAG}(n) = \text{KG_SLAG}(n-1) = 902.9 \text{ KG}$
 - $\text{KG_SAND}(n) = \text{KG_SAND}(n-1) = 902.9 \text{ KG}$
 - $\text{KG_CACO}_3(n) = \text{KG_CACO}_3(n-1) + \text{KG_CO}_2 + \text{KG_CACO}_3\text{_CAO}(n) = 3,276.7 + 828.7 + 1056.2 = 5,161.6 \text{ KG}$

32. Resulting MASS%_XX (of solids fraction) is determined:

- MASS%_CEMENT(*n*) = 57.0%
- 5 • MASS%_FLYASH (*n*) = 8.8%
- MASS%_SLAG (*n*) = 4.4%
- MASS%_SAND (*n*) = 4.4%
- MASS%_CACO3 (*n*) = 25.3%

AND solids% =

- 10 • %SOLIDS_TANK = (11,636.7 + 1805.84 + 902.9 + 902.9 + 5161.6) / [(11,636.7 + 1805.84 + 902.9 + 902.9 + 5161.6) + 91,966] = 18.2%

[0220] This Tank Solids characterization now becomes the new beginning of day material balance for the following day of operation at the concrete plant.

- 15 [0221] Additional or alternative scenarios are as follows:

An exemplary method for monitoring and controlling the reaction mechanism of CO₂ with concrete washwater slurry is as follows. Concrete wash water slurry with a known specific gravity / solids content and cementitious fraction of solids content can be treated with carbon dioxide to produce nano-calcium carbonate. Without being bound by theory, the reaction

20 mechanism is dependent on a number of factors, including: 1) Ionic calcium concentration, or the amount of free calcium in solution; 2) Rate of carbon dioxide injection; 3) Residence time of reaction.

[0222] Relative impact and mechanistic control strategy for each element is described below.

- 25 **1) Ionic Calcium:** Hydrating and hydrated portland cement is known to contain Calcium hydroxide (Ca(OH)₂), which dissociates in water to release Ca²⁺ ions in solution (as well as OH⁻), resulting in a caustic solution. Solubility of Ca(OH)₂ decreases with increasing temperature. Data presented as saturated solubility in grams per 100 grams of water.

T (deg C)	CaO	Ca(OH) ₂
0	0.140	0.185
10	0.133	0.176
20	0.125	0.165
25	0.120	0.159
30	0.116	0.153

40	0.106	0.140
50	0.097	0.128
60	0.088	0.116
70	0.079	0.104
80	0.070	0.092
90	0.061	0.081
100	0.054	0.071

[0223] Carbon dioxide reacts with the calcium oxide portion in cement / calcium hydroxide to create calcium carbonate. Without being bound by theory, in a slurry, the two CO₂

mineralization mechanisms are believed to occur are as follows: a) **Pathway 1:** Reaction of carbon dioxide with free calcium ions in solution and OH⁻ to form discrete nano-calcium

- 5 carbonate in solution (solution mechanism); b) **Pathway 2:** Reaction of carbon dioxide with cement solids to form calcite crystals on the surface of cement particles (surface reaction mechanism) The reaction pathway may be controlled by predicting the ionic calcium concentration in the wash water slurry and subsequently controlling the rate of carbon dioxide injection for a given residence time of reaction. **2) Rate of Carbon Dioxide**

- 10 **Injection:** The rate of carbon dioxide injection can be managed and controlled to ensure (1) maximum reaction efficiency and (2) targeted control of the reaction between carbon dioxide and calcium.

[0224] The rate of reaction of Pathway 1 as described above is hypothesized to be faster than Pathway 2. Further, the Pathway 1 reaction is hypothesized to be more predictable than

- 15 Pathway 2, and to create a more predictable product in the form of “free” nano-calcium carbonate. This can lead to higher reaction efficiencies, enhanced control and consistency in the application of produced nano-calcium carbonate, and greater predictability in the hydration characteristics and kinetics of the remaining cementitious fines. Consequently, a method for controlling the rate of carbon dioxide injection and method of reaction based on
20 predicted ionic calcium concentration, carbon dioxide bubble size, and reaction length can be created.

[0225] As described previously, the injection apparatus used for this application is comprised of a section of pipe length (the “injection length”, first conduit as described previously) installed as a sub-section of a longer conduit that has an inner diameter suitable to
25 allow for the insertion of a length of perforated expandable fine bubble expanding hose (second conduit as described previously), examples of which are used to create nano-bubbles

- such as for water oxygenation in fish farming/aquaculture applications. This method ensures an even distribution of nano-bubbles across the entire injection length. An increase in inner diameter of the pipe section accounts for lost volume due to the insertion of the expanding bubble hose, as well as the addition of CO₂ via injection. Alternately, the diameter can be
- 5 sized to slow the fluid velocity and hence increase the residence time that the slurry has in direct contact with the bubbled CO₂. The pressure drop (high-to-low) at the inlet of the injection length can encourage interruption in laminar flow in the preceding pipe section and results in turbulence, which encourages effective mixing of slurry with the injected CO₂.

Scenario Example

- 10 [0226] Consider a slurry with the following properties flowing through an 11-metre length of 2" I.D. pipe at 160 Gallons per Minute or GPM (equivalent to 607 litres per minute or LPM). CO₂ injection begins at injection length 0-metres and ends at injection length 1-metre in a 3" section of pipe. Outer diameter of the expanding bubble hose is 1 inch. CO₂ is injected evenly across said injection length using the injection mechanism described above. This is
- 15 followed by 10-metres of contained reaction length flow prior to discharge to the atmosphere and into a recirculation through.

SG_Slurry: 1.1

Temp_Slurry: 20 degrees Celsius

- 20 SG_Cement: 3.15

SG_FlyAsh: 2.2

Cement_fraction of solids (vol%): 85%

FlyAsh_fraction of solids: (vol%): 15%

- 25

Determination of Solids Content of Slurry:

%Solids = [(SG_Cement*Cement_fraction +

SG_FlyAsh*FlyAsh_fraction)]*[(SG_Slurry - 1)/((SG_Cement*Cement_fraction +

SG_FlyAsh*FlyAsh_fraction)-1)]/(SG_Slurry)

- 30

%Solids = 13.6%

%Water = 86.4%

Volume of slurry and CO₂ in injection length:

$$\text{slurry_flowrate} = [(160 \text{ gal/min}) * (3.7854 \text{ L/gal}) * (1\text{min}/60 \text{ sec})] = 6.3 \text{ L/s}$$

$$\text{CO}_2\text{_flowrate} = (100 \text{ L/min}) * (1\text{min}/ 60 \text{ sec}) = 1.6 \text{ L/s}$$

5

$$\text{volumetric flow ratio}_{\text{slurry}/\text{CO}_2} = \text{vol_slurry} / \text{vol_CO}_2$$

$$\text{volumetric flow ratio}_{\text{slurry}/\text{CO}_2} = 6.3 \text{ L/s} / 1.6 \text{ L/s}$$

$$\text{volumetric flow ratio}_{\text{slurry}/\text{CO}_2} = 3.9375$$

$$\text{volumetric flow ratio}_{\text{CO}_2/\text{slurry}} = 0.2540$$

10

$$2\text{-inch pipe_cross_sectional_area} = \pi * (d/2)^2$$

$$2\text{-inch pipe_cross_sectional_area} = \pi * [(2 \text{ in} * 0.0254 \text{ m/in})/2]^2$$

$$2\text{-inch pipe_cross_sectional_area} = 0.002027 \text{ m}^2$$

15

$$3\text{-inch pipe_cross_sectional_area} = \pi * (d/2)^2$$

$$3\text{-inch pipe_cross_sectional_area} = \pi * [(3 \text{ in} * 0.0254 \text{ m/in})/2]^2$$

$$3\text{-inch pipe_cross_sectional_area} = 0.00456 \text{ m}^2$$

20

$$3\text{-inch pipe volume} = \text{pipe cross sectional area} * \text{pipe length}$$

$$3\text{-inch pipe volume} = \pi * [(3 \text{ in} * 0.0254 \text{ m/in})/2]^2 * (1 \text{ m})$$

$$3\text{-inch pipe volume} = 0.00456 \text{ m}^3 = 4.56 \text{ L}$$

$$\text{expanding bubble hose volume} = \text{hose cross section} * \text{hose length}$$

25

$$\text{expanding bubble hose volume} = \pi * [(1 \text{ in} * 0.0254 \text{ m/in})/2]^2 * (1 \text{ m})$$

$$\text{expanding bubble hose volume} = 0.000507 \text{ m}^3 = 0.507 \text{ L}$$

$$\text{injection_length_volume_available} = \text{pipe volume} - \text{hose volume}$$

$$\text{injection_length_volume_available} = 4.56 \text{ L} - 0.507 = 4.05 \text{ L}$$

30

$$\text{injection_length_volume_available} = \text{vol_slurry} + \text{vol_CO}_2$$

$$\text{where: vol_CO}_2 = 0.2540 * \text{vol_slurry}$$

$\text{injection_length_volume_available} = \text{vol_slurry} + 0.254 * \text{vol_slurry}$
 $\text{injection_length_volume_available} = \text{vol_slurry} * (1 + 0.2540)$
 $\text{vol_slurry} = \text{injection_length_volume_available} / (1 + 0.2540)$
 5 $\text{vol_slurry} = (4.05 \text{ L}) / (1 + 0.2540)$
 $\text{vol_slurry} = 3.23 \text{ L}$

$\text{CO2_volume} = \text{vol_slurry} * \text{Volumetric flow ratio}_{\text{CO2/slurry}}$
 $\text{CO2_volume} = (3.23 \text{ L}) * 0.2540$
 10 $\text{CO2_volume} = 0.820 \text{ L}$

$\text{slurry_mass} = \text{slurry volume} * \text{slurry specific gravity}$
 $\text{slurry_mass} = 3.23 \text{ L} * 1.1 \text{ kg/L}$
 $\text{slurry_mass} = 3.55 \text{ kg}$

15 $\text{water_fraction} = \text{slurry mass} * \text{water fraction of slurry}$
 $\text{water_fraction} = 3.55 \text{ kg} * 0.864$
 $\text{water_fraction} = 3.07 \text{ kg} = 3.07 \text{ L}$

20

Slurry velocity change in pipe:

For 2-inch diameter section prior to injection:

25 $\text{slurry_flowrate} = 6.3 \text{ L/s} = 0.0063 \text{ m}^3/\text{s}$
 $\text{pipe_cross_sectional_area} = 0.002027 \text{ m}^2$

$\text{slurry velocity in 2-in pipe} = \text{slurry_flowrate} / \text{pipe_cross_sectional_area}$
 $\text{slurry velocity in 2-in pipe} = 0.0063 \text{ m}^3/\text{s} / 0.002027 \text{ m}^2$
 30 $\text{slurry velocity in 2-in pipe} = 3.11 \text{ m/s}$

For 3-inch diameter section where injection occurs:

$\text{slurry_flowrate} = [(160 \text{ gal/min}) * (3.7854 \text{ L/gal}) * (1 \text{ min} / 60 \text{ sec})]$

$$\text{slurry_flowrate} = 6.3 \text{ L/s} = 0.0063 \text{ m}^3/\text{s}$$

$$\text{vol_slurry} = 3.23 \text{ L} = 0.00323 \text{ m}^3$$

$$\text{effective_cross_sectional_area_slurry} = \text{slurry_volume} / \text{injection length}$$

$$\text{effective_cross_sectional_area_slurry} = 0.00323 \text{ m}^3 / 1\text{m} = 0.00323 \text{ m}^2$$

$$\text{slurry velocity in 3-in pipe} = \text{slurry_flowrate} / \text{effective_cross_sectional_area_slurry}$$

$$\text{slurry velocity in 3-in pipe} = 0.0063 \text{ m}^3/\text{s} / 0.00323 \text{ m}^2$$

$$\text{slurry velocity in 3-in pipe} = 1.95 \text{ m/s}$$

10

[0227] The slurry slows down in injection length which results in a pressure drop and encourages turbulence/disturbs laminar or plug flow. In another embodiment of the invention, a pitot tube sight glass assembly can be used to measure / monitor pressure drop across each pipe ID change.

15 [0228] *Slurry/CO₂ mixture velocity in 2-in pipe following injection length:* Assuming a negligible conversion of CO₂ within injection length (i.e. majority of reaction occurs in the 10-metres of 2-in pipe section to follow injection length)

$$\text{vol_flowrate_mixture} = \text{vol_flowrate_slurry} + \text{vol_flowrate_CO}_2$$

$$\text{vol_flowrate_mixture} = 6.3 \text{ L/s} + 1.6 \text{ L/s}$$

$$20 \quad \text{vol_flowrate_mixture} = 7.9 \text{ L/s} = 0.0079 \text{ m}^3/\text{s}$$

$$\text{2-inch pipe_cross_sectional_area} = 0.002027 \text{ m}^2$$

$$\text{slurry velocity in 2-in pipe} = \text{vol_flowrate_mixture} / \text{2-inch pipe}$$

$$25 \quad \text{_cross_sectional_area}$$

$$\text{slurry velocity in 2-in pipe} = 0.0079 \text{ m}^3/\text{s} / 0.002027 \text{ m}^2$$

$$\text{slurry velocity in 2-in pipe} = 3.9 \text{ m/s}$$

[0229] Increase in velocity results in pressure drop (high-to-low) in direction of flow when leaving 3-inch diameter injection length and entering the 2-inch diameter reaction length. In
30 another embodiment, additional venturis are installed along the reaction length to disrupt laminar / plug flow and encourage turbulence, thus increasing mixing and potentially the reaction efficiency.

[0230] Stoichiometric balance of Cao and CO₂:

[0231] CaO:

At 20 degrees celsius, the saturated solubility of Ca(OH)_2 in 100 grams water is 0.165 grams.

[0232] Therefore, it is predicted that there would be

$$\text{mass_Ca(OH)}_2 = \text{saturated solubility of Ca(OH)}_2 * \text{volume of solution}$$

$$\text{mass_Ca(OH)}_2 = (0.165 \text{ grams Ca(OH)}_2 / 100 \text{ grams}) * 3070 \text{ grams of solution}$$

5
$$\text{mass_Ca(OH)}_2 = 5.065 \text{ grams of Ca(OH)}_2 \text{ available in solution}$$

$$\text{moles_Ca(OH)}_2 = 5.065 \text{ g Ca(OH)}_2 / \text{molar mass of Ca(OH)}_2$$

$$\text{moles_Ca(OH)}_2 = 5.064 \text{ grams} / 74.093 \text{ g/mol}$$

$$\text{moles_Ca(OH)}_2 = 0.0684 \text{ moles}$$

10
$$\text{mass_Ca} = 0.0343 \text{ moles} * 40.08 \text{ g/mol Ca} = 2.74 \text{ grams Ca}$$

CO_2 :

$$\text{mass_CO}_2 = \text{mass of CO}_2 \text{ in injection length}$$

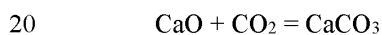
$$\text{mass_CO}_2 = \text{volume of CO}_2 \text{ in injection length} * \text{gas density}$$

15
$$\text{mass_CO}_2 = 0.820 \text{ L} * (1.98 \text{ g/L}) = 1.624 \text{ g}$$

$$\text{moles_CO}_2 = \text{mass CO}_2 / \text{molar mass CO}_2$$

$$\text{moles_CO}_2 = 1.624 \text{ g} / (44.01 \text{ g/mol}) = 0.0369 \text{ moles}$$

[0233] Simplified stoichiometric reaction of CO_2 with CaO is as follows:



[0234] The molar stoichiometric ratio ($\text{CaO}:\text{CO}_2$) is 1:1

For this example, this would indicate that the stoichiometric excess of CaO in solution

$$\text{is: stoichiometric_excess} = (\text{moles_Ca(OH)}_2 / \text{moles_CO}_2) - 1$$

$$\text{stoichiometric_excess} = (0.0684 \text{ moles} / 0.0369 \text{ moles}) - 1$$

25
$$\text{stoichiometric_excess} = +85.4\%$$

[0235] In this example, the reaction is expected to be controlled via Pathway 1, as the CO_2 is expected to react more readily / have a higher affinity for free calcium ions in solution, versus surface reaction with cement solids to form calcite crystals. For the purposes of this discussion, the reaction length that follows the injection length (10-metres), and based on the slurry flowrate, is assumed to provide a sufficient residence time to allow for 100% reaction efficiency - i.e., there would be no unreacted CO_2 discharged to the atmosphere at the end of the reaction length.

[0236] It is assumed that the replenishment rate of free calcium ions is low enough such that it can be deemed negligible in the reaction length (residence time = ~3-3.5 seconds in this

example). Free calcium replenishment will occur as a result of free calcium consumption / reaction with CO₂ during injection and subsequent reaction in the injection and reaction pipe, lowering CaO content below its saturated solubility point.

[0237] Free calcium can be predicted using solubility and flow characteristics, or alternatively it can be measured using a calcium ion sensor.

[0238] To provide further clarification of the proposed method of monitoring and controlling the incidence of Pathway 1 reaction vs Pathway 2 reaction, Let's consider the CO₂ flowrate that would equate to the stoichiometric equivalent of CaO in the reaction producing CaCO₃ :

10 stoichiometric_CO₂ = 0.0684 moles
 mass_CO₂ = 0.0684 moles *(44.01 g/mol CO₂) = 3.01 grams CO₂
 vol_CO₂ = 3.01 grams / (1.98 g/L) = 1.52 L
 vol_Slurry = 4.05 L - 1.52 L = 2.53 L
 Volumetric flow ratio (Vol_slurry/Vol_CO₂) = 2.53 L slurry / 1.52 L CO₂ = 1.664
 15 Stoichiometric_equivalent_CO₂_flowrate = slurry flow rate / volumetric flow
 ratio_{slurry/CO₂}
 Stoichiometric_equivalent_CO₂_flowrate = 6.3 L slurry/s / 1.664 L slurry/L CO₂
 Stoichiometric_equivalent_CO₂_flowrate = 3.79 L CO₂/s = 227 SLPM

[0239] This would indicate, based upon the specific inputs, that the maximum CO₂ flowrate
 20 allowed for stoichiometric reaction of free calcium ions in solution would be 227 SLPM. This
 does not address the required residence time following injection to achieve 100% reaction
 efficiency, which, as mentioned, would be dependent on rate of reaction and overall reaction
 length residence time.

[0240] In practice, a stoichiometric excess that maximizes the incidence of Pathway 1
 25 reaction vs Pathway 2 would be targeted. A method for determining extent of reaction (with
 respect to quantities of CO₂ consumed / CaCO₃ generated per pass) is described.

[0241] *g/s CaCO₃ generated per reaction pass:*

Assuming 100% reaction efficiency in the reaction length, and Pathway 1 reaction only, the
 amount of CaCO₃ generated during each pass using a CO₂ flowrate of 100 SLPM can be
 30 calculated. The Pathway 1 reaction is ensured by maintaining a target stoichiometric excess
 of CaO in solution (in this example 85.4% excess).

CO₂_flowrate = 100 SLPM

CO₂_flowrate = (100 L/min)*(1min/ 60 sec)

CO₂_flowrate = 1.6 L/s

$$\text{CO}_2_flowrate = 1.6 \text{ L/s} * (1.98 \text{ g/L}) = 3.168 \text{ g CO}_2/\text{s}$$

$$\text{rate_moles_CaCO}_3_generated = \text{CO}_2_flowrate * \text{molar_mass_CO}_2$$

$$\text{rate_moles_CaCO}_3_generated = 3.168 \text{ g/s} / (44.01 \text{ g/mol})$$

$$\text{rate_moles_CaCO}_3_generated = 0.0720 \text{ moles CO}_2/\text{s}$$

$$\text{moles_CaCO}_3_generated = \text{moles CO}_2 \text{ consumed}$$

$$\text{rate_CaCO}_3_generated = \text{moles_CaCO}_3_generated * \text{molar_mass_CaCO}_3$$

$$\text{rate_CaCO}_3_generated = 0.0720 \text{ moles CaCO}_3 * (100.0869 \text{ g/mol CaCO}_3)$$

$$\text{rate_CaCO}_3_generated = 7.21 \text{ grams CaCO}_3/\text{s}$$

[0242] For a given period of time, it can then be predicted the amount of nano-CaCO₃ generated “in-situ” in a washwater tank.

[0243] For a 10 hr overnight treatment period of an 80,000 L tank containing a slurry with a specific gravity of 1.1, for example, the mass CaCO₃ generated / CaCO₃ concentration would

be as follows:

$$\text{CaCO}_3_generated = 7.21 \text{ grams CaCO}_3/\text{s} * 3600 \text{ sec/hr} * 10 \text{ hr}$$

$$\text{CaCO}_3_generated = 259,560 \text{ grams}$$

$$\text{CaCO}_3_generated = 260 \text{ kg}$$

$$\text{slurry_mass_ (before treatment)} = \text{slurry_volume_ (before treatment)} * \text{slurry_specific_gravity}$$

$$\text{slurry_mass_ (before treatment)} = 80,000 \text{ L} * 1.1 \text{ kg/L}$$

$$\text{slurry_mass_ (before treatment)} = 88,000 \text{ kg}$$

$$\text{slurry_mass_ (after treatment)} = \text{slurry_mass_ (before treatment)} + \text{CaCO}_3_generated$$

$$\text{slurry_mass_ (after treatment)} = 88,000 \text{ kg untreated slurry} + 260 \text{ kg CaCO}_3$$

$$\text{slurry_mass_ (after treatment)} = 88,260 \text{ kg treated slurry}$$

Assuming the specific gravity of the slurry does not change,

$$\text{slurry_volume_ (after treatment)} = \text{slurry_mass_ (after treatment)} / \text{slurry_specific_gravity}$$

$$\text{slurry_volume_ (after treatment)} = 88,260 \text{ kg} / 1.1 \text{ kg/L}$$

$$\text{slurry_volume_ (after treatment)} = 80,236 \text{ L}$$

$\text{nano-CaCO}_3 \text{ concentration} = \text{CaCO}_3 \text{ _generated} / \text{slurry_volume_ (after treatment)}$

$\text{nano-CaCO}_3 \text{ concentration} = 260 \text{ kg CaCO}_3 / 80,236 \text{ L treated slurry}$

$\text{nano-CaCO}_3 \text{ concentration} = 3.23 \text{ g/L slurry}$

$\text{nano-CaCO}_3 \text{ concentration} = \sim 323 \text{ ppm}$

- 5 [0244] The incidence of reaction Pathway 1 vs Pathway 2 reaction can be identified by:

Monitoring free calcium concentration in solution via a calcium probe; evaluating particle size of an experimental slurry following controlled treatment.

- [0245] Consider a test that circulates slurry through an injection apparatus at a flowrate of 50 gallons per minute (GPM). In a mixing vessel of capacity 55 gallons the tank turnover is 55 gallons / 50 GPM = 1.1 min. The likelihood of short-circuiting is high in this system, so the control of Pathway 1 vs Pathway 2 reaction is difficult. Further, the replenishment rate of free calcium ions in solution is likely more than 1.1 minutes, especially as higher levels of treatment occur (CO₂ injection creates an exothermic reaction, and Ca(OH)₂ solubility drops with increased temperature).

- 15 [0246] At a commercial scale, following discharge to the atmosphere and into the recirculation conduit, the slurry will return to the washwater slurry tank. With proper management of tank infeed point for recirculation and tank out-feed point for CO₂ injection and reaction, short-circuiting of slurry is assumed to be negligible.

3) Reaction length of pipe / residence time of reaction

- 20 [0247] Using the scenario provided in the example, consider a system that monitors the energy inputs generated by the exothermic formation CaCO₃ (either Pathway 1 or Pathway 2). It is assumed that Pathway 1 reaction occurs at a much higher rate, and thus for a given length of pipe, at a greater efficiency than Pathway 2. Consequently, if CO₂ injection is controlled such that Pathway 1 is maintained, the incidence of over-injection with CO₂ (or 25 alternatively, a reduction in the required stoichiometric excess of free calcium ions in solution) can be observed by a loss in efficiency. This loss in efficiency can be observed by a reduction in exothermic reaction in a given pipe section, and from an operational / control level, this would be observed using temperature probes before / after injection and reaction. For this to be observed, it would be assumed that the residence time of reaction (in the 30 provided example, 3-3.5 seconds) would be low enough such that any ambient / environmental effects on slurry temperature would be negligible, and the only identifiable/measurable temperature change would result from the exothermic reaction.

[0248] A predictive model is provided, whereby MEASURED DEL-T can be changed to show the impact of variations of DEL-T on ACTUAL EFFICIENCY based on a theoretical calculation of 100% reaction efficiency. See Example 38.

[0249] Maintaining / controlling for Pathway 1 reaction results in a more predictable slurry in a concrete production environment. Predictability of cementitious solids in reclaimed washwater management systems is a significant challenge that impacts the rate of reuse in concrete production. This typically results in significant dilution of washwater to mitigate the impacts of hydration variability of cementitious solids on fresh properties of produced concrete. This in turn leads to a requirement to hold larger volumes in reclaimed washwater tanks, which then leads to larger sustained loads of solids and greater variability in age of cementitious solids contained in the reclaimer tank. With greater predictability in the hydration effects of cementitious solids, complemented by the “in-situ” generation of nano-calcium carbonate, the CO₂ treated washwater slurry can be used with little or no dilution, at higher replacement levels, and in a greater portion of concrete production, which leads to smaller sustained loads in reclaimer tanks and thus reduced variability in age of cementitious solids contained in the reclaimer tank.

[0250] Any reaction in the form of Pathway 2 is challenging to measure, and the corresponding impact on the reactivity / dynamics of Pathway 2 created solids creates even more challenges with respect to predictability. Conversely, if reaction is maintained as Pathway 1, the residual (unreacted) cementitious solids perform as expected as typical cementitious solids in water, and hydration kinetics can be managed using industry proven hydration stabilization / set retardation techniques. Further, the generation of nano-CaCO₃ results in a distinct “in-situ” product that carries an intrinsic performance enhancing value-add with it is currently accepted in the industry as such.

[0251] Introduction of carbon dioxide to the drum of the truck. In certain embodiments of the invention, carbon dioxide is introduced into the water in the drum of the ready mix truck, before the water leaves the drum. The carbon dioxide can be in any form, and introduced in any suitable manner.

[0252] 1) Introduction of carbon dioxide after concrete load has been poured and before truck reaches wash station. For example, carbonated water may be used as saddlebag water and/or as wash water at a wash station. Supersaturated carbonated water may be used, as described elsewhere (see, e.g., U.S. Patent Application Publication No. 2015/0202579). In addition, or alternatively, solid carbon dioxide may be introduced into the water. For example, a certain amount of dry ice may be added at the job site, before, during, or after the

addition of saddlebag water, and mix with the saddlebag water and residual concrete in the drum of the ready-mix truck during the drive back to the wash station; the dry ice will sublimate in the water and provide a steady source of carbon dioxide as the cement in the residual concrete reacts to produce reaction products, e.g., carbonates. The dry ice may be added as one dose or as more than one dose, e.g., as 2, 3, 4, 5, 6, 7, 8, 9, 10, or more than 10 doses, or continuously or semi-continuously. In addition or alternatively, gaseous carbon dioxide may be introduced into the drum, either as a single addition, or multiple additions, or as a stream of carbon dioxide that is injected into the drum, e.g., for some or all of the transport time from the job site. For example, carbon dioxide gas may be added as one dose or as more than one dose, e.g., as 2, 3, 4, 5, 6, 7, 8, 9, 10, or more than 10 doses, or continuously or semi-continuously. Carbon dioxide can also be introduced as mix of gaseous and solid carbon dioxide, e.g., by use of a snow horn; this can also be as one or more additions or continuous addition. For example, carbon dioxide as a mix of gas and solid may be added as one dose or as more than one dose, e.g., as 2, 3, 4, 5, 6, 7, 8, 9, 10, or more than 10 doses, or continuously or semi-continuously. In embodiments in which dry ice is used, there can be a further effect of cooling the wash water as cementitious materials react. It will be appreciated that one or more of the above options may be used for any given load.

[0253] For example, it is possible to add carbon dioxide to the drum after saddlebag water has been added, and while the truck is moving from the job site to a wash station: In one option, a certain amount of dry ice may be carried with the truck and introduced into the drum at the time that the saddlebag water is introduced; this is an easy and convenient method to get a relatively large amount of carbon dioxide into the drum. The dry ice may be used as pieces of a certain size, or within a certain range of sizes, that may be determined by, e.g., one or more of the volume of saddlebag water, the amount of cement in the mix, the expected amount of concrete coating the interior of the truck, the expected transport time back to the wash station, the desired level of carbon dioxide uptake, the efficiency of uptake, the temperature that the truck is likely to encounter, and the like, so that the dry ice sublimates at a rate that will match the expected rate of reaction with concrete residue and, in particular, with cement. This will tend to keep more of the carbon dioxide in the drum of the truck, since it will be reacting at approximately the rate that it is sublimated into gaseous form. In a second option, the saddlebag water is carbonated, or super-saturated, with carbon dioxide, generally at the batching facility before being loaded into its containers. The containers may be modified as necessary to preserve the carbonation of the water for the necessary time before use. Supersaturated solutions have been found to retain a large

percentage of introduced carbon dioxide over relatively long time periods; thus, little or no modification of the saddlebags may be necessary if a supersaturated solution is used. See, e.g., U.S. Patent Application Publication No. 2015/0202579. In a third option, gaseous carbon dioxide is added to the drum of the ready-mix truck, before, after, or during the addition of the saddlebag water. As described above, the addition may be in one dose, more than one dose, continuous, or a combination. The total amount of carbon dioxide added may be metered and regulated based on the same criteria as for dry ice. In a fourth option, a mixture of solid and gaseous carbon dioxide is added to the drum, for example by use of liquid carbon dioxide passed through a snow horn. Dosing and regulation would be as for gaseous carbon dioxide. Any combination of these options may be used, as desired and suitable for a particular load, truck, or operation.

[0254] Because the truck is empty, the drum provides a very large headspace for any gaseous carbon dioxide to be retained. In certain embodiments, the opening of the drum may be partially or completely closed in order to retain carbon dioxide within the drum, either during transport back to the wash station, or at the wash station, or both.

[0255] 2) Addition of carbon dioxide at a wash facility. Additionally or alternatively, carbon dioxide may be added to the drum of the ready-mix truck during the washing process at the wash station. Any or all of the options described above for addition of carbon dioxide after the load has been poured and before the truck returns to the wash facility may also be used during washing at the wash station: carbonated or super-carbonated wash water, dry ice, gaseous carbon dioxide, a mix of gaseous and solid carbon dioxide. If carbon dioxide has already been added to the drum prior to the truck reaching the wash station, one or more characteristics of the water can be useful to determine the extent of reaction of the carbon dioxide. Measurements such as pH, temperature, and the like, as described elsewhere herein, can be useful. The amount of additional carbon dioxide that would then be added can be calculated from the measurement(s).

[0256] The washing can be done as a single wash, or it can be split into two or more washes, one or more of which can include carbonation. Thus, the washing may be done as 1, 2, 3, or more than 3 washes. Of these, one or more may include carbonation. It is possible that by splitting the washes, in combination with carbonation, less water may be needed than if a single wash is used. If saddlebag water addition is counted as a wash, then, typically, a minimum of two washes would be used (first is saddlebag water, second is at wash station). If more than one wash is used at the wash station, then it is 3, 4, etc. washes. Of these total washes, one or more may include a carbonation step, e.g., there can be 2 total washes

(saddlebag and wash station) where one wash includes a carbonation step (e.g., addition of saddlebag water at job site, or the wash step at the wash station), or both washes include a carbonation step. As another example, there can be 3 washes (saddlebag and two separate washes at wash station) in which one wash includes a carbonation step (e.g., saddlebag at job site or one of the 2 washes at the wash station), or 2 washes include a carbonation step (e.g., saddlebag at job site and one of the 2 washes at the wash station, or both washes at the wash station), or all three washes include a carbonation step.

[0257] The carbon dioxide may be added manually, or automatically, or a combination of the two. If the carbon dioxide is added as carbonated wash water, typically, the usual wash routine can be used, and some or all of the wash water is carbonated or supercarbonated. If the concrete in the truck is already partially carbonated, e.g., if it has been carbonated during the trip to the wash facility, a desired additional amount of carbon dioxide may be calculated, possibly based on one or more characteristics as described above, e.g., pH, and the amount of carbonated wash water and normal (uncarbonated) wash water adjusted accordingly. If the concrete in the truck has not been carbonated, an amount of carbon dioxide may be calculated as described below, and the amount of carbonated wash water and normal (uncarbonated) wash water adjusted accordingly. Alternatively, the wash water may be used as normal, without any particular calculations or adjustments.

[0258] In some cases, additionally or alternatively, carbon dioxide may be added as solid carbon dioxide. Thus, dry ice, which may be adjusted to a particular size or range of sizes, may be added to the drum in a desired amount. The addition can be as simple as a manual addition by the truck driver or other personnel.

[0259] Additionally or alternatively, carbon dioxide may be added as gaseous carbon dioxide, or as a mixture of gaseous and solid carbon dioxide. In this case, an injection system is used. In these cases, in general, a delivery system for the carbon dioxide includes a source of carbon dioxide (e.g., a tank of liquid carbon dioxide), a conduit from the source to an injector for placing the carbon dioxide in the truck drum, and a system for positioning the injector so that the injection of carbon dioxide directs carbon dioxide into the drum of the truck, generally at a desired location in the drum, though in some cases very little is required beyond aiming the injector into the drum. A system may include a plurality of injectors to handle a plurality of trucks, e.g., simultaneously, such as at least 2, 3, 4, 5, 6, 7, 8, 9, 10, or more than 10 injectors. The injectors may all utilize the same source of carbon dioxide, with appropriate piping and valving. Typically, the system will also include a controller.

[0260] The injector is positioned so that delivery of carbon dioxide into the drum will occur into the opening of the drum and at a desired location of the drum. This can be as simple as the truck driver backing the truck to a designated spot, where the delivery system is situated so that it is properly aligned to inject carbon dioxide into the drum with little or no additional adjustment (e.g., injector is situated to be in proximity to opening of drum when truck backed in, then the truck driver may need to move the injector manually to the final position). In certain embodiments, an automated system may be used to assist in positioning the injector, or even to completely position it with no human intervention. The system further includes an actuator to start and stop delivery of carbon dioxide to the drum, e.g., a valve, and a connection between the valve and a controller that controls the start and stop of delivery. Generally, the system will also include a system to measure flow rate of the carbon dioxide. In a system that uses liquid→gas and solid, this can be, e.g., a system as described in U.S. Patent No. 9,376,345.

[0261] The controller can be as simple as a button or switch that the truck driver toggles after backing the truck to the bay. It will be appreciated that such a “switch” can be any suitable switch, such as the touchscreen of a wireless device, e.g., a smartphone. Flow can continue for a designated time, then halted. Again, the simplest method for this is for the truck driver to hit the switch again. However, it can be preferable to have an automatic controller, to avoid human error and to more finely modulate delivery, so that the flow of carbon dioxide is halted automatically on signal from the controller. This may be after a certain time, or a certain amount of carbon dioxide is delivered (from flow rate and time), and/or based on one or more characteristics of the wash water which can be measured, e.g., by sensors, such as pH, specific gravity, temperature, etc., and communicated to the controller, which then halts or adjusts flow based on a pre-determined algorithm. The automatic controller can also automatically start flow when the truck and injector are properly positioned, using appropriate positioning sensors to determine this point. The controller can also alert the truck driver as to when the truck is properly positioned in relation to the injector, or when the truck or injector is out of position.

[0262] An exemplary control system, which may be used for any suitable system in which wash water is treated with carbon dioxide, and, in particular in systems in which the carbonated wash water is re-used as mix water, utilizes input regarding one or more conditions of a wash water holder and/or its environment, such as at least 2, 3, 4, 5, or 6 conditions, processes the input, then signals one or more actuators, such as at least 2, 3, 4, 5, or 6 actuators, e.g., a valve that regulates carbon dioxide flow, based on the processing.

Inputs can include, but are not limited to, one or more of wash water pH, wash water temperature, carbon dioxide content of air in contact with wash water (e.g., air in a headspace above a tank), and/or a calculated amount of carbon dioxide to be added. In the latter case, the calculation can be based on, e.g., volume of wash water, known or estimated amount of concrete in wash water, known or estimated percentage of cement in the concrete, known or estimated carbon dioxide uptake required to reach an acceptable endpoint, e.g., acceptable pH, and/or acceptable carbon dioxide uptake. Thus, one exemplary control system utilizes inputs that include wash water pH, temperature, and/or carbon dioxide concentration directly above the water, e.g., in a holding tank or reclaimer. In certain embodiments all three of pH, temperature, and carbon dioxide concentration are used; in certain embodiments two of pH, temperature, and carbon dioxide concentration are used; in certain embodiments only one of pH, temperature, and carbon dioxide concentration are used, for example, carbon dioxide concentration above the wash water. Additional sensors and/or information that may input to a controller, can include a flow meter to determine carbon dioxide flow rate, a sensor to determine the level of water in the holding tank (which level may vary depending on a variety of conditions), and/or information from a pump or pumps, such as pumps that pump new wash water into a holding tank, e.g., from a reclaimer, and/or such as pumps that pump water into a recirculation loop. In the case of a pump from a reclaimer, the pump or pumps typically have a fixed flow rate, so information regarding time that the pump is on can be sufficient for the controller to determine an amount of new wash water that has been added to the system; given the typical amount of cement in a load, the controller can, e.g., adjust carbon dioxide flow to wash water to account for the anticipated amount of material to be carbonated, and keep ahead of the carbonation demand. Alternatively, or additionally, the controller may send signals to other sensors, e.g., pH, temperature, and/or carbon dioxide, to read values more frequently so that the system can adjust more quickly to the added load.

[0263] Additional sensors can also include a sensor to monitor pressure behind a carbon dioxide control valve (typically used to send an alarm signal if the pressure is outside acceptable limits), and a sensor for the temperature of incoming gas, which indicates whether the carbon dioxide source, e.g., tank, can keep up with demand; such a sensor can indicate whether the source is being overwhelmed by demand, because in such case liquid carbon dioxide droplets may form.

[0264] For convenience, the system will be described in terms of using all three sensors; it will be understood that fewer or more sensors may be used. Thus, in an exemplary embodiment, a pH sensor/meter, a temperature sensor such as a thermocouple, and a CO₂

- sensor/meter are used as sensors. The sensors are operably connected to a control system, e.g., wired connection, wireless connection, or a combination. The control system is also connected to the carbon dioxide addition equipment for the wash water, and, optionally, a pump or pumps. Any suitable control system can be used, such as a programmable logic
- 5 controller (PLC). The control system may be stand-alone, or integrated with an overall control system for the wash water facility, or a combination thereof. Additional equipment can include a first pneumatic cylinder and a second pneumatic cylinder, one or both of which can extend and contract, a mass flow meter for CO₂ gas flow metering and control, and a water line solenoid in a clean water line, to regulate flow of clean water to rinse the pH probe.
- 10 The system can include a pump; an exemplary pump is one that serves to agitate the water in a holding tank, so that solids don't settle. Pumps alternatively or in addition can include reclaimer pumps.
- [0265] The wash water temperature sensor, e.g., thermocouple, can be placed anywhere in contact with the wash water in the system, but typically is submerged to ensure the mass of
- 15 the sensor does not impact the reading. A single wash water temperature sensor may be used, or more than one temperature sensor may be used, such as at least 2, 3, 4, 5, or 6 wash water temperature sensors.
- [0266] The CO₂ sensor is placed above the surface of the wash water, e.g., in a location of upward-flowing wash water. The distance of the CO₂ sensor from the surface of the water
- 20 may be any suitable distance so long as the sensor can detect carbon dioxide emitted from the wash water, i.e., carbon dioxide that has been contacted with the wash water but that has not been absorbed in/reacted with the wash water, so that it is escaping to the atmosphere above the wash water (headspace). For example, the sensor may be 0.1-100, or 1-100, or 1-50, or 5-100, or 5-50 cm above the surface of the wash water, or any other suitable distance. If the
- 25 CO₂ sensor is in a fixed position, the distance from the surface of the water can vary as water level varies, e.g., from additional loads, use of water, etc. Thus, the system may also include a sensor to sense the level of the wash water in the tank. The controller may adjust the weight given to the carbon dioxide value depending on distance from the surface, e.g., if the sensor is further from the surface more carbon dioxide has to build up before the sensor will
- 30 read it, and the controller may adjust flow to a different degree, for example, reduce flow more, or at a different rate, for example, more quickly, than if the sensor is closer to the surface of the water. Additionally or alternatively, a CO₂ sensor may be configured to stay a constant distance, or within a constant range of distances, from the surface of the wash water. For example, a CO₂ sensor may be on a float, with the gas-sensing portion a certain distance

above the waterline of the float, or be provided with a mechanism to move the sensor based on, e.g., readings of the level of the wash water. Any other suitable method and apparatus for maintaining a constant distance from the surface of the wash water may be used. The system may use a single CO₂ sensor or more than one, such as at least 2, 3, 4, 5, or 6 CO₂ sensors.

- 5 [0267] Input from a sensor to signal the height of water in the tank may alternatively or additionally be used to regulate one or more aspects of the system. For example, when the water level is low, changes will tend to be more rapid, and the interval between samples may be decreased, and/or carbon dioxide flow rate decreased.

- [0268] The pH sensor or sensors can be used in any suitable location that allows accurate
10 readings of wash water pH. Any suitable sensor which can withstand the conditions typical of concrete wash water may be used. To obtain an accurate reading and prevent fouling of the sensor, the sensor is typically contacted with wash water in which the solids have been allowed to settle to a sufficient degree to obtain an accurate reading and to not foul the sensor. This may be done in any suitable manner. For example, a portion of wash water may
15 be removed from the tank for a pH measurement and, e.g., allowed to settle before a measurement is taken. In another example, a pneumatic cylinder can be extended into the wash water at a location of downward-flowing wash water, for example, about 12 inches into the wash water, or any other suitable distance. The water inside the cylinder will not be exposed to the motion of the overall wash water, and solids can settle out. After an
20 appropriate interval to allow sufficient solids to settle, for example, at least 5, 10, 15, 20, 30, 40, 50, or 60 seconds, a second pneumatic cylinder, which includes the pH sensor, is extended into the first cylinder to take a pH reading of the water inside the first cylinder. After a reading is complete, the probe is retracted from the first cylinder, and is subjected to appropriate treatment to prepare for the next reading, which can be, e.g., rinsing of the probe
25 with clean water released from a clean water line by action of a solenoid in the line. The first cylinder is also retracted from the wash water at some time between samples so that a fresh sample can be obtained for the next reading. A single pH sensor may be used, or more than one may be used, such as at least 2, 3, 4, 5, or 6 pH sensors.

- [0269] The sensor or sensors send signals to the control system. The readings from the
30 various sensors can be reviewed to ensure that proper sampling has occurred, for example confirmation logic checks that the reading is in the expected range based on reading time, that change in value between readings is reasonable, i.e., not too high or too low. If an anomaly is detected, an error signal can be sent and standby logic to ensure continued safe operation (e.g., for temperature, pH); in the case of CO₂ sensor malfunctioning, an alarm may sound

and/or the system may be shut down to ensure safety. If readings are determined to be proper, then the control system may determine, based on one or more readings, if any adjustment to CO₂ flow rate should be made.

[0270] Generally, the variable or variables will be determined to be within a suitable range, and if within the range, at what point in the range it is; this may be any suitable form of interpolation. The values for each variable may be combined, either as is or as weighted variables. The suitable ranges for each value can be determined by routine testing at the site. The range for pH may be any suitable range, such as from 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, 8.5, 8.6, 8.7, 8.8, 8.9, 9.0, 9.1, 9.2, 9.3, 9.4, 9.5, 9.6, 9.7, 9.8, 9.9, 10, 10.1, 10.2, 10.3, 10.4, 10.5, 10.6, 10.7, 10.8, 10.9, 11.0, 11.2, 11.4, 11.6, 11.8, 12.0, 12.2, 12.4, 12.6, 12.8, 13.0, 13.2, 13.4, 13.6, 13.8, 14.0, or 14.5 to 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, 8.5, 8.6, 8.7, 8.8, 8.9, 9.0, 9.1, 9.2, 9.3, 9.4, 9.5, 9.6, 9.7, 9.8, 9.9, 10, 10.1, 10.2, 10.3, 10.4, 10.5, 10.6, 10.7, 10.8, 10.9, 11.0, 11.2, 11.4, 11.6, 11.8, 12.0, 12.2, 12.4, 12.6, 12.8, 13.0, 13.2, 13.4, 13.6, 13.8, 14.0, 14.5, or 15.0. The range for temperature may be any suitable range, such as from 5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30 °C to 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 50, 52, or 55 °C; generally tanks are run in the open and the lower limit may be adjusted according to air temperature, while the upper limit may be determined by the concrete production facility, which may not use mix water above a certain temperature. The range for carbon dioxide may be any suitable range, such as from 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 520, 540, 560, 580, 600, 620, 640, 660, 680, 700, 720, 740, 760, 780, 800, 825, 850, 875, 900, 925, 950, 975, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350, 1400, 1450, 1500, 1550, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2400, 2600, 2800, 3000, 3200, 3400, 3600, 3800, 4000, 4200, 4400, 4600, or 4800 ppm to 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 520, 540, 560, 580, 600, 620, 640, 660, 680, 700, 720, 740, 760, 780, 800, 825, 850, 875, 900, 925, 950, 975, 1000, 1050, 1100, 1150, 1200, 1250, 1300, 1350, 1400, 1450, 1500, 1550, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2400, 2600, 2800, 3000, 3200, 3400, 3600, 3800, 4000, 4200, 4400, 4600, 4800, or 5000 ppm. Since tanks are generally open to the atmosphere, the lower limit typically will not be below the atmospheric level of carbon dioxide, which is rising, thus determined at the site or as of date. The maximum upper limit may be constrained by regulations regarding worker safety, which vary, and can be as low as

1000 ppm, or may be, e.g., 5000 ppm. However, in general the upper limit will be lower than worker safety limits in order to more efficiently control carbon dioxide use in the system, and to limit waste. A separate carbon dioxide sensor may be installed at the site in worker areas and be set to give an alarm at a certain level, or even to shut down carbon dioxide feed into the system. This sensor is not necessarily communicating with the overall system, e.g., it may be a standalone alarm.

[0271] Samples may be taken at any suitable interval, which may be constant or may vary depending on conditions, e.g., as described elsewhere, sampling rate may increase when a load from, e.g., a reclaimer is sensed. Exemplary sampling intervals are from 1, 2, 3, 4, 5, 7, 10, 20, 30, 40, or 50 seconds, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, or 20 minutes, to 2, 3, 4, 5, 7, 10, 20, 30, 40, or 50 seconds, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 20, 22, or 25 minutes. In order to obtain accurate readings at each sample time, several readings may be taken from one or more of the sensors, such as at least 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 17, or 20 readings. Such readings may be averaged, or the control system may contain logic that allows choice of the most likely accurate reading or readings from the group.

[0272] Exemplary control logic to control CO₂ flow rates, based on all three of pH, temperature, and CO₂ above the surface (e.g., in headspace), is as follows, using upper and lower limits that are merely exemplary (any suitable ranges may be used), and using linear interpolation (an suitable interpolation may be used):

[0273] Adjustable variables

Sensor interval (min) = 5

pH (Lower Limit, LL) = 7

pH (Upper Limit) = 13

CO₂ PPM (LL) = 400

CO₂ PPM (UL) = 1000

Temp C (LL) = 20 °C

Temp C (UL) = 40 °C

MAX FLOW = max flow determined onsite for the configuration used to ensure 100% uptake in new washwater. May be adjusted

according to factors that affect uptake, such as volume of water in the tank (e.g., water level in the tank).

[0274] Below is some of the logic that can be incorporated into the logic to control flow rates based on the condition of the wash water. This logic uses a linear interpolation between 100% and 0% of max uptake flow between expected min/max sensor readings for simplicity but changing the CO₂ factor, pH factor and temperature factor equations would be relatively simple when, e.g., data that supports the change. All variables are given equal weighting but that can be adjusted, as well, as appropriate.

[0275] Conditions:

- 10 - if **pH** < pH(LL) then **pH factor** = 0
- if **pH** > pH(UL) then **pH factor** = 1
- if pH (LL) < **pH** < pH(UL) then **pH factor** = (**pH** - pH(LL) / (pH(UL)-pH(LL)))
- if **CO₂** < CO₂ (LL), then **CO₂ factor** = 1
- 15 - if **CO₂** > CO₂ (UL) then **CO₂ factor** = 0
- if **CO₂** (LL) < **CO₂** < CO₂ (UL) then **CO₂ factor** = (CO₂ (UL) - **CO₂**) / (Co2 (UL) - Co2 (LL))
- if **Temp** < Temp C (LL) then **Temp factor** = 1
- 20 - if **Temp** > Temp C (UL) then **Temp factor** = 0
- if Temp C (LL) < **Temp** < Temp C (UL) then **Temp factor** = (Temp (UL) - **Temp**) / (Temp (UL) - Temp (LL))

Flow = MAX FLOW x ((pH Factor x CO₂ factor x Temp factor)/3).

- 25 This flow equation is merely exemplary; it will be appreciated that any suitable weighting of factors may be used; in the case of the example equation, a value of 0 for any factor would shut down carbon dioxide flow, as values are multiplied, but any suitable numerical manipulation may be used to produce a desired result. In general, the combination of factors should not be above 1.0, i.e., max flow.
- 30 Also, it may be desired, as in the example, that any one of the factors exceeding an upper or lower limit, depending on the factor, can shut down carbon dioxide flow.

[0276] Thus, in certain embodiments the invention provides a method of treating waste concrete in concrete mixer comprising adding water to the mixer to wash out the mixer and adding carbon dioxide to the mixer, to produce carbonated wash water in the mixer. At least a portion of the carbon dioxide added to the mixer is added as carbon dioxide dissolved in wash water for the mixer. The concentration of carbon dioxide in the wash water can be any concentration as described herein, such as at least 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 g/L water. In certain embodiments, such as when a supersaturated wash water is used, concentrations of carbon dioxide in the wash water can exceed 10 g/L, such as at least 12, 13, 14, 15, 16, 17, 18, 19, or 20 g/L. Additionally or alternatively, at least a portion of the carbon dioxide added to the mixer can be added as solid and/or gaseous carbon dioxide. The mixer can be any suitable mixer. In certain embodiments, the mixer is a transportable mixer, such as a drum of a ready-mix truck. The method can include transporting at least a portion of the carbonated wash water to a wash water treatment system. The wash water treatment system can, e.g., treat wash water comprising the carbonated wash water to remove aggregates. The wash water treatment system can additionally or alternatively add additional carbon dioxide to the wash water comprising carbonated wash water. Any suitable method for adding carbon dioxide, such as methods described herein, may be used to add the carbon dioxide.

[0277] Dosing of carbon dioxide Regardless of the form of the carbon dioxide, the total amount of carbon dioxide to be used in the truck on the drive back to the wash station and/or at the station may be determined by the cement content of the concrete mix in the truck, the expected amount of concrete that will be coating the inside of the truck, the expected or desired level of carbon dioxide uptake by the cement, and the expected efficiency of uptake (e.g., carbon dioxide loss due to leakage from the drum of the truck). For example, a truck with a capacity of 8 m³ may be carrying concrete with a cement content of 15%, and it is known or estimated that approximately 500 pounds of concrete remains in the truck after dumping its load, regardless of load size. A maximum uptake of 50% carbon dioxide bwc is expected for this cement type, and an efficiency of uptake of 80% is expected. The calculated dose of carbon dioxide for maximum carbonation would be $500 \times 0.15/0.50 \times 0.80 = \sim 188$ lb of carbon dioxide. In general, the amount of concrete in the empty truck will not be precisely known; a surrogate is the specific gravity of the wash water as soon as enough water is added to create a slurry; from the specific gravity and volume, a mass of solids may be calculated and, from that and the proportion of cement in the concrete mix that was carried in the truck, the amount of cement in the wash water can be calculated. Thus, in certain embodiments, the dose of carbon dioxide to be used for wash water (either in a single

truck or in a combination of more than one truck) may be expressed as an amount by weight solids, where a percentage of cement and other carbon-dioxide-reacting or -absorbing materials is known or estimated, and/or efficiency of carbonation is known or estimated, e.g., at least 1, 2, 5, 7, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95% carbon dioxide by weight solids, and/or not more than 2, 5, 7, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 or 100% carbon dioxide by weight solids. Higher doses may be used, e.g., beyond 100% by weight solids, depending on the cement content of the wash water, the expected efficiency of carbonation, etc.

[0278] Less than a complete (full) dose may be used in any embodiment of the invention.

This can be for any reason; e.g., the desired or available systems for carbon dioxide delivery will not allow sufficient carbon dioxide to be delivered, or it is desired to keep the carbon dioxide reactions to a certain level in the time period between dumping the load of concrete and final washing at the batching facility, or between washing and further treatment, etc. As described elsewhere herein, an aged wash water may require less than a complete dose (e.g., a dose calculated based on fresh concrete in the truck) to provide the desirable level of reaction. Although a full or complete dose may be calculated for a given truck, load, and mix design, as described elsewhere herein, less than a full or complete dose of carbon dioxide may be given, e.g., less than 95, 90, 80, 70, 60, 50, 40, 30, 20, or 10% of a complete dose, and/or more than 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, or 90% of a full dose. In certain embodiments of the invention, the dose of carbon dioxide used to treat wash water is such that the total amount of carbon dioxide delivered to a subsequent concrete mix using the carbonated mix water (and calculated only from carbon dioxide in the mix water, ignoring any other carbon dioxide added to the subsequent concrete mix), is less than 2.0, 1.5, 1.3, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1% by weight cement in the subsequent mix, for example, less than 1.0%, or less than 0.8%, or less than 0.5%, or less than 0.3%, or less than 0.1%, such as less than 0.5%. By weight of solids in the washwater, the carbon dioxide dose may be at least 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 5.0, 10.0, 15.0, 20.0, 25, 30, 35, or 40% by weight of solids in the wash water, and/or not more than 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 5.0, 10.0, 15.0, 20.0, 25, 30, 35, 40, or 50% by weight of solids in the wash water. The amount of carbon dioxide in the wash water may be determined, e.g., by multiplying the total amount of carbon dioxide delivered to the wash water by the efficiency (measured or calculated) of absorption of carbon dioxide by the wash water and dividing by volume of the wash water. Suitable adjustments may be made for the typical case where a holding tank contains wash water from multiple trucks, and may be used on an ongoing basis to provide mix water, based

on truck contents and water use, and other appropriate measurements. In certain embodiments, the carbon dioxide content the wash water (e.g., carbonates, bicarbonate, carbonic acid, and/or dissolved carbon dioxide) may be determined by chemical or other suitable measurements. It can be assumed that virtually all of the carbon dioxide content of a carbonated wash water, either dissolved or as reaction products with cementitious materials, is due to carbonation of the wash water.

[0279] In certain embodiments, a full dose, or dose that is calculated to be a full dose, may be delivered at the job site and/or during transport to the wash station; in some cases, less than a full dose is desired. In some cases, testing at the batching facility can show whether carbon dioxide uptake is complete; if not, additional carbon dioxide may be added at the batching facility, e.g., during washing of the drum or at a later step, to achieve a full dose or the desired less than full dose. In certain embodiments, no carbon dioxide until the truck is back at the batching facility. In certain embodiments, a partial dose is used at the job site and/or during the drive back to the batching facility, and one or more further partial doses are delivered at the batching facility, e.g., during washing or later, as described above.

[0280] In certain embodiments of the invention, the dose of carbon dioxide is determined mainly or exclusively by the methods above; e.g., no further pre-testing beyond, in some cases, specific gravity, is required. In some cases, dose is calculated simply from known or assumed amounts of concrete left in the truck and the mix design of the truck, including the amount of cement in the concrete and, in some cases, the type of cement in the concrete, as well as known or assumed efficiencies of carbonation, without the need to test wash water at all, and in particular, no need for testing for an initial dose of carbon dioxide.

[0281] The carbon dioxide added to the wash water will initially dissolve in the water and then form various products from reaction, such as bicarbonates, and carbonates (e.g., calcium carbonate). Carbon dioxide in the wash water, in the form of dissolved carbon dioxide, carbonic acid, bicarbonates, and carbonates, will be carried over into cement in which the wash water is used as mix water. Thus, the cement mix will contain a certain amount of carbon dioxide (including dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate) contributed by the carbonated wash water, which may be expressed as percent by weight cement in the mix. For example, a wash water may have a solids content 150,000 ppm, or 15%, which would give a specific gravity of approximately 1.10. If carbon dioxide is added to the wash water and the uptake by the wash water is 30%, then 4.5% of the water is carbon dioxide, mainly as carbonation products. If a concrete mix is then made using the carbonated wash water at a water/cement ratio of 0.5, then the amount of carbon dioxide (as

dissolved carbon dioxide, carbonic acid, bicarbonate, and carbonate) in the concrete mix is 2.25% bwc. These numbers are merely exemplary. Wash water solids content, efficiency of uptake, w/c ratio, amount of mix water that is wash water, and the like, can vary. Thus, the amount of carbon dioxide provided by carbonated wash water in a concrete mix that

5 comprises carbonated wash water can be at least 0.01, 0.05, 0.1, 0.2, 0.5, 0.7, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12, or 12.5% bwc, and/or not more than 0.05, 0.1, 0.2, 0.5, 0.7, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1,

10 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.5, 6.0, 6.5, 7.0, 8.0, 9.0, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0, 14, 15, 16, 17, 18, 19, 20, 22, 25, or 30% bwc. For example, the invention provides a method of preparing a concrete mix comprising (i) adding concrete materials to a mixer, wherein the concrete materials comprise cement; adding mix water to the mixer, wherein the mix water comprises carbonated concrete wash water in an

15 amount such that the total carbon dioxide or carbon dioxide reaction products (expressed as carbon dioxide) supplied by the carbonated mix water to the concrete mix is at least 0.01, 0.05, 0.1, 0.2, 0.5, 0.7, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12, or 12.5% bwc, and/or not more

20 than 0.05, 0.1, 0.2, 0.5, 0.7, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.2, 4.4, 4.6, 4.8, 5.0, 5.5, 6.0, 6.5, 7.0, 8.0, 9.0, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, or 13.0% bwc, for example, at least 0.5, 1.0, 1.5, or 2.0%, and/or not more than 2.5, 2.0, 1.5, or 1.0%, or for example, not more than 2%, or not more than 2.5%, or not more than 3.0%, or not more than 3.5%, or not

25 more than 4.0%; or, for example, at least 0.01% bwc, or at least 0.05% bwc, or at least 0.1% bwc, or at least 0.5% bwc, or at least 1.0% bwc, or at least 2.0% bwc, or at least 3.0% bwc, or at least 4.0% bwc, or at least 5.0% bwc; or, for example, in a range of between 0.01 and 13.0%, bwc, or a range of between 0.01 and 12.0% bwc, or a range of between 0.01 and 11.0%, bwc or a range of between 0.01 and 10.0%, bwc, or a range of between 0.01 and

30 8.0%, bwc, or a range of between 0.01 and 6.0%, bwc or a range of between 0.01 and 4.0%, bwc, or in a range of between 0.1 and 13.0%, bwc, or a range of between 0.1 and 12.0% bwc, or a range of between 0.1 and 11.0%, bwc or a range of between 0.1 and 10.0%, bwc, or a range of between 0.1 and 8.0%, bwc, or a range of between 0.1 and 6.0%, bwc or a range of between 0.1 and 4.0%, bwc, or in a range of between 1.0 and 13.0%, bwc, or a range of

between 1.0 and 12.0% bwc, or a range of between 1.0 and 11.0%, bwc or a range of between 1.0 and 10.0%, bwc, or a range of between 1.0 and 8.0%, bwc, or a range of between 1.0 and 6.0%, bwc or a range of between 1.0 and 4.0%, bwc and (iii) mixing the water and the concrete materials to produce a concrete mix. It will be appreciated that the amount of carbonated wash water in the total mix water may be any suitable amount, such as amounts described herein.

[0282] Carbon dioxide delivery in reclaimers and piping from reclaimer to pond or slurry tank. Some facilities utilize reclaimers to reclaim aggregate, e.g., sand and gravel, from the wash water. The water may then further be used, generally with more processing, either as part of mix water or as wash water; any remaining water is disposed of in the usual manner. In a typical reclaimer, water with grit and solid components is pumped through the process, and sand and gravel are separated out, e.g., by sieving. The water is then sent to a settlement pond, and/or to a tank for reuse. In the case of water sent to a settlement pond, water may be transported to a tank, where carbon dioxide is added to the water; e.g. a recirculation line allows carbon dioxide to be added to the water in the line, then sent back to the tank; if a tank is already present, then a carbonation apparatus may be added, for example, a recirculation line. This water can be carbonated or super-carbonated, additionally or alternatively with carbon dioxide added to the water during the pumping process, so that as carbon dioxide is consumed in carbonation reactions, more carbon dioxide is supplied to the water. Carbon dioxide can additionally or alternatively be supplied into piping as the water is pumped to a settlement pond or a slurry tank. In an optimum situation, sand and gravel are separated out as usual, but the water in, e.g., a slurry tank is available for use again without further dilution, or with less dilution than would otherwise be required. For example, the process may produce water, e.g., water in a slurry tank, from a reclaimer that has a specific gravity that is greater than, e.g., 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19, or 1.20, but that is suitable for use as mix water. This is different from existing reclaimers, where the water in, e.g., a slurry tank, typically requires dilution to lower the specific gravity to acceptable levels. In the present process, little or no additional processing may be needed (though additionally or alternatively carbonation at the slurry tank may be used, if necessary or desired) because the carbonation process halts or greatly retards deleterious reactions of the cementitious material while leaving it available for reaction in a second concrete batch, and also adjusts the pH of the water to more acceptable levels. For example, in the process, filtering and/or settling of solids is generally not necessary; indeed, an advantage of the methods and compositions of the invention is that materials from one

batch may be recycled into another batch or batches, potentially allowing less material, e.g., cement to be used, and decreasing or even eliminating costs associated with disposing of wash water materials.

[0283] Retrofit of existing facility to provide reclamation: Most concrete facilities do not include a reclaimer, but could benefit from being able to reuse wash water and, potentially, aggregates from wash water. At present, most solid material is simply allowed to settle out in one or more settlement ponds, and is periodically disposed of, with little or no reuse, while the water in the settlement pond must be further treated to meet environmental standards before disposal. If, instead, wash water is carbonated, either before placement in the pond, or during its time in the pond, or both, then some or all of the water may be used as mix water, reducing or eliminating the costs and equipment required to treat the water for disposal. In addition, some or all of the aggregates may be available for reuse, instead of hardening and becoming useless.

[0284] As an example, in one type of operation, wash waters from trucks are dumped into a first bay, where solids settle out, harden, and are generally dumped. The top water from the first bay goes over a weir into a second bay where, generally, solids are further allowed to settle, top water is taken off, often sent to a third bay, and the water, now essentially free of solids but still with a high pH, silicates, calcium etc., is treated for disposal or, in some cases, for at least partial reuse. In presently available systems, the treatment in the third bay, where there are no solids present, may be with carbon dioxide. The present invention allows for a retrofit of the first or second bay, where solids are still present, so that instead of being a settlement pond, it is a slurry pond where carbonation occurs; the carbonated wash water is then suitable for use as mix water, rather than merely being disposed of. This can be done by the use of agitators, recirculating pumps, or a combination of these, where carbon dioxide is added either directly into the pond (e.g., through bubble mats, as described elsewhere herein) or in the lines in the recirculation pumps, or both. Other methods of adding carbon dioxide, e.g., at impellers or eductors, etc., are as described herein. Other means of carbon dioxide addition, such as solid carbon dioxide, or a mixture of gaseous and solid, may also be used, as described herein.

[0285] In certain embodiments, a wall is added to the first bay, e.g., a wall with a notch to allow water to flow through the notch (e.g., a weir) to an area of the first tank beyond the wall. The wall can be placed to provide a division in the first tank to allow solids, such as aggregate, to settle, but allow the remaining water, with suspended solids, to flow over the notch into a second part of the first bay. Optionally, a second wall can be added on the other

- side of the first wall, in order to reduce the volume of the area into which water flows over the notch. The water can be pumped out of the area, e.g., with a sump pump or similar pump, into a holding tank, where it can be carbonated, e.g., by use of a recirculation loop, where water is pumped out of the tank into a pipe and carbon dioxide added to the water in the pipe, then the carbonated water is led back into the tank. The carbonated water in the holding tank can then be led back to the batching plant, for use in subsequent batches of concrete. Addition of carbon dioxide to the water can be controlled as described elsewhere herein. In these embodiments, it may not be necessary to have a second or third bay, or their volumes may be reduced.
- 10 **[0286]** With this retrofit, some or all of the water from the first or second pond becomes useable as mix water, often at a higher specific gravity than would otherwise be possible, for example, at a specific gravity greater than, e.g., 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.16, 1.17, 1.18, 1.19, or 1.20, whereas before the retrofit, little or none of the water from the pond was reused as mix water, but instead was disposed of. With the
- 15 retrofit, cementitious materials from previous batches also become available in subsequent batches (see calculations, below). Appropriate sensors and control systems may be used to monitor carbon dioxide addition, as well as monitor appropriate characteristics of the water, also as described herein, and to modify carbon dioxide delivery, as well as to control redirection of water back into the batching system for use as mix water. In this way, as
- 20 much as 100% of the wash water may be recycled into mix water, e.g., at least 10, 20, 30, 40, 50, 60, 70, 80, 90, or 95% of the wash water may be recycled into mix water. For a typical truck, which uses ~120L wash water/m³ of concrete carried in the truck to clean the truck, and a typical mix, which uses ~130L water/ m³ concrete, it is, indeed, possible to recycle 100% of the wash water into subsequent batches of concrete.
- 25 **[0287]** A retrofit may additionally or alternatively include a retrofit at the wash station, or at the truck, or both, to carbonate wash water before it reaches the ponds. At the truck level this includes addition of a source of carbon dioxide, which may be solid, gaseous (in solution or free), or a system to deliver both solid and gaseous carbon dioxide, as described elsewhere herein. For example, a truck may be retrofitted so that its saddlebags can hold carbonated
- 30 water, if necessary. The batching site may be retrofitted to include a system for carbonating water and for supplying it to truck saddlebags (this would include a source of carbon dioxide, appropriate piping and injection systems, optionally a system for supersaturating water with carbon dioxide, and delivery system to deliver carbonated water to saddlebags, and appropriate control systems). Alternatively or additionally, the truck may be retrofitted to

provide a system to carry dry ice for delivery to the drum after the load is delivered, which can be as simple as an insulated container. The batching facility may include a storage system for the dry ice and, optionally, a system for producing dry ice. If it is desired to produce dry ice of appropriate size range for a particular mix or load, as described elsewhere

5 herein, the batch facility or the truck itself may further be outfitted with a system for producing dry ice of the desired size. Additionally or alternatively, the truck may be retrofitted with a system to deliver gaseous carbon dioxide to the drum of the truck, which includes a source of carbon dioxide, a conduit to deliver the carbon dioxide from the source to the drum, and, typically, a metering and control system to regulate addition of carbon

10 dioxide to the drum. All of these retrofits may further include appropriate control systems, such as sensors (e.g., pH and other sensors, as described elsewhere herein, or in the simplest case, a timer, as well as sensors to determine the flow of carbon dioxide), a processor, and one or more actuators (e.g. valves) to control the flow of carbon dioxide according to the desired dose/rate, or other parameters. If it is desired to provide a mixture of solid and

15 gaseous carbon dioxide to the drum of the truck, then the same basic setup as for gaseous is used, except that piping must be such that it can withstand the temperature of liquid carbon dioxide, and the injector should be a snow horn of appropriate design to produce the desired mix of solid and gaseous carbon dioxide.

[0288] At the wash station level, this includes equipment as described elsewhere herein for

20 supplying carbon dioxide at the wash station, including the appropriate source or sources of carbon dioxide, appropriate conduits, injectors, positioning, metering, and control systems if carbon dioxide is injected into the drum, systems for carbonating or super-carbonating water if that method is used, and for delivering the carbonated water to the wash line.

[0289] It will be appreciated that, if a plant is retrofitted to carbonate the wash water, either

25 at the job site/during transport, or at the wash station, or both, sufficient carbonation of wash water may occur so that no further carbonation at the ponds need be pursued; in some cases, however, additional carbonation at the ponds is necessary. In addition, through carbonation in the truck after pouring and during transport, and/or during wash, aggregate in the concrete in the truck can become available for reuse. Using the example of a settlement system with

30 two ponds, if the wash station and/or truck is equipped to carbonate the leftover concrete, the aggregate material in the first pond can remain as discrete particles and be recovered and sieved, as appropriate, for use as aggregate in subsequent batches. The water may be ready at this point to be used as mix water, or it may require further treatment, e.g., further carbonation, to be so used.

[0290] Further possibilities, e.g., for retrofitting, are as follows:

[0291] Agitation of the wash water can be considered in three or more general approaches

[0292] **Customer has an existing wash water tank and an agitation system:** retrofit CO₂ treatment system can include a pump to move the water to/through the treatment step (either inline or in a separate tank). The pump is not the primary source of agitation and thus only needs to start when CO₂ treatment starts and is controlled based on one or all of the sensors (Temp, pH, CO₂ level in headspace)

[0293] **Storage tank with no agitation:** Pumps are used to keep material suspended in the tank. Pump moves the water to/through the treatment step (either inline, the same tank or in a separate tank). The pump is on at any time the CO₂ is injected with start/stop based upon the sensor logic.

[0294] **Customer has a pond with no agitation:** Retrofit CO₂ treatment adapted to pond. A pump is used to move the water to/through the treatment step (either inline or in a separate tank). The pump would need to be on all the time while CO₂ is injected. Pump and CO₂ start/stop are determined by the sensor logic examining the wash water supply.

[0295] In addition, there are various possibilities for the location of addition of carbon dioxide and/or admixture (described elsewhere herein) to wash water. In an exemplary ready-mix operation, wash water is added initially in the truck, after its load is dumped, to keep the remaining concrete from hardening. At this point, admixture, e.g., a set-retarding admixture, may be added to wash water in the drum of the truck. Alternatively or additionally, carbon dioxide may be added to wash water in the drum of the truck. The truck then proceeds to a wash station, where further water may be added to the drum. At this point, admixture, e.g., a set-retarding admixture, may be added to wash water in the drum of the truck. Alternatively or additionally, carbon dioxide may be added to wash water in the drum of the truck. The wash water is typically then pumped to a holding tank, and admixture and/or carbon dioxide can be added to the wash water in the line from the truck to the tank. In an operation in which a reclaimer is used, admixture and/or carbon dioxide may be added as described elsewhere herein. In some operations, additional holding tanks may be used, and at any one or more of these, admixture and/or carbon dioxide may be added. As described herein, the addition may occur in the tank itself or may occur in a recirculation line in which wash water is removed from the tank and circulated through a loop; see, e.g., Example 14. At some point, wash water is moved from, e.g., a holding tank, back to the drum of a ready-mix truck (or into a central mixer) to be used as part or all of the mix water

for a new batch of concrete. Carbon dioxide and/or admixture may be added in the line from the tank to the mixer (truck drum or central mixer).

[0296] The invention also provides kits as appropriate for the various types and combinations of retrofits, as described herein. These can be packaged at a central facility where appropriate components and sizes are selected, according to the operation to be retrofitted, and shipped to the operation, generally with all necessary parts and fittings so that installation at the facility is easy and efficient.

[0297] It will be appreciated that the above discussion regarding retrofits applies equally to the building of new facilities, though some modifications may not be necessary when a facility is built from scratch, whereas other modifications may become necessary, as will be apparent to one of skill in the art.

[0298] Benefits of carbonation of wash water The benefits of carbonation of wash water include a reduction in the carbon footprint of the concrete operation, reduced water usage, reduced waste output, and increased recycled content usage.

[0299] By use of the methods and compositions of the invention, it is possible to get back some percentage of cementitious quality of cement, say at least 10, 20, 30, 40, 50, 60, 70, 80, 90, or 95 of cementitious quality. The producer can then reduce amount of cement in next batch by corresponding amount. E.g., a truck with 500 lb residual concrete, 15% cement, is treated by process and compositions of invention and the resultant slurry contains the cement with 80% of its cementitious properties retained. If all the wash water can be transferred over to the next mix as mix water, then $500 \times 0.15 \times 0.80$ lb, or 60 lb less cement need be used in the next batch. If 90% of remainder of the concrete is aggregate that can be recovered because of the carbonation process, then an additional 450 lb of aggregate may be reduced in the subsequent load. These improvements contribute to a lower carbon footprint, reduced waste output, and increased recycled content usage.

[0300] In addition, as shown in the Examples and described herein, concrete made with wash water treated as described herein exhibits greater strength, especially greater early strength, than concrete made with untreated water. The greater strength may be, in some cases, over 40% of the strength of concrete made with the same mix design and procedure, except with normal mix water rather than carbonated mix water. Thus, less new cement may be used in a mix that uses carbonated wash water than in the same mix that uses normal mix water, which further reduces carbon footprint; for example, at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, or 40% less cement and/or not more than 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40 or 50% less cement to achieve the same compressive strength.

[0301] Further, carbonation of a cement mix, even one using normal water, results in strength increases in the resultant poured material, and correspondingly less need for cement in the batch. See, e.g., U.S. Patent No. 9,388,072. When used in conjunction with carbonated wash water, the results can be additive, or even synergistic, thus, with use of both methods the operator can reduce carbon footprint while at the same time saving money on the most expensive main component of concrete: cement; e.g., combining the two methods (carbonation of wash water and further carbonation of the concrete mix) can result in using for example, at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 50, or 60% less cement and/or not more than 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20, 25, 30, 35, 40, 50, 60, or 70% less cement to achieve the same compressive strength

[0302] Also as described herein, water reuse at a facility using the methods and compositions of the invention can be increased dramatically, in some cases to 100% (e.g., reuse of wash water in subsequent mixes of at least 10, 20, 30, 40, 50, 60, 70, 80, 90, or 95% of the wash water), with a corresponding reduction in waste output, again, in some cases, at or near 100% (e.g., decrease of waste water from wash water of at least 10, 20, 30, 40, 50, 60, 70, 80, 90, or 95% compared to using uncarbonated wash water). This imparts significant cost savings, as well as reducing carbon footprint further because of the reduction in energy use that would go toward treating and disposing of the wash water.

[0303] Disposal and regulatory costs, as well as cement costs, can be reduced by using the methods and compositions described herein. Admixtures, which normally may be needed, e.g. when wash water is used as mix water, related to workability, can often be reduced or eliminated when carbonated wash water is used.

[0304] In many cases, carbonated wash water may not only be used as mix water, but can be recycled as wash water.

[0305] Mechanism of carbonation of wash water. Without being bound by theory, it is thought that when carbon dioxide is introduced into wash water, it quickly is converted to carbonate anion due to the high alkalinity of the wash water; the carbonate anion reacts with calcium and forms a coating on suspended cement particles, reducing their reactivity in the wash water. They are thus “put to sleep” by the carbon dioxide, thus reducing/eliminating acceleration, but contributing to later strength. Variability is also reduced when using wash water that has been carbonated.

[0306] Sulfates The inventors have found that the methods and compositions of the invention also can help to favorably alter sulfate content in a concrete batch made with mix water that includes carbonated wash water. Carbon dioxide-treated wash water can be a tool

to deal with undersulfated binder. In general, a concrete mix that contains a high ratio of aluminates to sulfates may not be a viable mix when used as is. For example, the use of supplementary cementitious materials (SCMs) that contribute aluminates can mean that a cement that has a proper aluminate-sulfate balance is now in a cement blend that is under-sulfated. Carbonated wash water can contain significant concentrations of sulfates in solution. If the sulfate content of the carbonated wash water is known, then an appropriate amount of carbonated wash water mixes can be added to compensate for this. In this case the wash water could have a low solids content because the sulfates are in solution.

Compositions.

10 [0307] Further provided herein are compositions, such as carbonated wash water compositions. In certain embodiments, the invention provides a carbonated concrete wash water composition comprising (i) wash water from concrete; (ii) carbon dioxide and carbon dioxide reaction products with the wash water. The wash water can be primarily composed of water used to rinse out a concrete mixer, e.g., a drum of a ready mix truck, or a
15 combination of wash waters from a plurality of mixers, e.g., a plurality of ready-mix trucks. The amount of carbon dioxide and carbon dioxide reaction products in the carbonated concrete wash water can be at least 0.1, 0.2, 0.5, 0.7, 1.0, 1.2, 1.5, 1.7, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0, 13.0, 14.0, 15.0, 17.0, 20.0, or 25% by weight solids in the wash water composition; for example at least 0.5% by weight solids in the wash
20 water composition, in some cases at least 2% by weight solids in the wash water composition, such at least 5% by weight solids in the wash water composition, or at least 10% by weight solids in the wash water composition. The specific gravity of the carbonated wash water can be at least 1.01, 1.02, 1.03, 1.04, 1.05, 1.06, 1.07, 1.08, 1.09, 1.10, 1.11, 1.12, 1.13, 1.14, 1.15, 1.17, 1.20, or any other specific gravity as described herein; for example, at least 1.03,
25 such as at least 1.05, or at least 1.10. The pH of the carbonated wash water composition can be any pH or range of pHs as described herein, such as at least 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, or 8.5, and/or not more than 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, 7.0, 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, 8.5, 8.7, 9.0, 9.3, 9.5, 9.7, 10, 10.3, 10.5, 10.7, 11.0, 12.0, or 13.0;
30 for example, the pH of the carbonated wash water can be less than 9.0, such as less than 8.5, or less than 8.0. Compositions can further include (iii) additional cement, that is not cement in the wash water, e.g., a cement mix produced from dry cement and carbonated wash water. Such mixes can further include aggregates, admixtures, etc.

Carbon dioxide sequestration and economic advantages

[0308] A concrete production facility utilizing the methods and compositions described herein can incur considerable yearly savings, due to reuse of solids in wash water (thus avoiding use of a certain amount of new cement), avoided landfill costs, and other economic benefits, such as reduced or no additional water treatment costs because some or all of wash water is recycled. In addition, there will be considerable sequestration/offset of carbon dioxide. Thus, in certain embodiments, the invention provides a method of sequestering and/or offsetting carbon dioxide by treating wash water, concrete byproducts (such as returned concrete), or a combination thereof, with carbon dioxide, and optionally re-using some or all of the solids in the wash water as cementitious material in subsequent concrete batches. See Example 9. In certain embodiments, at least 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, 11, 12, 13, 14, or 15% of the carbon dioxide produced in manufacturing cement to be used at a concrete facility, transportation emissions, other emissions associated with concrete manufacture and use, or a combination thereof, is offset by the process. "Offset," as that term is used herein, includes the amount of carbon dioxide emissions avoided (e.g., through reduced cement use), as well as the amount of carbon dioxide actually sequestered, e.g., as part of carbonated wash solids and the like. In certain embodiments, the process provides a savings of at least 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, or 10% of the annual production costs of the concrete facility (e.g., compared to a period of time before carbonation, adjusted as appropriate for fluctuations in loads, costs, etc.). Further cost benefits may be realized in areas where there is a price on carbon, e.g., cap and trade or carbon tax, where the offset carbon dioxide may be a source of further revenue. Additional or alternative carbon dioxide offsets can be achieved by treating concrete produced in the facility with carbon dioxide while the concrete is being mixed, e.g., by applying gaseous carbon dioxide, or solid carbon dioxide, or a mixture of gaseous and solid carbon dioxide, for example in a dose of less than 3, 2, 1.5, 1.2, 1.0, 0.8, 0.6, 0.5, 0.4, 0.3, 0.2, or 0.1 bwc, to the mixing concrete mix. See, e.g., U.S. Patent Nos. 9,108,883 and 9,738,562. This treatment can result in a concrete product that requires less cement than the uncarbonated product, because, in addition to the carbon dioxide directly sequestered in the concrete, the carbonated concrete product has greater strength after setting and hardening than uncarbonated concrete product of the same mix design, and, consequently, a concrete product that requires at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 25, or 30% less cement than the uncarbonated product. In such a case, carbon dioxide offset merely from carbonating the concrete mix may

be at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 25, or 30%.

When concrete wash water treatment with carbon dioxide and, e.g., re-use of some or all of the solids in the wash water in subsequent concrete batches is combined with carbonation of concrete batches at a concrete facility, the total carbon dioxide offset can be at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 32, 35, 37, 40, 42 or 45%.

Admixtures

[0309] One or more admixtures may be added to the concrete wash water and/or to concrete made with the wash water. The addition may occur at one or more points in the process, as described elsewhere herein. Whether or not an admixture is used, the type of admixture, the point in the process at which admixture is added, and/or the amount of admixture added, can depend, e.g., on the type and amount of cement in the wash water. In some cases, addition of carbon dioxide to a wash water from a concrete batch can alter the properties of a subsequent batch which is made using the carbonated wash water as part or all of the mix water.

[0310] A decrease in the particle size of a powder in a binder system can lead to reduced workability (silica fume additions are an illustrative example). A workability impact can be observed for both CO₂-treated and untreated wash water, so the particle size distribution may not be pivotal. An admixture that flocculates fine particles to effectively serve to increase the median particle size and reduce the effective specific surface area, etc., can mitigate negative effects associated with the CO₂ induced reduction in particle size.

[0311] The use of chemicals in the flocculation of precipitated calcium carbonate (PCC) may act favorably on the CO₂ treated solids given their outward surface may effectively behave as calcium carbonate. With PCC, highly charged polyelectrolytes are known to produce strong large flocculants and higher flocculation rates. Both bridging and charge neutralization occur in polyelectrolyte induced PCC flocculation. See, e.g., R. Gaudreault, N. D. Cesare, D. Weitz, T. G. M. van de Ven; "Flocculation kinetics of precipitated calcium carbonate"; Colloids and Surfaces A: Physicochem. Eng. Aspects 340, p56-65, 2009 <https://doi.org/10.1016/j.colsurfa.2009.03.008>

[0312] Without being bound by theory, PCC flocculation with positively charged polyelectrolytes indicates two mechanisms. A polymer with a high charge density and low molar mass such as polyethylenimine could induce PCC flocculation by neutralizing the charge, thus eliminating the electrostatic repulsive force. Whereas a high molar weight polymer with low charge density, such as polyacrylamide, interacts with PCC by a combination of electrostatic and bridging forces. See, e.g., A. Vanerek, B. Alince, T. G. M.

- van de Ven, "Interaction of calcium carbonate fillers with pulp fibres: effects of surface charge and cationic polyelectrolytes", *J. Pulp Pap. Sci.*, 26(9), p317-322, 2000. Natural carbohydrates can also be used, e.g., starch (such as potato, corn, and/or tapioca starches), dextran, lignin. A starch derivative Glycidyl tetradecyl dimethylammonium chloride (GTDAC) can also be used. See, e.g., Y. Wei, F. Cheng, H. Zheng, "Synthesis and flocculating properties of cationic starch derivatives", *Carbohydr. Polym.*, 74(3), p673-679, 2008, Y. Wei, F. Cheng, H. Zheng, "Synthesis and flocculating properties of cationic starch derivatives", *Carbohydr. Polym.*, 74(3), p673-679, 2008. Another possible admixture is pectin (a biopolymer of D-galacturonic acid), whereon the addition of Al^{3+} and Fe^{3+} could greatly increase pectin's flocculating efficiency. Cationic ions neutralized and stabilized negatively charged pectin and bound particles by electrostatic attraction. See, e.g., H. Yokoi, T. Obita, J. Hirose, S. Hayashi, Y. Takasaki, "Flocculation properties of pectin in various suspensions", *Bioresour. Technol.*, 84(3), p287-290, 2002. [https://doi.org/10.1016/S0960-8524\(02\)00023-8](https://doi.org/10.1016/S0960-8524(02)00023-8).
- 15 **[0313]** Another potential admixture is cellulose or cellulose derivatives, e.g. electrosterically stabilized nanocrystalline cellulose (ENCC); dissolved carboxylated cellulose (DCC); rod-like dialdehyde cellulose (DAC) nanofibers, also referred to as sterically stabilized nanocrystalline cellulose (SNCC); dissolved DAC as dialdehyde modified cellulose (DAMC). ENCC/DCC showed a high flocculation efficiency with PCC particles and induced
- 20 PCC flocculation by a combination of electrostatic and bridging forces. ENCC/DCC induces the maximum PCC flocculation when PCC particles reach to isoelectric point. The flocculation of PCC induced by SNCC: SNCC particles can bridge PCC to induce flocculation at low dosage (above 1 mg/g). SNCC induced the maximum flocculation when its fractional coverage was more than half coverage because SNCC particles become unstable
- 25 after deposition on PCC. Adsorption isotherms of three SNCCs and dialdehyde modified cellulose (DAMC) on PCC particles were measured. It was found that DAMC had a higher affinity than three SNCCs with different aldehyde contents, and the affinity of SNCC increased with reaction time. This indicates DAMC chains adsorb stronger than nanocrystalline parts of SNCC on PCC. See, e.g., Dezhi Chen, Theo G.M. van de Ven, Flocculation kinetics of precipitated calcium carbonate induced by electrosterically stabilized nanocrystalline cellulose, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 504, 2016, Pages 11-17, ISSN 0927-7757, <https://doi.org/10.1016/j.colsurfa.2016.05.023>; Chen, Dezhi. "Flocculation Kinetics Of
- 30

Precipitated Calcium Carbonate Induced By Functionalized Nanocellulose." (2015). PhD Thesis.

- [0314] Another useful admixture is cationic polysaccharides, with N-alkyl-N,N-dimethyl-N-(2-hydroxypropyl)ammonium chloride pendent groups attached to a dextran backbone. The flocculation performance of the hydrophobically modified cationic dextran highly depended on its hydrophobicity and charge density, and was less dependent on molar mass. See, e.g., L. Ghimici, M. Nichifor, "Novel biodegradable flocculant agents based on cationic amphiphilic polysaccharides", *Bioresour. Technol.*, 101(22), p8549-8554, 2000. Doi: 10.1016/j.biortech.2010.06.049.
- 10 [0315] Another useful admixture is cationic derivatives of dialdehyde cellulose (CDAC). CDACs showed very good flocculation performance in neutral and acidic suspensions, while a low flocculation activity was observed in alkaline suspensions because CDACs were broken down into small fragments at alkaline pH. See, e.g., Liimatainen, H, Sirviö, J, Sundman, O, Visanko, M, Hormi, O & Niinimäki, J 2011, 'Flocculation performance of a cationic biopolymer derived from a cellulosic source in mild aqueous solution' *BIORESOURCE TECHNOLOGY*, vol 102, no. 20, pp. 9626-9632. DOI: 15 10.1016/j.biortech.2011.07.099.
- [0316] Another useful admixture is graft copolymers of carboxymethylcellulose (CMC) and polyacrylamide. Copolymers with fewer and longer PAM chains exhibited better flocculation performance. See, e.g., D. R. Biswal, R. P. Singh, "Flocculation studies based on water-soluble polymers of grafted carboxymethyl cellulose and polyacrylamide", *J. Appl. Polym. Sci.*, 102(2), p1000-1007, 2006. doi:10.1002/app.24016.
- 20 [0317] The flocculation kinetics of PCC has been studied in relation to cationic potato starch (C-starch), anionic potato carboxymethyl starch (A-starch), cationic polyacrylamide (C-PAM), Anionic polyacrylamide (A-PAM), Poly(ethylene oxide) (PEO), PEO cofactor, PVFA/NaAA, glyoxalated-PAM (PAM-glyoxal), cationic polyacrylamide (C-PAM), and polyamine (Pam) polyethylenimine (PEI). See, e.g., Gaudreault, R., Di Cesare, N., Weitz, D., & van de Ven, T. G. (2009). Flocculation kinetics of precipitated calcium carbonate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 340(1-3), 56-65. doi: 25 10.1016/j.colsurfa.2009.03.008. During polymer induced flocculation, the particle size increases from its initial value to a plateau value. PEO/cofactor, A-PAM and C-PAM retention aid systems, are very cost effective in inducing PCC aggregation, and create very large aggregates at high polymer dosage. C-PAM, glyoxalated-PAM and the polyamine coagulant (Pam) do not significantly induce filler aggregation. Both PEO/cofactor and C-

- PAM, gave higher flocculation rates and larger flocculant sizes making them useful, for process water clarification. Neither PEO nor cofactor alone, without salt, induce PCC aggregation. PCC aggregates induced by PVFA/NaAA and C-starch have floc sizes less sensitive to dosage in region I. PEO/cofactor, which is known to cluster, gave faster
- 5 flocculation rate and larger flocs; because the polymer cluster enlarge the effective polymer size leading to larger flocs. The A-PAM is highly charged and gives strong flocs due to strong binding to PCC. PAM-glyoxal, C-PAM (dry strength), and polyamine cause little or no flocculation, because they act as dispersants, similar to PEI.
- [0318] The effect of cationic polyacrylamide on precipitated calcium carbonate flocculation: Kinetics, charge density and ionic strength has also been studied. See, e.g., Peng, P. and Garnier, G., 2012. Effect of cationic polyacrylamide on precipitated calcium carbonate flocculation: Kinetics, charge density and ionic strength. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 408, pp.32-39. doi: 10.1016/j.colsurfa.2012.05.002. Cationic polyacrylamide (CPAM). The adsorption kinetics of
- 15 CPAM onto PCC can be explained by the balance of the electrostatic and van der Waals interactions, hydrogen bonding and steric hindrance between the adsorbed and dissolved CPAM molecules and CC. Increasing the ionic strength of the PCC suspension consistently screened the charge of CPAM molecules so that the initially dominant electrostatic attractions between CPAM and PCC in the absence of salt shifted to hydrogen bonding dominated
- 20 attraction at high ionic strength ($I = 0.1$). At low ionic strengths ($I = 0.01$), both electrostatic attractions and hydrogen bonding were important in controlling the interaction between CPAM and PCC.

Admixture to retain solids in suspension.

- [0319] In certain embodiments, carbonated wash water is treated with one or more
- 25 admixtures to create a mixture where the solids remain suspended with little or no agitation. These can include viscosity-modifying admixtures (VMAs). VMAs can be comprised of a wide range of different chemistries. Some VMAs are based on fine inorganic materials like colloidal silica, while others are comprised of more complex synthetic polymers such as styrene-maleic anhydride terpolymers and hydrophobically modified ethoxylated urethanes
- 30 (HEUR). The more common VMAs are based on cellulose-ethers and biopolymers (xanthan, welan, and diutan gums). Further VMAs include biopolymer polysaccharides such as S-657, welan gum, xanthan, rhamsan, gellan, dextran, pullulan, curdlan, and derivatives thereof; (b) marine gums such as algin, agar, carrageenan, and derivatives thereof; (c) plant exudates such as locust bean, gum arabic, gum Karaya, tragacanth, Ghatti, and derivatives thereof; (d) seed

gums such as guar, locust bean, okra, psyllium, mesquite, or derivatives thereof; and (e) starch-based gums such as ethers, esters, and derivatives thereof (f) associative thickeners such as hydrophobically modified alkali swellable acrylic copolymer, hydrophobically modified urethane copolymer, associative thickeners based on polyurethanes, cellulose, polyacrylates, or polyethers. In another classification scheme (Khayat, K.H., 1998. Viscosity-enhancing admixtures for cement-based materials — An overview. *Cement and Concrete Composites* 20, 171–188. [https://doi.org/10.1016/S0958-9465\(98\)80006-1](https://doi.org/10.1016/S0958-9465(98)80006-1)) VMAs are classified in various classes: Class A are water-soluble synthetic and natural organic polymers that increase the viscosity of the mixing water. Class A type materials include cellulose ethers, polyethylene oxides, polyacrylamide, polyvinyl alcohol, etc. Class B are organic water-soluble flocculants that become adsorbed onto cement grains and increase viscosity due to enhanced inter-particle attraction between cement grains. Class B materials include styrene copolymers with carboxyl groups, synthetic polyelectrolytes, and natural gums. Class C are emulsions of various organic materials which enhance interparticle attraction and supply additional superfine particles in the cement paste. Among the materials belonging to Class C are acrylic emulsions and aqueous clay dispersions. Class D are water-swellable inorganic materials of high surface area which increase the water retaining capacity of the paste, such as bentonites, silica fume and milled asbestos. Class E are inorganic materials of high surface area that increase the content of the fine particles in paste and, thereby, the thixotropy. These materials include fly ash, hydrated lime, kaolin, various rock dusts, and diatomaceous earth, etc. In another classification scheme, Kawai classified water-soluble polymers as natural, semi-synthetic, and synthetic polymers. Natural polymers include starches, guar gum, locust bean gum, alginates, agar, gum arabic, welan gum, xanthan gum, rhamsan gum, and gellan gum, as well as plant protein. Semi-synthetic polymers include: decomposed starch and its derivatives; cellulose-ether derivatives, such as hydroxypropyl methyl cellulose (HPMC), hydroxyethyl cellulose (HEC), and carboxy methyl cellulose (CMC); as well as electrolytes, such as sodium alginate and propyleneglycol alginate. Finally, synthetic polymers include polymers based on ethylene, such as polyethylene oxide, polyacrylamide, polyacrylate, and those based on vinyl, such as polyvinyl alcohol. In some cases, a viscosity-modifying agent can be used with a superplasticizer, such as a hydrocolloid such as welan gum or hydroxypropylmethyl cellulose and a superplasticizer such as sulfonated naphthalene, sulfonated melamine, modified lignosulfate, their derivatives and mixtures thereof. Thus, the wash water can include a stable hydrocolloid composition in which the hydrocolloid is uniformly dispersed in

- a superplasticizer such as sulfonated naphthalene, sulfonated melamine, modified lignosulfate, their derivatives and mixtures thereof. Suitable hydrocolloids include welan gum, methylcellulose, hydroxypropylmethyl cellulose (HPMC), hydroxyethyl cellulose (HEC), polyvinyl alcohol (PVA), starch, and the like. The mixture is then stabilized by a rheological control agent consisting of reticulated cellulose fibers. The composition is rapidly hydratable and useful as a stabilizing additive in many cement and drilling fluid applications. Further useful admixtures are described in Naik, H.K., Mishra, M.K., Rao Karanam, U.M., 2009, The Effect of Drag-Reducing Additives on the Rheological Properties of Fly Ash-Water Suspensions at Varying Temperature Environment. Coal Combustion and Gasification Products 1, 25-31, doi: 10.4177/CCGP-D-09-00005.1 https://www.researchgate.net/publication/209640967_The_Effect_of_Drag-Reducing_Additives_on_the_Rheological_Properties_of_Fly_Ash-Water_Suspensions_at_Varying_Temperature_Environment.
- [0320] In this case, the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) was selected for its eco-friendly nature. It is less susceptible to mechanical degradation) and also known potential to positively influence turbulent flow with very small amount. It is also least affected by the presence of calcium and sodium ions in tap water. The chemical formula of CTAB is $C_{19}H_{42}BrN$. The surfactant can be procured from, e.g., LOBA Chemie Pvt. Ltd., Mumbai, India. The molecular weight of the surfactant is 364.46.
- For the surfactant drag-reducing additives, the rod-like micelle structures are thought to be the key to give complicated rheological fluid properties including viscoelasticity. The counter-ion acts as a reagent to reduce ion radius of the surfactant to deform micellar shape from globular to rod-like micelles. These rod-like micelles entangle together to make a certain network structure. Counter-ions will play a role as catalysts for the breakdown and reformation of the entanglement points. The counter-ion selected for this investigation can be, e.g. sodium salicylate (NaSal) (HOC_6H_4COONa) having molecular weight 160.10 obtained from, e.g., LOBA Chemie Pvt. Ltd., Mumbai, India.

Set retarders

- [0321] In certain embodiments, a set retarder is added to the wash water before it is carbonated, e.g., while the wash water is still in the truck, or in any suitable manner to introduce the set retarder before carbonation of the wash water. **Set retarders** A set retarder is generally a substance that can delay the time before cement hydrates, for example, in a concrete mix. Set retarders are well-known in the concrete industry, and any suitable set retarder may be used. Set retarders include carbohydrates, i.e., saccharides, such as sugars,

e.g., fructose, glucose, and sucrose, and sugar acids/bases and their salts, such as sodium gluconate and sodium glucoheptonate; phosphonates, such as nitrilotri(methylphosphonic acid), 2-phosphonobutane-1,2,4-tricarboxylic acid; and chelating agents, such as EDTA, Citric Acid, and nitrilotriacetic acid. Other saccharides and saccharide-containing admixes include molasses and corn syrup. An exemplary set retarder is sodium gluconate. Other exemplary admixtures that can be of use as set retarders include sodium sulfate, citric acid, BASF Pozzolith XR, firmed silica, colloidal silica, hydroxyethyl cellulose, hydroxypropyl cellulose, fly ash (as defined in ASTM C618), mineral oils (such as light naphthenic), hectorite clay, polyoxyalkylenes, natural gums, or mixtures thereof, polycarboxylate superplasticizers, naphthalene HRWR (high range water reducer). Additional set retarders that can be used include, but are not limited to an oxy-boron compound, lignin, a polyphosphonic acid, a carboxylic acid, a hydroxycarboxylic acid, polycarboxylic acid, hydroxylated carboxylic acid, such as fumaric, itaconic, malonic, borax, gluconic, and tartaric acid, lignosulfonates, ascorbic acid, isoascorbic acid, sulphonic acid-acrylic acid copolymer, and their corresponding salts, polyhydroxysilane, polyacrylamide. Illustrative examples of retarders are set forth in U.S. Pat. Nos. 5,427,617 and 5,203,919, incorporated herein by reference.

[0322] The set retarder is added to the concrete or concrete wash water in any suitable amount; generally, dosing is well-established for a particular set retarder and desired effect. Exemplary percentages for sodium gluconate can be, e.g., at least 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, or 5% by weight solids in the washwater, and/or not more than 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5, or 10% by weight solids in the washwater. It will be appreciated that dosing may have to be approximate for some uses, e.g., when used with concrete coated on the inside of a ready-mix drum, and often operators will add excess set retarder to ensure that setting and hardening do not occur. This excess may be taken into account when carbonating the concrete or concrete wash water, and additional carbonation of the new concrete added to the old may be used in order to offset the excess set retarder, as necessary.

[0323] Thus, in certain embodiments, the invention provides methods and compositions for treating concrete wash water, that has been treated with set retarders, with carbon dioxide. This may be used when a truck is returned to the batch site and washed but the wash water is not removed from the truck; typically such a truck will sit overnight at the batching facility, then a new load of concrete will be introduced into the truck the next day. The wash water with set retarder contains components of the load that was in the truck, including cement. The wash water with set retarder may be treated with carbon dioxide after the addition of set

retarder and before and/or during the addition of a new load of concrete to the truck. For example, the concrete wash water may have been exposed to set retarder, and then have sat, e.g., in the truck drum, for at least 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 24, 28, 32 hours, and/or for not more than 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 24, 28, 32, or 36 hours, then carbon dioxide is added to the wash water. This may occur before a new load is added to the truck, e.g., at least 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 30, 40, 50, or 60 minutes before the new load, or at least 1, 1.5, 2, 2.5, 3, 4, 5, 6, or 8 hours before the new load, and/or not more than 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 30, 40, 50, or 60 minutes before the new load, or not more than 1, 1.5, 2, 2.5, 3, 4, 5, 6, 8, or 10 hours before the new load. Additionally or alternatively, carbon dioxide may be added as the new load is added, or carbon dioxide addition may occur both before and during addition of the new load. Carbon dioxide may be added in an amount sufficient to reverse some or all of the effect of the set retarder on the cement in the wash water with set retarder; the carbon dioxide dose may be any suitable dose, calculated as by weight cement in the wash water; it will be appreciated that such a calculation often must be based on estimates of the amount of concrete sticking to the drum of the truck, and typically in addition the mix design of the load or loads that were in the truck prior to washing is also used to estimate cement content. Alternatively, a fixed amount of carbon dioxide may be used, such as an amount known to provide an excess of carbon dioxide so that all cement will react. The carbon dioxide dose may also be adjusted according to the amount of set retarder in the wash water, which may be, e.g., recorded by the operator, or may be as specified by protocol, or may be estimated. It will be appreciated that if excess set retarder is used in the wash water, then additional carbon dioxide may be necessary in order to prevent effects on the next load added to the wash water. In such cases, it may be useful to add carbon dioxide as the next load is added, or immediately before, so that carbon dioxide will not exit the treated wash water into the atmosphere. Exemplary doses are described elsewhere herein, for example, a dose of 0.001-5.0% bwc. Additionally or alternatively, carbon dioxide may be added to the new batch of concrete; typically, such a dose will be below 2%, such as less than 1.5%, or less than 1%, or in some cases less than 0.5% by weight cement (bwc).

[0324] In certain embodiments, concrete wash water is moved to a holding tank; this water can be treated with one or more set retarders at some point, either in the truck, or in the tank, or a combination thereof, then carbon dioxide can be introduced at a later point, e.g., when it is desired to re-use the wash water in a new batch of concrete. For example, wash water treated with set retarder can be exposed to carbon dioxide before its use as mix water

and/or during its use as mix water. In this way, without being bound by theory, it is thought that the cement is kept in a “dormant” state by use of the set retarder, then that state is reversed by carbonation reactions from addition of the carbon dioxide.

- [0325] In certain embodiments, wash water is treated with a first dose of a first set retarder and then, at a later time, with a second dose of a second set retarder, where the first and second set retarders may be the same or different. Further doses may be used as appropriate. The time of the first dose may be within a few hours of formation of the wash water, and the time of the second dose may be, e.g., just before or after and/or during exposure of the wash water to carbon dioxide.
- [0326] In certain embodiments the invention provides methods and compositions for treating concrete, that has been treated with one or more set retarders, with carbon dioxide. This can occur, e.g., when a truck returns to a batching facility after only part of its load is used at a job site. In this case the concrete may be treated with set retarder at the job site or later; thus, the concrete may be batched then set retarder may be added a certain amount of time after batching, for example, at least 0.1, 0.2, 0.5, 0.7, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, or 8 hours after batching, and/or not more than 0.2, 0.5, 0.7, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 8, or 10 hours after batching. The truck generally returns to the batching facility, and it may be desired to load additional concrete into the truck in addition to the returned concrete. Carbon dioxide can be added to the returned concrete, that has been treated with one or more set retarders, in any suitable dose, as described elsewhere herein; for example, at a dose of 0.001-5.0% bwc; the carbon dioxide may be added at any suitable time after set retarders are added, though this may be dependent on a number of factors, such as return time to the batching facility, storage time at the batching facility, and the like; thus in certain embodiments, carbon dioxide may be added at least 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 20, 25, 30, 35, or 40 hours after set retarder is added to the concrete, and/or not more than 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 20, 25, 30, 35, or 40 hours after set retarder is added to the concrete. The concrete may then be used with additional concrete in a new batch of concrete; such use may occur simultaneously or nearly simultaneously with carbon dioxide addition, or may occur at any suitable time after carbon dioxide addition, such as at least 1, 2, 5, 7, 10, 15, 20, 25, 30, 40, or 50 min after carbon dioxide addition, or at least 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, or 6 hours after carbon dioxide addition, and/or not more than 2, 5, 7, 10, 15, 20, 25, 30, 40, or 50 min after carbon dioxide addition, or not more than 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6 or y hours after carbon dioxide addition. The new concrete may additionally be treated with carbon dioxide, so that in some

embodiments both the old concrete and the new concrete are treated with carbon dioxide; as discussed, this may happen simultaneously or the old concrete may be treated with carbon dioxide, then new concrete is treated, for example, as it is mixed with the old concrete. The dose of carbon dioxide for the new concrete may be any suitable dose as described herein.

- 5 [0327] In some cases, set retarder is added to a concrete batch at the batching facility, or in the truck on the way to the job site, because factors such as expected traffic on the way to the job site, temperature, and the like, necessitate that the batch not begin to set too soon. In this case, it can be desirable to reverse the effect of the set retarder before pouring at the job site, i.e., in this case and other cases described herein, the set retarder acts as an “off switch,”
- 10 and the carbon dioxide acts as an “on switch” for the cement in the concrete. Carbon dioxide will be added to the concrete at some other location than the batching facility in these embodiments, for example, in the truck on the way to, or at, the job site. A truck may be equipped with a portable carbon dioxide delivery system, such as a source of carbon dioxide and a conduit for transporting carbon dioxide to the drum of the truck. Additionally or
- 15 alternatively, a carbon dioxide delivery system may be sited at or near the job site, and trucks may arrive at the carbon dioxide delivery site, then the concrete contained therein may be treated with carbon dioxide at an appropriate time before its use at the job site; in this way, trucks may have a larger time window for transporting the concrete and its use, and factors such as traffic, delays at the job site, and the like, become less of an issue; the concrete is
- 20 “dormant” due to the set retarder, then activated by use of the carbon dioxide. The dose of carbon dioxide may be suitable any dose as described herein, such as a dose of 0.001-5.0% bwc; also as described elsewhere, the dose may be dependent on the type of cement in the concrete, the type and amount of set retarder, the expected time of use of the concrete after the addition of carbon dioxide, temperature, and the like. The carbon dioxide may be added
- 25 at any suitable time before the expected time of use of the concrete, for example, at least 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, or 50 minutes before the expected time of use, or at least 1, 1.5, 2, 2.5, or 3 hours before the expected time of use, and/or no more than 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, or 50 minutes before the expected time of use, or no more than 1, 1.5, 2, 2.5, 3, or 3.5 hours before the expected time of use. Thus in certain embodiments the invention
- 30 provides a method of treating concrete comprising treating concrete with a set retarder, then treating the concrete with carbon dioxide. The set retarder is generally added at a batching facility, though it may be added in the drum of the truck after it has left the batching facility, for example, if traffic delays and/or delays at the job site become known. The carbon dioxide is added en route to the job site and/or at the job site; typically it is added into the drum of the

ready-mix truck, though it may also be added during the transport of the concrete from the drum to, e.g., the forms at the job site.

[0328] In certain embodiments, set retarder and carbon dioxide are added to a concrete mix in order to provide a desired combination of improved workability and acceptable set time. One or more set retarders may be added to a concrete mix in order to improve workability; however, this often comes at the cost of a delayed set time. In order to shorten set time but retain workability, a set accelerant admixture may be used. However, although set retarders are generally relatively inexpensive, set accelerants are often expensive and also often contain undesirable chemical species, such as chloride. Thus, it is desirable to use a substance that can accelerate set to within a desired time frame that is not highly expensive; carbon dioxide is one such substance. In these cases, carbon dioxide and set retarder may be added in any suitable sequence, such as sequentially with set retarder first, then carbon dioxide; or as carbon dioxide first, then set retarder; or simultaneously or nearly simultaneously, e.g., the timing of addition of set retarder and carbon dioxide is such that they are both being added to a concrete mix during at least a portion of their respective addition times. Thus, in certain embodiments, carbon dioxide is added to a concrete mix, then a set retarder is added after carbon dioxide addition (i.e., after carbon dioxide addition begins; depending on the length of time for carbon dioxide addition, set retarder addition may start before carbon dioxide addition ends, though this would not typically be the case); the set retarder may be added, for example, at least 0.1, 0.5, 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, or 50 minutes after carbon dioxide addition, or at least 1, 1.5, 2, 2.5, 3, 3.5, or 4 hours after carbon dioxide addition; and/or not more than 0.5, 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, or 50 minutes after carbon dioxide addition, or not more than 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, or 6 hours after carbon dioxide addition. In other certain embodiments, set retarder is added to a concrete mix, then carbon dioxide is added after set retarder addition (i.e., after set retarder addition begins; depending on the length of time for set retarder addition, carbon dioxide addition may start before set retarder addition ends, though this would not typically be the case); the carbon dioxide may be added, for example, at least 0.1, 0.5, 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, or 50 minutes after set retarder addition, or at least 1, 1.5, 2, 2.5, 3, 3.5, or 4 hours after set retarder addition; and/or not more than 0.5, 1, 2, 3, 4, 5, 7, 10, 15, 20, 30, 40, or 50 minutes after set retarder addition, or not more than 1, 1.5, 2, 2.5, 3, 3.5, 4, or 4.5 hours after set retarder addition. It is also possible to add set retarder, carbon dioxide, or both, in divided doses, where the timing of each dose of one may be relative to the dose of the other in any suitable manner. For example, a certain amount of set retarder may be added, then carbon dioxide,

then a final dose of set retarder; this is merely exemplary, and any suitable number of doses for set retarder and/or carbon dioxide, as well as any suitable timing of addition, may be used.

[0329] It will be appreciated that set accelerants are available as admixtures; such set accelerants may be used in addition to carbon dioxide. However, these admixtures tend to be expensive, and also often contain undesirable chemical species such as chloride, and it is desirable to use carbon dioxide as a less expensive alternative as much as possible.

Dose of carbon dioxide

[0330] The concrete or concrete wash water, with set retarder, may be exposed to any suitable dose of carbon dioxide. For example, the dose may be not more than 5%, 4, 3%, 2.5%, 2%, 1.5%, 1.2%, 1%, 0.8%, 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2%, 0.1%, 0.05%, 0.01%, or 0.05% bwc and/or at least .001, .005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.5, 2.0, 2.5, 3.0, 4.0, or 4.5% bwc, such as a dose of 0.001-5%, or 0.001-4%, or 0.001-3%, or 0.001-2%, or 0.001-1.5%, 0.001-1.2%, 0.001-1%, 0.001-0.8%, 0.001-0.6%, 0.001-0.5%, 0.001-0.4%, 0.001-0.3%, 0.001-0.2%, or 0.001-0.1% bwc, or a dose of 0.01-5%, or 0.01-4%, or 0.01-3%, or 0.01-2%, 0.01-1.5%, 0.01-1.2%, 0.01-1%, 0.01-0.8%, 0.01-0.6%, 0.01-0.5%, 0.01-0.4%, 0.01-0.3%, 0.01-0.2%, or 0.01-0.1% bwc, or a dose of 0.02-1.5%, 0.02-1.2%, 0.02-1%, 0.02-0.8%, 0.02-0.6%, 0.02-0.5%, 0.02-0.4%, 0.02-0.3%, 0.02-0.2%, or 0.02-0.1% bwc, or a dose of 0.04-1.5%, 0.04-1.2%, 0.04-1%, 0.04-0.8%, 0.04-0.6%, 0.04-0.5%, 0.04-0.4%, 0.04-0.3%, 0.04-0.2%, or 0.04-0.1% bwc, or a dose of 0.06-1.5%, 0.06-1.2%, 0.06-1%, 0.06-0.8%, 0.06-0.6%, 0.06-0.5%, 0.06-0.4%, 0.06-0.3%, 0.06-0.2%, or 0.06-0.1% bwc, or a dose of 0.1-1.5%, 0.1-1.2%, 0.1-1%, 0.1-0.8%, 0.1-0.6%, 0.1-0.5%, 0.1-0.4%, 0.1-0.3%, or 0.1-0.2% bwc. The dose of carbon dioxide may be dependent on various factors, such as the type of cement in the concrete or concrete wash water, type and amount of set retarder used, timing of the addition of carbon dioxide after set retarder, temperature, expected time between addition of carbon dioxide and use of the concrete, and the like.

Form of carbon dioxide

[0331] The carbon dioxide may be added to the concrete or concrete wash water, with set retarder, in any suitable form, such as a gas, liquid, solid, or supercritical form; in certain embodiments, carbon dioxide comprising solid carbon dioxide can be used. This may be in the form of a mixture of solid and gaseous carbon dioxide, which can be formed from liquid carbon dioxide as it exits a conduit under pressure and is exposed to lower pressure, such as atmospheric pressure. See, e.g., U.S. Patent No. 9,738,562. Additionally or alternatively, solid carbon dioxide alone may be added, such as as pellets or shavings, or other suitable form, which may be determined at least in part by the desired speed of sublimation of the

carbon dioxide and its subsequent entry into solution. See, e.g., U.S. Patent No. 9,738,562. In certain embodiments, only gaseous carbon dioxide is used.

Further Admixtures

[0332] This section summarizes some further useful admixtures for use in the methods and compositions herein. For additional listings see Report on Chemical Admixtures for Concrete, Reported by ACI Committee 212, American Concrete Institute, ACI 212.3R-16, ISBN 978-1-942727-80-4, incorporated herein by reference in its entirety.

Admixtures useful in the methods and compositions herein include:

[0333] Accelerators: cause increase in the rate of hydration and thus accelerate setting and/or early strength development. In general, accelerating admixtures for concrete use should meet the requirements of ASTM C494/C494M for Type C (accelerating admixtures) or Type E (water-reducing and accelerating admixtures). Examples include inorganic salts, such as chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates, and alkali hydroxides. Of particular interest are calcium-containing compounds, such as CaO, Ca(NO₂)₂, Ca(OH)₂, calcium stearate, or CaCl₂, and magnesium-containing compounds, such as magnesium hydroxide, magnesium oxide, magnesium chloride, or magnesium nitrate. Without being bound by theory, it is thought that, in the case of carbonated cement, the added calcium or magnesium compound may provide free calcium or magnesium to react with the carbon dioxide, providing a sink for the carbon dioxide that spares the calcium in the cement mix, or providing a different site of carbonation than that of the cement calcium, or both, thus preserving early strength development. In addition, the anion, e.g., nitrate from a calcium-containing admixture may influence C-S-H particle structure. Other set accelerators include, but are not limited to, a nitrate salt of an alkali metal, alkaline earth metal, or aluminum; a nitrite salt of an alkali metal, alkaline earth metal, or aluminum; a thiocyanate of an alkali metal, alkaline earth metal or aluminum; an alkanolamine; a thiosulfate of an alkali metal, alkaline earth metal, or aluminum; a hydroxide of an alkali metal, alkaline earth metal, or aluminum; a carboxylic acid salt of an alkali metal, alkaline earth metal, or aluminum (preferably calcium formate); a polyhydroxylalkylamine; a halide salt of an alkali metal or alkaline earth metal (e.g., chloride). Stable C-S-H seeds may also be used as accelerators.

[0334] In certain embodiments an accelerator can include one or more soluble organic compounds such as one or more alkanolamines, such as triethylamine (TEA), and/or higher trialkanolamines or calcium formate. The term "higher trialkanolamine" as used herein

includes tertiary amine compounds which are tri(hydroxyalkyl) amines having at least one C₃-C₅ hydroxyalkyl (preferably a C₃-C₄ hydroxyalkyl) group therein. The remaining, if any, hydroxyalkyl groups of the subject tertiary amine can be selected from C₁-C₂ hydroxyalkyl groups (preferably C₂ hydroxyalkyl). Examples of such compounds include hydroxyethyl di(hydroxypropyl)amine, di(hydroxyethyl) hydroxypropylamine, tri(hydroxypropyl)amine, hydroxyethyl di(hydroxy-n-butyl)amine, tri(2-hydroxybutyl)amine, hydroxybutyl di(hydroxypropyl)amine, and the like. Accelerators can also include calcium salts of carboxylic acids, including acetate, propionate, or butyrate. Other organic compounds that can act as accelerators include urea, oxalic acid, lactic acid, various cyclic compounds, and condensation compounds of amines and formaldehyde.

[0335] Quick-setting admixtures may be used in some embodiments, e.g., to produce quick-setting mortar or concrete suitable for shotcreting or for 3D printing. These include, e.g., ferric salts, sodium fluoride, aluminum chloride, sodium aluminate, and potassium carbonate.

[0336] Miscellaneous additional accelerating materials include silicates, finely divided silica gels, soluble quaternary ammonium silicates, silica fume, finely divided magnesium or calcium carbonate. Very fine materials of various composition can exhibit accelerating properties. In certain embodiments, admixture can include nucleation seeds based on calcium-silicate hydrate (C-S-H) phases; see e.g. Thomas, J.J., et al. 2009 J. Phys Chem 113:4327-4334 and Ditter et al. 2013 BFT International, Jan, pp. 44-51, which are incorporated by reference herein in their entireties.

[0337] In certain embodiments, a set accelerator including one, two, or three of triisopropanolamine (TIPA), N,N-bis(2-hydroxyethyl)-N-(2-hydroxypropyl)amine (BHEHPA) and tri(2-hydroxybutyl) amine (T2BA) is used, for example, a set accelerator comprising TIPA. Any suitable dose may be used, such as 0.0001-0.5% bwc, such as 0.001-0.1%, or 0.005-0.03% bwc. See U.S. Patent No. 5,084,103.

[0338] In certain embodiments, carbonation of a cement mix is combined with use of an admixture comprising an alkanolamine set accelerator, e.g., TIPA, where the alkanolamine set accelerator, e.g., TIPA, is incorporated in an amount of 0.0001-0.5% bwc, such as 0.001-0.1%, or 0.005-0.03% bwc. In some of these embodiments, the alkanolamine, e.g., TIPA,-containing admixture is added before and/or during carbonation, e.g., as part of the initial mix water. In some of these embodiments, the alkanolamine, e.g., TIPA,-containing admixture is added after and/or during carbonation. In some embodiments, the alkanolamine, e.g., TIPA,-containing admixture is added as two or more doses, which may be added at different times

relative to carbonation (e.g., two doses, one before and one after carbonation, etc.).

Additionally or alternatively, carbonation may proceed in two or more doses with, e.g., one or more doses of an alkanolamine, e.g., TIPA,-containing admixture added before, after, or during one or more of the carbon dioxide doses. Other components may be present in the

- 5 alkanolamine, e.g., TIPA,-containing admixture, including one or more of set/strength controller, set balancer, hydration seed, dispersant, air controller, rheology modifier, colorant, or a combination thereof. Suitable commercially available products include BASF Master X-Seed 55 (BASF Corporation, Admixture Systems, Cleveland, OH). The total dose of carbon dioxide delivered to the cement mix in these embodiments may be
- 10 any suitable dose, such as those described herein, for example, 0.001-2% bwc, such as 0.001-1.0% bwc, or 0.001-0.5% bwc.

[0339] Air detrainers: also called defoamers or deaerators, decrease air content.

Examples include nonionic surfactants such as phosphates, including tributylphosphate, dibutyl phosphate, phthalates, including diisodecylphthalate and dibutyl phthalate, block

- 15 copolymers, including polyoxypropylene-polyoxyethylene-block copolymers, and the like, or mixture thereof. Air detrainers also include octyl alcohol, water-insoluble esters of carbonic and boric acid, and silicones. Further examples of air detrainers include mineral oils, vegetable oils, fatty acids, fatty acid esters, hydroxyl functional compounds, amides, phosphoric esters, metal soaps, polymers containing propylene oxide moieties,
- 20 hydrocarbons, alkoxylated hydrocarbons, alkoxylated polyalkylene oxides, acetylenic diols, polydimethylsiloxane, dodecyl alcohol, octyl alcohol, polypropylene glycols, water-soluble esters of carbonic and boric acids, and lower sulfonate oils.

[0340] Air-entraining admixtures: The term air entrainer includes any substance that will entrain air in cementitious compositions. Some air entrainers can also reduce the

25 surface tension of a composition at low concentration. Air-entraining admixtures are used to purposely entrain microscopic air bubbles into concrete. Air-entrainment dramatically improves the durability of concrete exposed to moisture during cycles of freezing and thawing. In addition, entrained air greatly improves concrete's resistance to surface scaling caused by chemical deicers. Air entrainment also increases the workability of

30 fresh concrete while eliminating or reducing segregation and bleeding. Materials used to achieve these desired effects can be selected from wood resin and their salts, natural resin and their salts, synthetic resin and their salts, sulfonated lignin and their salts, petroleum

- acids and their salts, proteinaceous material and their salts, fatty acids and their salts, resinous acids and their salts, alkylbenzene sulfonates, sulfonated hydrocarbons, vinsol resin, anionic surfactants, cationic surfactants, nonionic surfactants, natural rosin, synthetic rosin, an inorganic air entrainer, synthetic detergents, and their corresponding salts, and mixtures thereof. Solid materials can also be used, such as hollow plastic spheres, crushed brick, expanded clay or shale, or spheres of suitable diatomaceous earth. Air entrainers are added in an amount to yield a desired level of air in a cementitious composition. Examples of air entrainers that can be utilized in the admixture system include, but are not limited to MB AE 90, MB VR and MICRO AIR.RTM., all available from BASF Admixtures Inc. of Cleveland, Ohio.
- [0341] Alkali-aggregate reactivity inhibitors: Reduce alkali-aggregate reactivity expansion. Examples include barium salts, lithium nitrate, lithium carbonate, and lithium hydroxide.
- [0342] Antiwashout admixtures: Cohesive concrete for underwater placements. Examples include cellulose and acrylic polymer.
- [0343] Bonding admixtures: Increase bond strength. Examples include polyvinyl chloride, polyvinyl acetate, acrylics, and butadiene-styrene copolymers.
- [0344] Coloring admixtures: Colored concrete. Examples include modified carbon black, iron oxide, phthalocyanine, umber, chromium oxide, titanium oxide, cobalt blue, and organic coloring agents.
- [0345] Corrosion inhibitors: reduce steel corrosion activity in a chloride-laden environment. Examples include calcium nitrite, sodium nitrite, sodium benzoate, certain phosphates or fluosilicates, fluoaluminates, and ester amines.
- [0346] Dampproofing admixtures: retard moisture penetration into dry concrete. Examples include soaps of calcium or ammonium stearate or oleate, butyl stearate, and petroleum products.
- [0347] Foaming agents: produce lightweight, foamed concrete with low density. Examples include cationic and anionic surfactants, and hydrolyzed protein.
- [0348] Fungicides, germicides, and insecticides: Inhibit or control bacterial and fungal growth. Examples include polyhalogenated phenols, dieldrin emulsions, and copper compounds.

- [0349] Gas formers: Gas formers, or gas-forming agents, are sometimes added to concrete and grout in very small quantities to cause a slight expansion prior to hardening. The amount of expansion is dependent upon the amount of gas-forming material used and the temperature of the fresh mixture. Aluminum powder, resin soap and vegetable or animal glue, saponin or hydrolyzed protein can be used as gas formers.
- [0350] Hydration control admixtures: Suspend and reactivate cement hydration with stabilizer and activator. Examples include carboxylic acids and phosphorus-containing organic acid salts.
- [0351] Permeability reducers: Decrease permeability. Examples include latex and calcium stearate.
- [0352] Pumping aids: Improve pumpability. Examples include organic and synthetic polymers, organic flocculents, organic emulsions of paraffin, coal tar, asphalt, acrylics, bentonite and pyrogenic silicas, and hydrated lime.
- [0353] Retarders: Retard setting time, and can include water-reducing set-retarding admixtures, which reduce the water requirements of a concrete mixture for a given slump and increase time of setting (see water reducers), or those that increase set time of concrete without affecting the water requirements. In general, set retarders can be classified in four categories, any of which may be used in embodiments herein: 1) lignosulfonic acids and their salts and modifications and derivatives of these; 2) hydroxylated carboxylic acids and their salts and modifications and derivatives of these; 3) carbohydrate-based compounds such as sugars, sugar acids, and polysaccharides, and 4) inorganic salts such as borates and phosphates. Thus, set retarders include carbohydrates, i.e., saccharides, such as sugars, e.g., fructose, glucose, and sucrose, and sugar acids/bases and their salts, such as sodium gluconate and sodium glucoheptonate; phosphonates, such as nitrilotri(methylphosphonic acid), 2-phosphonobutane-1,2,4-tricarboxylic acid; and chelating agents, such as EDTA, Citric Acid, and nitrilotriacetic acid. Other saccharides and saccharide-containing admixes include molasses and corn syrup. In certain embodiments, the admixture is sodium gluconate. Other exemplary admixtures that can be of use as set retarders include sodium sulfate, citric acid, BASF Pozzolith XR, fumed silica, colloidal silica, hydroxyethyl cellulose, hydroxypropyl cellulose, fly ash (as defined in ASTM C618), mineral oils (such as light naphthenic), hectorite clay, polyoxyalkylenes, natural gums, or mixtures thereof, polycarboxylate superplasticizers, naphthalene HRWR (high range water reducer). Additional set retarders that can be used include, but are not limited to an oxy-

boron compound, lignin, a polyphosphonic acid, a carboxylic acid, a hydroxycarboxylic acid, polycarboxylic acid, hydroxylated carboxylic acid, such as fumaric, itaconic, malonic, borax, gluconic, and tartaric acid, lignosulfonates, ascorbic acid, isoascorbic acid, sulphonic acid-acrylic acid copolymer, and their corresponding salts, polyhydroxysilane, polyacrylamide.

- 5 Further retarders include nitrilotri(methylphosphonic acid), and 2-phosphonobutane-1,2,4-tricarboxylic acid. Illustrative examples of retarders are set forth in U.S. Pat. Nos. 5,427,617 and 5,203,919, incorporated herein by reference.

[0354] Shrinkage reducers: Reduce drying shrinkage. Examples include polyoxyalkylenes alkyl ether and propylene glycol.

- 10 [0355] Water reducers: Water-reducing admixtures (also called dispersants, especially HRWR) are used to reduce the quantity of mixing water required to produce concrete of a certain slump, reduce water-cement ratio, reduce cement content, or increase slump. Typical water reducers reduce the water content by approximately 5-10%; high range water reducers (HRWR) reduce water content even further. Adding a water-reducing admixture to concrete
15 without reducing the water content can produce a mixture with a higher slump; for example, in certain cases in which high doses of carbon dioxide are used to carbonate a cement mix, slump may be reduced, and use of a water reducer may restore adequate slump/workability.

[0356] Water reducers for use in the compositions and methods herein may meet one of the seven types of water reducers of ASTM C494/C494M, which defines seven types: 1)

- 20 Type A—water reducing admixtures; 2) Type B—retarding admixtures (described above); 3) Type C—accelerating admixtures (also described above); 4) Type D—water-reducing and retarding admixtures; 5) Type E—water reducing and accelerating admixtures; 6) Type F—water-reducing, high range admixtures; or 7) Type G—water-reducing, high-range, and retarding admixtures. Materials generally available for use as water-reducing admixtures
25 typically fall into one of seven general categories, and formulations useful herein may include, but are not limited to, compounds from more than one category: 1) lignosulfonic acids and their salts and modifications and derivatives of these; 2) hydroxylated carboxylic acids and their salts and modifications and derivatives of these; 3) carbohydrate-based compounds such as sugars, sugar acids, and polysaccharides; 4) salts of Sulfonated
30 melamine polycondensation products; 5) salts of sulfonated naphthalene polycondensation products; 6) polycarboxylates; 7) other materials that can be used to modify formulations, including nonionic surface-active agents; amines and their derivatives; organic phosphonates,

including zinc salts, borates, phosphates; and certain polymeric compounds, including cellulose-ethers, silicones, and Sulfonated hydrocarbon acrylate derivatives.

[0357] An increase in strength is generally obtained with water-reducing admixtures as the water-cement ratio is reduced. For concretes of equal cement content, air content, and slump, the 28-day strength of a water-reduced concrete containing a water reducer can be 10% to 25% greater than concrete without the admixture. Type A water reducers can have little effect on setting, while Type D admixtures provide water reduction with retardation (generally a retarder is added), and Type E admixtures provide water reduction with accelerated setting (generally an accelerator is added). Type D water-reducing admixtures usually retard the setting time of concrete by one to three hours. Some water-reducing admixtures may also entrain some air in concrete.

[0358] High range water reducer (HRWR, also called superplasticizer or plasticizer), Type F (water reducing) and G (water reducing and retarding), reduce water content by at least 12%.

[0359] Examples of water reducers include lignosulfonates, casein, hydroxylated carboxylic acids, and carbohydrates. Further examples, including HRWR (superplasticizers or plasticizers) include polycarboxylic ethers, polycarboxylates, polynaphthalene sulphonates (sulfonated naphthalene formaldehyde condensates (for example LOMAR D™, dispersant (Cognis Inc., Cincinnati, Ohio)), polymelamine sulphonates (sulfonated melamine formaldehyde condensates), polyoxyethylene phosphonates (phosphonates-terminated PEG brushes), vinyl copolymers. Further examples include beta naphthalene sulfonates, , polyaspartates, or oligomeric dispersants.

[0360] Polycarboxylate dispersants (water reducers which are also called polycarboxylate ethers, polycarboxylate esters) can be used, by which is meant a dispersant having a carbon backbone with pendant side chains, wherein at least a portion of the side chains are attached to the backbone through a carboxyl group or an ether group. Examples of polycarboxylate dispersants can be found in U.S. Pub. No. 2002/0019459 A1, U.S. Pat. No. 6,267,814, U.S. Pat. No. 6,290,770, U.S. Pat. No. 6,310,143, U.S. Pat. No. 6,187,841, U.S. Pat. No. 5,158,996, U.S. Pat. No. 6,008,275, U.S. Pat. No. 6,136,950, U.S. Pat. No. 6,284,867, U.S. Pat. No. 5,609,681, U.S. Pat. No. 5,494,516; U.S. Pat. No. 5,674,929, U.S. Pat. No. 5,660,626, U.S. Pat. No. 5,668,195, U.S. Pat. No. 5,661,206, U.S. Pat. No. 5,358,566, U.S. Pat. No. 5,162,402, U.S. Pat. No. 5,798,425, U.S. Pat. No. 5,612,396, U.S. Pat. No. 6,063,184, U.S. Pat. No. 5,912,284, U.S. Pat. No. 5,840,114, U.S. Pat. No. 5,753,744, U.S. Pat. No. 5,728,207, U.S. Pat. No. 5,725,657, U.S. Pat. No. 5,703,174, U.S. Pat. No.

5,665,158, U.S. Pat. No. 5,643,978, U.S. Pat. No. 5,633,298, U.S. Pat. No. 5,583,183, and U.S. Pat. No. 5,393,343. The polycarboxylate dispersants of interest include but are not limited to dispersants or water reducers sold under the trademarks GLENIUM.RTM. 3030NS, GLENIUM.RTM. 3200 HES, GLENIUM 3000NS.RTM. (BASF Admixtures Inc., Cleveland, Ohio), ADVA.RTM. (W. R. Grace Inc., Cambridge, Mass.), VISCOCRETE.RTM. (Sika, Zurich, Switzerland), and SUPERFLUX.RTM. (Axim Concrete Technologies Inc., Middlebranch, Ohio).

[0361] Viscosity and rheology modifying admixtures. Viscosity-modifying admixtures (VMAs) are typically water-soluble polymers used in concrete to modify its rheological properties. VMAs influence the rheology of concrete by increasing its plastic viscosity; the effect of yield stress widely varies with the type of VMA, from no increase to a significant one. Plastic viscosity is defined as the property of a material that resists change in the shape or arrangement of its elements during flow, and the measure thereof, and yield stress is defined as the critical shear stress value below which a viscoplastic material will not flow and, once exceeded, flows like a viscous liquid. Rheology modifying agents can be used to modulate, e.g., increase, the viscosity of cementitious compositions. Suitable examples of rheology modifier include fumed silica, colloidal silica, cellulose ethers (e.g., hydroxyethyl cellulose, hydroxypropyl methylcellulose), fly ash (as defined in ASTM C618), mineral oils (such as light naphthenic), hectorite clay, polyoxyalkylenes, polysaccharides, polyethylene oxides, polyacrylamides or polyvinyl alcohol, natural and synthetic gums, alginates (from seaweed), or mixtures thereof. Other materials include finely divided solids such as starches, clays, lime, and polymer emulsions. Rheology-modifying admixtures (RMA) are admixtures that affect the flow characteristics of concrete by lowering the yield stress or force required to initiate flow without necessarily changing the plastic viscosity. The addition of an RMA to concrete might not alter its slump but will improve workability and flow characteristics. RMAs have been used in low-slump concrete applications, for example, when concrete is placed using slipform paving machines to place concrete pavements, curbs, and barriers, and potentially in 3D printing. The can also be used in self-consolidating concrete (SCC) or highly workable concretes. Rheology-modifying admixtures include those reported by Bury and Bury, 2008, Concrete International, 30:42-45, incorporated herein by reference in its entirety.

[0362] Shrinkage reduction and compensation admixtures. The shrinkage compensation agent which can be used in the cementitious composition can include but is not limited to RO(AO)₁₋₁₀H, wherein R is a C₁₋₅ alkyl or C₅₋₆ cycloalkyl radical and A is a C₂₋₃ alkylene

radical, alkali metal sulfate, alkaline earth metal sulfates, alkaline earth oxides, preferably sodium sulfate and calcium oxide. TETRAGUARD.RTM. is an example of a shrinkage reducing agent and is available from BASF Admixtures Inc. of Cleveland, Ohio. Exemplary shrinkage reduction admixtures (SRAs) include polyoxyalkylenes alkyl ethers or similar compositions. Exemplary shrinkage compensation admixtures (SCAs) include calcium sulfoaluminate and calcium aluminate, calcium hydroxide, magnesium oxide, hard-burnt and dead-burnt magnesium oxide.

[0363] Extended set-control admixtures. Extended set-control admixtures (ESCs) or hydration-controlling admixtures (HCAs) are used to stop or severely retard cement hydration process in unhardened concrete. They may be used to shut down ongoing hydration of cementitious products in returned/waste concrete or in wash water that has been treated in the truck or in a concrete reclaimer system, which allows these products to be recycled back into concrete production so that they need not be disposed of; or to stabilize freshly batched concrete to provide medium- to very long-term set retardation, which allows concrete to remain plastic during very long hauls or in long-distance pumping situations that require long slump life in a more predictable fashion than normal retarders. These differ from conventional set control admixtures because they stop the hydration process of both the silicate and aluminate phases in Portland cement. Regular set-control admixtures act only on the silicate phases. Examples include carboxylic acids and phosphorus-containing organic acids and salts.

[0364] Workability-retaining admixtures. Help retain workability retention of concrete. Examples include hydration-controlling and retarding admixtures that meet the requirements of ASTM C494/C494M Type B or D, or neutral set workability-retaining admixtures meeting the requirements of ASTM C494/C494M Type S. See, e.g., Daczko, 2010, Proceedings from the 6th International Symposium on Self-compacting Concrete and the 4th North American Conference on the Design and Use of Self-Consolidating Concrete, Sept.

[0365] Corrosion-inhibiting admixtures. Reduces corrosion of steel in concrete, e.g., rebar. Examples include chromates, phosphates, hydrophosphates, alkalies, nitrites, and fluorides; aine carboxylate, amine-ester organic emulsion, and calcium nitrite.

[0366] Permeability-reducing admixtures. Permeability-reducing admixtures (PRAs) have been developed to improve concrete durability though controlling water and moisture movement, as well as by reducing chloride ion ingress and permeability. These typically include, but are not limited, to: 1) hydrophobic water repellants, such as materials based on soaps and long-chain fatty acid derivatives, vegetable oils such as tallows, soya-based

- materials, and greases, and petroleum such as mineral oil and paraffin waxes., e.g, calcium, ammonium, and butyl stearates; 2) polymer products, such as organic hydrocarbons supplied either as emulsions (latex) or in liquid form, such as coal tar pitches, bitumen or other resinous polymer, or prepolymer materials; 3) finely divided solids, such as inert and
- 5 chemically active fillers such as talc, bentonite, silicious powders, clay, lime, silicates, and colloidal silica. Supplementary cementitious materials (SCMs) such as fly ash, raw or calcined natural pozzolans, silica fume, or slag cement, although not technically chemical admixtures, can contribute to reducing concrete permeability be be a complementary component; 4) hydrophobic pore blockers; 5) crystalline products, which can be proprietary
- 10 active chemicals provided in a carrier of cement and sand.
- [0367] Bonding admixtures include an organic polymer dispersed in water (latex).
- [0368] Coloring admixtures include natural or synthetic materials, in liquid or dry forms. Pigments include black iron oxide, carbon black, phthalocyanine blue, cobalt blue, red iron oxide, brown iron oxide, raw burnt umber, chromium oxide, phtalocyanine green, yellow iron
- 15 oxide, and titanium dioxide.
- [0369] Flocculating admixtures include synthetic polyelectrolytes, such as vinyl acetate-maleic anhydride copolymer.
- [0370] Fungicidal, germicidal, and insecticidal admixtures include polyhalogenated phenols, dieldrin emulsion, and copper compounds.
- 20 [0371] Lithium admixtures to reduce deleterious expansion from alkali-silica reaction. Deleterious expansions from alkali-silica reaction (ASR) can occur in concrete when susceptible siliceous minerals are present in the aggregate. Exemplary admixtures that prevent these deleterious expansion reactions include solid forms (lithium hydroxide monohydrate and lithium carbonate) and liquid form (30 percent by weight lithium nitrate
- 25 solution in water). Additional examples include lithium nitrite.
- [0372] Expansive/gas forming admixtures include metallic aluminum, zinc or magnesium, hydrogen peroxide, nitrogen and ammonium compounds, and certain forms of activated carbon or fluidized coke.
- [0373] Admixtures for cellular concrete/flowable fill include those based on protein or on
- 30 synthetic surfactants.
- [0374] Shotcrete admixtures. Shotcrete is define as “mortar or concrete pneumatically projected at high velocity onto a surface.” Materials useful as shotcrete admixtures include accelerators, such as alkali-based accelerators, e.g., aqueous silicate or aluminate solutions or alkali-free accelerators such as those based on aluminum sulfates and aluminum

hydroxysulfates; high-range water-reducing admixtures such as those known in the art specifically formulated for shotcrete mixtures; and extended set-control admixtures.

[0375] Admixtures for manufactured concrete products. These may be used to add production efficiency, improve or modify surface texture, enhance and maintain visual
5 appeal, or provide value-added performance benefits. These include plasticizers such as soaps, surfactants, lubricants, and cement dispersants; accelerators both calcium chloride and non-chloride-based; and water-repellant/efflorescence control admixtures such as calcium/aluminum stearates, fatty acids, silicone emulsions, and wax emulsions.

[0376] Admixtures for flowing concrete. Flowing concrete is defined as “concrete that is
10 characterized as having a slump greater than 7-1/2 in (190 mm) while maintaining a cohesive nature.” Various admixtures may be used, such as mid-range water reducers and high-range water reducers, viscosity-modifying admixtures, set retarders, set accelerators, and workability-retaining admixtures, as described herein.

[0377] Admixtures for self-consolidating concrete (SCC). Exemplary admixtures for
15 inclusion in SCC include high-range water-reducing admixtures, e.g., polycarboxylate-based HRWRAs such as blends of different polycarboxylate polymers that have different rates of absorption on the powder substrates; and viscosity-modifying admixtures.

[0378] Admixtures for very cold weather concrete. These allow placement of concrete in
20 temperatures below freezing, and include water reducers, accelerators, retarders, corrosion inhibitors, and shrinkage reducers (for their added freezing point depression).

[0379] Admixture for very-high-early-strength concrete. VHESC is designed to achieve extremely high early strengths within the first few hours after placement. Admixture systems can include a high-range water reducer, set accelerator, and optionally air-entraining admixture. Also include may be workability-retaining admixtures.

25 [0380] Admixtures for pervious concrete. Pervious concrete is a low-slump, open-graded material consisting of portland cement, uniform-sized aggregate, little or no fine aggregate, chemical admixtures, and water, which, when combined, produces hardened concrete with interconnected pores, or voids, that allow water to pass through the concrete easily. Exemplary admixtures include air-entraining admixtures, extended set-control admixtures,
30 water-reducing admixtures, internal curing admixtures, viscosity-modifying admixtures, and latex admixtures.

[0381] Admixtures for 3D printing concrete. These include admixtures that allow the printed concrete to stand without forms and other admixtures suited to the requirements of 3D printing.

[0382] Modification or influence on calcium carbonate In certain embodiments, an admixture is used that modulates the formation of calcium carbonate, e.g., so that one or more polymorphic forms is favored compared to the mixture without the admixture, e.g., modulates the formation of amorphous calcium carbonate, e.g., aragonite, or calcite.

- 5 Exemplary admixtures of this type include organic polymers such as polyacrylate and polycarboxylate ether, phosphate esters such as hydroxyamino phosphate ester, phosphonate and phosphonic acids such as nitrilotri(methylphosphonic acid), 2-phosphonobutane-1,2,4-tricarboxylic acid, chelators, such as sodium gluconate, ethylenediaminetetraacetic acid (EDTA), and citric acid, or surfactants, such as calcium stearate.
- 10 **[0383]** Further admixtures of interest include those that influence calcium carbonate formation, reactions, and other aspects of calcium carbonate. For example, magnesium can be a strong inhibitor to calcite growth, and the Mg/Ca ratio may affect the lifetime of amorphous calcium carbonate, e.g., high ratios may increase lifetime, and may influence the type of crystalline polymorph that forms as the initial and long-term product. $\text{CO}_3^{2-}/\text{Ca}^{2+}$
- 15 may also affect these, as may physical mixing, either or both of which may be manipulated. See, e.g., see Blue, C.R., Giuffre, A., Mergelsberg, S., Han, N., De Yoreo, J.J., Dove, P.M., 2017. Chemical and physical controls on the transformation of amorphous calcium carbonate into crystalline CaCO_3 polymorphs. *Geochimica et Cosmochimica Acta* 196, 179–196. <https://doi.org/10.1016/j.gca.2016.09.004>, incorporated herein by reference in its entirety.
- 20 **[0384]** In certain embodiments, admixture can include one or more 2D substrates terminated with functional groups, which may also influence crystal phase, size, shape, and/or orientation. Exemplary strategies for preparing functional group substrates include Langmuir monolayer, surface carbonylation, and alkanethiol self-assembling monolayer (SAM). For example, a stearic acid monolayer has been used to direct CaCO_3 crystallization.
- 25 Various functional groups can be micro-patterned on a substrate to guide CaCO_3 crystallization. Thus, in certain embodiments 2D substrates with $-\text{COOH}$, $-\text{NH}_2$, $-\text{OH}$, SO_3H , $-\text{CH}_3$, $-\text{SH}$, and/or PO_4H_2 , can be used to control CaCO_3 mineralization. The physical and/or chemical properties of the substrate may be manipulated as suitable for desired outcome. These include chemical character, hydrophilicity, charge (or coordination number)
- 30 and geometry (or spatial structure) of terminated functional groups, substrate metals and length of alkanethiol molecule. Additionally or alternatively, environmental factors such as temperature and/or initial concentration of Ca^{++} may be manipulated. ACC formation and transformation may be preferred on strong hydrophilic surfaces, for example, on $-\text{OH}$ or $-\text{SH}$ terminated SAMs. Without being bound by theory, it is thought that CaCO_3 nucleates via the

same mechanism on –OH, NH₂, and –CH₃ terminated SAMs. Double-hydrophilic block copolymers based on poly(ethyleneglycol)(PEG), carboxylated polyanilines (c-PANIs) can be used to mediate CaCO₃ crystallization, and can provide control over crystal size, shape, and modification, e.g., promote production of purely crystalline calcite and/or vaterite.

- 5 Addition of –OH and –COOH tailored functional polymer can potentially stabilize ACC precursor phase, which may gradually transform to calcites, if desired. Additionally or alternatively, charged functional groups can be coupled with Ca²⁺ ions to facilitate CaCO₃ crystallization. See, e.g., Deng, H., Shen, X.-C., Wang, X.-M., Du, C., 2013. Calcium carbonate crystallization controlled by functional groups: A mini-review. *Frontiers of Materials Science* 7, 62–68. <https://doi.org/10.1007/s11706-013-0191-y>, incorporated herein by reference in its entirety; in particular, see Table 1 for potential influences of various admixtures on morphologies.

[0385] In certain embodiments admixture may include one or more complexing agents, such as Ethylenediaminetetraacetic acid (EDTA) and/or 1-hydroxyethyl- lidene-1,1-

- 15 diphosphonic acid (HEDP). For example, without being bound by theory, EDTA is reported to retard the crystal growth of calcite and aragonite. Aquasoft 330, a commercial grade HEDP is reported to control the morphology of CaCO₃ and calcium oxalate. See, e.g., Gopi, S.P., Subramanian, V.K., Palanisamy, K., 2015. Synergistic Effect of EDTA and HEDP on the Crystal Growth, Polymorphism, and Morphology of CaCO₃. *Industrial & Engineering Chemistry Research* 54, 3618–3625. <https://doi.org/10.1021/ie5034039>, incorporated herein by reference in its entirety.

[0386] In certain embodiments, admixture may include low molecular weight and polymeric additives, such as block copolymers, poly(ethylene glycol) (PEG), polyelectrolyte, polyacrylamide and cellulose, which can exhibit large influence on the crystallization of

- 25 CaCO₃. See, e.g., Xie et al., 2006; Xu et al., 2008; Xu et al., 2011, Sadowski et al., 2010; Su et al., 2010, all of which are incorporated by reference herein in their entireties. Among various templates, PEG is of particular interest because its molecules contain hydrophilic groups, which can act as a donor to metal ions to form metal complexes with diverse conformation. CaCO₃ mineralized without PEG polymer formed rhombohedral calcite crystals of an average size of 12.5 and 21.5 μm after 5 min and 24 h of incubation, respectively. In contrast, CaCO₃ precipitates obtained in the presence of PEG but collected after 24 hours of incubation exhibited particles with diameters ranging from 13.4 to 15.9 μm. The slight increase in the particle size observed at a high polymer concentration may be

caused by the flocculation effect. Thus, without being bound by theory, it is thought that the presence of poly(ethylene glycol) inhibits the growth of CaCO_3 particles in the system. It is known that low and high molecular weight additives can stabilize nonequilibrium morphologies by changing the relative growth rates of different crystal faces through

5 molecular, specific interactions with certain surfaces that modify the surface energy or growth mechanism, or both. Further without being bound by theory, it is also thought that in aqueous solution, Ca^{2+} and CO_3^{2-} firstly form ACC, which quickly transforms into vaterite and calcite within minutes, but at the same time the polymer molecules adsorb on the surface of the particles, which can inhibit the growth of crystal during the process resulting in

10 formation small particles. See, e.g., Polowczyk, I., Bastrzyk, A., Kozlecki, T., Sadowski, Z., 2013. Calcium carbonate mineralization. Part 1: The effect of poly(ethylene glycol) concentration on the formation of precipitate. Faculty of Geoengineering, Mining and Geology, Wrocław University of Technology, Wrocław.

<https://doi.org/10.5277/ppmp130222>, which is incorporated by reference herein in its

15 entirety.

[0387] In certain embodiments, admixture may include water-soluble macro-molecules as soluble additives which may, e.g., affect the crystallization of CaCO_3 ; such additives may be present with insoluble matrices. Exemplary soluble additives include poly(acrylic acid) (PAA); PAAm: Poly(allylamine); PGA: Poly(glutamic acid) sodium salt; DNA:

20 deoxyribonucleic acid, such as sodium salt from salmon sperm (DNA); these admixtures can be used with one or more substrates, when suitable, such as glass, Poly(ethylene- co-acrylic acid) (PEAA) (20wt% acrylic acid), or chitosan. PEAA and chitosan contain carboxylic acid and amino groups, respectively. These polymers can be spin-coated on glass substrates. In the absence of soluble additives, rhombohedral calcite crystals can grow on all three

25 substrates. Different substrate/macro-molecule combinations can have different effects. For example, for glass, there may be no crystallization with PAA or PAAm, whereas spherical crystals may be obtained with PGA additive (vaterite and calcite) or DNA (calcite). The same effects can be seen with additives on PEAA. With chitosan, PAA and PGA may give thin film states of CaCO_3 . Without being bound by theory, the carboxylic acid of PAA and

30 PGA and the amino group of chitosan may cause interactions, which results in the formation of thin film crystals. Spherical particles sporadically grow on the surfaces in the presence of DNA. For further discussion of these potential admixtures see, e.g., Kato, T., Suzuki, T., Amamiya, T., Irie, T., Komiyama, M., Yui, H., 1998. Effects of macromolecules on the

crystallization of CaCO_3 the Formation of Organic/Inorganic Composites. *Supramolecular Science* 5, 411–415. [https://doi.org/10.1016/S0968-5677\(98\)00041-8](https://doi.org/10.1016/S0968-5677(98)00041-8), incorporated by reference herein in its entirety.

[0388] The admixture (or each admixture) may be added to any suitable final percentage (bwc), such as in the range of 0.01-0.5%, or 0.01-0.3%, or 0.01-0.2%, or 0.01-0.1%, or 0.01-1.0%, or 0.01-0.05%, or 0.05% to 5%, or 0.05% to 1%, or 0.05% to 0.5%, or 0.1% to 1%, or 0.1% to 0.8%, or 0.1% to 0.7% per weight of cement. The admixture (or each admixture in a combination of admixtures) may be added to a final percentage of greater than 0.0001, 0.0002, 0.0005, 0.001, 0.002, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5%, 0.6%, 0.7%, 0.8%, 0.9, or 1.0% bwc; in certain cases also less than 10, 5, 4, 3, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.005, 0.002, 0.001, 0.0005, or 0.002% bwc. Other ranges and quantities are as described herein.

[0389] In certain embodiments, sodium gluconate is used as a set-retarding admixture, in combination with carbonation of wash water. The sodium gluconate can be added at one or more times in the process as described herein. Any suitable timing and/or amount of sodium gluconate can be used, which, as with any admixture, may depend on the mix design, e.g., type and amount of cement, in the concrete that is in the wash water, and/or the mix design, e.g., type and amount of cement, in the concrete that is produced in a subsequent batch from the carbonated mix water. The exact amount of sodium gluconate can be important and may be determined in testing with the mix designs to be treated. In certain embodiments, the amount of sodium gluconate, expressed by weight cement in the wash water, may be 0.1-5%, or 0.2-4%, or 0.5-3%, or 0.7-2%, or 1.0-2.0%, or 1.2-1.8%, or 1.4-1.6%.

[0390] In certain embodiments, carbonated wash water may itself be used to accelerate set, e.g., to produce a concrete that will stick to a desired surface when used as, e.g., shotcrete. In a shotcrete operation concrete mix can be sent to the nozzle as a wet mix, i.e., already mixed with water, or as a dry mix that is mixed with water just before ejection from the nozzle. In the latter case, some or all of the mix water may be carbonated wash water, and the use of carbonated wash water may reduce or eliminate flow of the concrete delivered to the desired surface by the nozzle.

EXAMPLES

EXAMPLE 1

[0391] For Examples 1-23 the following general protocols were used, unless otherwise noted:

5 **[0392] Concrete Mixing Procedure:**

1. Add sand and stone, mix for 15 seconds
2. Add 80% of the water, mix for 15 seconds
3. Add cementitious material, mix 15 seconds
4. Add remaining water/concrete admixtures, mix 3 minutes
- 10 5. Rest 3 minutes
6. Mix 2 minutes

[0393] Washwater preparation procedure

1. Weigh out cementitious material and water in separate buckets at ratios required to produce desired specific gravity.
- 15 2. Add the cement to the water and mix with drill with a grout mixing paddle attachment for approximately 15 seconds.
3. Mix again every 30 minutes to prevent settling.
4. At appropriate time add to the treatment reactor for CO₂ injection (as shown in specific Examples) and/or add sodium gluconate (as shown in specific Examples).

20 **[0394] Washwater carbon dioxide injection system**

[0395] The washwater treatment injection system included a steel container (oil drum) to hold the water, a standing sump pump for washwater agitation, a CO₂ line tapped into PVC piping and a copper cooling coil. The washwater sits in the container and is pumped continuously through the PVC piping system, which acts as a reaction chamber for the CO₂ and the washwater slurry. The CO₂ is controlled with a flowmeter which is attached to a CO₂ gas line. The copper coil has water passed through it to cool the system during the CO₂ reaction.

[0396] All admixture concentrations are as % w/w with washwater solids, unless otherwise noted.

30 **[0397]** Provided herein is an exemplary embodiment of the use of dried treated washwater solids as a replacement for cement at levels of 10% and 25%. In this exemplary embodiment, washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration, the washwater was added to the CO₂ injection system and was treated to a CO₂ uptake of 24%. After 3 days, the washwater solids were dried out using hot plates. The solids were then used as a cement replacement.

35 **[0398]** Concrete batches were made as follows: a control concrete batch made with no washwater solids; a concrete batch made with treated washwater solids that replaced at 10% cement; and a concrete batch made with treated washwater solids replaced at 25% cement.

[0399] **Figures 1-4** show the impact for treated washwater solids on concrete. The batches of concrete with the dried washwater solids saw a loss in workability (**Figure 1**). There was also an acceleration in setting time and the compressive strength was reduced significantly at 24 hours, but the reduction decreased with time (**Figure 2**; **Figure 3** shows calorimetry, as power vs. time). After 28 days, the samples were still not as strong as the control. **Figure 4** shows the composition of the concrete batches used in this Example.

EXAMPLE 2

[0400] In another exemplary embodiment, concrete washwater was treated using a lab simulated flue gas to see if the washwater and produced concrete properties would be the same. General conditions were as in Example 1.

[0401] The washwater was made at a specific gravity of 1.05 and allowed to hydrate for three hours. After the initial hydration, the washwater was added to the CO₂ injection system and was treated with the simulated flue gas. The flue gas was a combination of compressed air and CO₂ where 85% of the flow was air and 15% was CO₂. The simulated flue gas was injected into the washwater until a CO₂ uptake of 27% was achieved.

[0402] Concrete batches made were as follows: a control batch made with no washwater; a concrete batch made with flue gas treated washwater with full washwater replacement; a concrete batch made with flue gas treated washwater with full washwater replacement and with a cement reduction; and a concrete batch made with flue gas treated washwater with full washwater replacement and with a cement and water reduction.

[0403] **Figures 5-8** show the impact of flue gas treatment. The concrete saw comparable workability (**Figure 5**) and a slight acceleration in the setting time. There was a large strength reduction at 24 hours that was lessened at 7 and 28 days (**Figure 6**; **Figure 7** shows calorimetry, as power vs. time). The Final compressive strength was still lower than the control, with the exception of the batch with a cement and water reduction. The simulated flue gas appears to have had a negative impact on the concrete strength that is not seen with pure CO₂. **Figure 8** shows the composition of the concrete batches used in this Example.

EXAMPLE 3

[0404] In another exemplary embodiment, concrete was made with full treated washwater replacement, with sodium gluconate being added after treatment. Concrete batches were made with varying specific gravity levels in the treated washwater. Desired specific gravity

was achieved by diluting down the washwater with potable water. General conditions were as in Example 1.

[0405] The washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration, the washwater was added to the CO₂ injection system and was treated to a CO₂ uptake of 25%. After 24 hours, the washwater was used in concrete production with 1.5% sodium gluconate by weight of washwater solids added to the washwater before batching.

[0406] Concrete batches made were as follows: a control concrete made with no washwater; concrete batch made with 1.10 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; a concrete batch made with 1.075 specific gravity treated washwater with full washwater replacement and 1.5% sodium gluconate; and a concrete batch made with 1.05 specific gravity treated washwater batch with full washwater replacement and 1.5% sodium gluconate.

[0407] Figures 9-12 show the impact for specific gravity and sodium gluconate on concrete. The concrete produced had a reduction in workability that was lessened with the decrease of washwater specific gravity (Figure 9). There was some set acceleration in all the washwater batches and a minor strength increase in all cases at 28 days (Figures 10 and 11). The strength was also impacted by specific gravity, as the specific gravity increased so did the increase in compressive strength. Figure 12 shows the compositions of the various concrete mixes used.

EXAMPLE 4

[0408] In an exemplary embodiment, the addition timing of sodium gluconate to both treated and untreated washwater was determined. Addition of gluconate before carbonation (at three hours of hydration) was compared with addition of gluconate after carbonation (immediately before batching). General conditions were as in Example 1.

[0409] The washwater batches were made as follows: untreated washwater comprising no gluconate; untreated washwater comprising gluconate which was added after 3 hours of hydration; untreated washwater comprising gluconate which was added after 24 hours of hydration and immediately before concrete batching; treated washwater comprising no gluconate; treated washwater comprising gluconate which was added before treatment and after 3 hours of hydration; and treated washwater comprising gluconate which was added after 24 hours and immediately before concrete batching. All gluconate dosages were 3% by weight of washwater solids. The treated washwater was treated to a CO₂ uptake of 24% by weight of cement.

[0410] Concrete batches made were as follows: a control concrete batch made with no washwater; a concrete batch made with untreated washwater with no gluconate; a concrete batch made with untreated washwater with gluconate added after 3 hours; a concrete batch made with untreated washwater with gluconate added after 24 hours; a concrete batch made with treated washwater with no gluconate; a concrete batch made with treated washwater with gluconate added before treatment; and a concrete batch made with treated washwater with gluconate added after treatment.

[0411] Figures 13-16 show the impact of the addition timing of sodium gluconate to treated and untreated washwater on the properties of concrete. Concrete batches comprising treated washwater with gluconate had comparable workability to the control (Figure 13), slight set retardation and a large compressive strength increase (Figures 14 and 15). The concrete batches comprising washwater without gluconate had a reduction in workability (Figure 13), set acceleration and a minor strength improvement (Figures 14 and 15). The concrete batches comprising untreated washwater with gluconate saw a very large set retardation.

Compositions of the various concrete mixes are shown in Figure 16.

EXAMPLE 5

[0412] In other exemplary embodiments, the properties of concrete comprising untreated washwater with the addition of sodium gluconate were compared with those of concrete comprising treated washwater with sodium gluconate and cement reductions. General conditions were as in Example 1.

[0413] The washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration, sodium gluconate was added to two samples of washwater at a dosage of 0.6% and 1.2% by weight of washwater solids. The remaining washwater was added to the CO₂ injection system and was treated to a CO₂ uptake of 29%. After 24 hours, the washwater was used in concrete production. In the treated washwater concrete batches, sodium gluconate was added to the water immediately before batching at a dosage of 3% by weight of washwater solids.

[0414] The concrete batches made were as follows: a control concrete batch made with no washwater; a concrete batch made with untreated washwater with 0.6% sodium gluconate, with full washwater replacement; a concrete batch made with untreated washwater with 1.2% sodium gluconate with full washwater replacement; a concrete batch made with treated washwater batch with 3% sodium gluconate and 5% cement reduction, and full washwater

replacement; and a concrete batch made with treated washwater with 3% sodium gluconate and 10% cement reduction, with full washwater replacement.

[0415] Figures 17-20 show the results. The concrete produced in all batches had acceptable workability (Figure 17) with some set retardation in the washwater batch with 1.2% sodium gluconate and the treated washwater batches. The set retardation could be adjusted in future batches with less sodium gluconate. There was a compressive strength increase in all washwater batches (Figures 18 and 19). The treated washwater batch with a 5% cement reduction was the strongest batch and the one with a 10% cement reduction was equivalent to the untreated batches. Compositions of the various concrete batches are shown in Figure 20.

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EXAMPLE 6

[0416] Provided herein is exemplary concrete made with full treated washwater replacement with sodium gluconate being added before treatment. The washwater was aged 6 days before being batched in concrete. General conditions were as in Example 1.

15 [0417] The washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration, the washwater was added to the CO₂ injection system and was treated to a CO₂ uptake of 24%. After 6 days, the washwater was used in concrete production. Sodium gluconate was added to the washwater of two concrete batches before production at a dosage of 2.4 and 4.8% by weight of washwater solids.

20 [0418] The concrete batches were made as follows: a control concrete batch made with no washwater; a concrete batch made with aged treated washwater with no sodium gluconate and full washwater replacement; a concrete batch made with aged treated washwater comprising 2.4% sodium gluconate with full washwater replacement; and a concrete batch made with aged treated washwater comprising 4.8% sodium gluconate with full washwater replacement.

25 [0419] Figures 21-23 reveal that the concrete produced saw workability issues in the batch without gluconate and the batch with the lower amount of gluconate (Figure 21). Setting time data was not able to be gathered for this test. There was a large 7- and 28-day compressive strength increase in both gluconate samples (Figure 22). This shows the possible benefit of treated washwater can exceed 6 days of storage. Compositions of concrete mixes are shown in Figure 23.

30

EXAMPLE 7:

[0420] This Example compares the addition of sodium gluconate or a lignosulfonate added after washwater treatment immediately before batching. General conditions were as in Example 1.

- 5 [0421] Washwater: Washwater was made at a specific gravity of 1.10 and hydrated for three hours. After the initial hydration it was added to the treatment system and injected with CO₂ until it achieved a CO₂ uptake of 23%.

[0422] A small separate batch of untreated washwater was produced. The washwater was made at the same time and same specific gravity.

- 10 [0423] Concrete: The concrete batches made were as follows: Control (no washwater); Untreated washwater control (2.7% gluconate immediately before batching); Treated washwater (no gluconate); Treated washwater (2.7% gluconate added immediately before batching); Treated washwater control (8.1% lignosulfonate added immediately before batching)

- 15 [0424] Results are shown in Figures 24-27. All samples had comparable workability (Figure 24). The untreated sample had a very large set retardation (Figure 26). The treated sample without admixture saw some set acceleration and the admixture batches had comparable set to the control. All washwater batches saw a large compressive strength increase (Figure 26). Compositions of the concrete mixes are shown in Figure 27). This Example demonstrates
20 that admixtures comparable to sodium gluconate, such as lignosulfate, may be added to carbon dioxide-treated washwater with comparable results.

EXAMPLE 8:

- [0425] In this Example, concrete was made with full treated washwater replacement with
25 sodium gluconate being added before treatment. One batch had additional gluconate added after treatment and another had a cement reduction. General conditions were as in Example 1.

- [0426] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration sodium gluconate was added to the
30 washwater (dosage = 1.4% by weight of washwater solids). The washwater was added to the CO₂ injection system and was treated to a CO₂ uptake of 26%. After 24 hours the washwater was used in concrete production.

[0427] Concrete: The concrete batches made were as follows: Control (no washwater); Treated washwater batch, full washwater replacement, 1.4% sodium gluconate; Treated

washwater batch, full washwater replacement, 1.4% sodium gluconate before carbonation and 0.7% sodium gluconate after carbonation; Treated washwater batch with 5% cementitious reduction, full washwater replacement, 1.4% sodium gluconate.

[0428] The results are shown in Figures 28-31. The concrete produced in all batches had acceptable workability (Figure 28). The setting time of the washwater batches were comparable to the control, with the exception of the batch with gluconate before and after carbonation, which saw some set retardation. The set retardation could be adjusted in future batches with less sodium gluconate. There was a large compressive strength increase in the treated washwater samples, even the sample with the cementitious reduction (Figures 29 and 30). Compositions of the various concrete mixes are shown in Figure 31.

EXAMPLE 9:

[0429] This Example relates to testing the slump life of treated washwater concrete with and without gluconate relative to a control. General conditions were as in Example 1.

15 [0430] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration the washwater was added to the CO₂ injection system and was treated until it achieved a CO₂ uptake of 24% by weight of cement. The washwater was used 24 hours later for concrete production.

[0431] Concrete: The concrete batches made were as follows: Control (no washwater);
20 Treated washwater, full replacement, 1.4% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids

[0432] The results are shown in Figures 32-35. The treated washwater samples lost slump slightly faster than the control (Figure 32). The batch with the higher gluconate dosage had a longer slump life (Figure 32). The samples had a slight set retardation (Figure 34) with an increase in compressive strength (Figure 33). Compositions of the concrete mixes are shown in Figure 35.

EXAMPLE 10:

30 [0433] This Example demonstrates effects on concrete mixes using treated washwater to make concrete with a cement from Lyon, France and a mix design that uses limestone filler. General conditions were as in Example 1.

[0434] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial the washwater was added to the CO₂ injection system

and was treated until it achieved a CO₂ uptake of 31% by weight of cement. The washwater was used 24 hours later for concrete production.

- [0435] Concrete: The concrete batches made were as follows: Control (no washwater); Treated washwater, full replacement, no gluconate; Treated washwater, full replacement, 1.6% gluconate by weight of washwater solids.
- The results are shown in Figures 36-39. The treated washwater batches required more admixture but were able to achieve the same workability as the control (Figure 36). The treated washwater sample without gluconate had the same setting time as the control, whereas the sample with gluconate had some set retardation (Figure 38). The compressive strength was significantly increased in both treated washwater batches (Figure 37). The compositions of the various concrete batches are shown in Figure 39.

EXAMPLE 11

- [0436] This Example demonstrates using treated washwater to make concrete with a low w/c cement ratio with and without a cementitious reduction.
- [0437] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial the washwater was added to the CO₂ injection system and was treated until it achieved a CO₂ uptake of 24% by weight of cement. The washwater was used 24 hours later for concrete production.
- [0438] Concrete: The concrete batches made were as follows: Control (no washwater); Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids; Treated washwater, full replacement, 1.7% gluconate by weight of washwater solids with a 5% cementitious reduction.
- [0439] The results are shown in Figures 40-43. The workability of all the batches was comparable (Figure 40). There was a slight retardation in the treated washwater set times (Figure 42), but they had an increase in compressive strength, even in the sample with the cementitious reduction (Figure 41). Compositions of the various concrete batches are shown in Figure 43.

EXAMPLE 12

- [0440] This Example demonstrates adding treated washwater as mix water in concrete with different addition timings. The batches were produced with a 50/50 mix of potable water and treated washwater. The goal was to determine if there is a difference when potable water or treated washwater is added first. General conditions are as in Example 1.

[0441] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration the washwater was added to the CO₂ injection system and was treated until it achieved a CO₂ uptake of 28% by weight of cement. The washwater was used 24 hours later for concrete production.

- 5 [0442] Concrete: The concrete batches made were as follows: Control (no washwater); Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater mixed with potable water and added upfront; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, washwater added upfront with the potable water added later; Treated washwater, half replacement, 2% gluconate by weight of washwater solids, potable added upfront with the washwater added later.

[0443] The results are shown in Figures 44-47. The upfront and the delayed washwater had an equivalent slump (Figure 44) and setting time (Figure 46). Both samples had an increase in compressive strength vs the control, with the strength of the upfront washwater sample being slightly higher (Figure 45). Compositions of the concrete mixes are shown in Figure 47.

15

EXAMPELE 13:

[0444] This Example demonstrates adding treated washwater as mix water in to a ternary blend (cement, fly ash, slag) concrete mix with a low water to cement ratio. The washwater was added in dosages of 100, 75, and 50% replacement of mix water. General conditions were as in Example 1.

20

[0445] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial the washwater was added to the CO₂ injection system and was treated until it achieved a CO₂ uptake of 27% by weight of cement. The washwater was used 24 hours later for concrete production.

25

[0446] Concrete: The concrete batches made were as follows: Control (no washwater). Treated washwater, full replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 75% replacement, 2.5% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2.5% gluconate by weight of washwater solids.

30

[0447] The results are shown in Figures 48-51. The treated washwater batches all had comparable slumps to the control (Figure 48) with a bit of set retardation (Figure 50). All washwater samples had a compressive strength increase (Figure 49). The compositions of the concrete batches are shown in Figure 51.

EXAMPLE 14

[0448] This Example demonstrates adding treated washwater as mix water in to a ternary blend (cement, fly ash, slag) concrete mix with a low water to cement ratio. The treated washwater was compared to untreated washwater at 50 and 100% water replacement.

5 General conditions were as in Example 1.

[0449] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to hydrate for three hours. After the initial hydration the washwater was added to the CO₂ injection system and was treated until it achieved a CO₂ uptake of 28% by weight of cement. The washwater was used 24 hours later for concrete production.

10 [0450] Concrete: The concrete batches made were as follows: Control (no washwater; Untreated washwater, full replacement, 2% gluconate by weight of washwater solids; Treated washwater, full replacement, 2% gluconate by weight of washwater solids; Untreated washwater, 50% replacement, 2% gluconate by weight of washwater solids; Treated washwater, 50% replacement, 2% gluconate by weight of washwater solids,

15 [0451] The results are shown in Figures 52-55. The workability of all mixes was comparable (Figure 52) with setting time retardation in all washwater samples (Figure 54). All washwater samples also saw a strength increase from the control, with the treated samples being stronger than the untreated samples (Figure 53). Compositions of the concrete mixes are shown in Figure 55.

20

EXAMPLE 15

[0452] This Example demonstrates using different flow rates while treating washwater to determine if it impacts the washwater properties. General conditions were as in Example 1.

[0453] Washwater: Washwater was made at a specific gravity of 1.10 and allowed to
 25 hydrate for three hours. After the initial hydration the washwater was added to the CO₂ injection system and was treated with a flow rate of 2.23 (low), 4.46 (med), and 6.69 (high) LPM. The washwater was sampled at intervals calculated to make sure all sample points have the same CO₂ uptake.

[0454] Mortar: The mortar batches made were as follows (test was repeated for each flow
 30 rate): Control ; Untreated washwater, full replacement, no CO₂; Treated washwater, full replacement, 7-8% CO₂; Treated washwater, full replacement, 10-13% CO₂; Treated washwater, full replacement, 14-15% CO₂; Treated washwater, full replacement, 16-17% CO₂; Treated washwater, full replacement, 19-21% CO₂.

[0455] The results are shown in Figures 56-62. Figure 56 shows % carbon dioxide by weight cement at various time for the different flow rates. The point from 210- and 360-minute marks in the low flow sample appear to be outliers in the data. 7-day compressive strength is comparable for all conditions except 19-21 min at the low flow rate, and is about the same as control (Figure 57). There appears to be a strong correlation between the increase in set (Figures 59 and 60), loss in workability (Figure 58) and temperature increase in the washwater (Figure 61). The medium and high flow additions showed a similar effect on pH, whereas the low flow rate showed a slower decrease in pH (Figure 62).

10 **EXAMPLE 16**

[0456] In this Example, washwater was made with increasing specific gravity. General conditions for washwater carbon dioxide exposure were as in Example 1, with modifications as noted.

[0457] Washwater: Washwater was made at a specific gravity of 1.10, 1.20, 1.30 and 1.35 and allowed to hydrate for three hours. After the initial hydration the washwater was added to the treatment reactor. The washwater reactor was equipped with a cooling coil to compensate for the expected large temperature increase due to the high solids in the washwater. The washwater was sampled for carbon analysis every 20-30 minutes depending on the specific gravity (1.10 and 1.20 every 20 minutes, 1.30 and 1.35 every 30 minutes). Temperature was recorded at all times with a temperature logger.

[0458] The results are shown in Figures 63 and 64. With the addition of proper cooling and an on/off switch for the pump and CO₂ injection (to allow more cooling with added heat, see the dips in the temperature graph, Figure 64) the system was able to treat the washwater samples even with the highest specific gravity up to 28% by weight of the cement (Figure 63). Thus, the system could potential handle a 1.35 specific gravity slurry provided there was sufficient cooling.

EXAMPLE 17

[0459] In this Example, a slurry was made with just class C fly ash and water with the purpose of being carbonated in a reactor. Class C fly ash is known to be very variable and the addition of CO₂ may be able to reduce the variability. The slurry was then used in mortar mixes.

[0460] Washwater: Washwater (all class C fly ash) was made at a specific gravity of 1.25 and allowed to hydrate for three hours. The slurry was treated with CO₂ at a flow rate of 10

LPM and sampled at 11, 26, 41, 114 and 180 minutes of treatment. The sampled water was tested for carbon analysis and used to make mortar.

- [0461] Mortar: Control, no washwater; Untreated washwater, full replacement; Treated washwater, full replacement, 1.2% CO₂; Treated washwater, full replacement, 2.2% CO₂;
 5 Treated washwater, full replacement, 2.4% CO₂; Treated washwater, full replacement, 3.2% CO₂; Treated washwater, full replacement, 3.5% CO₂.

[0462] The mortar made contained a blend of 70% cement and 30% class C fly ash. The batches made with the added slurry had no virgin fly ash added. All the fly ash was added through the slurry.

- 10 [0463] The results are shown in Figures 65-67. There was a reduction in compressive strength in all washwater samples vs the control containing the virgin material (Figure 65). The addition of CO₂ caused set retardation in all samples (Figure 66). This testing is not able to determine whether or not this improves variability as all the batches were made from the same class C fly ash supply. Figure 67 shows the compositions of various mortars used in the
 15 Example.

EXAMPLE 18

[0464] The Example demonstrates using treated washwater, with lower CO₂ dosages, to make concrete. General conditions were as in Example 1.

- 20 [0465] Washwater: Washwater was made at a specific gravity of 1.10 (straight cement) and allowed to hydrate for three hours. After the initial hydration 0.8% sodium gluconate was added to the washwater by weight of cement. The gluconate was used to prevent any future hydration of the cement, "putting it to sleep". After 24 hours, CO₂ was injected in the washwater at a flow rate of 3LPM. Without being bound by theory, it is thought that the CO₂
 25 reactivates the washwater. The washwater was sampled at 20 minutes of treatment (estimated 5% uptake) and 40 minutes of treatment (estimated 10% uptake).

[0466] Concrete: Control, no washwater; Untreated washwater, full replacement; Treated washwater, 20 minutes of CO₂ injection; Treated washwater, 40 minutes of CO₂ injection.

- [0467] The results are shown in Figures 68-71. Slumps were comparable across all samples
 30 (Figure 68). The washwater sample with 40 minutes of CO₂ injection had acceptable setting time (Figure 70), workability (Figure 68) and saw a large strength increase (Figure 69). The compositions of the various concretes are shown in Figure 71.

EXAMPLE 19

[0468] In this Example, treated washwater concrete was produced with the addition of air entraining admixture to ensure there were no incompatibilities. General conditions were as in Example 1.

- 5 [0469] Washwater: Washwater was produced at a specific gravity of 1.10 (straight cement) and allowed to hydrate for three hours. After the initial hydration the washwater was added to the treatment reactor and had CO₂ injected at a flow rate of 12.1LPM until it achieved a CO₂ uptake of 27%. The washwater was used after 24 hours to make concrete.

- [0470] Concrete: Control, no washwater, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture; Treated washwater, full replacement, 15g air entraining admixture, sodium gluconate added 2% by weight of washwater solids

[0471] The results are shown in Figures 72-76. The addition of treated washwater into a concrete mix did not reduce the impact of the air entraining admixture on workability (Figure 72), amount of air entrained (Figure 73), compressive strength (Figure 74), or set (Figure 75).

- 15 The compositions of the various concrete mixes are shown in Figure 76.

EXAMPLE 20

[0472] This Example demonstrates using treated washwater to produce concrete, in which increasing amounts of washwater were added to the concrete to correct the workability (no increase in admixtures). This explored the idea of available water in washwater being less than the theoretical amount. General conditions were as for Example 1.

- [0473] Washwater: Washwater was produced at a specific gravity of 1.05 (straight cement) and allowed to hydrate for three hours. After the initial hydration it was added to the reactor for CO₂ injection. The washwater was treated until it achieved a CO₂ uptake of 25% by weight of cement. The washwater was used after 24 hours to make concrete.

[0474] Concrete: Control, no washwater; Treated washwater, full replacement, added assuming 12% of the washwater was unavailable for concrete hydration; Treated washwater, full replacement, added assuming 17% of the washwater was unavailable for concrete hydration.

- 30 [0475] Results are shown in Figures 77-80. The theoretical unavailable water at 1.05 specific gravity is 8%. The concrete produced assuming the washwater had 12% unavailable water had comparable setting time (Figure 79) and workability (Figure 77) to the control with nearly equal strength after 28 days (Figure 78). Compositions of the concrete mixes are shown in Figure 80.

EXAMPLE 21

[0476] This Example demonstrates using commercially available admixtures to stabilize the washwater and comparing them to the effectiveness of sodium gluconate. The commercial
5 admixtures used were hydration stabilizing admixtures. General conditions were as for Example 1.

[0477] Washwater: Washwater was produced at a specific gravity of 1.10 (straight cement) and allowed to hydrate for three hours. After the initial hydration the washwater was added to the reactor for CO₂ injection. The washwater was treated until it achieved an uptake of 26%
10 CO₂ by weight of washwater solids. The washwater was used after 24 hours to produce concrete. The stabilizing admixtures were added to the washwater 10 minutes before batching.

[0478] Concrete: Control, no washwater; Treated washwater, full replacement, sodium gluconate added 1% by weight of washwater solids; Treated washwater, full replacement,
15 Daratard 17 added 5% by weight of washwater solids; Treated washwater, full replacement, Recover added 5% by weight of washwater solids.

[0479] The results are shown in Figures 81-84. All three admixtures produced comparable workability (Figure 81), setting time (Figure 83) and compressive strength (Figure 82) to each other. However, the amount of Daratard or Recover required to have the same impact as
20 the sodium gluconate is five times more. The compositions of the concrete mixes are shown in Figure 84.

EXAMPLE 22

[0480] This Example demonstrates treating washwater with CO₂ with two different injection
25 methods. The first is the lab reactor that was used in Examples 1-21 (pump circulating system), the second is a CO₂ bubbler system with a fixed drill used to keep the washwater solids suspended (carbon dioxide added in same container as wash water, no circulation). This testing was completed to see if the high shearing of the pump system treated the washwater differently than the low shearing of the drill/bubbler system.

30 [0481] Washwater: Two sets of washwater were produced at a specific gravity of 1.10 (straight cement) and allowed to hydrate for three hours. After the initial hydration the washwater was added to its respective treatment system. Both batches were treated until achieving 29% CO₂ uptake and 26% uptake for the drill and pump system respectively. After 24 hours each washwater batch was used to produce concrete.

[0482] Concrete: Control, no washwater; Treated washwater, full replacement, washwater from pump system; Treated washwater, full replacement, washwater from drill system.

- [0483] The results are shown in Figures 85-88. There was a difference between the treatment methods. The drill system saw an increase in washwater specific gravity resulting in more workability loss in the concrete (Figure 85). Also, the drill system saw more of an increase in set acceleration (Figure 87). The compressive strengths of the two treatment systems were comparable with the higher strength going to the drill system (Figure 86). The compositions of the concrete mixes are shown in Figure 88.

10 **EXAMPLE 23**

[0484] The following is the procedure used in Examples 24-26

Washwater inline injection trials (1,000L washwater mixing tank with continuous mechanical agitation)

[0485] CO₂ preparation procedure

- 15 Obtain 60 gallon header tank to store CO₂ gas required for experimental trials.
Install inline CO₂ gas heaters to ensure full conversion of CO₂ supply to gas prior to infeed to header tank.

[0486] **Washwater preparation procedure** Fill slurry mixing vessel with water to 80% of ratio required to produce desired specific gravity and initiate agitator.

- 20 Weight out cementitious material and slowly pour into agitated tote.
Add the remaining water required to produce desired specific gravity.

Description of Trial Apparatus and Method

- [0487] In this trial method, water and cementitious material are received in a mixing vessel and continuously agitated using a mechanical agitation method, such as a dual vane impeller operating at 1800 rpm. Concurrently, CO₂ in either gas or liquid phase is heated via an inline heater and then CO₂ gas is collected in a CO₂ header tank at a predetermined pressure, such as 100 psig, in preparation for experimental trials.

EXAMPLE 24

- 30 [0488] Treating a simulated washwater slurry with CO₂ gas via inline injection, without inline mixing of the CO₂ gas and simulated washwater slurry, at varying CO₂ gas injection flowrates.

[0489] Experiment Description: 975 L of simulated washwater was prepared in a slurry mixing vessel at a specific gravity of 1.05 (straight cement) and mechanically agitated for 10

minutes. The slurry was then pumped at a flowrate of 115 GPM through a pipe section with a CO₂ gas injection point, followed by a 20-ft length of hose and collected in a slurry collection vessel. The slurry discharged to the atmosphere (i.e. was not submerged in the slurry collection vessel) to ensure that any unreacted CO₂ gas would be discharged to the atmosphere rather than react further in the slurry collection vessel. CO₂ gas was injected into the slurry at varying flowrates, and the CO₂ uptake (by weight of cement) and uptake efficiency was measured for each experimental trial.

[0490] Results are shown in Figure 89. Without inline mixing: Uptake increased slightly with an increase in CO₂ injection flowrate; uptake efficiency dropped 49% with a doubling of CO₂ injection flowrate.

EXAMPLE 25

[0491] This Example demonstrates treating a simulated washwater slurry with CO₂ gas via inline injection, with / without inline mixing of the CO₂ gas and simulated washwater slurry, at a constant CO₂ gas injection flowrate of 400 SLPM.

[0492] Experiment Description: 975 L of simulated washwater was prepared in a slurry mixing vessel at a specific gravity of 1.05 (straight cement) and mechanically agitated for 10 minutes.

[0493] For the first trial, the slurry was then pumped at a flowrate of 115 GPM through a pipe section with a CO₂ gas injection point, followed by a 20-ft length of hose and collected in a slurry collection vessel.

[0494] For the second trial, the slurry was then pumped at a flowrate of 115 GPM through a pipe section with a CO₂ gas injection point followed by a series of baffles inside the pipe section to facilitate mixing and enhance surface-to-surface interaction of the simulated washwater slurry and the CO₂ gas immediately after injection.

[0495] For both trials, the simulated washwater slurry / CO₂ gas mixture then passed through a 20-ft length of hose and collected in a slurry collection vessel. The slurry discharged to the atmosphere (i.e. was not submerged in the slurry collection vessel) to ensure that any unreacted CO₂ gas would be discharged to the atmosphere rather than react further in the slurry collection vessel.

[0496] Results are shown in **Figure 90**. With / without inline mixing: Uptake increased by 40% with inline mixing compared to without inline mixing; uptake efficiency increased by 38% with inline mixing compared to without inline mixing.

EXAMPLE 26

- [0497] This Example demonstrates treating a simulated washwater slurry with CO₂ gas via inline injection, with inline mixing of the CO₂ gas and simulated washwater slurry, at a constant CO₂ gas injection flowrate of 400 SLPM per injection point. # of injection points was increased from 1 to 2 (in series).
- [0498] Experiment Description: 975 L of simulated washwater was prepared in a slurry mixing vessel at a specific gravity of 1.05 (straight cement) and mechanically agitated for 10 minutes. The slurry was then pumped at a flowrate of 115 GPM through a pipe section with a CO₂ gas injection point followed by a series of baffles inside the pipe section to facilitate mixing and enhance surface-to-surface interaction of the simulated washwater slurry and the CO₂ gas immediately after injection.
- [0499] For each injection point, the simulated washwater slurry / CO₂ gas mixture then passed through a 20-ft length of hose and collected in a slurry collection vessel. The slurry discharged to the atmosphere (i.e. was not submerged in the slurry collection vessel) to ensure that any unreacted CO₂ gas would be discharged to the atmosphere rather than react further in the slurry collection vessel.
- [0500] CO₂ gas was injected into the slurry at 1 or 2 injection points (in series) with a CO₂ gas flowrate of 400 SLPM per injection point. The CO₂ uptake (by weight of cement) and uptake efficiency was measured for each experimental trial.
- [0501] Results are shown in **Figure 91**. With inline mixing / varying # of injection points: Uptake (per injection point / 20-ft hose length) increased slightly with additional injection points (in series); uptake efficiency increased by 20% with an increased # of injection points / total hose length.

EXAMPLE 27**In-line Injection Predictive Model**

- [0502] Design and control of an inline CO₂ injection system has been evaluated via a predictive model to facilitate the design of experimental programs. Through this exercise, a set of theoretical assumptions and critical process variables has been identified that is expected to provide the foundation for an inline injection control system architecture.

Input Variables

[0503] An objective of this invention is to develop a CO₂ injection system that can optimize operation based on a specific set of process inputs. These include, but are not limited to, the following:

[0504] I1 → Target CO2 uptake (%by weight of cement) - This will be a process variable that is constrained by the physical limitations for a given system, and is to be manipulated depending on the desired end-product usage objectives.

5 [0505] I2 → Washwater slurry flowrate (LPM) - this is anticipated to be either a constant/setpoint, or a measurement/input variable depending on the system / process availability.

[0506] I3 → CO2 injection rate (% by weight of cement) - this reflects the maximum CO2 injection rate per injection point, and will be a variable to be manipulated on a system-by-system / day-to-day basis, depending on physical system constraints and daily process
10 operating variables.

[0507] I4 → Maximum CO2 bubble diameter (% of Pipe Inner Diameter) - this will be a system setpoint to be optimized depending on the physical orientation of slurry piping and/or length of pipe available for a given system.

15 [0508] I5 → Full reaction residence time required (sec) - this will be an optimized control system setpoint resulting from experimental and operational data, and will be dependent on the pipe size / maximum bubble diameter.

[0509] I6 → Pipe Inner Diameter (in.) - This will be a control system setpoint to reflect physical system constraints for a given washwater system/concrete plant.

20 [0510] I7 → Vertical Pipe length available (ft) - This will be a control system setpoint to reflect physical system constraints for a given washwater system/concrete plant.

[0511] I8 → Washwater Slurry SG - This will be an online process measurement that will impact specific injection system outputs such as max. CO2 injection rate, slurry flowrate, and maximum CO2 uptake achieved.

25 [0512] I9 → %Cement - This will be a day-to-day process measurement or setpoint that will impact specific injection system outputs such as max. CO2 injection rate, slurry flowrate, and maximum CO2 uptake achieved.

[0513] I10 → %Fly Ash - This will be a day-to-day process measurement or setpoint that will impact specific injection system outputs such as max. CO2 injection rate, slurry flowrate, and maximum CO2 uptake achieved.

30 [0514] I11 → %Slag - This will be a day-to-day process measurement or setpoint that will impact specific injection system outputs such as max. CO2 injection rate, slurry flowrate, and maximum CO2 uptake achieved.

CO₂ Uptake Efficiency & Reaction Efficiency

[0515] As documented herein, *CO₂ uptake efficiency* refers to the reaction efficiency between a CO₂ gas flow and a cementitious washwater slurry flow. Specifically, efficiency refers to the extent to which the reaction takes place between a CO₂ gas flow and a cementitious washwater slurry flow for a given pipe section (or hose). As documented herein, the *reaction pipe section (or length)* refers to the length of pipe between two injection points.

[0516] For the purposes of this predictive model, 100% uptake efficiency is assumed, and the length of pipe (or hose) required to achieve 100% uptake efficiency (i.e. injected CO₂ gas is fully consumed/converted to a mineralized byproduct via reaction with calcium ions contained in the washwater slurry) is documented herein as the *pipe length required for full reaction*.

[0517] As documented herein, *Reaction efficiency* refers to the speed of the reaction between a CO₂ gas flow and a cementitious washwater slurry flow to full conversion (i.e. injected CO₂ gas is fully consumed/converted to a mineralized byproduct). The primary output that quantifies the *reaction efficiency* in such a way that can be used to control and optimize the inline CO₂ injection system is documented herein as the *full conversion residence time*.

Plug Flow vs. Encapsulated Flow

[0518] If the volumetric flow of CO₂ gas is greater than the volumetric flow of the slurry, intermittent/unpredictable plug flow will occur in the vertical pipe sections, and the reaction efficiency and effectiveness of inline mixing will be significantly reduced. Conversely, if the volumetric flow of CO₂ gas is less than the volumetric flow of washwater slurry, the injected CO₂ gas stream will be broken into a series of bubbles encapsulated entirely by washwater slurry inside the pipe section, resulting in a maximized surface area for reaction.

[0519] The above hypothesis provides the basis for the experimental predictive modelling developed herein, and results in the following process assumptions to ensure an optimized inline CO₂ injection system.

[0520] *Maximize reaction efficiency → Minimize full conversion residence time → Minimize pipe length required for full reaction*

[0521] Following these assumptions, a CO₂ injection system can be optimized for a given washwater system/concrete plant, depending on the process variables and physical system constraints. For example, for a given total pipe length at a concrete plant, minimizing the pipe length required for full reaction will allow for more injection points and thus a higher uptake potential.

Injection System Sizing and Control

[0522] The system will be sized and controlled with respect to the process inputs as listed (but not limited to the) above.

[0523] **Figure 92** illustrates an inline injection system for a vertical pipe section. For the purposes of the theory detailed herein, it is assumed that all CO₂ injection is performed in a vertical pipe section.

[0524] The theory developed is guided by a set of process assumptions to allow for effective control and efficient operation of the inline injection system. Based on this theory, it is believed that uptake efficiency and reaction efficiency will drop dramatically if any of the following performance conditions are not satisfied / validated.

Performance Condition #1 - Encapsulated flow of CO₂ and washwater slurry in a vertical pipe section

[0525] The first process assumption involves the ratio of volumetric flow of washwater slurry to CO₂ gas in a section of vertical pipe.

[0526] For a bubble of CO₂ gas to exist within a section of vertical pipe, a *maximum bubble diameter* (*I4*) as a function of the *vertical pipe inner diameter* (*I6*) must be established to reduce the risk of plug flow and a corresponding drop in reaction efficiency. Consequently, a *minimum bubble spacing* (*O2*) is established to ensure that bubbles remain separated and that reaction surface area is not negatively impacted via bubble agglomeration. This has been quantified as the *bubble section length* (*O3*).

EXAMPLE 1

[0527] Constants:

C1 → density of CO₂ gas = 1.9 kg/m³

C2 → 0.0163871 L/cubic-in.

[0528] Inputs:

[0529] Process calculations:

I4 → Maximum bubble diameter = 90% of *I6*

I6 → Pipe Inner Diameter = 4 inches

30

$$V_{\text{bubble}} = 4/3 * \pi r^3$$

$$V_{\text{bubble}}(L) = [4/3 * (\pi * (I6 * I4 / 2)^3)] * C2$$

$$= 0.28 \text{ L}$$

$$M_{\text{bubble}} (\text{g}) = V_{\text{bubble}} * C1 * 1000 / 1000$$

$$= 0.28 * C1 * 1000 / 1000$$

$$= 0.53 \text{ g}$$

Outputs:

O2 → Minimum bubble spacing

O3 → Bubble section length

$$(O2) \text{ Required bubble spacing} = I6 * (I - I4) / 2$$

$$= 0.4 \text{ in.}$$

$$(O3) \text{ Bubble section length} = I6 * I4 + O2 * 2$$

$$= 4.0 \text{ in.}$$

Performance Condition #2 - Required slurry velocity

[0530] Following the outputs of assumption #1, specifically the *bubble section length (O3)*, the second process assumption involves the required slurry velocity of a system to maximize the reaction of CO₂ for each injection point / reaction pipe section.

[0531] For a specified bubble mass (as shown in EXAMPLE 1) and a specified CO₂ injection rate, the number of bubbles required per second can be determined, and using the *bubble section length (O3)*, a *required slurry velocity (O4)* can be determined to ensure encapsulated flow is maintained. If the *actual slurry velocity (O5)* (which is a function of slurry flowrate and pipe diameter) is less than the *required slurry velocity (O4)*, then it cannot be assumed that encapsulated flow is occurring inside the pipe and thus reaction efficiency will begin to be negatively impacted.

EXAMPLE 2

Constants:

$C2 \rightarrow 0.0163871 \text{ L/cubic-in.}$

$C3 \rightarrow \text{SG Cement} = 3.15$

Inputs:

5 $I2 \rightarrow \text{Slurry flowrate} = 1,000 \text{ LPM}$

$I3 \rightarrow \text{CO}_2 \text{ injection point rate (\% by weight cement)} = 0.85\%$

$I6 \rightarrow \text{Pipe Inner Diameter} = 4 \text{ inches}$

$I8 \rightarrow \text{SG Slurry} = 1.05$

$I9 \rightarrow \text{\%Cement in solids} = 100\%$

10

From EXAMPLE 1:

$M_{\text{bubble}} = 0.53 \text{ g}$

$O3 \rightarrow \text{bubble section length} = 4 \text{ inches}$

15 Process calculations:

$$\% \text{Cement}_{\text{Slurry}} = [C3 * (I8 - 1) / (C3 - 1)] / I8$$

20

$$= 6.98\%$$

$$\text{MassFlow}_{\text{Cement}} = I2 * I8 * \% \text{Cement}_{\text{Slurry}}$$

25

$$= 73 \text{ kg per min.}$$

$$30 \quad \text{MassFlow}_{\text{CO}_2} = \text{MassFlow}_{\text{Cement}} * I3$$

$$= 0.92 \text{ kg per min}$$

$$= 0.0153 \text{ kg per sec.}$$

$$\# \text{ of bubbles required (per sec)} = \text{MassFlow}_{\text{CO}_2} / (M_{\text{bubble}}/1000)$$

5

$$= 20 \text{ bubbles per second}$$

10 Outputs:**O4** → Required slurry velocity**O5** → Actual slurry velocity

15

$$(O4) \text{ Velocity}_{\text{Slurry-required}} = O3 * [\# \text{ of bubbles required (per sec)}]$$

$$= 80.3 \text{ inches per second}$$

20

$$= 6.7 \text{ ft per second}$$

$$(O5) \text{ Velocity}_{\text{Slurry-Actual}} = I2 / [C2 * 60 * \pi * (I6/2)^2]$$

25

$$= 80.9 \text{ inches per second}$$

$$= 6.74 \text{ ft per second}$$

30 Evaluation:

$$\text{Velocity}_{\text{Slurry-Actual}} > \text{Velocity}_{\text{Slurry-Required}} ;$$

therefore, the system can be assumed to be operating in an encapsulated flow environment.

System Sizing / Maximum Potential

[0532] The above performance conditions provide basis for optimizing the inline CO₂ injection system for each injection point. With an optimized system, projections can be made as to the *maximum CO₂ uptake that can be achieved (O8)* for a given washwater system/concrete plant.

[0533] It should be noted that, if one of the performance conditions cannot be met, or if the maximum *CO₂ uptake that can be achieved (O8)* is less than required, changes to the physical infrastructure of the washwater system / concrete plant may be required before a system can be installed (i.e. increased pump flowrate, or increased vertical pipe length).

10 **EXAMPLE 3**

[0534] Using the slurry characterization from EXAMPLE 2, and assuming the system has been previously optimized as per Performance condition #1 and #2:

Inputs:

I2 → Slurry flowrate = 1,000 LPM

15 I3 → CO₂ injection rate per injection point (% by weight cement) = 1.25%

I5 → Full conversion residence time = 0.5 sec

I6 → Pipe inner diameter = 4 inches

I7 → Vertical pipe length available at concrete plant = 50 ft

From EXAMPLE 2:

20 O5 → Velocity_{Slurry-Actual} = 6.75 ft per second

[0535] Outputs:

O6 → Pipe length required for full reaction = O5*I5

25

= 3.4 ft

30 O7 → Maximum number of injection points / reaction sections = I7/O6

= 14.8 injection points

$$\begin{aligned} \text{O8} \rightarrow \text{Maximum CO}_2 \text{ uptake achieved (\% by weight cement)} &= \text{I3} * \text{O7} \\ \text{[0536]} &= 18.5\% \end{aligned}$$

- 5 [0537] The following conditions were used for Examples 28-37, except where otherwise indicated:

Concrete Mixing Procedure (Pan Mixer):

Add sand, cement and stone, mix for 60 seconds

Add water slowly over 60 seconds

- 10 Add remaining water/concrete admixtures, mix 3 minutes

Rest 3 minutes

Mix 2 minutes

Washwater preparation procedure

- 15 Weigh out cementitious material and water in separate buckets at ratios required to produce desired specific gravity.

Add the cement to the water and mix with drill with a grout mixing paddle attachment for approximately 15 seconds.

Mix again every 30 minutes to prevent settling.

- 20 After three hours of hydration either add sodium gluconate (if the water is being treated after 24 hours) or add the treatment reactor for CO₂ injection.

EXAMPLE 28

- [0538] In this Example, washwater was prepared and treated at a high specific gravity (1.15) and used to make concrete at low replacement levels (10, 20, 30%).

[0539] Washwater: Washwater was prepared at a specific gravity of 1.15 and allowed to hydrate for 3 hours. This washwater was then treated with CO₂ to an uptake of 15% by weight of cement. Sodium gluconate was added to the washwater at a dose of 1.5% by weight of cement immediately before batching.

- 30 [0540] Concrete: Control, no washwater; Treated washwater, 10% replacement; Treated washwater, 20% replacement; Treated washwater, 30% replacement

[0541] Conclusions: The concrete produced was all comparable in setting time and workability. The batches that had the washwater addition saw a large increase in compressive strength. See Figures 93-96.

EXAMPLE 29

[0542] In this Example, two batches of washwater were made at two different specific gravities, 1.10 and 1.05. The 1.05 washwater was treated and used to make concrete and the
5 1.10 washwater was treated and then diluted down to 1.05 specific gravity. The diluted washwater was also used to make concrete and was compared to the batched 1.05 washwater.

[0543] Washwater: Two batches of washwater were prepared with straight cement. Both washwater batches were allowed to hydrate for 3 hours and were then treated to full saturation with CO₂. The washwater batches were made at different specific gravities, one
10 was batched at 1.05 and the other at 1.10. Both washwater samples were dosed with 1% sodium gluconate immediately before batching.

[0544] Concrete: Control, no washwater; Treated washwater, 1.05 SG, 100% replacement; Treated washwater, 1.10 SG diluted to 1.05 SG, 100% replacement

[0545] Conclusions: There was a slump loss in the washwater batches, more noticeable in
15 the diluted 1.10 SG sample. The setting time was comparable among all samples batched and the compressive strength was increased in both washwater samples, more so in the diluted 1.10 SG samples. The diluted sample had a larger strength increase and a larger loss in workability; this points towards there being less water in the concrete produced. This indicates that diluting washwater does not guarantee that it will have the same available water
20 as washwater batches at that specific gravity. See Figures 97 – 100.

EXAMPLE 30

[0546] In this Example, washwater was produced at a specific gravity of 1.10 and was treated with CO₂ to 0, 5, 10, 15, 20 and 25% by weight of cement. Each CO₂ point was
25 tested for x-ray diffraction analysis after 0, 3, 6, 24 and 72 hours of hydration.

[0547] Washwater: Washwater was batched at a specific gravity of 1.10 and was allowed to hydrate for 3 hours. It was then treated to 0, 5, 10, 15, 20 and 25% CO₂ by weight of cement. At each CO₂ dose it the water was sampled and tested at 0, 3, 6, 24 and 72 hours.

[0548] Conclusions: It can be seen that 15% CO₂ by weight of cement is enough to stop the
30 formation of calcium hydroxide for as much as 3 days. This indicates that once 15% CO₂ is added to washwater, the washwater will stop hydrating for a minimum of 3 days. See Figures 101-105.

EXAMPLE 31

- [0549] In this Example, concrete samples were produced using treated washwater for the purpose of testing durability in treated washwater concrete. Washwater was made at two different treatment levels (5, 25%) and compared to a potable water reference and an untreated washwater reference. All conditions were made with and without a 3% cementitious reduction. Samples were tested for compressive strength, flexural strength, absorption, carbonation, freeze/thaw, salt scaling, abrasion, corrosion, bulk diffusion and chloride penetration.
- [0550] Washwater: Washwater was made at a specific gravity of 1.10 (75% cement, 25% fly ash) and allowed to hydrate for 3 hours. The washwater was treated to 3 different conditions. The untreated condition was dosed with 0.6% sodium gluconate after initial hydration and rested for 24 hours until concrete batching. The low CO₂ condition was dosed with 0.6% sodium gluconate after initial hydration and rested for 24 hours. Before batching the washwater was treated to 5% CO₂ by weight of cement solids at a flow rate of 5 LPM. The high CO₂ condition was treated to 25% CO₂ by weight of cement solids after its initial hydration and rested for 24 hours. Immediately before batching concrete the high CO₂ washwater was dosed with 1.5% sodium gluconate by weight of cement solids.
- [0551] Concrete: Control, no washwater; Untreated washwater, 100% replacement; Untreated washwater, 100% replacement, 3% cementitious reduction; 5% treated washwater, 100% replacement; 5% treated washwater, 100% replacement, 3% cementitious reduction; 25% treated washwater, 100% replacement; 25% treated washwater, 100% replacement, 3% cementitious reduction.
- [0552] Conclusions: Minor reductions in workability in the samples with washwater relative to the potable water control with negligible change in setting time. Noticeable compressive strength increases in all washwater samples at 28-days with the most strength coming from the highest CO₂ dose, low CO₂ dose being the next strongest. Cement reduction samples still had a strength increase with the exception of the untreated washwater condition. Still waiting on results for the flexural strength, absorption, carbonation, freeze/thaw, salt scaling, abrasion, corrosion, bulk diffusion and chloride penetration testing. See Figures 106-109.

EXAMPLE 32

[0553] Washwater was produced at a large scale (1000L) and treated in a way to simulate the treatment that would be used in a reclaimer. Since a reclaimer is so large the turnover time could be multiple hours. Washwater was transferred from one tank to another with CO₂

being injected in the transfer line. The washwater was transferred/treated every 30 minutes. The washwater was used to make concrete at CO₂ levels of 0, 3, 6 and 9% by weight of cement solids.

5 [0554] Washwater: Washwater was made at a specific gravity of 1.10 (100% cement) and allowed to hydrate for 3 hours. After the initial hydration, Recover (commercial hydration stabilizing admixture) was added at a dose of 2% by weight of washwater solids. After the admixture addition, the treatment of the washwater was started. The washwater was sampled at 0, 3, 6 and 9% CO₂ by weight of cement solids.

[0555] Concrete: Control, no washwater; Untreated washwater, 100% replacement; 3%
10 treated washwater, 100% replacement; 6% treated washwater, 100% replacement; 9% treated washwater, 100% replacement

[0556] Conclusions: There was a loss in slump when the CO₂ was added to the washwater as compared to the control and the untreated case. The untreated and 3% treated washwater samples showed retardation in set, whereas the 6% and 9% washwater samples showed set
15 acceleration. There was a significant strength increase in all washwater samples relative to the control with the largest increase coming from the 6% treated sample. See Figures 110-113.

EXAMPLE 33

20 [0557] In this Example, the same experiment and washwater as Example 32 was conducted except the washwater samples were allowed to age 24 hours after treatment.

[0558] Washwater: Washwater was made at a specific gravity of 1.10 (100% cement) and allowed to hydrate for 3 hours. After the initial hydration, Recover (commercial hydration stabilizing admixture) was added at a dose of 2% by weight of washwater solids. After the
25 admixture addition, the treatment of the washwater was started. The washwater was sampled at 0, 3, 6 and 9% CO₂ by weight of cement solids. Each sample was allowed to age for 24 hours and then was used to make concrete.

[0559] Concrete: Control, no washwater; Untreated washwater, 100% replacement; 3%
treated washwater, 100% replacement; 6% treated washwater, 100% replacement; 9% treated
30 washwater, 100% replacement.

[0560] Conclusions: There was a loss in slump when the CO₂ was added to the washwater as compared to the control and the untreated case. The untreated washwater sample showed retardation in set, whereas the 3%, 6% and 9% washwater samples showed set acceleration (all were within an acceptable range). There was a significant strength increase in all

washwater samples relative to the control at 24 hours. With minor strength increases at 7- and 28-days. The largest strength increase was in the 9% treated sample. See Figures 114-117.

EXAMPLE 34

5 [0561] In this Example, washwater was treated to an uptake of 8% CO₂ by weight of washwater solids. This washwater was used to make mortar at a 100% water replacement. A commercial set retarding admixture (Eucon DS) was added to the washwater before batching to try to correct for workability and set issues. The admixture was used at two different dosages and was compared to treated washwater without the retarder, untreated washwater
10 and a potable water reference.

[0562] Washwater: Washwater was prepared at a specific gravity of 1.10 (straight cement) and allowed to hydrate for 3 hours. It was then treated to an uptake of 8% CO₂ by weight of cement solids over a span of 16 hours at a flow rate of 0.36 LPM. Commercial set retarding admixture (Eucon DS) was added to the washwater immediately before batching.

15 [0563] Mortar: Control, no washwater; Untreated washwater, 100% replacement; 8% treated washwater, 100% replacement; 8% treated washwater, 100% replacement, Eucon DS 2.4% by weight of washwater solids; 8% treated washwater, 100% replacement, Eucon DS 7.3% by weight of washwater solids

[0564] Conclusions: There was a reduction in slump with the treated washwater samples,
20 the 2.4 and 7.3% Eucon samples had comparable slump to the control but each received 0.5g of water reducer to correct workability. The washwater samples with the Eucon did show set retardation demonstrating the set could be corrected by the addition of a commercial admixture. Compressive strength samples were comparable throughout all batches. See Figures 118-121.

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EXAMPLE 35

[0565] In this Example, two washwater batches were prepared, one with 100% cement and the other with a blend of 75% cement and 25% slag. Both washwater samples were treated to 0, 5, 10, 15, 20 and 25% CO₂ by weight of cement. This washwater was tested for XRD after
30 3 hours of hydration and again after 24 hours of hydration at each CO₂ interval.

[0566] Washwater: Two batches of washwater were prepared at a specific gravity of 1.10 (straight cement and 75/25 slag blend) and allowed to hydrate for 3 hours. The water was then treated to 0, 5, 10, 15, 20 and 25% CO₂ uptake by weight of cement solids.

[0567] Conclusions: The 100% cement sample required 20% CO₂ addition to stop the hydration (formation of calcium hydroxide) for 24 hours, whereas the blended sample only required the addition of 10% CO₂. See Figures 122-125.

5 **EXAMPLE 36**

[0568] In this Example, two batches of washwater were prepared and treated with two different flow rates (5LPM and 10LPM). Each washwater batch was treated to 0, 5, 10, 15, 20 and 25% CO₂ by weight of cement solids. This washwater was tested for XRD after 3 hours of hydration and again after 24 hours of hydration.

10 [0569] Washwater: Two batches of washwater were prepared at a specific gravity of 1.10 (straight cement) and allowed to hydrate for 3 hours. One was treated at a flowrate of 5LPM and the other at 10LPM. Each washwater batch was treated to 0, 5, 10, 15, 20 and 25% CO₂ by weight of cement solids.

15 [0570] Conclusions: The 5 LPM sample required 20% CO₂ addition to stop the hydration (formation of calcium hydroxide) for 24 hours, whereas the 10 LPM sample only required the addition of 10% CO₂. See Figures 126-129.

EXAMPLE 37

20 [0571] In this Example, two batches of washwater were prepared at two different specific gravities (1.05 and 1.15) and allowed to hydrate for 3 hours. Each washwater batch was treated to 0, 5, 10, 15, 20, 25 and 30% CO₂ by weight of cement solids. This washwater was tested for XRD after 3, 24 and 48 hours of hydration.

25 [0572] Washwater: Two batches of washwater were prepared at different specific gravities (straight cement). One was batched at 1.05 and the other at 1.15, they were both allowed to hydrate for 3 hours. After hydration they were treated with CO₂ to an uptake levels of 0, 5, 10, 15, 20, 25 and 30% by weight of cement.

[0573] Conclusions: The 1.05 sample required 5% CO₂ addition to stop the hydration (formation of calcium hydroxide) for 48 hours, whereas the 1.15 sample required the addition of 10% CO₂. See Figures 130-135.

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EXAMPLE 38

[0574] A trial was performed whereby CO₂ was injected at 100 SLPM. Slurry was circulated at 100 GPM from a 260 gallon vessel, resulting in a tank turnover of 2.6 minutes.

[0575] A graph would show the temperature difference between two probes placed 12 meters apart along an injection/reaction length, one measuring temp (T_o) before injection of CO_2 (length 0) and one measuring temp (T_n) after injection / reaction of CO_2 (length 12 m). The graph shows that for a period of time, the ΔT remained at an elevated level and continued to climb - this is as a result of the exothermic reaction iteratively creating a new T_o for each tank volume iteration (assuming no short circuiting, each injection / reaction iteration).

[0576] In this trial, there was an observable drop in the ΔT ($T_n - T_o$) after 2 hours of treatment. This has been attributed to the possibility that at this point in the reaction, the free calcium in solution was depleted and the remaining reaction was dominated by Pathway 2 reaction, such that the rate of free calcium replenishment was less than the rate of free calcium consumption via reaction with CO_2 . The correlative reaction efficiency was measured and a noticeable drop in efficiency was observed at this specific point in treatment, and continued to remain at a reduced level thereafter.

[0577] While preferred embodiments of the present invention have been shown and described herein, it will be obvious to those skilled in the art that such embodiments are provided by way of example only. Numerous variations, changes, and substitutions will now occur to those skilled in the art without departing from the invention. It should be understood that various alternatives to the embodiments of the invention described herein may be employed in practicing the invention.