

We claim:

1. A method of producing a cement material, the method comprising steps of:
first reacting a calcium-bearing starting material with a first acid to produce an
5 aqueous first calcium salt;
second reacting the aqueous first calcium salt with a second acid to produce a
solid second calcium salt; wherein the second acid is different from the first
acid and the second calcium salt is different from the first calcium salt; and
thermally treating one or more calcium salts to produce a first cement material.
- 10 2. The method of claim 1, wherein the one or more calcium salts is the second
calcium salt.
3. The method of claim 1 or 2, wherein, during the second reacting step, reaction
between the first calcium salt and the second acid regenerates the first acid.
4. The method of any one of claims 1-3 being characterized by a net reaction free of
15 an acid-forming gas product.
5. The method of any one of claims 1-4 comprising forming the solid second
calcium salt characterized by a purity of greater than or equal to 90 wt. % purity.
6. The method of any one of claims 1-5 comprising a first separating step after the
first reacting step and before the second reacting step; the first separating step
20 comprising separating a first aqueous fraction from a first solid fraction; wherein
the first aqueous fraction comprises the aqueous first calcium salt and the first
solid fraction comprises one or more solid byproducts formed during the first
reacting step.
7. The method of any one of claims 1-6 comprising a second separating step after
25 the second reacting step and before the thermally treating step; the second
separating step comprising separating a second solid fraction from a second
aqueous fraction; wherein the second solid fraction comprises the solid second
calcium salt and the second aqueous fraction comprises one or more aqueous
byproducts formed during the second reacting step.
- 30 8. The method of claim 7, wherein the solid fraction is characterized by a dry mass
at least 90 dry wt. % of which is the second calcium salt.

9. The method of any one of claims 1-8 comprising a second acid regeneration step; wherein the second acid regeneration step comprises converting one or more gas products of the thermally treating step to the second acid.
10. The method of claim 9, wherein the second acid regeneration step is a non-electrochemical process performed according to formula **FX1A**:

$$\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad (\text{FX1A});$$
 wherein:
 the SO_2 in **FX1A** is a gas product of the thermally treating step;
 the H_2SO_4 generated in **FX1A** is used as at least a fraction of the second acid during the second reacting step.
11. The method of claim 9, wherein the second acid regeneration step is a non-electrochemical process performed according to formula **FX1B**:

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \quad (\text{FX1B});$$
 wherein:
 the SO_2 in **FX1B** is a gas product of the thermally treating step;
 the H_2SO_3 generated in **FX1B** is used as at least a fraction of the second acid during the second reacting step.
12. The method of claim 9, wherein the second acid regeneration step comprises (i) electrochemically oxidizing sulfur dioxide to sulfuric acid and (ii) forming hydrogen gas via a reduction reaction; and wherein the second acid regeneration step is performed according to formula **FX2**:

$$\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \quad (\text{FX2});$$
 wherein:
 the SO_2 in **FX2** is a gas product of the thermally treating step;
 the H_2SO_4 generated in **FX2** is used as at least a fraction of the second acid during the second reacting step.
13. The method of claim 12, wherein the thermally treating step comprises using energy generated from oxidizing the hydrogen gas formed as a result of the second acid regeneration.
14. The method of claim 12, wherein electrochemically oxidizing sulfur dioxide comprises using energy generated as a result of the second acid regeneration step.
15. The method of any of claims 1-14, wherein, during the second reacting step, reaction between the first calcium salt and the second acid regenerates the first acid according to formula **FX3**:

$$\text{CaCl}_{2(\text{aq})} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_{4(\text{s})} + 2\text{HCl} \quad (\text{FX3});$$
 wherein:

the first calcium salt is CaCl_2 ;
the first acid is HCl ;
the second acid is H_2SO_4 ; and
the second calcium salt is CaSO_4 .

- 5 16. The method of any one of claims 1-15, wherein the calcium-bearing starting material has at least 1 dry wt.% of Ca.
17. The method of any one of claims 1-16, wherein the calcium-bearing starting material comprises at least one multinary metal oxide material having a composition comprising Ca and at least one other metal element selected from
10 the group consisting of Al, Si, Fe, Mn, and Mg.
18. The method of claim 17, wherein the composition of the at least one multinary metal oxide comprises less than or equal to 55 dry wt.% of Ca.
19. The method of any one of claims 1-18, wherein the calcium-bearing starting material comprises at least one natural rock or mineral.
- 15 20. The method of any one of claims 17-18, wherein the at least one multinary metal oxide material is at least one natural rock or mineral.
21. The method of any one of claims 19-20, wherein the at least one natural rock or mineral comprises basalt, igneous appetites, wollastonite, anorthosite, montmorillonite, bentonite, calcium-containing feldspar, anorthite, diopside,
20 pyroxene, pyroxenite, mafurite, kamafurite, clinopyroxene, colemonite, grossular, augite, pigeonite, margarite, calcium serpentine, garnet, scheilite, skarn, limestone, natural gypsum, appetite, fluorapatite, or any combination of these.
22. The method of any one of claims 1-21, wherein calcium-bearing starting material comprises cement, concrete, Portland cement, fly ash, slag, or any combination
25 of these.
23. The method of any one of claims 1-22, wherein the first acid is hydrochloric acid.
24. The method of any one of claims 1-23, wherein the second acid is sulfuric acid and/or sulfurous acid.
25. The method of any one of claims 1-24, wherein the aqueous first calcium salt is
30 calcium chloride.

26. The method of any one of claims 1-25, wherein the solid second calcium salt is calcium sulfate and/or calcium sulfite.
27. The method of any one of claims 1-26, wherein the first cement material is calcium oxide.
- 5 28. The method of any one of claims 1-27, wherein the acid-forming gas product is SO₂ and/or CO₂.
29. The method of any one of claims 1-28, wherein the first reacting step comprises reacting the calcium-bearing starting material with hydrochloric acid to form at least aqueous calcium chloride, aqueous aluminum chloride, and solid silica.
- 10 30. The method of claim 29, wherein the first separating step comprises separating a first aqueous fraction comprising the aqueous calcium chloride and the aqueous aluminum chloride from a first solid fraction comprising the solid silica.
31. The method of claim 30, wherein the second reacting step comprises reacting at least the aqueous calcium chloride, the aqueous aluminum chloride, and sulfuric acid to form at least solid calcium sulfate, aqueous aluminum sulfate, and hydrochloric acid.
- 15 32. The method of claim 31, wherein the thermally treating step comprises heating the calcium sulfate to form calcium oxide.
33. The method of any one of claims 1-32 comprising a step of forming a composite cement material; wherein: (i) the thermally treating step comprises the step of forming the composite cement material and the first cement material is the composite cement material or (ii) the step of forming the composite material is performed using the first cement material formed during the thermally treating step.
- 20 34. The method of claim 33, wherein the step of forming the composite cement material comprises heating the second calcium salt and/or the first cement material together with one or more additives.
35. The method of any one of claims 33-34, wherein the step of forming the composite cement material is performed simultaneously with the thermally treating step.
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36. The method of any one of claims 33-35, wherein the step of forming the composite cement material is performed subsequently after the thermally treating step.
37. The method of any one of claims 33-36, wherein the composite cement material is ordinary Portland cement or a Portland cement clinker, and/or the first cement material is calcium oxide.
38. The method of any one of claims 34-37 comprising forming the one or more additives from the calcium-bearing starting material.
39. The method of any one of claims 34-38, wherein the one or more additives are one or more byproducts of the first reacting step and/or are formed from one or more byproducts of the first reacting step and/or are one or more byproducts of the second reacting step and/or are formed from one or more byproducts of the second reacting step.
40. The method of any one of claims 34-39, wherein a combined composition of the one or more additives comprises Al and Si.
41. The method of any one of claims 34-40, wherein the one or more additives are at least Al_2O_3 and SiO_2 .
42. The method of any one of claims 1-41 comprising forming and isolating silica-fume grade silica, nano-silica, and/or micro-silica from the calcium-bearing starting material.
43. The method of any one of claims 1-42 comprising forming and isolating alumina from the calcium-bearing starting material.
44. The method of claim 43, wherein the first reacting step comprises reacting the calcium-bearing starting material with hydrochloric acid to form at least aqueous aluminum chloride; wherein the method further comprises:
precipitating the aluminum chloride in the presence of hydrochloric acid;
reacting the precipitated aluminum chloride with sulfuric acid to form solid aluminum sulfate;
heating the aluminum sulfate and/or aluminum chloride to form alumina.
45. The method of claim 44, wherein the reaction of the precipitated aluminum chloride forms hydrochloric acid.

46. The method of claim 44 or 45, wherein the second reacting step comprises the step of reacting the precipitated aluminum chloride.
47. The method of any one of claims 44-46, wherein the thermally treating step comprises the heating the aluminum sulfate and/or aluminum chloride step.
- 5 48. The method of any one of claims 1-47 comprising forming and isolating iron oxide from the calcium-bearing starting material.
49. The method of claim 48, wherein the step of forming and isolating the iron oxide comprises:
forming an aqueous solution having aqueous iron sulfate and/or iron chloride and
10 optionally at least one other metal magnesium sulfate salt and/or chloride salt formed as byproducts during the second reacting step; wherein the aqueous solution is free of a calcium salt and free of an aluminum salt;
drying the aqueous solution to form solid iron sulfate and/or solid iron chloride and optionally the at least one other metal sulfate salt;
15 heating the solid iron sulfate and optionally the at least one other metal sulfate salt to form a water-insoluble iron oxide; and
optionally, dissolving the at least one other metal sulfate salt to isolate the water-insoluble iron oxide.
50. The method of any one of claims 1-49 further comprising a step of forming the
20 first acid; wherein: (i) the first reacting step comprises the step of forming the first acid and the step of forming the first acid is occurs simultaneously with the first reacting step, or (ii) the step of forming the first acid is performed separately from the first reacting step.
51. The method of any one of claims 1-50 further comprising a step of forming the
25 second acid; wherein: (i) the second reacting step comprises the step of forming the second acid and the step of forming the second acid is occurs simultaneously with the second reacting step, or (ii) the step of forming the second acid is performed separately from the second reacting step.
52. The method of claim 51, wherein the step of forming the second acid comprises
30 reacting SO₂ with water to form H₂SO₃ and/or H₂SO₄; wherein the second acid is H₂SO₃ and/or H₂SO₄.

53. The method of claim 52, wherein the second acid is H_2SO_3 and/or H_2SO_4 and wherein the second calcium salt is CaSO_3 and/or CaSO_4 , respectively.
54. The method of any one of claims 1-53, wherein the first acid and/or the second acid is a bulk acid.
- 5 55. The method of any one of claims 1-53, wherein the step of forming the first acid comprises forming a pH gradient via water electrolysis; wherein the first acid is formed via the water electrolysis.
56. The method of any one of claims 1-53, wherein the step of forming the second acid comprises forming a pH gradient via water electrolysis; wherein the second acid is formed via the water electrolysis.
- 10 57. The method of claim 10, wherein the second acid regeneration step according to formula **FX1A** is performed at a temperature selected from the range of 400 °C to 1800 °C, is exothermic, and is performed in the presence of a catalyst.
58. The method of any one of claims 1-57, wherein the method is characterized by a net energy selected from the range of -2 to +2 GJ per metric ton of produced cement material.
- 15 59. The method of any one of claims 1-58, wherein the first reacting step is exothermic.
60. The method of any one of claims 1-59, wherein the second acid regeneration step is exothermic.
- 20 61. The method of any one of claims 1-60, wherein the first reacting step is performed at a temperature of at least 50 °C.
62. The method of any one of claims 1-61, wherein the thermally treating step is performed at a temperature selected from the range of 1100 °C to 1800 °C.
- 25 63. The method of any one of claims 1-61, wherein the thermally treating step is performed in the presence of a chemical reductant and is performed at a temperature selected from the range of 800 °C to 1200 °C.
64. The method of any one of claims 1-62, further comprising an ion exchange step; wherein the ion exchange step comprises exchanging one or more anions of the first calcium salt and/or the second calcium salt for one or more hydroxyl anions to form a third calcium salt.
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65. The method of claim 64, wherein the ion exchange step comprises reacting the first calcium salt and/or the second calcium salt with a chelating agent to form a calcium-chelator compound and reacting the calcium-chelator compound with a base to form the third calcium salt.
- 5 66. The method of claim 64 or 65, wherein the ion exchange step comprises reacting the first calcium salt and/or the second calcium salt with a base to form the third calcium salt.
67. The method of any one of claims 64-66, wherein the ion exchange step comprises using an ion exchange membrane to perform the exchanging one or more anions of the first calcium salt and/or the second calcium salt for one or more hydroxyl anions to form the third calcium salt.
- 10 68. The method of any one of claims 64-67, wherein the one or more calcium salts of the thermally treating step is the third calcium salt.
69. The method of any one of claims 64-68, wherein the third calcium salt is $\text{Ca}(\text{OH})_2$.
- 15 70. A method for producing a cement material via reductive thermal decomposition, the method comprising steps of:
reacting a calcium-bearing material with a chemically reducing gas to produce methane and a cement material.
- 20 71. The method of claim 70, wherein the calcium-bearing material comprises CaCO_3 , CaSO_4 , CaS , a calcium salt, or any combination thereof.
72. The method of claim 70, wherein the calcium-bearing material is CaCO_3 , CaSO_4 , CaS , or any combination thereof.
73. The method of any one of claims 70-72, wherein the chemically reducing gas is hydrogen gas or a gas that comprises hydrogen gas.
- 25 74. The method of any one of claims 70-73, wherein the cement material is CaO or the cement material comprises CaO .
75. The method of any one of claims 70-74, wherein a molar ratio of calcium-bearing material reacting with the chemically reducing gas is 1:4 or 1:2.
- 30 76. The method of any one of claims 70-75, wherein the reacting is performed in the presence of water.

77. The method of any one of claims 70-75, wherein the reacting is performed in the absence of water.
78. The method of any one of claims 70-77, wherein oxygen gas, water, or a combination of oxygen gas and water is produced during the step of reacting.
- 5 79. The method of any one of claims 70-78, further comprising a step of decomposing the methane to produce hydrogen gas and one or more carbon materials.
80. The method of any one of claims 70-79, wherein the method does not comprise forming CO₂.
- 10 81. The method of any one of claims 70-80, wherein the step of reacting is characterized by a lower heating value (LHV) of 720 kJ/mol or less and a high heating value (HHV) of 800 kJ/mol or less.
82. The method of any one of claims 70-81, wherein the step of reacting is performed at a temperature of at least 700 °C.
- 15 83. A method of producing a cement material, the method comprising steps of:
first reacting a calcium-bearing starting material with a first acid to produce a first aqueous fraction comprising an aqueous first calcium salt and a first solid fraction comprising one or more solid byproducts ; wherein:
the calcium-bearing starting material has a chemical composition
20 comprising a plurality of metal elements including at least Ca and Si;
the one or more solid byproducts comprises a silicon salt;
first separating the first aqueous fraction from the first solid fraction; and
treating the first calcium salt to produce a first cement material.
84. The method of claim 83, wherein the treating step comprises thermally treating
25 the first calcium salt in the presence of water to produce the first cement material.
85. The method of claim 84, wherein thermally treating the first calcium salt regenerates the first acid.
86. The method of any one of claims 83-85, wherein the treating step comprises an ion exchange step; wherein the ion exchange step comprises exchanging the one
30 or more anions of the first calcium salt for one or more hydroxyl anions to form a third calcium salt.

87. The method of claim 86, wherein the ion exchange step comprises reacting the first calcium salt with a chelating agent to form a calcium-chelator compound and reacting the calcium-chelator compound with a base to form the third calcium salt.
- 5 88. The method of claim 86 or 87, wherein the ion exchange step comprises reacting the first calcium salt with a base to form the third calcium salt.
89. The method of any one of claims 86-88, wherein the ion exchange step comprises using an ion exchange membrane to perform the exchanging one or more anions of the first calcium salt for hydroxyl anions to form the third calcium salt.
- 10 90. The method of any one of claims 86-89, wherein the third calcium salt is $\text{Ca}(\text{OH})_2$.
91. The method of any one of claims 86-90, wherein the treating step comprises thermally treating the third calcium salt to produce the first cement material.
- 15 92. The method of any one of claims 83-91, wherein the first acid is hydrogen chloride.
93. The method of any one of claims 83-92, wherein the one or more solid byproducts comprise SiO_2 .
94. The method of any one of claims 83-93, wherein the calcium-bearing starting material comprises at least one natural rock or mineral.
- 20 95. The method of any one of claims 49-69, wherein the step of forming and isolating the iron oxide further comprises: using SO_2 to precipitate MgSO_3 ; separating the aqueous iron salt from the solid magnesium salt; drying the aqueous solution to form solid iron sulfate or chloride and optionally the at least one other metal sulfate salt; heating the solid iron sulfate and optionally the at least one other metal sulfate salt to form a water-insoluble iron oxide; and optionally, dissolving the at least one other metal sulfate salt to isolate the water-insoluble iron oxide.
- 25 96. The method of any one of claims 1-69, wherein the first reacting step comprises reacting the calcium-bearing starting material with hydrochloric acid to form at least aqueous calcium chloride, aqueous aluminum chloride, aqueous iron chloride, aqueous magnesium chloride, and solid silica.
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97. The method of claim 96, wherein the first separating step comprises separating a first aqueous fraction comprising the aqueous calcium chloride and the aqueous aluminum chloride from a first solid fraction comprising the solid silica.
98. The method of any one of claim 96-97, wherein the second reacting step
5 comprises reacting at least the aqueous calcium chloride, and sulfuric acid to form at least solid calcium sulfate, solid calcium sulfate, and hydrochloric acid.
99. The method of any one of claims 96-98, wherein the thermally treating step comprises heating the calcium sulfate to form calcium oxide.
100. The method of any one of claim 1-69 and 95-99, comprising forming and isolating
10 aluminum chloride and forming aluminum metal via electrowinning the aluminum chloride.
101. The method of claim 100, wherein the forming and isolating aluminum chloride comprises co-forming chlorine gas; the method further comprising reacting the chlorine gas with hydrogen to regenerate hydrochloric acid.
- 15 102. The method of any one of claim 1-69 and 95-99, comprising forming and isolating iron sulfate and forming iron metal via electrowinning the iron sulfate.
103. The method of claim 102, further comprising regenerating sulfuric acid.