

A Process and Apparatus for the Production of Hydrogen

Technical Field

[0001] The present disclosure broadly relates to a process and apparatus for producing hydrogen, and in particular a process and apparatus for producing hydrogen from silicon.

Background Art

[0002] Any discussion of the prior art throughout this specification should in no way be considered as an admission that such prior art is widely known or forms part of the common general knowledge in the field.

[0003] At present, fossil fuels are the primary energy source used throughout the world. However, fossil fuels are a finite resource and their use results in significant adverse environmental impacts. As reserves of fossil fuels become scarcer and environmental concerns increase, the world will increasingly turn to renewable, clean energy sources. Hydrogen is expected to play a significant role in energy generation in the future.

[0004] At present, the majority of industrial hydrogen (~95%) is produced from fossil fuels by steam reforming or partial oxidation of methane and coal gasification. Small quantities of hydrogen are also produced by other routes, such as biomass gasification or electrolysis of water.

[0005] The present inventors have developed an alternative process for the production of hydrogen from a silicon material.

Summary of the Invention

[0006] In a first aspect there is provided a process for preparing hydrogen, the process comprising:

- (a) providing an alkaline solution; and
- (b) reacting the alkaline solution with a silicon material so as to produce hydrogen.

[0007] The process may further comprise:

- (c) separating solids from the alkaline solution.

[0008] The process may further comprise:

(d) separating dissolved silicates from the alkaline solution.

Step (d) may be performed by mechanical vapour recompression.

[0009] The process may further comprise:

(d1) precipitating dissolved silicates from the alkaline solution to provide precipitated silicates; and

(e) separating the precipitated silicates from the alkaline solution.

[0010] The process may further comprise collecting, compressing and storing the hydrogen.

[0011] The alkaline solution in step (a) and/or (b) may have a temperature between about 20 °C and about 80 °C.

[0012] The alkaline solution in step (a) and/or step (b) may have a temperature below 0° C.

[0013] Step (a) may comprise providing the alkaline solution by mixing water with hydroxide.

[0014] Excess heat produced during the mixing of water with hydroxide may be recovered.

[0015] Excess heat produced during the mixing of water with hydroxide may be recovered and transferred to a thermoelectric generator.

[0016] The hydroxide may be a water-soluble hydroxide.

[0017] The water-soluble hydroxide may be one or more of: ammonium hydroxide, lithium hydroxide, sodium hydroxide, potassium hydroxide or cesium hydroxide.

[0018] Step (a) may comprise providing the alkaline solution by mixing water with (i) one or more of ammonium hydroxide, lithium hydroxide, sodium hydroxide, potassium hydroxide or cesium hydroxide, and (ii) calcium hydroxide.

[0019] The water may be tap water, distilled water, waste water or natural surface water.

[0020] The silicon material may be a porous silicon material. In some embodiments the silicon material is a microporous silicon material or a nanoporous silicon material

[0021] In some embodiments, the silicon material is a silicon-containing alloy.

[0022] The silicon material may be pure, or substantially pure silicon.

[0023] The silicon material may have a high surface area.

[0024] Following step (b), the hydrogen may be stripped of water vapour and/or caustic vapour.

[0025] The solids separated in step (c) may be silicon, oxides of silicon or silicates..

[0026] Step (d1) may be performed by adding calcium hydroxide and/or calcium chloride to the alkaline solution.

[0027] Following any one or more of steps (c), (d) and (e) at least a portion of the alkaline solution may be re-used in step (b).

[0028] Following step (e), at least a portion of, or all of the alkaline solution may be concentrated to provide water and a concentrated alkaline solution, wherein the concentrated alkaline solution is re-used in step (b).

[0029] Excess heat produced during step (b) may be recovered.

[0030] Excess heat produced during step (b) may be recovered and transferred to a thermoelectric generator.

[0031] Steps (c) and/or (e) may comprise filtration, centrifugation or sedimentation.

[0032] Steps (c) and/or (e) may comprise use of a hydrocyclone.

[0033] The process may be a batch, semi-batch, continuous, or a semi-continuous process.

[0034] Steps (a) and (b) may be carried out in separate vessels.

[0035] Steps (b) and (c) may be carried out in separate vessels.

[0036] Steps (c) and (d1) may be carried out in separate vessels.

[0037] Steps (d1) and (e) may be carried out in separate vessels.

[0038] In a second aspect there is provided an apparatus for producing hydrogen, the apparatus comprising:

a caustic dissolution vessel having one or more inlets suitable for introducing water and hydroxide, and an outlet for exiting an alkaline solution;

one or more hydrogen reaction vessels for producing hydrogen having one or more inlets suitable for introducing silicon material and the alkaline solution, an outlet for exiting hydrogen produced and an outlet for exiting the alkaline solution, the one or more hydrogen reaction vessels being in fluid communication with the caustic dissolution vessel;

a first solid-liquid separator in fluid communication with the one or more hydrogen reaction vessels for removing unreacted solids present in the alkaline solution received from the one or more hydrogen reaction vessels;

a precipitation vessel in fluid communication with the first solid-liquid separator for precipitating dissolved silicates in the alkaline solution received from the first solid-liquid separator; and

a second solid-liquid separator in fluid communication with the precipitation vessel for separating precipitated silicates from the alkaline solution received from the precipitation vessel.

[0039] The caustic dissolution vessel and the one or more hydrogen reaction vessels may be made of an alkaline-resistant material, such as for example stainless steel.

[0040] The caustic dissolution vessel may comprise a cooling jacket and/or one or more cooling members, such as coils, within the vessel.

[0041] The caustic dissolution vessel may comprise a stirrer, such as for example a mechanical stirrer.

[0042] The one or more hydrogen reaction vessels may comprise a stirrer, such as for example a mechanical stirrer.

[0043] The one or more hydrogen reaction vessels may comprise a condenser to condense water vapour produced in the one or more hydrogen reaction vessels.

[0044] The precipitation vessel may comprise a stirrer, such as for example a mechanical stirrer.

[0045] The apparatus may further comprise a thermoelectric generator.

[0046] The thermoelectric generator may receive heat from one or both of the caustic dissolution vessel and the one or more hydrogen reaction vessels.

[0047] The first and second solid-liquid separators may be hydrocyclones, filtration devices, centrifugation devices or sedimentation tanks.

[0048] The apparatus may further comprise a conduit between the second solid-liquid separator and the caustic dissolution vessel for transporting caustic solution back to the caustic dissolution vessel.

[0049] The apparatus may further comprise one or more pumps for moving the alkaline solution through the apparatus.

[0050] In a third aspect there is provided hydrogen, whenever obtained by the process of the first aspect.

Definitions

[0051] The following are some definitions that may be helpful in understanding the description of the present disclosure. These are intended as general definitions and should in no way limit the scope of the present disclosure to those terms alone, but are put forth for a better understanding of the following description.

[0052] Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

[0053] The terms "a" and "an" are used herein to refer to one or to more than one (i.e. to at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

[0054] In the context of this specification the term "about" is understood to refer to a range of numbers that a person of skill in the art would consider equivalent to the recited value in the context of achieving the same function or result.

[0055] Any numerical range recited herein is intended to include all sub-ranges of the same numerical precision subsumed within the recited range. For example, a range of 1.0 to 5.0 is intended to include all sub-ranges between (and including) the recited minimum value of 1.0 and the recited maximum value of 5.0, that is, having a minimum value equal to or greater than 1.0 and a maximum value equal to or less than 5.0, such as 2.1 to 4.5. Any maximum numerical limitation recited herein is intended to include all lower numerical limitations

subsumed therein and any minimum numerical limitation recited herein is intended to include all higher numerical limitations subsumed therein.

Brief Description of the Drawings

[0056] Figure 1: Schematic illustration of a process and apparatus in accordance with one embodiment of the disclosure.

[0057] Figure 2: Comparison of hydrogen-producing ability of a porous silicon with that of non-porous, solid silicon.

Detailed Description

[0058] In one aspect of the disclosure there is provided a process for preparing hydrogen, the process comprising:

- (a) providing an alkaline solution; and
- (b) reacting the alkaline solution with a silicon material so as to produce hydrogen.

[0059] The process may further comprise:

- (c) separating solids from the alkaline solution.

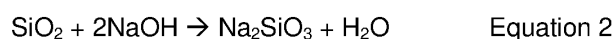
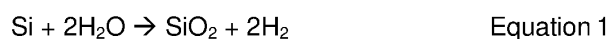
[0060] The process may further comprise:

- (d) separating dissolved silicates from the alkaline solution.

[0061] The process may further comprise:

- (d1) precipitating dissolved silicates from the alkaline solution to provide precipitated silicates; and
- (e) separating the precipitated silicates from the alkaline solution.

[0062] The process involves reaction of an alkaline solution with a silicon material so as to produce hydrogen gas. When using sodium hydroxide to produce the alkaline solution, the following reactions take place in step (b):



[0063] In some embodiments, step (a) may comprise providing the alkaline solution by mixing water with a water-soluble hydroxide, such as for example ammonium hydroxide, lithium hydroxide, sodium hydroxide, potassium hydroxide or cesium hydroxide. The water may be waste water (such as for example grey water), natural surface water (such as for example seawater, lake water or rain water), tap water or distilled water.

[0064] The alkaline solution in step (a) and/or (b) preferably has a temperature between about 20 °C and about 80 °C. In an alternative embodiment, the alkaline solution in step (a) and/or step (b) may have a temperature below 0 °C by making use of the lowered melting point of aqueous caustic solutions, where the eutectic melting point can be as low as -33.4 °C for an alkaline solution containing 20% NaOH. This circumvents the need for antifreeze where the process is performed in a cold environment.

[0065] Heat produced during the mixing of water with hydroxide may be used to increase the temperature of the alkaline solution to a desired temperature, the excess of which may be recovered. In some embodiments, the excess heat may be recovered and transferred to a thermoelectric generator, a heat exchanger or some other auxiliary unit that utilises the heat.

[0066] Heat produced during reaction of the alkaline solution with the silicon material may be used to increase the temperature of the alkaline solution in step (b) to a desired temperature, the excess of which may be recovered. In some embodiments, the excess heat may be recovered and transferred to a thermoelectric generator, a heat exchanger or some other auxiliary unit that utilises the heat. In other embodiments, excess heat generated during any part of the process may be recovered via thermoelectric generators. In some embodiments, the silicon material is in the form of a porous silicon material. In other embodiments the silicon material is a microporous silicon material or a nanoporous silicon material. In one embodiment, the silicon is in the form of micron-sized microporous particles, or micro-sized nanoporous particles.

[0067] The silicon material may be a silicon-containing alloy, such as for example a silicon-containing alloy having the formula SiX , wherein X is a transition metal or a post-transition metal. Preferably, the alloy comprises at least 80%, at least 85%, at least 90%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99%, or at least 99.5% silicon. Impurities and or dopants in the silicon material may beneficially enhance reactivity.

[0068] In some embodiments, the silicon material is pure, or substantially pure silicon. The silicon may be greater than 90%, greater than 95%, greater than 96%, greater than 97%, greater than 98%, greater than 99%, or greater than 99.5% pure.

[0069] The extent of reaction and kinetics of the system may be managed by controlling the pH, amount of silicon material, type and concentration of caustic solution, as well as the reaction temperature.

[0070] In some embodiments the silicon material has one or more of the following properties:

- A specific surface area (SSA) as determined by BET of at least 1.5 m²/g, 1.6 m²/g, 1.7 m²/g, 1.8 m²/g, 1.9 m²/g, 2.0 m²/g or 2.1 m²/g, or a surface area between about 2.0 m²/g and about 2.5 m²/g, or between about 2.0 m²/g and about 2.4 m²/g, or between about 2.0 m²/g and about 2.3 m²/g, or between about 2.0 m²/g and about 2.2 m²/g, or between about 2.1 m²/g and about 2.2 m²/g, or between about 1.9 m²/g and about 2.3 m²/g, or about 2.1 m²/g.
- An agglomerate particle size distribution having one or more of the following: D10 0.512 μm, D25 1.115 μm, D50 2.305 μm, D75 3.980 μm or D90 5.842 μm.
- An average pore volume between about 0.004 mL/g and about 0.007 mL/g, or between about 0.005 mL/g and about 0.006 mL/g, or up to about 0.01 mL/g.
- An average pore diameter (4V/A by BET) between about 0.5 nm and about 50 nm, or between about 0.5 nm and about 25 nm, or between about 1 nm and about 20 nm, or between about 10 nm and about 15 nm, or between about 11 nm and about 15 nm, or between about 12 nm and about 15 nm, or between about 12 nm and about 14 nm, or between about 11 nm and about 13 nm, or between about 11 nm and about 12 nm.
- A SSA as determined by BET between about 0.85 m²/g and about 2.5 m²/g, correlating to a particle size of 0.5mm to 5mm.

[0071] Methods for preparing porous silicon that may be used in the process of the disclosure are described in WO2018019266, the disclosure of which is herein incorporated by reference in its entirety.

[0072] Figure 2 shows a comparison between the hydrogen-producing ability of a porous silicon (denoted as "EAT-Si") and a non-porous, solid silicon (denoted as Solid-Si).

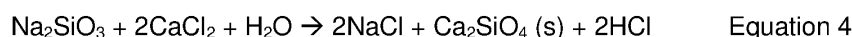
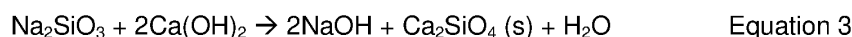
[0073] The EAT-Si silicon has the following characteristics:

- A SSA as determined by BET of about 2.1 m²/g, and a particle size distribution as follows: D10 0.512 μm, D25 1.115 μm, D50 2.305 μm, D75 3.980 μm or D90 5.842 μm.

- A SSA as determined by BET of about 0.85 m²/g, and a particle size of 5mm.

[0074] Following the reactions shown above in Equations 1 and 2, unreacted solids, such as silicon, undissolved SiO_x and silicates (if the dissolved concentration in the liquid exceeds the solubility limit), present in the alkaline solution are removed using a suitable solid-liquid separation technique, such as for example filtration, centrifugation or sedimentation. Solid-liquid separation techniques are well known amongst those skilled in the art. In one embodiment, separation is performed using a hydrocyclone.

[0075] In step (d1) dissolved silicates are then precipitated and subsequently separated from the alkaline solution. Precipitation may be achieved by adding a compound or compounds that convert the silicate into a water-insoluble form. In some embodiments, precipitation is achieved by addition of calcium hydroxide or calcium chloride according to Equations 3 and 4 below:



[0076] Both reactions lead to the formation of solid Ca₂SiO₄ which precipitates due to its insolubility in water. Precipitation involves low cost and low energy expenditure, thereby contributing to the overall efficiency of the process.

[0077] Following any one or more of steps (c), (d) and (e), at least a portion of the alkaline solution may be re-used in step (b). In an alternative embodiment, following step (e), at least a portion of, or all of the alkaline solution may be concentrated to provide water and a concentrated alkaline solution, wherein the concentrated alkaline solution is re-used in step (b). Re-use of the alkaline solution improves process efficiency by preserving water and hydroxide, and also avoids the need for disposal.

[0078] In some embodiments calcium hydroxide is provided in the alkaline solution in step (a). While the hydrogen generation kinetics and efficiencies are marginally higher when performing step (b) (as a result of higher hydroxide concentration as contributed by dissolved Ca(OH)₂) longer incubation time post hydrogen generation is required to complete the reaction in Equation 3, which is limited by the dissolution kinetics of Ca(OH)₂. The resultant Ca₂SiO₄ precipitates can be removed by simple solid-liquid separation as described in step (c) and/or step (e).

[0079] The advantages of inclusion of calcium hydroxide in the alkaline solution of step (a) are two-fold: (i) the ability to recover aqueous NaOH at, or close to, the original

concentration without needing to reconcentrate, such as that described above in [0077], and (ii) operation under zero-liquid addition since all of the water and NaOH are recovered and recycled as shown in Equation 3. The latter is well-suited to operation under water-scarce conditions. Moreover, since the water contains dissolved NaOH at all times, it remains as a liquid even at sub-zero temperature (as described in [0064]) thereby allowing reaction under such conditions.

[0080] In an alternative embodiment the alkaline solution may be neutralised as part of step (d1). This may be achieved by equally splitting the alkaline solution into first and second solutions and adding $\text{Ca}(\text{OH})_2$ to the first solution and CaCl_2 to the second solution. The first and second solutions contain NaOH (Eq. 3) and HCl (Eq. 4) respectively in equimolar amounts, which can be combined to neutralize one another ($\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$).

[0081] The process may further comprise collecting, compressing and storing the hydrogen gas that is produced in step (b). In some embodiments, following step (b), the hydrogen may be stripped of water vapour and/or caustic vapour.

[0082] Hydrogen gas is highly flammable and readily forms explosive mixtures with air and oxygen. As such, transportation of hydrogen gas is problematic. The process of the present disclosure allows safe preparation of hydrogen for a given application *in situ*, thereby avoiding the need for transport. The processes are also environmentally friendly, in that no toxic by-products are produced. In fact, the major by-product of the process (silicates) find use in a number of industries, such as for example as an absorbent, a food additive, a refractory material and a fertilizer additive, to name a few. This adds to the commercial value of the processes.

[0083] In another aspect of the disclosure there is provided an apparatus for producing hydrogen, the apparatus comprising:

a caustic dissolution vessel having one or more inlets suitable for introducing water and hydroxide, and an outlet for exiting an alkaline solution;

one or more hydrogen reaction vessels for producing hydrogen having one or more inlets suitable for introducing silicon material and the alkaline solution, an outlet for exiting hydrogen produced and an outlet for exiting the alkaline solution, the one or more hydrogen reaction vessels being in fluid communication with the caustic dissolution vessel;

a first solid-liquid separator in fluid communication with the one or more hydrogen reaction vessels for removing unreacted solids present in the alkaline solution received from the one or more hydrogen reaction vessels;

a precipitation vessel in fluid communication with the first solid-liquid separator for precipitating dissolved silicates in the alkaline solution received from the first solid-liquid separator; and

a second solid-liquid separator in fluid communication with the precipitation vessel for separating precipitated silicates from the alkaline solution received from the precipitation vessel.

[0084] Figure 1 shows an example of a process and apparatus in accordance with one embodiment of the disclosure.

[0085] The apparatus 100 comprises a caustic dissolution vessel 101 having an inlet 102 for introducing water and an inlet 103 for introducing hydroxide. The caustic dissolution vessel may be made of an alkaline-resistant material, such as for example stainless steel, and may be fitted with a cooling jacket (not shown). Caustic dissolution vessel 101 further comprises an outlet 104 for exiting alkaline solution and a mechanical stirrer 105. Caustic dissolution vessel 101 is in fluid communication with hydrogen reactor vessel 106 via conduit 107. The hydrogen reactor vessel 106 may be made of an alkaline-resistant material, such as for example stainless steel, and may be fitted with a cooling jacket (not shown). The hydrogen reactor vessel 106 may also comprise a condenser (not shown). Hydrogen reactor vessel 106 comprises inlet 108 for introducing the alkaline solution received from the caustic dissolution vessel 101 and inlet 109 for introducing silicon material. Hydrogen reactor vessel 106 further comprises outlet 110 for exiting hydrogen produced in the hydrogen reactor vessel 106, outlet 112 for exiting the alkaline solution, and a mechanical stirrer 111. First solid-liquid separator 113 is in fluid communication with hydrogen reactor vessel 106 via conduit 114. Precipitation vessel 115 is in fluid communication with first solid-liquid separator 113 via conduit 116 and further comprises mechanical stirrer 117. Second solid-liquid separator 118 is in fluid communication with precipitation vessel 115 via conduit 119. The second solid-liquid separator 118 is also in fluid communication with the caustic dissolution vessel 101 via conduit 120. The first and second solid-liquid separators may be hydrocyclones, filtration devices, centrifugation devices or sedimentation tanks. The apparatus 100 further comprises thermoelectric generator 121. The apparatus 100 may further comprise pumps (not shown) located between one or more of: the caustic dissolution vessel and the hydrogen reactor vessel, the hydrogen reactor vessel and the first solid-liquid

separator and the precipitation vessel and the second solid-liquid separator, for moving the alkaline solution between these components of the apparatus.

[0086] In use, water and hydroxide are introduced into caustic dissolution vessel 101 via inlets 102 and 103 respectively. Stirring of the resultant mixture causes dissolution of the hydroxide to provide the alkaline solution and heat. The heat typically maintains the alkaline solution at a temperature of about 50 °C (although temperature and reaction kinetics can be tuned accordingly) in the caustic dissolution vessel 101. Excess heat is transported to the thermoelectric generator 121. The alkaline solution exits outlet 104 and travels via conduit 107 through inlet 108 to hydrogen reactor vessel 106. Silicon material is introduced to the hydrogen reactor vessel 106 via inlet 109. The reactions noted above in equations 1 and 2 then take place resulting in the formation of hydrogen gas, silicon dioxide and silicate. Hydrogen gas produced exits hydrogen reactor vessel 106 via outlet 110, and may be subsequently compressed and stored. Following the reactions of equations 1 and 2, the resulting alkaline solution exits outlet 112 and travels via conduit 114 to first solid-liquid separator 113. Solid-liquid separator 113 separates unreacted silicon material and/or undissolved silicon dioxide from the alkaline solution. The alkaline solution is then transported to precipitation vessel 115 via conduit 116. Precipitation of dissolved silicate is performed in precipitation vessel 115, such as for example, by adding calcium hydroxide and/or calcium chloride to the alkaline solution. The alkaline solution containing the precipitated silicates is then transported to the second solid-liquid separator 118 by conduit 119, wherein the precipitated silicates are separated from the alkaline solution. The resulting alkaline solution is then transported back to the caustic dissolution vessel via conduit 120. In an alternative embodiment, the alkaline solution may be transported back to the hydrogen reactor vessel 106.

[0087] In some embodiments, the process may be carried out as a batch process, a semi-batch process, a continuous process, or a semi-continuous process.

Examples

[0088] The present disclosure is further described below by reference to the following non-limiting example.

[0089] The following example describes a process in which 150 kg of hydrogen are produced per day using porous silicon.

[0090] Water is combined with NaOH with vigorous stirring in a 1.41m³ capacity stainless steel tank fitted with a cooling jacket to give a hydroxide concentration of 8.9 M. The

production rate of the alkaline solution is maintained at 470 L/h, whereby the exothermic heat of dissolution (0.11 kWh per L solution) is used to maintain the alkaline solution at a temperature of about 50 °C. Excess heat of up to 51.7 kWh is transferred to a thermoelectric generator.

[0091] The caustic solution is transferred to a pair of hydrogen reaction vessels having a total capacity of 941 L. The process is operated in a semi-continuous manner according to the following schedule:

Operation (hours)	Batch												Batch											
	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	10.5	11	11.5	12
Caustic Dissolution Tank																								
Hydrogen Reactor 1																								
Hydrogen Reactor 2																								

[0092] Controlled dispensing of silicon (90 kg per batch) ensures evolution of hydrogen over a reaction period of 1.5 hours. The net exothermic heat of reaction (23.8 kWh per kg H₂) will result in self-heating of the reaction medium in the hydrogen reaction vessels, and this is maintained at the optimum operation condition of about 80 °C. Excess heat is transferred to the thermoelectric generator. The hydrogen reaction vessels also include internal condensers in the headspace to condense saturated water vapor (up to 15 kg per batch) that accompanies the hydrogen gas stream leaving the reactor. Operating temperature of the system will largely depend on the ambient temperature.

[0093] Unreacted silicon and/or undissolved silicon dioxide is separated from the alkaline solution using a hydrocyclone. The recovered alkaline solution contains dissolved Na₂SiO₃ (up to a concentration of about 3.5 M). The Na₂SiO₃ is precipitated using calcium hydroxide, which results in formation of Ca₂SiO₄. To treat the alkaline solution, a volumetric ratio of saturated calcium hydroxide solution to the clarified solution of 300 is required to precipitate Na₂SiO₃ in its entirety. The stirring speed of the precipitation process is kept low in order to promote the formation of large Ca₂SiO₄ precipitates. The Ca₂SiO₄ precipitates are separated from the alkaline solution using a hydrocyclone (1.5 m³). The resulting caustic solution (about 0.032 M) is further concentrated to about 8.9 M and then recycled back to the stainless steel tank.

[0094] Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described without departing from the scope of the invention. All such variations and modification which become apparent to persons skilled in the art, should be considered to fall within the spirit and scope of the invention as broadly hereinbefore described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all of

the steps and features, referred or indicated in the specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

Claims

1. A process for preparing hydrogen, the process comprising:
 - (a) providing an alkaline solution; and
 - (b) reacting the alkaline solution with a silicon material so as to produce hydrogen.
2. The process of claim 1, further comprising:
 - (c) separating solids from the alkaline solution.
3. The process of claim 1 or claim 2, further comprising:
 - (d) separating dissolved silicates from the alkaline solution.
4. The process of claim 3, wherein step (d) is performed by mechanical vapour recompression.
5. The process of claim 2, further comprising:
 - (d1) precipitating dissolved silicates from the alkaline solution to provide precipitated silicates; and
 - (e) separating the precipitated silicates from the alkaline solution.
6. The process of any one of claims 1 to 5, further comprising collecting, compressing and storing the hydrogen.
7. The process of any one of claims 1 to 6, wherein the alkaline solution in step (a) and/or (b) has a temperature between about 20 °C and about 80 °C.
8. The process of any one of claims 1 to 6, wherein the alkaline solution in step (a) and/or step (b) has a temperature below 0° C.
9. The process of any one of claims 1 to 8, wherein step (a) comprises providing the alkaline solution by mixing water with hydroxide.
10. The process of claim 9, wherein excess heat produced during the mixing of water with hydroxide is recovered.
11. The process of claim 10, wherein the excess heat is recovered and transferred to a thermoelectric generator.

12. The process of any one of claims 9 to 11, wherein the hydroxide is a water-soluble hydroxide.
13. The process of claim 12, wherein the water-soluble hydroxide is one or more of: ammonium hydroxide, lithium hydroxide, sodium hydroxide, potassium hydroxide or cesium hydroxide.
14. The process of any one of claims 1 to 11, wherein step (a) comprises providing the alkaline solution by mixing water with (i) one or more of ammonium hydroxide, lithium hydroxide, sodium hydroxide, potassium hydroxide or cesium hydroxide, and (ii) calcium hydroxide.
15. The process of any one of claims 9 to 14, wherein the water is tap water, distilled water, waste water or natural surface water.
16. The process of any one of claims 1 to 15, wherein the silicon material is microporous silicon or nanoporous silicon.
17. The process of claim 16, wherein the silicon material is in the form of micron-sized microporous particles.
18. The process of any one of claims 1 to 15, wherein the the silicon material has one or more of the following properties:
- A specific surface area as determined by BET of at least $1.5 \text{ m}^2/\text{g}$;
 - An agglomerate particle size distribution having one or more of the following: D10 $0.512 \text{ }\mu\text{m}$, D25 $1.115 \text{ }\mu\text{m}$, D50 $2.305 \text{ }\mu\text{m}$, D75 $3.980 \text{ }\mu\text{m}$ or D90 $5.842 \text{ }\mu\text{m}$;
 - A specific surface area as determined by BET of at least $0.85 \text{ m}^2/\text{g}$, with a particle size of $0.5\text{mm} - 5\text{mm}$
 - An average pore volume of up to about 0.01 mL/g ; and
 - An average pore diameter ($4V/A$ by BET) between about 0.5 nm and about 50 nm .
19. The process of any one of claims 1 to 18, wherein the silicon material is a silicon-containing alloy.
20. The process of any one of claims 1 to 18, wherein the silicon material is pure or substantially pure silicon.

21. The process of any one of claims 1 to 20, wherein following step (b), the hydrogen is stripped of water vapour and/or caustic vapour.
22. The process of any one of claims 2 to 21, wherein solids separated in step (c) are silicon, oxides of silicon or silicates.
23. The process of any one of claims 5 to 22, wherein step (d1) is performed by adding calcium hydroxide and/or calcium chloride to the alkaline solution.
24. The process of any one of claims 2 to 23, wherein following any one or more of steps (c), (d) or (e), at least a portion of the alkaline solution is re-used in step (b).
25. The process of any one of claims 5 to 24, wherein following step (e), at least a portion of, or all of the alkaline solution is concentrated to provide water and a concentrated alkaline solution, wherein the concentrated alkaline solution is re-used in step (b).
26. The process of any one of claims 1 to 25, wherein excess heat produced during step (b) is recovered.
27. The process of claim 26, wherein the excess heat is recovered and transferred to a thermoelectric generator.
28. The process of any one of claims 1 to 27, which is a batch, semi-batch, continuous or semi-continuous process.
29. An apparatus for producing hydrogen, the apparatus comprising:
- a caustic dissolution vessel having one or more inlets suitable for introducing water and hydroxide, and an outlet for exiting an alkaline solution;
 - one or more hydrogen reaction vessels for producing hydrogen having one or more inlets suitable for introducing a silicon material and the alkaline solution, an outlet for exiting hydrogen produced and an outlet for exiting the alkaline solution, the one or more hydrogen reaction vessels being in fluid communication with the caustic dissolution vessel;
 - a first solid-liquid separator in fluid communication with the one or more hydrogen reaction vessels for removing unreacted solids present in the alkaline solution received from the one or more hydrogen reaction vessels;

a precipitation vessel in fluid communication with the first solid-liquid separator for precipitating dissolved silicates in the alkaline solution received from the first solid-liquid separator; and

a second solid-liquid separator in fluid communication with the precipitation vessel for separating precipitated silicates from the alkaline solution received from the precipitation vessel.

30. The apparatus of claim 29, wherein the caustic dissolution vessel and the one or more hydrogen reaction vessels are made of an alkaline-resistant material.

31. The apparatus of claim 29 or claim 30, wherein the caustic dissolution vessel comprises a cooling jacket and/or one or more cooling members within the vessel.

32. The apparatus of any one of claims 29 to 31, wherein the caustic dissolution vessel comprises a stirrer.

33. The apparatus of any one of claims 29 to 32, wherein the one or more hydrogen reaction vessels may comprise a stirrer, such as for example a mechanical stirrer.

34. The apparatus of any one of claims 29 to 33, wherein the one or more hydrogen reaction vessels comprise a condenser to condense water vapour produced in the one or more hydrogen reaction vessels.

35. The apparatus of any one of claims 29 to 34, wherein the precipitation vessel comprises a stirrer.

36. The apparatus of any one of claims 29 to 35, further comprising a thermoelectric generator.

37. The apparatus of claim 36, wherein the thermoelectric generator receives heat from one or both of the caustic dissolution vessels and the one or more hydrogen reaction vessels.

38. The apparatus of any one of claims 29 to 37, wherein the first and second solid-liquid separators are hydrocyclones, filtration devices, centrifugation devices or sedimentation tanks.

39. The apparatus of any one of claims 29 to 38, further comprising a conduit between the second solid-liquid separator and the caustic dissolution vessel for transporting caustic solution back to the caustic dissolution vessel.

40. The apparatus of any one of claims 29 to 39, further comprising one or more pumps for moving the alkaline solution through the apparatus.
41. Hydrogen, whenever obtained by the process of any one of claims 1 to 28.