

METHOD FOR PRODUCTION OF PURIFIED SILICA

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore Patent Application No. 10202008639Q, filed 4 September 2020, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various aspects of this disclosure relate to a method for producing purified silica (SiO_2). Various aspects of this disclosure also relate to a purified SiO_2 produced by the method as described herein.

BACKGROUND

[0003] Conventional industrial production of sodium silicate involves melting sodium carbonate (Na_2CO_3) at 1,200 °C and then reacting it with pure quartz. This is an established process, which is widely practiced in industry.

[0004] Mukunda et al. (2004, W02004073600A3) describes a method to produce precipitated SiO_2 from rice husk ash. In their method, an aqueous NaOH solution is used to extract SiO_2 from rice husk ash, for obtaining an aqueous sodium silicate (Na_2SiO_3) solution in a concentration of between 2.5 - 10%. While the starting concentration of the NaOH solution used therein is not explicitly stated, it can be estimated that the starting NaOH solution is in the range of 1.6 - 6.5% assuming full conversion at stoichiometric ratios. The Na_2SiO_3 solution is sparged with CO_2 and then filtered, and the obtained sodium carbonate (Na_2CO_3) solution is sent for regeneration using calcium hydroxide (CaOH). Mukunda appears to be silent regarding the concentration of the Na_2CO_3 solution.

[0005] Considering that the concentration of obtained Na_2SiO_3 solution is only between 2.5 - 10%, there is still room for improvement for the methods disclosed in the prior art.

[0006] Therefore, there remains a need to provide an improved method for producing purified SiO_2 .

SUMMARY

[0007] In a first aspect, the present disclosure provides a method for producing purified SiO_2 . The method may comprise the following step a): providing an aqueous solution

containing Na_2CO_3 and mixing it with an oxide or hydroxide of an alkaline earth metal to produce an aqueous solution containing NaOH and a precipitated carbonate of an alkaline earth metal. The method may comprise the following step b): adding acid-pretreated crude SiO_2 , containing more than 50 wt% of SiO_2 , to the aqueous solution of step a) and scavenging NaOH from the aqueous solution to form an aqueous Na_2SiO_3 solution at a temperature of 100 °C or lower. The method may comprise the following step c): filtering the aqueous Na_2SiO_3 solution to remove the precipitated carbonate of an alkaline earth metal. The method may comprise the following step d): partitioning the aqueous Na_2SiO_3 solution into at least two portions, wherein a mixture comprising a first portion of the purified SiO_2 alongside NaHCO_3 solution is produced by adding gaseous CO_2 to a first portion of the aqueous Na_2SiO_3 solution. The method may comprise the following step e): filtering the mixture from d) to separate and obtain the purified SiO_2 and the NaHCO_3 solution, wherein the NaHCO_3 solution is added to a further portion of the aqueous Na_2SiO_3 solution from step d) to precipitate an additional portion of the purified SiO_2 .

[0008] In a second aspect, there is provided a purified SiO_2 produced by the method as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

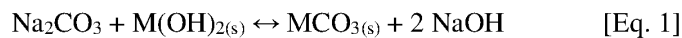
- **FIG. 1** is a block diagram illustrating one embodiment in which the method may be practiced;
- **FIG. 2** is a block diagram illustrating one embodiment in which the method may be practiced;
- **FIG. 3** is an X-ray powder diffraction (XRD) illustrating the approximate components of the feed for silica upgrading;
- **FIG. 4** is an XRD illustrating the purity of the purified SiO_2 obtained by the method as described herein; and
- **FIG. 5** shows the characteristics of the surface area measured for the purified SiO_2 obtained by the method as described herein, illustrating a surface area in excess of 500 m^2/g as measured with the Brunauer-Emmett-Teller (BET) method.

DETAILED DESCRIPTION

[0010] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the disclosure may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the disclosure. Other embodiments may be utilized and structural, and logical changes may be made without departing from the scope of the disclosure. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0011] In a first aspect, the present disclosure provides a method for producing purified SiO_2 . The method may comprise the following step a): providing an aqueous solution containing Na_2CO_3 and mixing it with an oxide or hydroxide of an alkaline earth metal to produce an aqueous solution containing NaOH and a precipitated carbonate of an alkaline earth metal. The method may comprise the following step b): adding acid-pretreated crude SiO_2 , containing more than 50 wt% of SiO_2 , to the aqueous solution of step a) and scavenging NaOH from the aqueous solution to form an aqueous Na_2SiO_3 solution at a temperature of 100 °C or lower. The method may comprise the following step c): filtering the aqueous Na_2SiO_3 solution to remove the precipitated carbonate of an alkaline earth metal. The method may comprise the following step d): partitioning the aqueous Na_2SiO_3 solution into at least two portions, wherein a mixture comprising a first portion of the purified SiO_2 alongside NaHCO_3 solution is produced by adding gaseous CO_2 to a first portion of the aqueous Na_2SiO_3 solution. The method may comprise the following step e): filtering the mixture from d) to separate and obtain the purified SiO_2 and the NaHCO_3 solution, wherein the NaHCO_3 solution is added to a further portion of the aqueous Na_2SiO_3 solution from step d) to precipitate an additional portion of the purified SiO_2 .

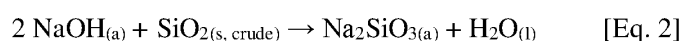
[0012] Advantageously, the method described herein represents the combination of two initial chemical reactions that synergistically support each other to 1) shift the reaction equilibrium towards the products; and/or 2) proceed at comparably mild conditions that allow for easy onward processing of the reaction products. One of the two chemical reactions (termed as the regeneration) is described as step a) of this method may involve a reaction between an aqueous solution containing Na_2CO_3 and an oxide or hydroxide of an alkaline earth metal (MO or $\text{M}(\text{OH})_2$) to produce an aqueous solution containing NaOH and a precipitated carbonate of an alkaline earth metal, having a reaction equation as follows:



[0013] In this reaction, the alkaline earth metal carbonate ($\text{MCO}_{3(s)}$) precipitates as a solid, whereby the solid is signified with (s). While the terminology $\text{M}(\text{OH})_2$ has been used, it is understood that an alkaline earth metal oxide (MO) in an aqueous solution could equally be used, which would react in situ with water to give the alkaline earth metal hydroxide ($\text{M}(\text{OH})_2$).

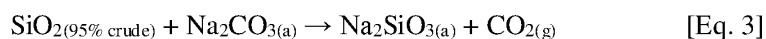
[0014] Conventionally, there are physical limitations to the implementation of the reaction outlined as [Eq. 1], since it is an equilibrium reaction that highly depends on solution concentrations. For example, conventionally, the $\text{Na}_2\text{CO}_3/\text{NaOH}$ solutions have to be dilute (typically <1M) for the reaction to proceed towards the right hand side of the equation, *i.e.* towards the product. A reaction proceeding towards the “right hand side of the equation”, as used herein, is commonly understood to refer to a reversible reaction, wherein formation of the product is favored over the back reaction, which would return the starting materials.

[0015] The other of the two initial reactions, described as step b) in this method, is the reaction of using NaOH to dissolve silica and produce Na_2SiO_3 (termed herein as the dissolution). Advantageously, the NaOH generated in step a) is immediately consumed via reaction with the crude SiO_2 in the mixture in step b), and is therefore less likely to undergo the reverse reaction with precipitated alkaline earth metal carbonate to re-form Na_2CO_3 as in step a). Hence, the back reaction of step a) is advantageously hindered by removing NaOH from the reaction equation. The equation describing the reaction of step b) is shown below:



[0016] Advantageously, it was observed that the combination of these two reactions in one unit operation enables several synergistic effects to take place. By combining the two steps into one unit operation, the concentration limitations in the regeneration step (allowing concentrations up to 20wt% or more of Na_2CO_3 in solution) can be circumvented, since the NaOH is continuously scavenged by the reaction of step b), thereby driving the reaction equilibrium towards the right hand side of the equation, *i.e.* towards the product. More advantageously, the SiO_2 dissolution kinetics are also increased via the increased alkalinity in the aqueous solution environment resulting from the continuous regeneration of NaOH from

step a). Advantageously, addition of an alkaline earth metal oxide or hydroxide may accelerate the conventional reaction carried out towards the Na_2SiO_3 , outlined as follows:



[0017] The overall reaction of step a) and b) can thus be described as follows:



[0018] Further advantageously, the reaction to form aqueous sodium silicate ($\text{Na}_2\text{SiO}_{3(a)}$) in this method is significantly milder than that in conventional processes. For example, the reaction outlined in [Eq. 4] may occur at 100 °C and atmospheric pressure. In conventional processes, a mixture of solid Na_2CO_3 and pure quartz is melted at 1,200 °C, filtered, cooled, and then washed with water to obtain the Na_2SiO_3 . Corrosion, safety and energy requirements are major costs/issues encountered in the conventional production processes. The significant improvements that the disclosed method offers are self-evident.

[0019] Further advantageously, in the process, the spent aqueous Na_2CO_3 solution after silica precipitation can be reused directly without further treatment. In conventional precipitated silica production processes, the recycling of this Na_2CO_3 involves its recovery from its aqueous solution via evaporation of excess water. Depending on the concentration of the Na_2CO_3 solution, the energy needed for evaporation can be anywhere from 10 to 40 GJ per ton SiO_2 produced. For comparison, the energy consumption in this method due to the use of MO is estimated to be in the range of 3 to 5 GJ/ton SiO_2 , which is significantly lower.

[0020] Further advantageously, in contrast with conventional sodium silicate production processes, the method is capable of using impure starting materials (95% crude silica instead of >99% pure quartz). The less stringent requirements mean that the raw material costs can be much lower as well.

[0021] Finally, pure carbon dioxide (CO_2) gas is produced from dilute CO_2 streams at the end of a cycle of the process, which can be sold, sequestered or used for mineralization.

[0022] According to various embodiments, the acid-pretreated crude SiO_2 may be an acid-treated mineral residue that is rich in silica content (>90wt% SiO_2). According to various embodiments, the acid-pretreated crude SiO_2 may be obtained from an alkaline earth silicate rock, which is optionally thermally treated.

[0023] The acid pre-treatment step may involve the reaction of a mineral acid with a mineral residue that is rich in silica content. The mineral acid may be selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid and a combination thereof. The quantity of mineral acid that is used may depend on the composition of the mineral residue to be treated. In some embodiments, between 1 to 5, or 1 to 3, or 1 to 1.2 times the stoichiometric amounts relative to the metal components from the mineral residue may be employed. The mineral acid may leach out the metal components from the mineral residue. The acid pre-treatment step may be conducted room temperature or at slightly elevated temperatures to accelerate the metal leaching reaction.

[0024] In some embodiments, the acid-pretreated crude SiO_2 may contain more than about 60 wt% of SiO_2 , optionally more than about 70 wt% of SiO_2 , optionally more than about 80 wt% of SiO_2 , optionally more than about 90 wt% of SiO_2 , optionally between about 75 wt% and about 95 wt% of SiO_2 , or about 95 wt% of SiO_2 .

[0025] The acid pretreatment step advantageously enriches the relative content of SiO_2 in the material and also converts SiO_2 into a more reactive form. The acid pretreatment step to obtain the acid-pretreated crude SiO_2 (acid-leached residue) also helps to greatly reduce the heating and pressurization requirements. This enables faster reactions to take place under milder conditions, and also removes impurities such as aluminum that might necessitate additional downstream purification/separation steps to ensure that a high purity SiO_2 product is obtained. Reaction conversions under these circumstances as outlined in this method can reach >85% within one hour of reaction for the silica dissolution step (step b)). This reaction conversion is contrasted with conversions in the prior art, for which only a conversion of about ~71% may be obtained after 3 hours at 95 °C, e.g. by using rice husk ash as the SiO_2 source. Accordingly, an acid pretreatment step may be present prior to the SiO_2 dissolution step itself, which “activates” the starting material and allows the dissolution reaction to proceed rapidly under mild conditions.

[0026] According to various embodiments, the Na_2CO_3 in step a) may be present in the aqueous solution in a concentration higher than about 10 wt%, optionally higher than about 20 wt%, optionally higher than about 30 wt%, optionally between about 10 wt% and about 50 wt%, or about 20 wt% and about 40 wt%, or of about 20 wt%. In particular, a high concentration of between 10 wt% and 30 wt% is part of the advantages discussed above, which is enabled by continuously removing the NaOH from the reaction equilibrium by the reaction outlined in step b).

[0027] Since step a) and step b) are carried out in one unit operation, the terminology into “step a)” and “step b)” does not imply that these steps are sequential in chronology. Rather, they may be carried out either sequentially or concurrently, as soon as NaOH has been produced by step a). Accordingly, in one embodiment, step a) may be initiated first, and subsequently, in the same container step b) may be initiated.

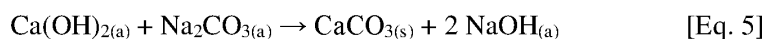
[0028] According to various embodiments, the step a) may subsequently comprise a step a)i): filtering the aqueous solution obtained from step a) to remove the precipitated carbonate of an alkaline earth metal before addition of the acid-pretreated crude SiO₂. In this embodiments, step a) and step b) would be carried out sequentially.

[0029] One of the key advantages in this method is that the NaOH concentration in the aqueous solution is kept at a virtual minimum at all times, since any generated NaOH is immediately consumed via reaction with crude silica to form Na₂SiO₃. Because NaOH is not allowed to accumulate in the system, its concentration never gets high enough to enable the reverse reaction (re-formation of Na₂CO₃) to occur, thus circumventing the aforementioned concentration limitations.

[0030] Accordingly, and in accordance with various embodiments, the concentration of the NaOH in the aqueous solution of step b) may be kept below about 5 wt%, optionally below about 1 wt%, optionally below about 0.5 wt%, optionally below about 0.1 wt%, optionally infinitesimal due to being removed continuously by reaction with the acid-pretreated crude SiO₂.

[0031] According to various embodiments, the oxide or hydroxide of an alkaline earth metal may be an oxide or hydroxide of calcium or magnesium.

[0032] According to various embodiments, the oxide or hydroxide of calcium or magnesium may be an oxide or hydroxide of calcium. The reaction of step a), in one embodiment, may thus be described as follows:



[0033] Advantageously, when CaO/(OH)₂ is chosen, it can perform two functions in the reaction system. Firstly, it can regenerate Na₂CO₃ into NaOH for reaction with SiO₂ under mild aqueous conditions. Secondly, it binds tightly with any formed CO₂ in the system and prevents the reverse reactions from happening, thus pushing the equilibrium to the right and increasing overall conversions. These pull factors drive the reaction to very high degrees of conversion

under very mild conditions and in a relatively short timeframe, and are examples of the practical application of Le Chatelier's principle in the method. In addition, by using the disclosed process, there is a potential to refine the calcium carbonate by-product mixture into high value precipitated CaCO_3 , which is a specialty chemical used in many applications.

[0034] Accordingly, according to various embodiments, step b) may be carried out at a temperature of about 90 °C or lower, or at a temperature of about 80 °C or lower, or at a temperature of about 70 °C or lower, or at a temperature of about 60 °C or lower, or at a temperature of about 50 °C or lower, or at a temperature of about 40 °C or lower, or between about 20 °C and about 100 °C, or between about 30 °C and about 90 °C, or between about 40 °C and about 80 °C, or between about 50 °C and about 70 °C, or at room temperature. "Room temperature", as used herein, refers to a temperature greater than 4 °C, preferably being in the range from 15 °C to 40 °C, or in the range from 15 °C to 30 °C, or in the range from 20 °C to 30 °C, or in the range from 15 °C to 24 °C, or in the range from 16 °C to 21 °C, or around 25 °C. Such temperatures may include, 14 °C, 15 °C, 16 °C, 17 °C, 18 °C, 19 °C, 20 °C, 21 °C, and 25 °C, each of these values including ± 0.5 °C. Advantageously, such low temperature conditions are enabled by the above mentioned pull factors, driving the reaction to very high degrees of conversion under very mild conditions.

[0035] According to various embodiments, carrying out the reaction of step b) may comprise stirring the solution of the reactants for about between 0.5 and 3 hours. Advantageously, such low reaction times are enabled by the above mentioned pull factors, driving the reaction to very high degrees of conversion under very mild conditions.

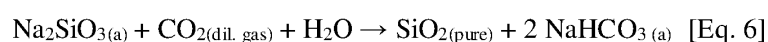
[0036] Moreover, according to various embodiments, step b) may be carried out at a pressure of between about 1 bar to about 5 bar, or at a pressure of between about 1 bar to about 4 bar, or at a pressure of between about 1 bar to about 3 bar, or at a pressure of between about 1 bar to about 2 bar, or at ambient pressure. The pressure may refer to an absolute pressure. As mentioned, such relatively pressure is enabled by the above mentioned pull factors, driving the reaction to very high degrees of conversion under very mild conditions.

[0037] In a further step c), the aqueous Na_2SiO_3 solution obtained from step b) may be filtered for removal of the precipitated carbonate of the alkaline earth metal. Advantageously, this step also helps to remove impurities from the aqueous Na_2SiO_3 solution.

[0038] According to various embodiments, step c) may be carried out at a lower temperature than the temperature in step b), optionally at a temperature of about 40 °C or lower, or at a temperature of about 30 °C or lower, or at room temperature.

[0039] According to various embodiments, the precipitated carbonate of an alkaline earth metal, which is removed in step c) or optionally in step a)i), may be decomposed into an oxide or hydroxide of an alkaline earth metal and recycled in step a).

[0040] In a subsequent step d), the filtered and aqueous Na_2SiO_3 solution from step c) may be partitioned into at least two portions. One of the two portions (the first portion) is reacted into the final product (purified silica) and sodium bicarbonate (NaHCO_3), according to the following equation:



[0041] According to various embodiments, the pH of the aqueous Na_2SiO_3 solution prior to the addition of gaseous CO_2 may be at about 9 to about 14, or at about 10 to about 13, or at about 11 to about 13, or at about 12 to about 13, or at about 13. Subsequently, the addition of gaseous CO_2 in step d) may lower the pH of the aqueous Na_2SiO_3 solution to about 6 to about 10, or about 7 to about 9, or about 8 to about 9, or to about 8. This may be carried out by adding the gaseous CO_2 in step d) in more than stoichiometric amount. Advantageously, due to the lower pH of about 7 to about 9, the precipitated purified SiO_2 is obtained as a hydrous gel.

[0042] Advantageously, by partitioning the filtered and aqueous Na_2SiO_3 solution from step c) in step d), the NaHCO_3 produced in the reaction of [Eq. 6] may be recycled for a second or subsequent precipitation of Na_2SiO_3 and the NaHCO_3 , in such a subsequent precipitation of Na_2SiO_3 , is reacted into Na_2CO_3 . This has the advantage that the Na_2CO_3 may be reused in step a) of the method, and only half the amount of oxides or hydroxides of an alkaline earth metal has to be used. In comparison, in the event that NaHCO_3 was recycled in step a), the chemical reaction for step a) would be as follows:



[0043] As can be seen, the reaction outlined in [Eq. 1] is more atom efficient than the reaction outlined in [Eq. 7], due to using Na_2CO_3 instead of NaHCO_3 .

[0044] The method in step d) may involve the use of dilute CO_2 streams to dissolve and precipitate NaHCO_3 and pure SiO_2 , respectively. Subsequent to the precipitation of silica, this CO_2 may form a carbonate/bicarbonate with the alkaline earth metal. Ultimately, this alkaline earth metal (bi)carbonate may be decomposed and a pure stream of CO_2 may be generated,

which can be sold, sequestered or used in mineralization reactions. Thus advantageously, the method also provides a mechanism wherein CO₂ may be concentrated (up to 100%) and purified from dilute flue gas streams.

[0045] In step e) of the method, the remaining solution after precipitation of the purified SiO₂ from the solution in step d) may be added to a further partition of the filtered and aqueous Na₂SiO₃ solution from step c), yielding a further portion of the further purified SiO₂ and produces Na₂CO₃, according to the following equation:



[0046] Accordingly, step e) may comprise a step e)i): precipitating the additional portion of the purified SiO₂ to further produce Na₂CO₃. The Na₂CO₃ of step e)i) may be reused in step a). Hence, the Na₂CO₃ of step e)i) may be present in an aqueous solution for recycling in step a). This recycling step may advantageously be carried out directly, without any further treatment, which is also attributed to the mild conditions that were used in step b).

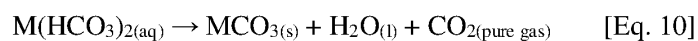
[0047] According to various embodiments, the purified SiO₂ of step d) and/or step e) may be precipitated in form of a hydrous gel. The precipitation of step e) is deemed complete once the pH of the solution is between about 8 to about 10, or about 9.

[0048] According to various embodiments, the method may further comprise a step f): decomposing the precipitated carbonate of an alkaline earth metal into an oxide or hydroxide of the alkaline earth metal and purified CO₂.

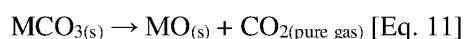
[0049] According to various embodiments, the additional step f) may advantageously further enhance the recycling capabilities of the method described herein. The precipitated carbonate of an alkaline earth metal may be obtained from the reaction described in step a) of the method and removed in an optional filtration a)i) or the filtration step c). The reaction in step f) may involve purifying the precipitated carbonate of an alkaline earth metal by reacting the precipitated carbonate of an alkaline earth metal with diluted CO₂ to give an aqueous solution of a bicarbonate of an alkaline earth metal, as shown in the following reaction scheme:



[0050] Subsequent decomposition of the bicarbonate of an alkaline earth metal may give a purified carbonate of an alkaline earth metal, as shown in the following reaction scheme:

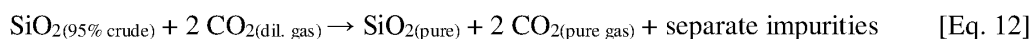


[0051] According to various embodiments, the purified carbonate of an alkaline earth metal may be filtered off and further decomposed into the oxide or hydroxide of an alkaline earth metal and the purified CO₂. The decomposition into the oxide or hydroxide of an alkaline earth metal may be affected by applying heat, which may have a drying effect. Further decomposition into pure CO₂ and MO, which is recycled back into the process, is shown in the below reaction:



[0052] The oxide or hydroxide of an alkaline earth metal thus obtained may be recycled in step a).

[0053] Hence, the net effect of the method is the refinement of crude SiO₂ into high purity precipitated SiO₂ and the concentration of dilute CO₂ sources into pure CO₂ streams, as shown in the following reaction scheme:



[0054] In a further aspect, there is provided a purified SiO₂ produced by the method of the method described herein, being present in a purity of at least 98.5%, optionally in a purity of at least 99%.

[0055] According to various embodiments, the purified SiO₂ may have a surface area in excess of 500 m²/g, optionally measured through nitrogen adsorption using a Brunauer-Emmett-Teller (BET) method.

[0056] According to various embodiments, the purified SiO₂ may be amorphous and may be obtained by precipitation.

[0057] The term “solution” as used herein refers to a mixture of components. The liquid to bring the mixture of components into solution may be water, which is indicated in the equations as (a). Components that are added as solids or precipitate therefrom may be signified in the equations with (s). Components that are added as gas may be signified in the equations with

(g). Similarly, subscripts such as (dil.) would refer to “diluted”, and (l) would refer to “liquid”. The abbreviations used in the reaction schemes are well known to the person skilled in the art.

[0058] By “about” in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10 % of the specified value.

[0059] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0060] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

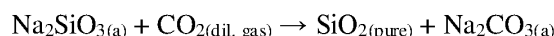
[0061] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

EXAMPLES

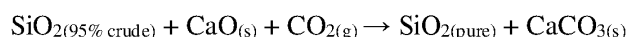
[0062] Herein, there is provided a less energy-intensive method of refining a residual crude silica material (obtained after acid treatment of serpentine minerals) into commercial-grade precipitated silica. This crude silica material is first mixed with calcium oxide powder and stirred into a sodium carbonate aqueous solution. The mixture is then heated to 100 °C and refluxed for several hours to allow the reaction



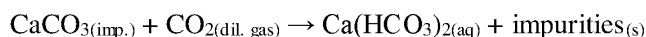
to take place. After that, the mixture is filtered and the calcium carbonate is removed together with undissolved impurities. The sodium silicate solution is cooled and then transferred into another vessel, where dilute CO₂ is sparged into it. This results in the precipitation of purified silica as a hydrous gel and also the regeneration of sodium carbonate for recycling:



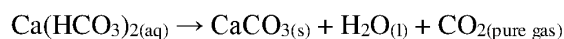
[0063] The precipitated silica is washed, dried and ground into a white powder, where characterization reveals that it is comparable in quality with commercial grade chromatographic silica gels. The net reaction is thus:



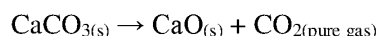
The impure calcium carbonate by-product (circa 85% purity, metal oxides basis) is then mixed with water to form a slurry and sparged with more dilute CO₂. This dissolves the calcium as Ca(HCO₃)₂, and leaves behind the unreacted residue:



[0064] A filtration step separates the two phases and the impurities are discarded, while the bicarbonate solution is transferred into a regeneration system to regenerate the CaO reagent and produce pure CO₂ gas, which can be sold, sequestered or used in mineralization reactions. Here, the bicarbonate is first decomposed into solid CaCO₃, water and pure CO₂ gas at low temperatures:



The calcium carbonate is then filtered off and sent into a furnace to be dried and further decomposed into pure CO₂ and CaO, which is recycled back into the process:



The net effect of the process is the refinement of crude silica into high purity precipitated silica and the concentration of dilute CO₂ sources into pure CO₂ streams.

[0065] $\text{SiO}_{2(95\% \text{ crude})} + 2\text{CO}_{2(\text{dil. gas})} \rightarrow \text{SiO}_{2(\text{pure})} + 2\text{CO}_{2(\text{pure gas})} + \text{separate impurities}$

[0066] Key features of this disclosure relate to a method for refining crude silica residue after acid leaching into commercial-grade precipitated silica gel involving a reaction to form sodium silicate from amorphous silica at mild operating conditions (100 °C and atmospheric pressure), using calcium oxide and aqueous sodium carbonate solutions as reagents. Precipitated silica obtained from this method was found to be amorphous, having surface areas in excess of 500m²/g, and of at least 98.5% purity. Advantageously, the method allows direct reuse of sodium carbonate solution after silica precipitation reaction. There is also potential to produce a high quality precipitated calcium carbonate by-product from process. Moreover, dilute CO₂ streams (*i.e.* flue gas) are concentrated into pure CO₂ (up to 100%) in the process.

[0067] A method is developed to produce precipitated silica at significantly milder reaction conditions compared to conventional production processes. The key to achieving this breakthrough is the application of process intensification principles, more specifically the combination of two unit operations resulting in much higher overall process efficiencies.

[0068] The concept of using of $\text{CaO}/(\text{OH})_2$ to regenerate spent Na_2CO_3 into NaOH is known. This method is found in the Kraft process (pulp-making for paper manufacture) and is also mentioned elsewhere.

[0069] However, there are physical limitations to the implementation of this reaction. The regeneration reaction ($\text{Na}_2\text{CO}_{3(a)} + \text{CaO}_{(s)} \leftrightarrow \text{CaCO}_{3(s)} + \text{NaOH}_{(a)}$) is an equilibrium reaction that highly depends on solution concentrations. The $\text{Na}_2\text{CO}_3/\text{NaOH}$ solutions have to be dilute (typically $<1\text{M}$) for the reaction to proceed towards the right hand side of the equation.

[0070] On the other hand, the concept of using NaOH to dissolve silica and produce sodium silicates is also known. However, it was observed that the combination of these two steps (regeneration and dissolution) in one unit operation enables a synergistic effect to take place. By combining the two steps into one unit operation, we can circumvent the concentration limitations in the regeneration step (allowing concentrations up to 20wt% or more of Na_2CO_3 in solution) and also enhance the SiO_2 dissolution kinetics via the increased alkalinity in the aqueous solution environment.

[0071] In this method, calcium oxide or hydroxide is added to accelerate the reaction ($\text{SiO}_{2(95\% \text{ crude})} + \text{Na}_2\text{CO}_{3(a)} \rightarrow \text{Na}_2\text{SiO}_{3(a)} + \text{CO}_{2(g)}$). The overall reaction is a combination of two distinct reactions. Firstly, calcium oxide/hydroxide dissolves in solution and reacts with sodium carbonate to precipitate calcium carbonate and generate sodium hydroxide.

[0072] $\text{Ca}(\text{OH})_{2(a)} + \text{Na}_2\text{CO}_{3(a)} \rightarrow \text{CaCO}_{3(s)} + 2\text{NaOH}_{(a)}$

[0073] Next, the generated sodium hydroxide is immediately consumed via reaction with the silica component in the mixture, and is therefore less likely to undergo the reverse reaction with precipitated calcium carbonate and re-form sodium carbonate.

[0074] $2\text{NaOH}_{(a)} + \text{SiO}_{2(s, \text{ crude})} \rightarrow \text{Na}_2\text{SiO}_{3(a)} + \text{H}_2\text{O}_{(l)}$

[0075] The overall reaction is thus:

[0076] $\text{Ca}(\text{OH})_{2(a)} + \text{Na}_2\text{CO}_{3(a)} + \text{SiO}_{2(s, \text{ crude})} \rightarrow \text{CaCO}_{3(s)} + \text{Na}_2\text{SiO}_{3(a)} + \text{H}_2\text{O}_{(l)}$

[0077] One of the key elements in this method is that the NaOH concentration in the aqueous solution is kept at a virtual minimum at all times, since any generated NaOH is immediately consumed via reaction with crude silica to form sodium silicate. Because NaOH is not allowed to accumulate in the system, its concentration never gets high enough to enable the reverse reaction (re-formation of Na_2CO_3) to occur, thus circumventing the aforementioned concentration limitations.

[0078] Also, $\text{CaO}/(\text{OH})_2$ was chosen because it can perform two functions in the reaction system. Firstly it can regenerate Na_2CO_3 into NaOH for reaction with SiO_2 under mild aqueous

conditions. Secondly it binds tightly with any formed CO_2 in the system and prevents the reverse reactions from happening, thus pushing the equilibrium to the right and increasing overall conversions. These pull factors drive the reaction to very high degrees of conversion under very mild conditions and in a relatively short timeframe, and are examples of the practical application of Le Chatelier's principle in method.

[0079] Additionally, since the method allows for the silica dissolution reaction to be conducted under mild conditions (100 °C at 1 bar, in aqueous environments), the spent aqueous sodium carbonate solution after silica precipitation can be reused directly without further treatment.

[0080] Finally, the method proposed here utilizes dilute CO_2 streams to dissolve and precipitate CaCO_3 and pure SiO_2 respectively. The penultimate fate of this CO_2 is that it forms a carbonate/bicarbonate with calcium. Ultimately, this calcium (bi)carbonate is calcined and a pure stream of CO_2 is generated, which can be sold, sequestered or used in mineralization reactions. Thus in essence, the process is also a mechanism where CO_2 is concentrated and purified from dilute flue gas streams.

[0081] A block diagram showing one embodiment in which the method may be practiced is shown in **FIG. 1**.

[0082] The reaction to form aqueous sodium silicate in the method is significantly milder than that in conventional processes. The reaction in the method: $\text{SiO}_{2(95\% \text{ crude})} + \text{CaO}_{(s)} + \text{Na}_2\text{CO}_{3(a)} \rightarrow \text{Na}_2\text{SiO}_{3(a)} + \text{CaCO}_{3(s)}$ occurs at 100 °C and atmospheric pressure. In conventional processes, a mixture of solid sodium carbonate and pure quartz is melted at 1,200 °C, filtered, cooled, and then washed with water to obtain the sodium silicate. Corrosion, safety and energy requirements are major costs/issues in the conventional production processes. The significant improvements that the disclosed method offers are self-evident.

[0083] In addition, in the process, there is a potential to refine the calcium carbonate by-product mixture into high value precipitated calcium carbonate, which is a specialty chemical used in many applications.

[0084] Thirdly, in the process, the spent aqueous Na_2CO_3 solution after silica precipitation can be reused directly without further treatment. In conventional precipitated silica production processes, the recycling of this sodium carbonate involves its recovery from aqueous solution via evaporation of excess water. Depending on the concentration of the Na_2CO_3 solution, this energy for evaporation can be anywhere from 10 to 40 GJ per ton SiO_2 produced. For

comparison, the energy consumption in this method due to the use of CaO is estimated to be in the range of 3 to 5 GJ/ton SiO₂, which is significantly lower.

[0085] Fourthly, in contrast with conventional sodium silicate production processes, the method is capable of using impure starting materials (95% crude silica instead of >99% pure quartz). The less stringent requirements mean that the raw material costs can be much lower as well.

[0086] Finally, pure CO₂ gas is produced from dilute CO₂ streams at the end of a cycle of the process, which can be sold, sequestered or used for mineralization.

[0087] Some further work relating to this method has been done to clarify and refine the key details of the present technology. The key aspects are outlined in a block diagram as shown in **FIG. 2**, and numbers for method steps mentioned herein refer to the numbers used in the block diagram as shown in **FIG. 2**.

[0088] The preferred starting material for the process is an acid-treated mineral residue that is rich in silica content (>90wt% SiO₂). The acid pretreatment step enriches the relative content of silica in the material and also converts it into a more reactive form.

[0089] In a parallel step, (recycled) aqueous sodium carbonate in a concentration of between 10 and 30 wt% is mixed with an oxide or hydroxide of calcium or magnesium, for example to give the reaction: $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + 2\text{NaOH}$ [Eq. 12]. This gives solid calcium or magnesium carbonate, and aqueous sodium hydroxide. This mixture is filtered to separate out the carbonate solids and give an aqueous sodium hydroxide solution.

[0090] The solid carbonate byproduct from [Eq. 12] is regenerated via heating to give the metal oxide and CO₂ for recycling back into the system.

[0091] The resultant sodium hydroxide solution from [Eq. 12] is then used to react with the silica-rich, acid-treated mineral residue from the acid pretreatment at room temperature and pressure, though this can obviously also be done at other conditions, for example between 20 – 100 °C and/or between 1 to 5 bars of pressure.

[0092] The pretreatment step to obtain the acid-leached residue is important to greatly reduce the heating and pressurization requirements. This enables faster reactions to take place under milder conditions, and also removes impurities such as aluminum that might necessitate additional downstream purification/separation steps to ensure a high purity SiO₂ product is obtained. Reaction conversions under these circumstances as outlined in our process can reach >85% within 1 hour of reaction for the silica dissolution step (cf. ~71% conversion after 3 hours at 95 °C, by using rice husk ash as the silica source).

[0093] This mixture after reaction is filtered again to separate out the unreacted remnants and obtain an aqueous Na_2SiO_3 solution ($\text{pH} \approx 13$).

[0094] The addition of gaseous CO_2 to the aqueous Na_2SiO_3 solution will lower the pH of the solution to around 8 or so, and thus precipitate pure SiO_2 as a gel. An excess of CO_2 above the stoichiometric amount needs to be supplied to the solution in order to lower the pH to 8. This silica gel is washed and dried to give the final product (precipitated silica). The mixture consisting of silica gel and the residual aqueous phase is separated via filtration.

[0095] The resultant aqueous phase from this method is a NaHCO_3 solution, which cannot be recycled directly back into the system. If NaHCO_3 is recycled directly, twice the amount of oxides or hydroxides of calcium or magnesium is needed to regenerate the same amount of aqueous NaOH for reaction: $2\text{NaHCO}_3 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + 2\text{NaOH} + 2\text{H}_2\text{O}$ (see, e.g. [Eq. 12]).

[0096] To overcome this, the aqueous Na_2SiO_3 solution was split into two streams for separate reactions in two steps. The first stream is contacted with gaseous CO_2 to precipitate SiO_2 as described previously.

[0097] The NaHCO_3 solution obtained from the processing of the first stream is then mixed with the second stream of aqueous Na_2SiO_3 , resulting in precipitation of more SiO_2 . The pH of the mixture, after precipitation is deemed complete, is around 9.

[0098] The silica gel thus precipitated is filtered off and the aqueous byproduct is substantially composed of Na_2CO_3 , which can now be recycled back into the system.

[0099] This splitting of streams to obtain aqueous Na_2CO_3 instead of NaHCO_3 is important, because it ensures that the use of the oxides or hydroxides of calcium or magnesium are kept to a minimum. A simple mass balance would show that without the splitting, at least twice the amount of $\text{Ca}(\text{OH})_2$ and heat energy (for example) would have been needed for the steps in [Eq. 12].

[00100] The silica precipitation is conducted in two steps instead of one, in order to control the $\text{CO}_3^{2-}/\text{HCO}_3^-$ speciation in the final aqueous phase. Proper control to obtain recycled solutions that consist substantially of CO_3^{2-} will reduce the $\text{Ca}(\text{OH})_2$ requirements in the regeneration step.

[00101] **Example 1 – Acid-Pretreatment of the Mineral Residue**

[00102] A 150g sample of magnesium-depleted serpentine was mixed with 575ml of 20wt% HCl and heated to 80°C under constant stirring. The reaction was allowed to proceed for one hour, and the resulting product mixture was filtered to separate the leachate solution and solid

residues. The degree of extraction of the metal components into the solution was measured to be as follows: Mg (95.5%), Al (91.5%), Ca (47.3%), Cr (23.3%), Fe (89.0%), Mn (100%).

[00103] **Example 2 – Characterization of the crude silica**

[00104] The acid-pretreated crude SiO₂ (feed for silica upgrading) is obtained after acid leaching to recover metal components (see, Example 1). The starting material is mainly composed of amorphous silica, mixed with unreacted mineral fractions. The silica content is approximately 75% – 95% depending on acid leaching conditions. In the following Table 1, the approximate components of the feed for silica upgrading is outlined.

[00105] **Table 1:** crude silica starting material

XRF (Oxides)	Mg-depleted Residue	Acid-leached Residue
MgO	28.04%	2% - 12%
Al ₂ O ₃	5.47%	0.7% – 1.5%
SiO ₂	50.16%	75% – 95%
CaO	2.61%	2.5% - 3.3%
Cr ₂ O ₃	0.99%	1.2% - 1.4%
MnO	0.18%	ND
Fe ₂ O ₃	12.12%	1.8% - 6.9%
NiO	0.32%	ND

[00106] In **FIG. 3**, an X-ray powder diffraction (XRD) also shows the approximate components of the feed for silica upgrading.

[00107] **Example 3 – Production of sodium silicate**

[00108] Example A: 110.5g of 10wt% Na₂CO₃ solution was preheated to 100°C, and mixed under stirring with 3.00g of CaO. After 30 minutes, 3.17g of crude silica (85.6% SiO₂ content) was added to the mixture. The mixture was stirred for 1 hour and then cooled to room temperature for filtration. The filtered solids were washed, weighed and analysed to determine the amount of SiO₂ reacted. The conversion of SiO₂ into sodium silicate was found to be 88.0%.

[00109] Example B: 110.5g of 5wt% Na₂CO₃ solution was mixed with 3.00g of CaO and stirred at room temperature for 1 hour. 3.17g of crude silica (66.8% SiO₂ content) was subsequently added to the mixture, and stirred for another hour. The product mixture was then

filtered, and the filtered solids were washed, weighed and analysed to determine the amount of SiO_2 reacted. The conversion of SiO_2 into sodium silicate was found to be 85.5%.

[00110] **Example 4 – Precipitation of purified silica**

[00111] Example C: 45ml of Na_2SiO_3 solution obtained from Example 3A was transferred into a beaker, with attached pH probe and gas sparger. Pure CO_2 gas was sparged into the solution under constant stirring, and the pH of the mixture (initial value of around 12) was monitored. Once the pH reached a value of 8, the sparging was stopped and the mixture was filtered. The filtrate was retained for further processing. The solid silica gel component was washed with de-ionised water, dried and weighed. The weight of the precipitated silica was found to be 0.62g.

[00112] Example D: 45ml of a filtrate prepared in a similar manner as that from Example C (i.e. Na_2SiO_3 solution sparged with CO_2 to pH 8 and filtered) was stirred in a beaker, and an additional 45ml of Na_2SiO_3 solution was gradually added to the solution. Upon completion of addition, the mixture was stirred for another 48 hours to allow for the formation of silica gels. The mixture was then filtered, and the solid silica gel component was washed with de-ionised water, dried and weighed. The weight of the precipitated silica was found to be 0.52g. The filtrate was also retained for further processing.

[00113] **Example 5 - Recycling of precipitation filtrate**

[00114] Example E: 86.5g of the filtrate from Example D was mixed with 2.36g of CaO and stirred at 100°C for 30 minutes. The mixture was filtered, and the filtrate was transferred back into the reactor. 2.48g of crude silica (40.8% SiO_2 content) was then added to the solution and stirred at 100°C for 1 hour. The mixture was then cooled and filtered, and the filtered solids were washed, weighed and analysed to determine the amount of SiO_2 reacted. The conversion of SiO_2 into sodium silicate was found to be 94.7%.

[00115] **Example 6 – Characterization of the purified SiO_2**

[00116] The purified SiO_2 obtained by the method as described herein has been measured by an XRD, which is shown in **FIG. 4**. Therein, it can be seen that the SiO_2 is obtained in a high purity, compared with the XRD for the starting material. **FIG. 5** shows the characteristics of the surface area measured for the purified SiO_2 obtained by the method as described herein, illustrating a surface area in excess of 500 m^2/g as measured with the Brunauer-Emmett-Teller (BET) method.

[00117] While the disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes

in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A method for producing purified SiO_2 , the method comprising the following steps:
 - a) providing an aqueous solution containing Na_2CO_3 and mixing it with an oxide or hydroxide of an alkaline earth metal to produce an aqueous solution containing NaOH and a precipitated carbonate of an alkaline earth metal;
 - b) adding acid-pretreated crude SiO_2 , containing more than 50 wt% of SiO_2 , to the aqueous solution of step a) and scavenging NaOH from the aqueous solution to form an aqueous Na_2SiO_3 solution at a temperature of 100 °C or lower;
 - c) filtering the aqueous Na_2SiO_3 solution to remove the precipitated carbonate of an alkaline earth metal;
 - d) partitioning the aqueous Na_2SiO_3 solution into at least two portions, wherein a mixture comprising a first portion of the purified SiO_2 alongside NaHCO_3 solution is produced by adding gaseous CO_2 to a first portion of the aqueous Na_2SiO_3 solution; and
 - e) filtering the mixture from d) to separate and obtain the purified SiO_2 and the NaHCO_3 solution, wherein the NaHCO_3 solution is added to a further portion of the aqueous Na_2SiO_3 solution from step d) to precipitate an additional portion of the purified SiO_2 .
2. The method of claim 1, wherein the Na_2CO_3 is present in the aqueous solution in a concentration higher than about 10 wt%.
3. The method of claim 1 or 2, wherein the oxide or hydroxide of an alkaline earth metal is an oxide or hydroxide of calcium or magnesium.
4. The method of claim 3, wherein the oxide or hydroxide of calcium or magnesium is an oxide or hydroxide of calcium.
5. The method of any of claims 1 to 4, step a) subsequently comprising

- a)i) filtering the aqueous solution obtained from step a) to remove the precipitated carbonate of an alkaline earth metal before addition of the acid-pretreated crude SiO_2 .
6. The method of any of claims 1 to 5, wherein the acid-pretreated crude SiO_2 contains more than about 60 wt% of SiO_2 .
7. The method of any of claims 1 to 6, wherein the concentration of the NaOH in the aqueous solution of step b) is kept below about 5 wt%.
8. The method of any of claims 1 to 7, wherein step b) is carried out at a temperature of about 90 °C or lower.
9. The method of any of claims 1 to 8, wherein step b) is carried out at a pressure of between about 1 bar to about 5 bar.
10. The method of any of claims 1 to 9, wherein step c) is carried out at a lower temperature than the temperature in step b).
11. The method of any of claims 1 to 10, wherein the precipitated carbonate of an alkaline earth metal, which is removed in step c) or optionally in step a)i), is decomposed into an oxide or hydroxide of an alkaline earth metal and recycled in step a).
12. The method of any of claims 1 to 11, wherein the pH of the aqueous Na_2SiO_3 solution prior to the addition of gaseous CO_2 is at about 9 to about 14.
13. The method of any of claims 1 to 12, wherein the addition of gaseous CO_2 in step d) lowers the pH of the aqueous Na_2SiO_3 solution to about 6 to about 10.
14. The method of any of claims 1 to 13, step e) subsequently comprising
e)i) precipitating the additional portion of the purified SiO_2 to further produce Na_2CO_3 .
15. The method of claim 14, wherein the Na_2CO_3 of step e)i) is recycled in step a).

16. The method of claim 15, wherein the Na_2CO_3 of step e)i) is present in an aqueous solution for recycling in step a).
17. The method of any of the claims 1 to 16, further comprising
- f) decomposing the precipitated carbonate of an alkaline earth metal into an oxide or hydroxide of the alkaline earth metal and purified CO_2 .
18. The method of claim 17, wherein the reaction in step f) involves purifying the precipitated carbonate of an alkaline earth metal by reacting it with diluted CO_2 to give an aqueous solution of a bicarbonate of an alkaline earth metal and decomposing the bicarbonate of an alkaline earth metal to give a purified carbonate of an alkaline earth metal.
19. A purified SiO_2 produced by the method of any of claims 1 to 18, being present in a purity of at least 98.5%.
20. The purified SiO_2 of claim 19, having a surface area in excess of $500 \text{ m}^2/\text{g}$.