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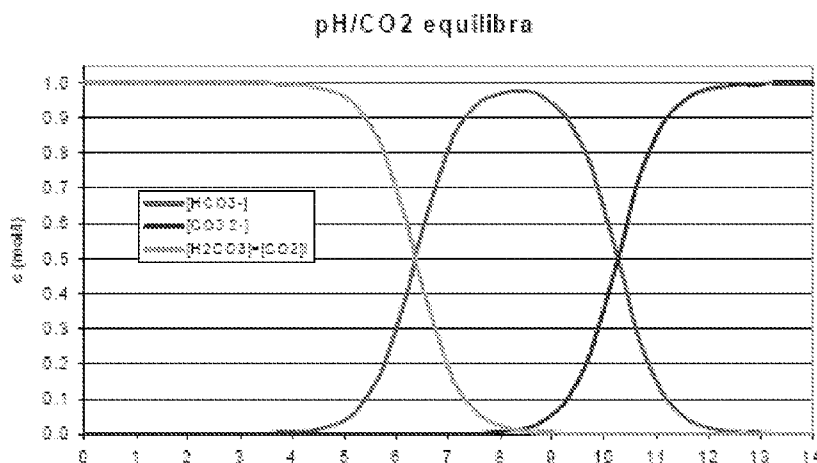


FIGURE 1

(57) Abstract: The present invention provides methods and apparatuses for removing carbon dioxide from gaseous emissions. In particular, the present invention provides methods and apparatuses for removing carbon dioxide from gaseous emissions as a metallic carbonate precipitate.

REMOVING CARBON DIOXIDE FROM GASEOUS EMISSIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the priority benefit of U.S. Provisional Application No. 61/027,808, filed February 11, 2008, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to methods and apparatuses for removing carbon dioxide from gaseous emissions. In particular, the present invention relates to methods and apparatuses for removing carbon dioxide from gaseous emissions as a metallic carbonate precipitate.

BACKGROUND OF THE INVENTION

[0003] Many conventional methods for reducing industrial carbon dioxide emissions have focused on reducing the amount of carbon dioxide generated during specific industrial processes. Some attempts have been made to reduce the amount of carbon dioxide released into the atmosphere by capturing and removing some of the carbon dioxide that is generated during industrial processes.

[0004] The technologies conventionally developed for reducing the amount of CO₂ released into the atmosphere from various industrial processes (e.g., from thermal power plants or cement producing plants) include a method of chemically absorbing CO₂ by organic amine compounds, an isolation or dissolution method for transferring recovered CO₂ to the ocean, a chemical conversion method for reforming CO₂ and methane to resource materials (such as synthesis fuel gas), as well as other technologies. In addition, as a global reduction method for the concentration of atmospheric CO₂ emitted and accumulated in the atmosphere, natural immobilization methods such as afforestation, algal growth, fertilizer application to the ocean, and coral reef growth have been studied and attempted.

[0005] However, the above mentioned methods are either too costly, require a large amount of energy (which generally comes from the combustion of fossil fuels – thereby creating

even more CO₂), are not sufficiently efficient enough to be used in industrial scale, and/or create other environmental problems.

[0006] Therefore, there is a continuing need for other methods for removing carbon dioxide from gaseous emissions.

SUMMARY OF THE INVENTION

[0007] Some aspects of the present invention provide methods and apparatuses for removing carbon dioxide from gaseous emissions. Other aspects of the invention provide methods for removing carbon dioxide from a gas emission stream by converting at least a portion of the carbon dioxide in the gaseous emission stream to carbonate ion and then reacting the carbonate ion with a metallic ion to form a metallic carbonate precipitate. Thus, removal of carbon dioxide in the form of a solid metallic carbonate reduces the amount of carbon dioxide gas being released into the atmosphere from a gaseous emission stream.

[0008] Yet in other aspects of the invention provide methods for reducing the amount of carbon dioxide gas being released into the atmosphere from a gaseous emission stream that comprises carbon dioxide. In these aspects of the invention, methods generally include contacting the gaseous emission stream with an aqueous solution comprising a metallic ion under conditions sufficient to produce a metallic carbonate precipitate, thereby reducing the amount of carbon dioxide gas being released into the atmosphere. Typically, the metallic carbonate has K_{sp} of about 10^{-3} or less under standard conditions.

[0009] In some embodiments, the pH of the aqueous solution is maintained at about pH 8 or higher. Still in other embodiments, the pH of the aqueous solution is maintained at about pH 10 or higher.

[0010] Yet in other embodiments, the pH of the aqueous solution is adjusted constantly or periodically.

[0011] Still in other embodiments, a hydroxide ion source is added or hydroxide ion is generated in situ via a non-chemical means to maintain the pH of aqueous solution at about pH 8 or higher, typically at about pH 10 or higher. Within these embodiments, in some instances the hydroxide ion is generated by electron beam, corona discharge, particle beam, ultrasonic

cavitation, hydrodynamic cavitation, ultraviolet light, plasma, electrolysis, radio or microwave radiation, or a combination thereof. In one particular embodiment, the hydroxide ion is generated in situ. In some instances, within this embodiment, the hydroxide ion is generated using corona discharge.

[0012] Without being bound by any theory, it is believed that carbon dioxide dissolves in the aqueous solution and forms carbonate ion, which then forms the metallic carbonate precipitate. Thus, metallic ions that are sparingly soluble in an aqueous solution are typically used. However, it should be appreciated that any metallic ions can be used as long as the aqueous solution can reach the saturation point of metallic carbonate. As expected, once the saturation point of any metallic carbonate is reached, it precipitates out of the solution.

[0013] The metallic ion typically comprises sodium ion, calcium ion, magnesium ion, manganese ion, barium ion, strontium ion, or a combination thereof. It should be appreciated that sodium ion combines with carbonate to form a various sodium carbonate precipitates, e.g., trona, sodium carbonate decahydrate, sodium bicarbonate, etc. Typically, the metallic ion comprises calcium ion, magnesium ion, manganese ion, barium ion, strontium ion, or a combination thereof.

[0014] The source of gaseous emission is generally those emission stream produced from an industrial process. Such a process typically generates a large amount of carbon dioxide. Such a gaseous emission stream can be first scrubbed or purified to concentrate the amount of carbon dioxide or it can be used without any prior purification. Typically, the industrial process comprises an oil refinery, power plants, cement plants, coal industry, auto, airline, mining, food, lumber, paper and manufacturing industries, or a combination thereof.

[0015] In other embodiments of the invention, the step of contacting the gaseous emission stream with an aqueous solution is conducted under pressure.

[0016] It should be appreciated that for an industrial scale process, a vast quantity of aqueous solution is required. Thus, typically the aqueous solution comprises industrial process water, water from an aquifer, sea water, oil field produced water, frac flowback water, or a combination thereof. Accordingly, in some aspects of the invention, industrial waste or by-

products (e.g., gaseous emission stream and aqueous solution) are used to reduce the amount of the total industrial waste.

[0017] It should also be appreciated that methods of the invention can optionally include recycling the unreacted gaseous emission and/or the aqueous solution. In this manner, the overall yield of removing the carbon dioxide removal and/or metallic water pollutants can be increased.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Figure 1 is a graph showing the relative amount of carbon dioxide, bicarbonate ions, and carbonate ions present at various pH levels.

[0019] Figure 2 is a graph showing quantum efficiencies of photoionization and photodissociation in liquid water as functions of photon energy.

[0020] Figures 3A and 3B are graphs showing the result of Barnett Shale water samples that were treated with NaHCO_3 and soda ash Na_2CO_3 , respectively. The amount of calcium ion concentration decreased significantly as the amount of sodium bicarbonate and sodium carbonate addition increased.

[0021] Figure 4 is a 3-D plot showing the relationship between pH, CO_2 pressure, and NaOH Concentration.

[0022] Figure 5 is a 3-D graph showing the relationship between total hardness (mg/L), CO_2 and NaOH.

[0023] Figure 6 is a 3-D graph showing the relationship between the total alkalinity, CO_2 , and NaOH

DETAILED DESCRIPTION OF THE INVENTION

[0024] Descriptions of well known processing techniques, components, and equipment are omitted so as not to unnecessarily obscure the methods and devices in unnecessary detail. The descriptions of the methods and devices disclosed herein are exemplary and non-limiting. Certain substitutions, modifications, additions and/or rearrangements falling within the scope of

the claims, but not explicitly listed in this disclosure, will become apparent to those of ordinary skill in the art based on this disclosure.

[0025] Unless the context requires otherwise, the terms “sequestration” and “removal” are used interchangeably herein and refer generally to techniques or practices whose partial or whole effect is to remove carbon dioxide from point emissions sources and to store that carbon dioxide in some form so as to prevent its return to the atmosphere. Use of this term does not exclude any form of the described embodiments from being considered carbon dioxide “sequestration” or “removal” techniques.

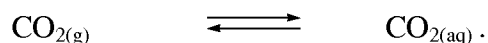
[0026] Some aspects of the invention relate to sequestration processes in which carbon dioxide is removed from gaseous emissions and converted into solid metallic carbonate and/or solid metallic bicarbonate products. Embodiments of the methods and apparatuses of the invention comprise one or more of the following general components: an aqueous carbonation process whereby gaseous carbon dioxide is dissolved or absorbed into an aqueous solution to form carbonate and/or bicarbonate ions; and a precipitation process whereby the carbonate and/or bicarbonate ions are precipitated from the aqueous solution. It should be appreciated that these two processes can be combined into a single process to provide an efficient process. That is, as carbon dioxide is dissolved and forms carbonate ion, the metallic ion that is present in the aqueous solution combines with carbonate to form a metallic carbonate precipitate.

[0027] As noted above, in certain embodiments, the apparatuses and methods of the invention employ an aqueous carbonation process, whereby gaseous carbon dioxide is dissolved into an aqueous solution to form carbonate and/or bicarbonate ions. It should be noted, however, that at room temperature, the solubility of carbon dioxide is about 90 cm³ of CO₂ per 100 mL of water. In some embodiments, the carbon dioxide or the gaseous emission stream is pressurized to increase the amount of carbon dioxide which dissolves in the aqueous solution. When pressurization is used, typically the gaseous emission stream is pressurized to at least about 1 psi, often to at least about 10 psi, and more often to at least about 2 atm. In some embodiments, the gaseous emission stream is pressurized to from about 1 to about 10 psi. In other embodiments from about 10 psi to about 2 atm. Still in other embodiments from about 2 atm to about 10 atm. It should be appreciated, however, that the scope of the invention is not limited to these

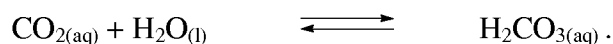
particular pressures as different pressurization and/or temperature can also be used to achieve desired carbonation of aqueous solution.

[0028] In other embodiments a mixture of air or other inert gases and CO₂ is used to achieve carbonate ion concentrations less than that achieved by using pure CO₂.

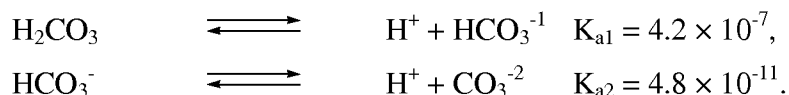
[0029] In aqueous solution, carbon dioxide exists in many forms. First, it simply dissolves in water, as described by the reaction



Then, an equilibrium reaction condition is established between the dissolved CO₂ and H₂CO₃, carbonic acid as described by



Without being bound by any theory, it is believed that in pure water only about 1% of the dissolved CO₂ exists as H₂CO₃. That is because carbonic acid is a weak acid which dissociates in two steps, shown below



[0030] Figure 1 shows equilibrium concentration curves for carbon dioxide, bicarbonate, and carbonate at various pH values. As shown in Figure 1, when carbon dioxide is brought into contact with an aqueous solution, a continuum of products that range from pure dissolved carbon dioxide to bicarbonate ions (HCO₃⁻¹) to pure carbonate ions (CO₃⁻²) can be formed, depending on the pH of the solution. Accordingly, in order to form carbonate ions from the dissolved carbon dioxide, the aqueous solution needs to be at a certain pH level. In some embodiments, the aqueous solution is at least about pH 8, often at least about pH 8.2, more often at least about pH 8.5, and still more often at least about 10.5. The equilibrium curve shown in Figure 1 represents equilibrium at a particular condition, e.g., at a certain pressure and temperature. Thus, it should be appreciated that the pH necessary to convert dissolved carbon dioxide to carbonate ions can vary depending on the reaction conditions, such as the nature of ions present, etc. One skilled in the art can readily determine the minimum pH required for such a conversion at any give reaction condition and derive at an equilibrium curve similar to that shown in Figure 1. Accordingly, while certain pH ranges are discussed above, it should be appreciated that the pH values of the aqueous solution are not limited to these specific ranges and examples given herein.

The desired pH of the aqueous solution can vary depending on particular reaction conditions used, e.g., temperature, pressure, nature of the ions present, and the presence of other ions including salts.

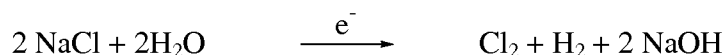
[0031] One of the factors for consideration is the rate at which gaseous carbon dioxide dissolves in the aqueous solution. For economic reasons, it is desirable to dissolve carbon dioxide with the least energy possible. However, dissolving carbon dioxide in the aqueous solution is generally considered by one skilled in the art to be mass-transfer-limited. In practice, the impact of such a limitation can be reduced significantly or completely eliminated, for example, by using packed or un-packed columns with wide-area gas-liquid contact absorption in bubble-rising-through-fluid methods. Thus, in some embodiments, a large liquid/gas contact area is provided to aid mass transport. For example, one can employ bubble-column reactors (packed or unpacked and with/without horizontal fluid flow) that create large liquid/gas contact area to aid mass transport. In this configuration, the overall design benefits by the freedom to utilize stages with short stage height (e.g., 3 m or less) that yet achieve 90%+ absorption with little resistance or pressure head to overcome in pumping the fluids. Therefore, the stages are designed with wide horizontal area to achieve industrial scaling (wide shallow pools or the equivalent in vessels), potentially with horizontal movement to accommodate continuous operation. Some embodiments of the present invention can utilize gas-liquid contactors of many other configurations, provided those devices attain the required gas-liquid contact. Some embodiments of the present invention use a wide-area liquid-gas transfer surface (bubble-column, packed or clear, or its equivalent in static or moving fluid vessels) to dissolve a relatively high amount of carbon dioxide in the aqueous solution by lowering the resistance necessary to bring the fluids into contact.

[0032] While not necessary, one can concentrate the amount of carbon dioxide in the gaseous emission stream prior to contacting with the aqueous solution; for example, by using carbon dioxide absorber(s) or scrubber(s). In general, the efficiency of the methods of the present invention can be enhanced by reducing the amount of work required to dissolve carbon dioxide. To that end, high-efficiency absorber(s) (capable of removing 99% of the carbon dioxide from an incoming flue-gas stream or gaseous emission stream) can be used to achieve high carbon dioxide absorption, i.e., separation, rate. The separated carbon dioxide can then be

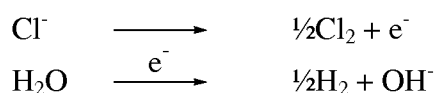
contacted with the aqueous solution to form carbonate ion. Such pre-concentration of carbon dioxide gas reduces the amount of energy required to dissolve carbon dioxide in the aqueous solution by providing a higher concentration of carbon dioxide. In addition, pre-concentration of carbon dioxide may increase the efficiency of dissolving carbon dioxide in the aqueous solution.

[0033] As stated above, when carbon dioxide is brought into contact with an aqueous solution, a continuum of products that range from pure dissolved carbon dioxide to bicarbonate ions to pure carbonate ions can be formed depending on the pH of the solution. Thus, reaction conditions such as pH, temperature, and pressure will drive the equilibrium in either direction, even unto complete formation of carbonate ions. The pH of the aqueous solution can be adjusted using any one of a variety of methods known to one skilled in the art. For example, a base (e.g., a hydroxide ion source such as metallic hydroxides, metallic hydrides, and/or metallic oxides) can be added to the aqueous solution or hydroxide ions can be generated in situ by non-chemical means. While the scope of present invention includes all manners for adjusting the pH of the aqueous solution, in some embodiments, adjustment of pH is achieved by in situ generation of base, such as hydroxides. There are a wide variety of non-chemical means known to one skilled in the art for generating hydroxide ion from various aqueous solutions. Such methods include photolysis, hydrodynamic cavitation, electrolysis, electron beam, corona discharge, plasmas, ultrasonic cavitation, ultraviolet light, radio and microwave frequency and others. Each of these methods is well known to one skilled in the art.

[0034] For example, the electrolysis of water which contains sodium chloride produces hydroxide compounds according to the following equation:



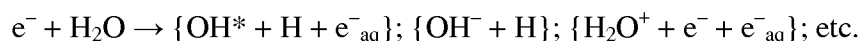
The half reaction in each electrolytic cell is:



[0035] Hydrodynamic cavitation and ultrasonic cavitation generally involve the production of highly localized regions of extreme pressure. Without being bound by any theory, it is believed that both hydrodynamic cavitation and ultrasonic cavitation produce small or microscopic bubbles that collapse producing high temperatures and pressures internally, which produce large quantities of OH• radicals by dissociation of water molecules. The use of

ultrasonic cavitation produces an effect known as sonoluminescence, as high energy photons are produced in the process. It has been estimated that the gas temperature inside of the collapsing bubble can reach 20,000 degrees Kelvin. The collapse of bubbles also produces blue and UV light. Hydroxyl radicals (OH•) can be formed by direct dissociation of the H₂O but also by collisions of excited oxygen and hydrogen with water molecules.

[0036] Beams of electrons, x-rays, gamma-rays, and energetic electrons generated from electrical discharges also can be used to form hydroxyl radicals (OH•), hydrogen radicals, and other highly-reactive chemical species. They ionize water molecules, producing a large number of energetic electrons per ionization event that cascade to lower energies dissociating H₂O into H radicals and OH radicals as they lose energy in collisions with water molecules. Gamma-radiation and e-beams also produce solvated (aqueous) electrons in irradiated pure water. This generation of reactive species is shown by the reaction products of e⁻ + H₂O shown in the braces {...} below:



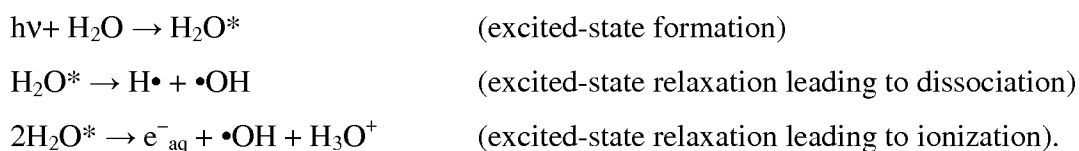
There are a number of possible combinations of product atomic and molecular species. From many past radiolysis experiments, the yields (G-values) for these species are well known, typically being about 2.7 (for OH radicals), 0.55 (for H radicals), 2.6 (for solvated electrons), and 0.71 (for H₂O₂), in units of molecules/100 eV deposited energy. In contrast, for dielectric-barrier discharges (DBDs, which are electrical-discharge streamers similar to corona discharge) in moist gases, the G-values are about 5 to 10 times smaller. For other types of electrical discharges in water (like a form of pulsed corona), generally higher production rates for hydroxide radicals and H₂O₂ in aqueous electrical discharges is observed than in radiation/e-beam techniques. It should be appreciated that different aqueous solutions provide different yield, for example, the presence of carbonate ions can scavenge active species and reduce the effective yields.

[0037] In some embodiments of the invention, hydroxyl ions are generated by electron beams, dielectric-barrier/corona discharges, particle beams, ultrasonic cavitation, hydrodynamic cavitation, ultraviolet light, plasmas, electrolysis, radio or microwave radiation, or a combination thereof.

[0038] The chlorine (i.e., Cl₂) in salt water at normal pH value typically forms HClO as well as other chloride species. Ultraviolet light at wavelengths of less than about 300 nm, which

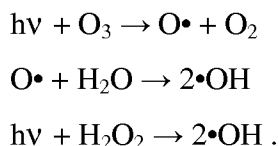
can be generated readily, dissociate the HClO molecule. Without being bound by any theory, it is believed that HClO molecule dissociates into chlorine, which can emerge from the water as Cl₂ gas, and OH radicals. It is believed that some, but not necessarily all, of the OH will combine with a solvated electron (i.e., e_{aq}⁻) to produce hydroxide ions (i.e., OH⁻).

[0039] The photolysis (splitting) of water can be accomplished by illuminating it with ultraviolet (UV) light. This process can be described in terms of the following reactions:

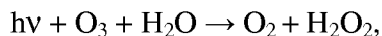


The quantum yields (products per light photon) for the dissociation and ionization processes in pure water are shown in Figure 2. As Figure 2 shows, the yield for the dissociation reaction peaks at around 8.5 eV (around a wavelength of 146 nm), while that for ionization peaks at a higher energy of around 11.7 eV (around a wavelength of 106 nm; a value thought to be the ionization potential of water/H₂O). Practical UV-light sources like mercury lamps have wavelengths of 254 nm/~ 4.9 eV, which according to Figure 2 would have quantum yields at about < 0.25. One skilled in the art can choose an appropriate light source for the photolytic process, depending on the particular type of water and the compounds it contains (e.g., hardness ions, organic materials, etc.). Some compounds entrained in water can actually assist in forming OH radicals by the absorption of UV light. It is generally believed that UV absorption for water in the wavelength range of from about 200nm to about 300 nm is mainly due to organic matter, while common inorganic salts (except transition metal ions) have significant absorption only for wavelengths shorter than 250 nm. Nitrate has strong absorption around 210 nm. Sodium has strong absorption around 589 nm.

[0040] Without being bound by any theory, it is believed that by adding ozone or hydrogen peroxide (H₂O₂) to the water, one can obtain enhanced production of OH-radicals by the reactions:



In some instances, H₂O₂ can be generated by a UV-ozone reaction:



thus further increasing the OH production.

[0041] Analogous to the radiolysis and photolysis processes described above, $\bullet\text{OH}$, $\bullet\text{H}$, e^-_{aq} , and H_2O_2 can be generated by the energetic electrons in a plasma or electrical discharge in water or water vapor. One embodiment is to flow water down a grounded metal ramp which has an array or arrays of needles (or other sharp points) facing the water. The needles are typically connected to a high voltage source and enhancement of the electric field at the points produces electrical discharge corona (a form of non-equilibrium plasma), which contains electrons of sufficient energy to dissociate water molecules. Another embodiment is to spray water through an array of fine wires (alternately connected to ground and high voltage), which also produces corona discharges similar to that described above. Yet another embodiment is to immerse electrodes directly into water and produce electrical discharges in the bulk liquid. Still another embodiment uses plexiglass with a copper foil on the bottom of the trough for the cathode.

[0042] As stated, some methods of the invention include precipitating carbonate ions from the aqueous solution. Many metallic carbonates are insoluble in water. In fact, carbonates are frequently considered to be insoluble, i.e., they have solubility constants (K_{sp}) of less than 1×10^{-4} . In general, group II carbonates (e.g., Ca, Sr, and Ba) are insoluble. Some other insoluble carbonates include FeCO_3 and PbCO_3 . Table 1 below shows some of the representative solubility constants of metallic carbonates in pure (or neutral pH) water at 25 °C.

Table 1. K_{sp} of some of the metallic carbonates at ambient atmosphere.

Compound	Formula	K_{sp} (25 °C)
Barium carbonate	BaCO_3	2.58×10^{-9}
Cadmium carbonate	CdCO_3	1.0×10^{-12}
Calcium carbonate (calcite)	CaCO_3	3.36×10^{-9}
Calcium carbonate (aragonite)	CaCO_3	6.0×10^{-9}
Cobalt(II) carbonate	CoCO_3	1.0×10^{-10}
Iron(II) carbonate	FeCO_3	3.13×10^{-11}
Lead(II) carbonate	PbCO_3	7.40×10^{-14}
Lithium carbonate	Li_2CO_3	8.15×10^{-4}
Magnesium carbonate	MgCO_3	6.82×10^{-6}
Magnesium carbonate trihydrate	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	2.38×10^{-6}
Magnesium carbonate pentahydrate	$\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$	3.79×10^{-6}
Manganese(II) carbonate	MnCO_3	2.24×10^{-11}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Neodymium carbonate	$\text{Nd}_2(\text{CO}_3)_3$	1.08×10^{-33}

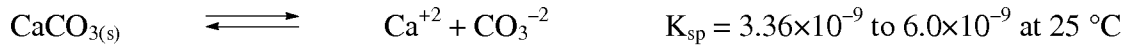
Nickel(II) carbonate	NiCO_3	1.42×10^{-7}
Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Strontium carbonate	SrCO_3	5.60×10^{-10}
Yttrium carbonate	$\text{Y}_2(\text{CO}_3)_3$	1.03×10^{-31}
Zinc carbonate	ZnCO_3	1.46×10^{-10}
Zinc carbonate monohydrate	$\text{ZnCO}_3 \cdot \text{H}_2\text{O}$	5.42×10^{-11}

[0043] It is apparent from Table 1 that carbonates in general form insoluble salts with Group II metals and transition metals. However, most carbonates of Group IA (i.e., alkali) metals, such as sodium and potassium but not lithium carbonate (see Table 1), are considered to be soluble in water (i.e., have K_{sp} of about 1×10^{-3} or higher, and often about 1×10^{-2} or higher). Some methods of the invention take advantage of this relative insolubility of carbonate ion by reacting the carbonate ions with metallic ions to produce a metallic carbonate precipitate. By precipitating out carbonate ions, methods of the invention effectively reduce the amount of carbon dioxide gas being released into the atmosphere. In some embodiments of the invention, the metallic ions comprise calcium ions, magnesium ions, manganese ions, barium ions, strontium ions, or a combination thereof. In other embodiments of the invention, the metallic ion is chosen such that at standard temperature and pressure ("STP", i.e., at 1 atmosphere of pressure at 25 °C), the K_{sp} of the metallic carbonate is about 1×10^{-5} or less, and often 1×10^{-6} or less.

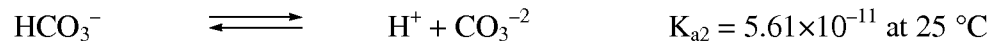
[0044] In some embodiments of the invention, the aqueous solution that is used to generate carbonate ion from carbon dioxide includes one or more metallic ions that form a precipitate with carbonate ions. Thus, when the gaseous emission stream containing carbon dioxide is brought in contact with the aqueous solution under appropriate conditions, some methods of the invention remove carbon dioxide from the gaseous emission stream in the form of a solid precipitate without the need for any additional steps. It should be appreciated, however, that the step of dissolving carbon dioxide in an aqueous solution to generate carbonate ion and precipitating the carbonate ion in the form of a solid metallic carbonate can occur in stepwise fashion. And the scope of the present invention includes all methods for precipitating carbonate ion from the aqueous solution.

[0045] While methods of the invention include using any metallic ion that forms a precipitate with carbonate ions, for the sake of brevity and clarity the present invention will now be described in reference to forming a solid precipitate with calcium ion.

[0046] As shown in Table 1 above, calcium carbonate is poorly soluble (i.e., insoluble) in pure water. The equilibrium of its dissolving is given by the equation (with dissolved calcium carbonate on the right):



where the solubility constant K_{sp} depends on the nature of solid calcium carbonate. What the above equation means is that the product of molar concentration of calcium ions (moles of dissolved Ca^{2+} per liter of solution) with the molar concentration of dissolved CO_3^{2-} cannot exceed the value of K_{sp} . It should be appreciated that this equation is a simplified form in that other factors need to be considered when calculating a true solubility constant of calcium carbonate for a given condition. For example, some of the CO_3^{2-} combines with H^+ in the solution according to the equation:

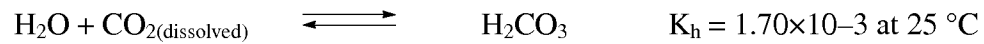


And calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$) is many times more soluble in water than calcium carbonate.

[0047] Some of the HCO_3^- combines with H^+ in solution according to the equation:



Some of the H_2CO_3 dissociate into water and dissolved carbon dioxide according to the equation:

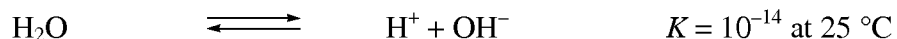


And dissolved carbon dioxide is in equilibrium with atmospheric carbon dioxide according to the equation:

$$P_{\text{CO}_2} / [\text{CO}_2] = K_h$$

where K_h (also known as Henry constant) = 29.76 atm/(mol/L) at 25 °C, and P_{CO_2} being the partial pressure of CO_2 .

[0048] For ambient air, P_{CO_2} is around 3.5×10^{-4} atmospheres (i.e., 35 Pascal). The last equation above fixes the concentration of dissolved CO_2 as a function of P_{CO_2} , independent of the concentration of dissolved CaCO_3 . At one atmosphere partial pressure of CO_2 , the dissolved CO_2 concentration is about 1.2×10^{-5} moles/liter. The equation before that fixes the concentration of H_2CO_3 as a function of $[\text{CO}_2]$. For $[\text{CO}_2] = 1.2 \times 10^{-5}$, it results in $[\text{H}_2\text{CO}_3] = 2.0 \times 10^{-8}$ moles per liter. When $[\text{H}_2\text{CO}_3]$ is known, the remaining three equations together with the reaction below:



(which is true for all aqueous solutions), and the fact that the solution must be electrically neutral (represented by the relation below),



makes it possible to solve simultaneously for the remaining five unknown concentrations. It should be appreciated that the above form of the neutrality equation is valid for water at a neutral pH solution; in the case where the original water solvent pH is not neutral, the equation must be modified.

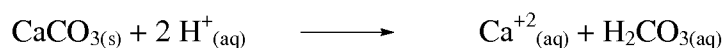
[0049] Table 2 below shows the calcium ion solubility and the concentration of H^+ (in the form of pH) as a function of ambient partial pressure of CO_2 ($K_{\text{sp}} = 4.47 \times 10^{-9}$).

Table 2. Calcium ion solubility as a function of CO_2 partial pressure at 25°C .

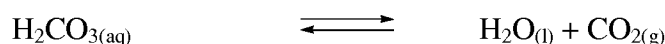
P_{CO_2} (atm)	pH	$[\text{Ca}^{+2}]$ (mol/L)
10^{-12}	12.0	5.19×10^{-3}
10^{-10}	11.3	1.12×10^{-3}
10^{-8}	10.7	2.55×10^{-4}
10^{-6}	9.83	1.20×10^{-4}
10^{-4}	8.62	3.16×10^{-4}
3.5×10^{-4} (ambient air)	8.27	4.70×10^{-4}
10^{-3}	7.96	6.62×10^{-4}
10^{-2}	7.30	1.42×10^{-3}
10^{-1}	6.63	3.05×10^{-3}
1	5.96	6.58×10^{-3}
10	5.30	1.42×10^{-2}

As Table 2 shows, at atmospheric levels of ambient CO_2 , the solution becomes slightly alkaline. And as more CO_2 gas is present (i.e., at higher CO_2 partial pressure), dissolved carbon dioxide forms carbonic acid, thereby decreasing the pH of the aqueous solution. Accordingly, larger amounts of base are required at higher CO_2 partial pressure to convert the dissolved carbon dioxide into carbonate.

[0050] Although “insoluble” (i.e., $K_{\text{sp}} < 1 \times 10^{-3}$) in water, calcium carbonate dissolves in acidic solutions. The carbonate ion behaves as a Brønsted base.



And in acidic solution, the aqueous carbonic acid dissociates, producing carbon dioxide gas.



Therefore, one needs to consider the various equilibria when attempting to precipitate out carbonate ions as a metallic carbonate solid. Thus, in many embodiments of the invention, the pH of the aqueous solution is adjusted to favor formation of carbonate ions, and hence formation of a metallic carbonate precipitate. Typical pH of the aqueous solution that favors formation of the metallic carbonate precipitate has been disclosed above.

[0051] Carbonates of other metallic ions present similar properties. Thus, regardless of the particular metallic ion(s) in the aqueous solution, similar consideration of pH, temperature, and pressure is employed. Typically, at lower temperatures higher precipitates of carbonates are formed. In some embodiments, the expansion (endothermic) of solid or liquid CO₂ can be used efficiently in the process to chill or cool the aqueous solution that is used to dissolve CO₂.

[0052] While one can add a suitable metallic ion source to the aqueous solution to precipitate out carbonate ions, it has been found by the present inventors that many natural water sources and industrial waste waters comprise various concentrations of metallic ion(s) that are suitable for methods of the invention. For example, industrial process water (such as water from oil refinery process), some natural aquifers, sea water, oil field produced water, and frac flowback water contain various amounts of calcium ions, and in many instances other metallic ion(s) that can form a precipitate with carbonate ions. Thus, in many embodiments of the invention, the aqueous solution used to dissolve carbon dioxide and/or to remove carbonate ions comprises industrial process water, water from an aquifer, sea water, oil field produced water, frac flowback water, or a combination thereof.

[0053] In many instances, the aqueous solution that is used to dissolve carbon dioxide and/or precipitate out carbonate ions comprises other materials, for which their removal is often desirable. For example, oil field produced water, frac flowback water and sea water contain a large amount of chloride ions. Chloride ions in water are typically removed by filtration such as reverse osmosis or distillation. Another method to remove chloride is by conversion to chlorine gas by electrolysis. Electrolysis of chloride ions also produces hydrogen gas and hydroxides from water. Such process can be advantageously employed by using the hydroxides that are generated from the electrolysis to adjust the pH of the aqueous solution. In this manner, it is possible to reduce or even to eliminate any need for adding a hydroxide source to the aqueous solution to achieve the desired pH level of the aqueous solution for conversion of dissolved

carbon dioxide to carbonate ions. Furthermore, the hydrogen gas that is generated can be used as a fuel source to reduce the overall energy consumption.

[0054] Methods of the invention are suitable for removing carbon dioxide from any gaseous emission stream that comprises carbon dioxide. Typically, however, the gaseous emission is produced from an industrial process. Exemplary industries that produce a significant amount of carbon dioxide that can be removed by methods of the invention include, but are not limited to, the energy industry (such as oil refineries, the coal industry, and power plants), cement plants, and the auto, airline, mining, food, lumber, paper, and manufacturing industries.

[0055] Generally, methods of the invention removes at least 50% of carbon dioxide from the emission stream, typically at least about 60%, often at least about 75%.

[0056] In some embodiments, carbon dioxide from the emission stream is removed as hardness ion carbonate precipitate. Of the amount of carbon dioxide that is removed from the emission stream, typically at least about 50%, often at least about 75%, more often at least about 85%, and still more often at least about 95% is removed as precipitate of hardness ion carbonate.

[0057] Additional objects, advantages, and novel features of this invention will become apparent to those skilled in the art upon examination of the following examples thereof, which are not intended to be limiting.

EXAMPLES

Example 1

[0058] Source waters from three separate oil & gas geological basins having different levels of metallic ions were evaluated and treated (Barnett Shale, Piceance and Denver Julesburg). See Table I. Hardness ions are considered to be calcium, magnesium, strontium, manganese, barium, iron, copper, and other metallic ions which readily form insoluble carbonate compounds.

[0059] Barnett Shale water samples were treated with NaHCO_3 and soda ash Na_2CO_3 . The amount of calcium ion concentration decreased significantly as the amount of sodium bicarbonate and sodium carbonate addition increased as shown in Figures 3A and 3B.

[0060] Experiments were conducted using pressurized CO₂ as the carbonate source instead of adding solid sodium bicarbonate or sodium carbonate.

[0061] Experiments were conducted on Barnett Shale water and Piceance Basin water using water which had been carbonated with CO₂ and then dosed with NaOH. Test results are shown below:

Table 1: Basin Water Starting and Ending Characteristics

Source of Water	Starting Total Hardness	Ending Total Hardness	Drinking Water Std*
Barnett Shale	23,000 mg/L	350 mg/L	500 mg/L
Piceance Basin	3,000 mg/L	150 mg/L	500 mg/L

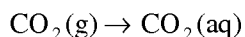
*500 mg/L is generally accepted as an upper limit for Total Hardness in Drinking Water

[0062] Produced water from the Denver Julesburg Basin was treated. This experiment forced carbonated water (Dissolved CO₂ provided in-situ source of carbonate ions according to Equation 3) at 3 discrete pressure levels (2.5, 4.0 & 10 psi) and treat with 4 discrete amounts of NaOH (3, 5, 7 & 9 grams). This process caused the precipitation of the above listed insoluble metallic carbonates. The response variables are pH, Total Alkalinity (mg/L) and Total Hardness (mg/L). pH was measured with a Hach calibrated pH probe and Alkalinity and Hardness were measured using industry standard Hach titration methods.

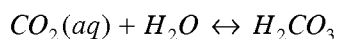
[0063] A statistical model was developed to predict the 3 response variables (pH, Total Hardness, Total Alkalinity) from the 2 input variables (CO₂ pressure, NaOH concentration). Concentrations of carbonic acid and hydroxide ions was varied with 3 separate pressure settings for CO₂ (2.5, 4.0 & 10 psi) and 4 separate concentration levels with NaOH (3, 5, 7 & 9 grams).

[0064] Equations 1 & 2 describe the first two steps in the equilibrium relationships of dissolved CO₂ in water. And equation 3 describes the reaction of a hydroxide source with carbonic acid to form free carbonate ions in solution. Equation 4 describes the formation of insoluble metallic carbonates.

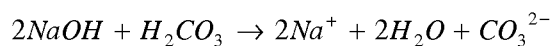
Equation 1: CO₂ Dissolves in Water



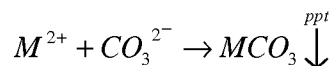
Equation 2: CO₂ Reacts with Water to form Carbonic Acid



Equation 3: Hydroxide Reacts with Carbonic Acid to form Carbonate Ions



Equation 4: Formation of Insoluble Metallic Carbonate Precipitates



Experimental Procedure:

[0065] The following is a standard experimental protocol that was used to determine the effectiveness of hardness ion removal from various water sources:

- Step 1: Measure & record starting pH, Total Hardness & Total Alkalinity of water to be treated.
- Step 2: Weigh out 4 discrete masses of NaOH (3, 5, 7, 9 grams), place in 4 separate reaction vessels.
- Step 3: Set CO₂ pressure to 1st pressure level.
- Step 4: Process produced water containing hardness ions through a soda fountain carbonation pump.
- Step 5: Fill buckets to 4-gal mark with carbonate produced water.
- Step 6: Wait for precipitation process to complete (complete settling of floc).
- Step 7: Sample about 1L of each bucket, process through vacuum filter to remove floc.
- Step 8: Measure and record pH, Total Hardness and Total Alkalinity for each sample.
- Step 9: Reset pressure of CO₂ to next discrete level.
- Step 10: Repeat Steps 1 – 6.
- Step 11: Reset pressure of CO₂ to next discrete level.
- Step 12: Repeat Steps 1 – 6.

Experimental Results:

[0066] The following table shows the results of hardness ion reduction using the experimental protocol above.

CO ₂ Pressure (psi)	NaOH Concentration (g)	Total Hardness (mg/L as CaCO ₃)	Total Alkalinity (mg/L)	pH
0 (Blank)	0	1150	232	7.65
2.5	3	1040	1150	8.21
2.5	5	230	810	9.16
2.5	7	105	1270	10.4
2.5	9	35	1720	11.5

CO ₂ Pressure (psi)	NaOH Concentration (g)	Total Hardness (mg/L as CaCO ₃)	Total Alkalinity (mg/L)	pH
4.5	3	595	790	7.66
4.5	5	385	1125	7.87
4.5	7	175	1400	8.72
4.5	9	125	1280	9.66
10	3	575	740	7.93
10	5	295	1010	8.13
10	7	185	1590	8.72
10	9	140	1900	9.15

Graphs and Statistical Data Analysis

[0067] The pH data fit very well to a Cosine Series Bivariate Order 3 equation with resulting r^2 of 0.996 and Fit Standard Error of 0.131. The F-Statistic of 173 high level of significance to the fit. See Figure 4. The surface showed a saddle point near NaOH ~ 3 grams and CO₂ ~ 3-4 psi.

The fit statistics are presented below:

r^2 Coef Det	DF Adj r^2	Fit Std Err	F-value
0.9961798356	0.9885395067	0.1319368309	173.84589124

Parm	Value	Std Error	t-value	95.00% Confidence Limits		P> t
a	8.483690365	0.095074931	89.23162285	8.25105039	8.71633034	0.00000
b	0.961118065	0.066566195	14.43853089	0.798236453	1.123999676	0.00001
c	-1.42117145	0.048156256	-29.511668	-1.53900556	-1.30333733	0.00000
d	0.572220362	0.052499729	10.89949169	0.443758153	0.700682572	0.00004
e	-0.6990775	0.086295779	-8.10094653	-0.91023566	-0.48791933	0.00019
f	0.066050586	0.043797239	1.50809931	-0.0411174	0.173218569	0.18226
g	0.137724203	0.130901464	1.052121182	-0.18258014	0.458028545	0.33326
h	-0.43301684	0.077007288	-5.62306315	-0.62144689	-0.2445868	0.00135
i	0.288456411	0.061342643	4.702379929	0.138356372	0.43855645	0.00332
j	-0.3059942	0.043160168	-7.0897361	-0.41160333	-0.20038508	0.00040

[0068] Figure 5 is a graph that shows a fit using a Lowess curve smoothing algorithm. However, the nature of the surface is apparent from this technique. As can be seen from the surface, there is a trough in the surface located where CO₂ psi ~ 3-3.5 psi and NaOH ~ 5 grams.

[0069] Figure 6 is a graph that shows a fit using a Lowess curve smoothing algorithm. However, the nature of the surface is apparent from this technique. Also, it is apparent that Total Alkalinity and Total hardness are inverses of each other, e.g., as Total Hardness is reduced, Total Alkalinity is increased.

[0070] As can be seen, there is a local minima where CO₂ psi ~ 3.5 psi and NaOH ~ 3-4 grams. This point appears to be the optimal setting to achieve the desired goals of neutral pH, Total Hardness < 500 mg/L and Total Alkalinity < 600 mg/L for this water sample.

[0071] Analysis of the graphs showed that a process near CO₂ pressure of about 3.0 psi, NaOH amount of about 4.5 grams results in pH of about pH 8.0, total hardness of about 500 mg/L or less and total alkalinity of about 600 mg/L or less. Such results are similar to drinking water standards (See Table 1 above).

[0072] Pressurized CO₂ and Hydroxide treatment of high hardness water resulted in significant reduction of hardness ion concentrations (Total Hardness) with minimal increase in pH and Alkalinity when optimized input variables are used. The process can be used to remove the concentrations of hardness ions present in the water to be treated.

Example 2

[0073] The Corona Discharge was produced through a needle apparatus. For these experiments a single needle was used. However, for treating a large volume of water, multiple needles resistively coupled in parallel can be used. It is believed that Corona Discharge produces OH⁻, OH radicals, and other ions in-situ. These ions react with the hardness ions, Ca²⁺, Mg²⁺, Sr²⁺, to produce hydroxides, Ca(OH)₂, Mg(OH)₂, and Sr(OH)₂. These hydroxides are insoluble in water and precipitate out. Under standard conditions, the solubility of these hydroxides are: Ca(OH)₂ is 0.185g per 100mL; Mg(OH)₂ is 0.0012g per 100mL; and Sr(OH)₂ is 1.77g per 100mL. Thus, by forming hydroxides and precipitating out these metal ions, the corona discharge reduces the overall hardness of the water. This experiment examines whether enough OH was produced by corona discharge to soften the water and quantifies the amount or percentage of hardness ion reduction.

[0074] The corona discharge for this experiment utilized a Franceformer 15000V Neon Transformer, a 10A-120 volt Variable Autotransformer, a full wave rectifying HV07-15 diode bridge, a pure 1/8 inch tungsten welding rod, aluminum foil, a 250mL beaker, and high voltage wire.

[0075] Each test consisted of a Calcium Hardness titration, unless Magnesium was present then the solution was additionally titrated for Total Hardness, a pH reading, a

Conductivity reading, a Voltage reading, and a current reading. The titrations were done with a Hach digital titrator and Hach test kits. These test kits are easily found on Hach's website. See www.hach.com. The pH was measured using a Thermo Scientific Orion Ross Sure-Flow pH probe with a Hach SenseIon 3 meter. Conductivity was measured using a Hach CDC401 IntelliCAL Standard Conductivity probe. Voltage was measured using a Tektronix TDS2014B Oscilloscope and a Tektronix 1000x high voltage probe. The current was measured using a Wide Band Current Transformer.

[0076] Briefly, the set-up for corona discharge is as follows: The variable auto transformer (15kV neon transformer) was connected the wall outlet. From the transformer, one end was connected to one side of the HV07-15 diode bridge, while the other end of the transformer was attached to the other side of the diode bridge. The diode bridge connected the neon transformer to the tungsten electrode and the aluminum foil strip. The high voltage probe was attached to the tungsten rod, and the current transformer was attached to the outgoing cable of the neon transformer.

[0077] Three experiments were conducted. The first experiment contained a solution of 2.2159 grams of Calcium Chloride (CaCl_2) in 200 mL distilled water. The solution was placed in a 250 mL beaker. An aluminum foil strip was placed into the solution. The tungsten rod was suspended over the solution by a lab stand. The tungsten rod was powered with the full wave rectified diode bridge to be positive (+). This effect caused a (+) corona discharge. For this experiment, the voltage going to the tungsten rod read 1.78kV. This was achieved through adjusting the variac to the appropriate power setting. However, before turning on the power, calcium hardness, pH, and conductivity were measured. The calcium hardness was measured using Hach's Calcium Hardness titration kit and a Hach digital titrator. The pH was measured with the Thermo Scientific Orion Ross Sure-Flow pH probe. The conductivity was measured with the Hach CDC401 IntelliCAL Standard Conductivity probe. With the initial measurements taken, the experiment began. The tungsten rod was placed above the solution and power given to the system. After 1 hour, the system was shut off. The solution was filtered and the final volume was measured. Using the filtrate, final measurements were taken and % hardness removal was calculated.

[0078] The second experiment included a solution with only 0.4434 grams of CaCl_2 in 200 mL of distilled water. The same procedure as above was utilized. Measurements were gathered before and after the corona discharge took place.

[0079] The third experiment included 2.2126 grams of CaCl_2 in 200 mL of distilled water. The same procedure as above was used except that in this experiment run time was only 15 minutes instead of an hour.

[0080] Two additional experiments were conducted. The first consisted of AC power, no diode bridge, with 2.2156 grams CaCl_2 in 200 mL of distilled water. The same procedure as described above was performed. Initial measurements were taken before the corona discharge. The experiment lasted 15 minutes. Then the final measurements were taken.

[0081] Another experiment included a 200 mL sample of Barnett shale water. Barnett Shale water contains both magnesium and calcium. Thus, Total Hardness and Calcium Hardness were measured through titrations. The same procedure as described above was performed. Measurements were taken before and after the corona discharge. The experiment ran for 15 minutes.

[0082] The final experiment was conducted using a 200 mL sample of Barnett Shale water. However, for this experiment, the solution was filtered before measurements were performed. This was to remove any suspended solids. After the first filtering, the initial hardness levels were measured. Then the solution was exposed to the corona discharge for 15 minutes. After the corona discharge, another set of titrations were conducted. Then the solution was filtered, and the post-filter measurements were taken. With the post-filter measurements, the solution was run under the corona discharge for a second time. After another 15 minutes, another set of measurements were taken. The solution was then filtered, and final measurements were taken. This experiment was to show that a step wise approach would remove hardness after every run through the corona discharge.

Results

[0083] Data was gathered by calculating the mass of the hardness ions, Ca^{2+} and Mg^{2+} , through stoichiometry. Each test consisted of a titration number based on mg/L of Ca^{2+} . The

first test contained an initial titrated calcium (Ca^{2+}) hardness value of 3540 mg/L. This number is then converted to grams of Ca^{2+} . The stoichiometry is shown below.

$$3540 \frac{\text{mg}}{\text{L}} \{ \text{Ca}^{2+} \} \times 0.200 \text{L} \times \frac{1 \text{g}}{1000 \text{mg}} = 0.7080 \text{g} \{ \text{Ca}^{2+} \} \quad (1)$$

This gave the amount of Ca^{2+} in solution. After the experiment was completed, another titration for calcium hardness was performed yielding a value of 3752 mg/L Ca^{2+} , which is equal to 0.6679 g of Ca^{2+} :

$$3752 \frac{\text{mg}}{\text{L}} \{ \text{Ca}^{2+} \} \times 0.178 \text{L} \times \frac{1 \text{g}}{1000 \text{mg}} = 0.6679 \text{g} \{ \text{Ca}^{2+} \} \quad (2)$$

With these numbers, the total amount of calcium reduction was calculated. Thus, 0.0401g of Ca^{2+} was removed using the corona discharge. The precipitate formed was $\text{Ca}(\text{OH})_2$. Without being bound by any theory, it is believed that OH^- and OH radicals produced by corona discharge reacted with Ca^{2+} to form $\text{Ca}(\text{OH})_2$. Thus, the percentage of Ca^{2+} removal using the corona discharge was 5.67%. In all subsequent experiments, the mass and percentages were also calculated. The below table shows the results obtained using the procedure described above.

Table: Masses compared to Experiments and the correlating % of Hardness Reduction

Experiment	Pre-Treatment Mass (g)	Post-Treatment Mass (g)	% Hardness Reduction
Test 1	0.7080	0.6679	5.6010
Test 2	0.1438	0.1320	8.2481
Test 3	0.7320	0.6443	11.9836
AC Test	0.7520	0.6582	12.4681
BS Ca^{2+}	1.8800	1.5288	18.6809
BS Mg^{2+}	0.3157	0.2652	16.0000
BS Step 1 Ca^{2+}	1.8520	1.7410	6.0108
BS Step1 Mg^{2+}	0.2000	0.1340	33.0909
BS Step2 Ca^{2+}	1.7410	1.5030	13.6473
BS Step2 Mg^{2+}	0.1340	0.1350	-0.8831
BS Total Step-wise Ca^{2+}	1.8520	1.5030	18.8380
BS Total Step-wise Mg^{2+}	0.2000	0.1350	32.5000
BS = Barnett Shale water			

[0084] According to the table, it can be seen that the percentage of hardness reduced is from 5.601% to 18.838% for Ca^{2+} . For Magnesium, one test showed a 16.0% reduction, while the Barnett Shale Step-wise test showed a decrease in 33.09%. Interestingly, the second step of the Step-wise experiment showed a slight increase in Mg^{2+} concentrations. The reason for this

increase is unknown for this deviation. However, it can be seen that hardness was decreased as precipitate formation was observed during the second step.

Discussion

[0085] The data show that dissolved metallic ions in water were removed by corona discharge. The percentage of hardness removed ranged from 5% to 18% for Ca^{2+} , and about 16% to 32% for Mg^{2+} . The formation of precipitates, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, shows that the corona discharge produced hydroxide, and OH radicals in-situ. A higher production of hydroxide using corona discharge can be achieved, for example, by using a higher voltage, more electrodes, longer exposure to corona discharge, etc. In addition, a UV lamp can be used in conjunction with corona discharge to increase the amount of hydroxide formation by dissociating hydrogen peroxide, H_2O_2 that is formed by the corona discharge.

Example 3

[0086] Barnett Shale water is extremely hard water coming from Texas. See Table 1 in Example 1. It includes a large amount of the following ions sodium, calcium, strontium, magnesium, potassium, barium, ferrous iron, aluminum, chloride, bicarbonate, and sulfate. Because of the quality of Barnett Shale water, it cannot be used for fracking due to scaling. An experiment was conducted to remove these hardness ions, which included adding baking soda (sodium bicarbonate, NaHCO_3) and raising the pH, as well as adding soda ash (sodium carbonate, Na_2CO_3) in a step wise fashion.

Experimental

[0087] Conductivity and pH measurements of Barnett Shale water were taken initially using a Hach CDC401 IntelliCAL Standard Conductivity probe connected to a Hach HQ 40d meter and a Thermo Scientific Orion Ross Sure-Flow pH probe connected to a Hach SenseIon3 pH meter, respectively. Total hardness and calcium hardness were determined using Hach methods 8213 and 8204, respectively. The calcium hardness titration allowed one to determine calcium hardness as CaCO_3 in mg/L. This can be converted to ionic calcium concentration.

[0088] The total hardness titration allowed one to determine the concentration of all hardness ions, including calcium, as CaCO_3 . Since this method did not allow for determination

of individual concentrations of hardness ions, except for magnesium, other hardness ions such as strontium or iron are included in the concentration of the calcium hardness. Magnesium hardness was determined by subtracting the calcium hardness concentration from the total hardness concentration. Once magnesium hardness (as MgCO_3) has been determined it can be converted to ionic magnesium concentration.

[0089] After determining the concentration of ionic calcium and magnesium, the stoichiometric amount of baking soda was determined, verified, and measured. The appropriate amount of baking soda was then added to 200mL of Barnett Shale water. Immediately a precipitate formed, which was removed by filtration. The pH and conductivity of the filtrate were measured, and the concentrations of ionic calcium and magnesium were confirmed.

[0090] Two other solutions were prepared in a similar manner as described above. However, instead of filtering after additions and dilutions of baking soda, the pH of one solution was raised to about 10.50 and the other to a pH of about 12.00. These solutions were then filtered and the pH, conductivity, ionic calcium concentration (i.e., total hardness ion concentration minus magnesium ion concentration), and ionic magnesium concentration were determined. Referring again to Figure 1, at pH of approximately 10.50 the ratio of bicarbonate to carbonate is about 0.5, i.e., about 50% exists as bicarbonate and about 50% exists as carbonate. At a pH of 12.00, almost 100% exists as carbonate. It should be appreciated that calcium carbonate is a substantially insoluble solid whereas calcium bicarbonate has a significantly higher solubility.

[0091] The experiment with soda ash was performed in a similar manner as the baking soda experiment, with the same instrumentation, except that the pH of the solution was not altered. A stoichiometric amount of soda ash was added to 200 mL of Barnett Shale water, which formed a precipitate similar to the baking soda experiment. The precipitate was filtered. The filtrate was titrated for calcium and magnesium, and the pH and conductivity were determined. Another stoichiometric amount of soda ash was added to the filtrate. Once again the precipitate that was formed was filtered. The second filtrate was titrated for calcium and magnesium, and the pH and conductivity were once again determined.

Results

Baking Soda

[0092] The initial pH of the Barnett Shale water was 7.21, the conductivity was 141.0 mS/cm, calcium hardness was 21,000 mg/L, and the total hardness was 26,000 mg/L. From the calcium and total hardness data, it was determined that ionic calcium and ionic magnesium concentrations were 8409 mg/L and 1214 mg/L, respectively. After adding 4.3763 g of baking soda to 200 mL of Barnett Shale water, the pH dropped to 5.96 while the conductivity increased from 141.0 mS/cm to 141.1 mS/cm. This mixture of baking soda and Barnett Shale water formed a precipitate almost immediately, which was filtered. The precipitate had a mass of 1.7933g. Following the filtration, the pH of filtrate was measured to be 5.97 and a conductivity was measured at 142.3 mS/cm. It was determined that the ionic calcium and magnesium concentrations decreased to 5400 mg/L and 729 mg/L, respectively. Thus, the amount of calcium and magnesium reduction was 35.78% and 39.95%, respectively. The data and results for the baking soda experiment without pH adjustment are shown in the Table below.

Baking Soda and Barnett Shale Water without pH Adjustment

Measurement	Barnett Shale	Barnett Shale and Baking Soda	Post Filter
pH	7.21	5.96	5.97
conductivity (mS/cm)	141.00	141.10	142.30
Total Hardness as CaCO ₃ (mg/L)	26000.00	N/A	16500.0
Calcium Hardness as CaCO ₃ (mg/L)	21000.00	N/A	13500.0
[Ca ²⁺] (mg/L)	8409.00	N/A	5400.00
[Mg ²⁺] (mg/L)	1214.00	N/A	729.00
Volume of Barnett Shale (mL)	200.00	200.00	200.00
Mass of filter paper (g)	N/A	N/A	1.78
Mass of filter paper and precipitation (g)	N/A	N/A	3.57
Mass of precipitation (g)	N/A	N/A	1.79
Mass of baking soda (g)	N/A	4.38	N/A
% reduction in [Ca ²⁺]	N/A	N/A	35.78
% reduction in [Mg ²⁺]	N/A	N/A	39.95

[0093] After adding the baking soda (4.3661 g) to 200 mL with Barnett Shale water, the pH dropped from 7.211 to 5.74, and conductivity increased from 141.00 mS/cm to 143.40mS/cm.

[0094] The solution that was brought to a pH of 10.5 had a conductivity of 95.20 mS/cm after filtration. The ionic calcium and magnesium was found to have decreased from 8409 mg/L

and 1214 mg/L to 1612 mg/L and 77.76 mg/L, respectively, which is 80.83% and 93.59% reduction, respectively. The mass of the precipitate recovered was discovered to be 4.52 g.

[0095] The solution whose pH was adjusted to 12.0 had a conductivity of 95.70 mS/cm after filtration. The amount of calcium and magnesium ions was found to decrease from 8409 mg/L and 1214 mg/L to 1612 mg/L and 31.59 mg/L, respectively, which is 80.83% and 97.40% reduction, respectively. The mass of the precipitate recovered was 4.38 g. The data and results for the baking soda experiment with pH adjustments are shown in the following Table.

Baking Soda and Barnett Shale Water with pH Adjustment

Measurement	Barnett Shale	Barnett Shale + Baking Soda	pH	pH
pH	7.21	5.74	10.51	12.00
conductivity (mS/cm)	141.00	143.40	95.20	95.70
Total Hardness as CaCO ₃ (mg/L)	26000.00	N/A	4350.0	4160.0
Calcium Hardness as CaCO ₃ (mg/L)	21000.00	N/A	4030.0	4030.0
[Ca ²⁺] (mg/L)	8409.00	N/A	1612.0	1612.0
[Mg ²⁺] (mg/L)	1214.00	N/A	77.76	31.59
Volume of Barnett Shale (mL)	200.00	200.00	200.00	200.00
Mass of filter paper (g)	N/A	N/A	1.60	5.94
Mass of filter paper and ppt (g)	N/A	N/A	5.84	10.33
Mass of precipitation (g)	N/A	N/A	4.52	4.38
Mass of baking soda (g)	N/A	4.37	N/A	N/A
% reduction in [Ca ²⁺]	N/A	N/A	80.83	80.83
% reduction in [Mg ²⁺]	N/A	N/A	93.59	97.40

[0096] The initial pH of the Barnett Shale water was 7.21, the conductivity was 141.5 mS/cm, calcium hardness was 23,000 mg/L, and the total hardness was 27,000 mg/L. From the calcium and total hardness data, it was determined that ionic calcium and ionic magnesium concentrations were 9200 mg/L and 972 mg/L, respectively. After 5.7130g of soda ash was added to 200 mL of Barnett Shale water, the pH dropped to 6.397, while the conductivity decreased to 141.4 mS/cm. This mixture of soda ash and Barnett Shale water formed a precipitate almost immediately, which was filtered. The precipitate had a mass of 7.0206g. Following the filtration, the filtrate had a pH of 7.4 and a conductivity of 155.1 mS/cm. It was determined that the ionic calcium and magnesium concentrations decreased to 1088 mg/L and 811.62 mg/L, respectively, which corresponds to 88.17% and 16.50% reduction, respectively.

[0097] Additional 1.1157g of soda ash was added to the filtrate (145 mL) from the previous step. Once again, a precipitate formed (1.4693 g). This solution had a pH of 9.3 and a

conductivity of 160.0 mS/cm. After filtering for the second time, the pH dropped to 9.1 and the conductivity increased to 164.4 mS/cm. Titrations for the total and calcium hardness showed that the calcium and magnesium ion concentrations decreased to 180 mg/L and 716 mg/L, respectively, which corresponds to 98.04% and 26.34% reduction, respectively. The data and results for the step-wise addition of soda ash to Barnett Shale water experiment are shown in the following Table.

Soda Ash and Barnett Shale Water: Two Step Additions

Measurement	Barnett Shale Initially	Step 1 Pre-filter	Step 1 Post-filter	Step 2 Pre-filter	Step 2 Post-filter
pH	7.30	5.74	7.44	9.28	9.08
conductivity (mS/cm)	141.50	143.40	155.10	160.00	164.40
Total Hardness as CaCO ₃ (mg/L)	27000.00	N/A	6060.00	N/A	3400.00
Calcium Hardness as CaCO ₃ (mg/L)	23000.00	N/A	2720.00	N/A	450.00
[Ca ²⁺] (mg/L)	9200.00	N/A	1088.00	N/A	180.00
[Mg ²⁺] (mg/L)	972.00	N/A	811.62	N/A	716.00
Volume of Barnett Shale (mL)	200.00	200.00	200.00	145.00	145.00
Mass of filter paper (g)	N/A	N/A	6.83	N/A	5.05
Mass of filter paper and precipitation (g)	N/A	N/A	13.85	N/A	6.52
Mass of precipitation (g)	N/A	N/A	7.02	N/A	1.47
Mass of soda ash (g)	N/A	5.71	N/A	1.12	N/A
% reduction in [Ca ²⁺]	N/A	N/A	88.17	N/A	98.04
% reduction in [Mg ²⁺]	N/A	N/A	16.50	N/A	26.34

Discussion

[0098] It can be seen from the percent reduction in ionic calcium and magnesium between the baking soda and soda ash experiments, that adding baking soda to Barnett Shale water and adjusting the pH resulted in a higher amount of magnesium removal than adding carbonate. On the other hand, adding soda ash (sodium carbonate) in a step wise fashion to Barnett Shale water, as described above, was much more efficient at removing calcium than magnesium.

[0099] In the experiment where baking soda (sodium bicarbonate) was added to Barnett Shale water, hydroxides were also added via a sodium hydroxide solution. The reason such a higher reduction of magnesium was obtained compared to calcium in the same reaction or magnesium in the soda ash experiment is believed to be that magnesium hydroxide is the least

soluble product formed. Therefore, in the baking soda experiment where the pH was adjusted, it is believed that magnesium was reacting with the hydroxides being added first and falling out of solution. Magnesium hydroxide has a solubility of 0.012 g/L compared to 1.85 g/L of calcium hydroxide.

[0100] In the experiment where soda ash was added to Barnett Shale water the opposite was true, in that, a greater reduction in calcium was observed than magnesium. Once again this is believed to be due to the solubility of the products that were formed. Calcium carbonate is almost an order of magnitude less soluble than magnesium carbonate. Calcium carbonate has a solubility of 0.015 g/L, while magnesium carbonate has a solubility of 0.101 g/L. Because of this difference in the solubility, it is believed that calcium carbonate forms and falls out of solution at a faster rate than magnesium carbonate resulting in a greater reduction in calcium.

Example 4

[0101] A bottle of carbonated water that can be readily purchased was titrated for carbon dioxide concentration using Hach method 8205. It was found to have a concentration of 1824 mg/L as carbon dioxide. This concentration was then used to determine the concentration of carbonic acid by multiplying by 1.41 (the ratio of the molar mass of carbonic acid to the molar mass of carbon dioxide), which was found to be 2570.87 mg/L. Then by assuming that all of the carbonic acid could be converted to ionic carbonate by raising the pH of the solution to about 12, it was calculated that the concentration of ionic carbonate was 2487 mg/L. It should be noted that the pH and conductivity of the 100 mL sample of carbonated water solution were 3.594 and 66.2 μ S/cm, respectively, and that the pH and conductivity of the carbonated water after pH adjustment were 12.004 and 4.95 mS/cm, respectively.

[0102] Using the calculated concentration of ionic carbonate, it was determined that at least 0.4599 g of calcium chloride was needed. Twice this amount (0.8940 g) was dissolved into 200 mL of distilled water so that analysis could be done and allow 100 mL left over for the actual reaction. This calcium chloride solution had pH of 9.970, a conductivity of 8.18 mS/cm, and from the Hach calcium hardness titration (method 8204) it was determined that it had a calcium hardness as calcium carbonate of 3700 mg/L, which equated to a ionic calcium concentration of 1480 mg/L.

[0103] After the pH adjusted carbonated water solution and calcium chloride solution were mixed the combined solution formed a milky white precipitate immediately. This solution had a pH of 11.125 and a conductivity of 3.91 mS/cm. The mass of the filter paper prior to filtering was 5.0644 g. After filtering the solution had a pH of 9.343 and a conductivity of 4.56 mS/cm. Following another calcium hardness titration it was determined that the calcium hardness as calcium carbonate decreased to 180 mg/L, which in turn was a decrease in ionic calcium concentration to about 72 mg/L. This reduction equates to about 95% reduction in ionic calcium concentration.

[0104] By raising the pH of water and subsequently carbonating it, carbonates can be generated. This carbonate solution can then be mixed with hard water to simultaneously remove hardness and sequester carbon dioxide in the form of metallic carbonates.

Measurement	Carbonated Water Initial	Carbonated Water After pH Adjustment	CaCl ₂ Solution Initial	Mixed Pre-filter	Mixed Post-filter
pH	3.59	12.00	9.97	11.13	9.34
conductivity (μS/cm)	66.20	4950.00	8180.00	3910.00	4560.00
Carbon Dioxide (mg/L)	1824.00	N/A	N/A	N/A	N/A
Carbonic Acid (mg/L)	2570.00	N/A	N/A	N/A	N/A
Carbonate (mg/L)	N/A	2487.00	N/A	N/A	N/A
Calcium Hardness as CaCO ₃ (mg/L)	N/A	N/A	3700.00	N/A	180.00
[Ca ²⁺] (mg/L)	N/A	N/A	1480.00	N/A	72.00
Volume of Carbonated Water (mL)	100.00	100.00	N/A	N/A	100.00
Volume of Calcium Chloride Solution (mL)	N/A	N/A	100.00	N/A	100.00
Mass of filter paper (g)	N/A	N/A	N/A	5.0644	N/A
Mass of filter paper and precipitation (g)	N/A	N/A	N/A	N/A	
Mass of precipitation (g)	N/A	N/A	N/A	N/A	
Mass of Calcium Chloride (g)	N/A	N/A	0.8940	N/A	N/A
% reduction in [Ca ²⁺]	N/A	N/A	N/A	N/A	95.14

[0105] The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. Although the description of the invention has included description of one or more embodiments and certain variations and modifications, other variations and

modifications are within the scope of the invention, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter.

What is Claimed is:

1. A method for reducing the amount of carbon dioxide gas being released into the atmosphere from a gaseous emission stream that comprises carbon dioxide, said method comprising:
contacting the gaseous emission stream with an aqueous solution comprising a metallic ion under conditions sufficient to produce a metallic carbonate precipitate, thereby reducing the amount of carbon dioxide gas being released into the atmosphere.
2. The method of Claim 1, wherein the metallic carbonate has K_{sp} of about 10^{-3} or less.
3. The method of Claim 1, wherein the pH of aqueous solution is about pH 8 or higher.
4. The method of Claim 1, wherein the pH of aqueous solution is about pH 10 or higher.
5. The method of Claim 1, wherein said method further comprises adding a hydroxide ion source or generating hydroxide ion to maintain the pH of aqueous solution at about pH 8 or higher.
6. The method of Claim 5, wherein said hydroxide ion is generated by electron beam, corona discharge, particle beam, ultrasonic cavitation, hydrodynamic cavitation, ultraviolet light, plasma, electrolysis, radio or microwave radiation, or a combination thereof.
7. The method of Claim 1, wherein the metallic ion comprises sodium, calcium ion, magnesium ion, manganese ion, barium ion, strontium ion, or a combination thereof.
8. The method of Claim 1, wherein the metallic ion comprises calcium ion, magnesium ion, manganese ion, barium ion, strontium ion, or a combination thereof.
9. The method of Claim 1, wherein the gaseous emission stream is produced from an industrial process.

10. The method of Claim 9, wherein the industrial process comprises an oil refinery, power plants, cement plants, coal industry, auto, airline, mining, food, lumber, paper and manufacturing industries, or a combination thereof.

11. The method of Claim 1, wherein said step of contacting the gaseous emission stream with an aqueous solution is conducted under pressure.

12. The method of Claim 1, wherein the aqueous solution comprises industrial process water, water from an aquifer, sea water, oil field produced water, frac flowback water, or a combination thereof.

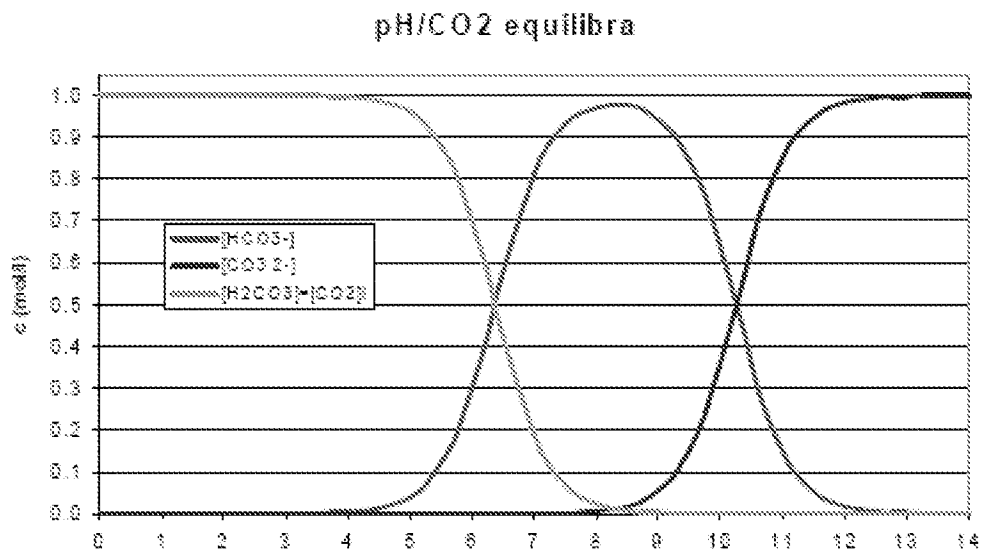


FIGURE 1

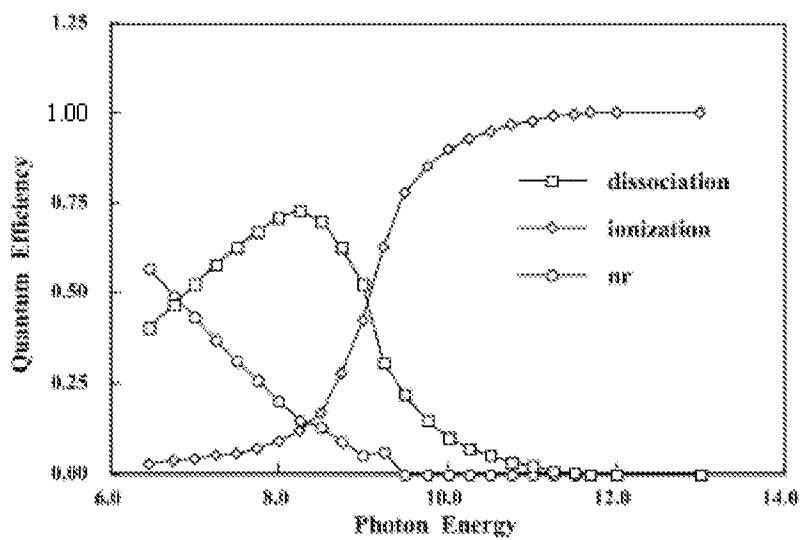


FIGURE 2

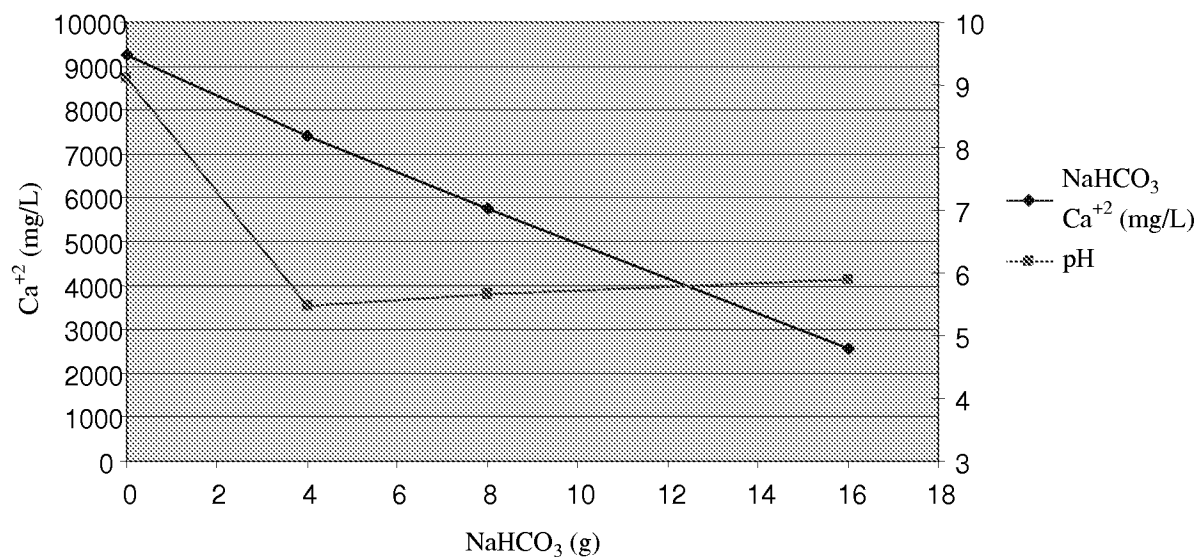


FIGURE 3A

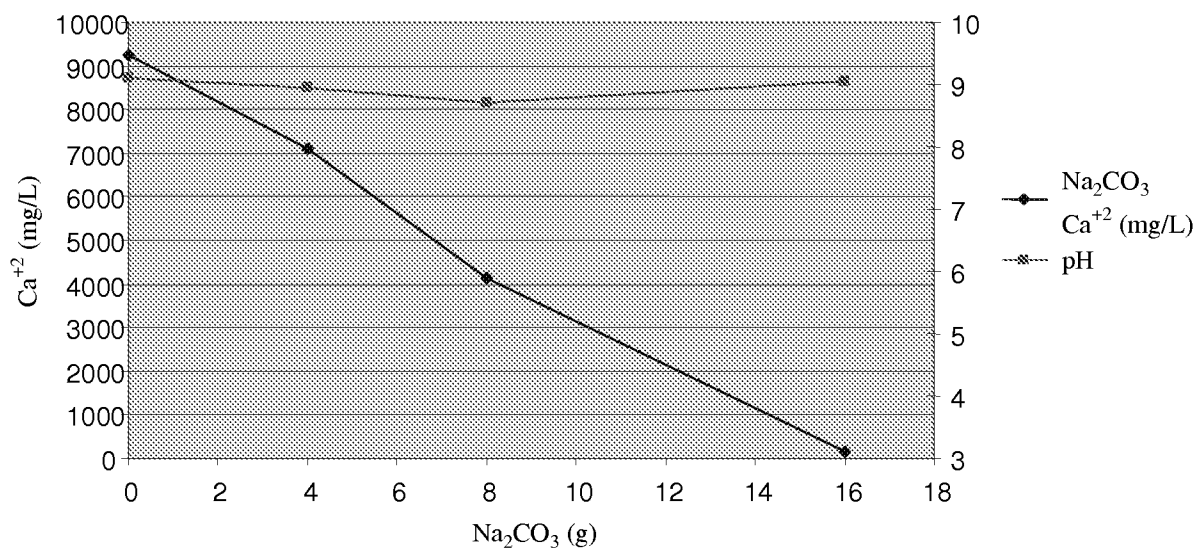


FIGURE 3B

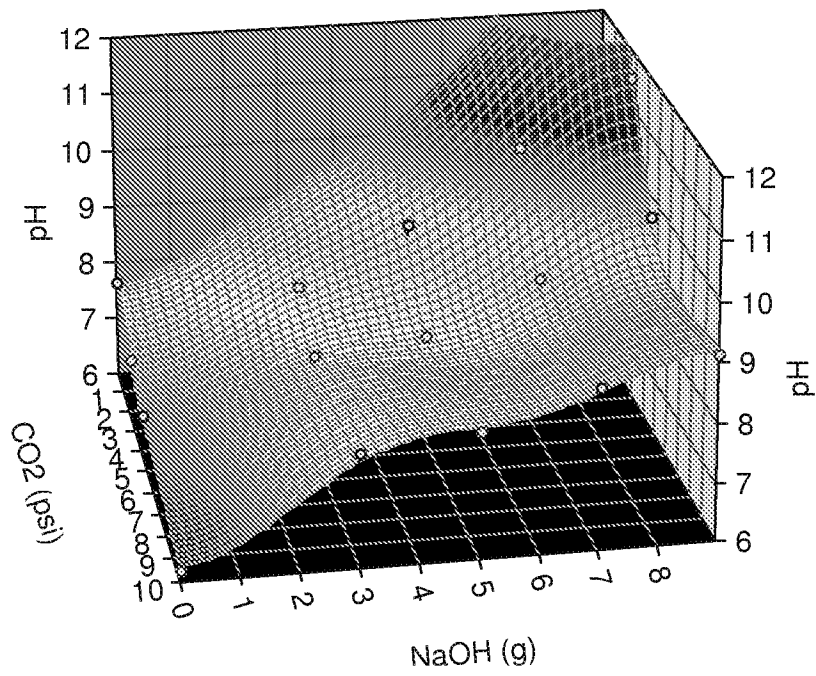


FIGURE 4

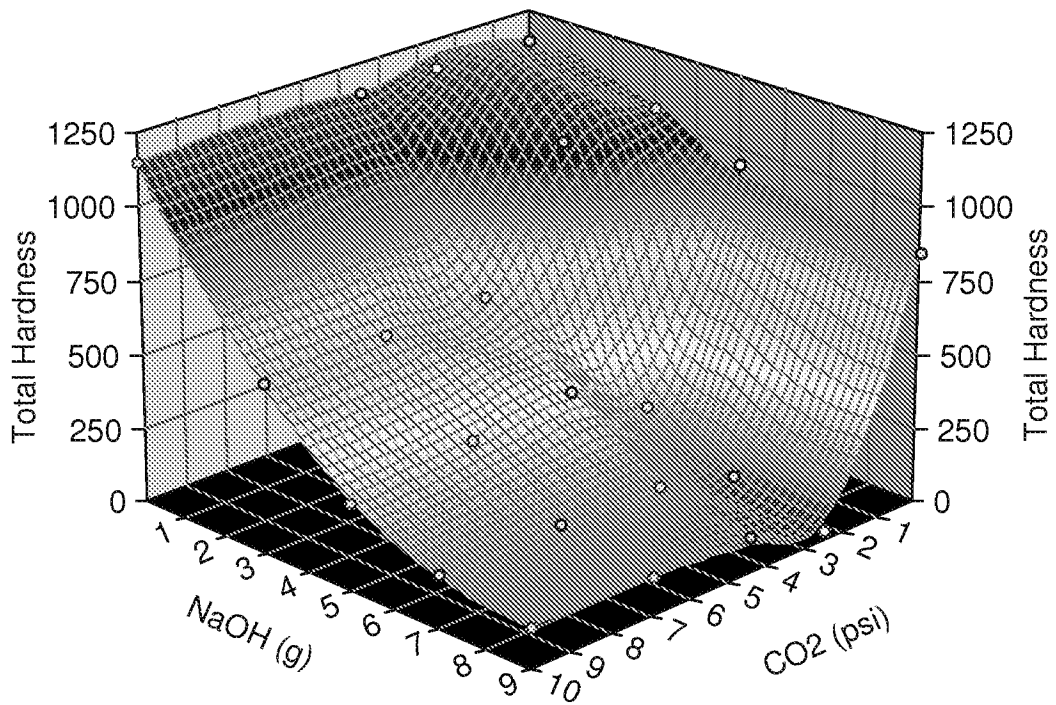


FIGURE 5

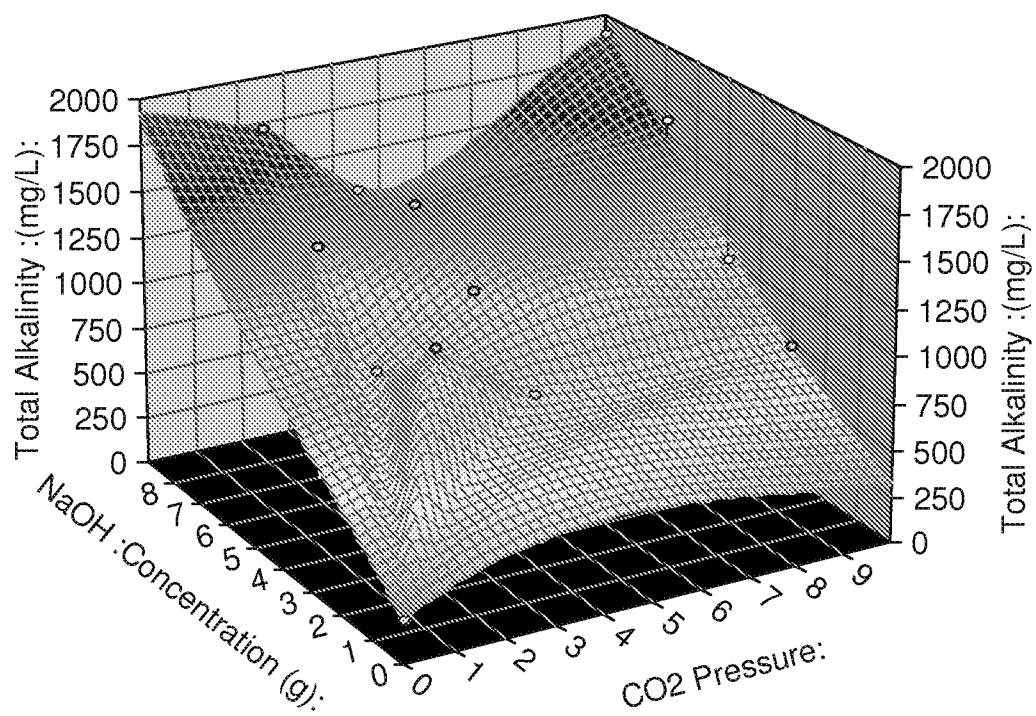


FIGURE 6