A Novel Strategy for CO_2 Sequestration and Clean Air Protection

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Abstract

Upon ratification, the recent climate treaty negotiated in Kyoto, Japan, would require the United States and other developed nations to reduce their emissions of greenhouse gases below 1990 levels by the year 2010. Because most anthropogenic greenhouse-gas emissions (particularly CO_2) come from the use of fossil energy, this agreement has the potential to affect the entire fabric of society. Here, we present a practical and revolutionary method that can sequester greenhouse-gas emissions and at the same time benefit both agriculture and the economy. The proposed strategy utilizes an innovative application of chemical processes to convert CO_2, NO_x, and SO_x emissions into valuable fertilizers [mainly, NH_4HCO_3 and $(NH_2)_2CO$] that can enhance sequestration of CO_2 into soil and subsoil earth layers, reduce NO_3^- contamination of groundwater, and stimulate photosynthetic fixation of CO_2 from the atmosphere. This systematic technology concept (Fig. 1) could contribute importantly to global CO_2 sequestration and environmental protection.

Introduction

The current CO_2 problem from fossil fuel consumption. Fossil fuels—coal, oil, and natural gas—have long been a prime "engine" of our industrialized society. They supply abundant energy at low cost. At the same time, most anthropogenic emissions are related to the use of these fuels. At present, 22 gigatons (Gt) of CO_2 per year (equivalent to 6 Gt C/yr) is emitted as a result of the use of fossil fuels.[1] Coal is the fuel most widely used for the generation of electricity worldwide because it is readily available, easily transportable, and relatively inexpensive. Today 70% of all electricity in the United States is generated from coal and natural gas, while oil-derived products dominate transportation fuels. Worldwide, coal-fired power plants alone result in 1.8 of the 6 Gt C/yr CO_2 emission, while the rest (4.2 Gt C/yr) is from the use of fossil fuels in transportation, industry, and private homes. The increasing anthropogenic CO_2 emission and global warming (thus climate change) have challenged the United States and other countries to find new and better ways to meet the world's increasing needs for energy while reducing greenhouse gases.[2] An effective strategy is needed to solve this increasingly urgent problem.

Enhancement of global photosynthetic activity as a viable solution. Photosynthesis is the biggest CO_2 sink on Earth. Each year, the land-based green plants remove about 403 Gt CO_2 (equivalent to 110 Gt C) from the atmosphere, while the oceans draw approximately 385 Gt CO_2 from the atmosphere.[3] Therefore, an enhancement as small as 6% for terrestrial or oceanic photosynthesis is sufficient to remove the 22 Gt CO_2 (6 Gt C) that is emitted annually into the atmosphere from the use of fossil fuels. To meet the stipulations of the recent Kyoto Treaty for a 22% reduction of global CO_2 emissions by the year 2010, an increase in annual global photosynthetic biomass production of only 0.62% is required if the increased biomass is in a stable form such as woody products.

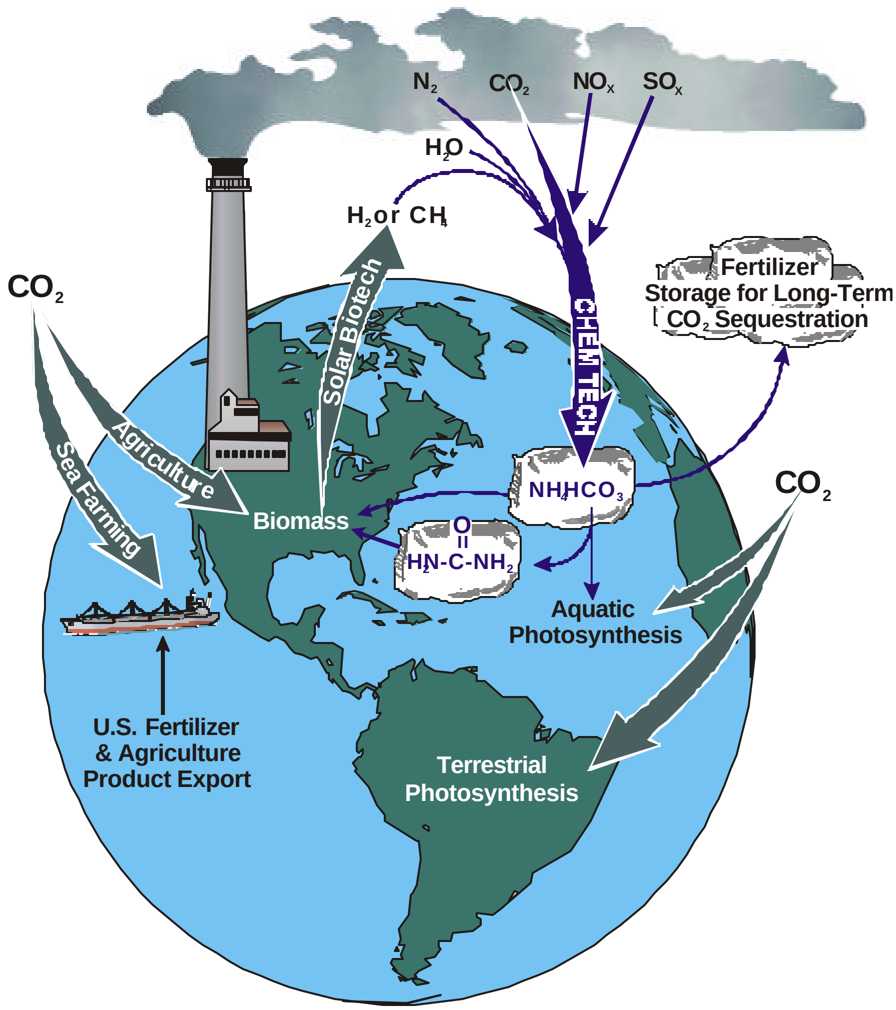

Fig. 1. A systematic technology concept for global CO_2 sequestration and clean air protection.

Enhancement of global photosynthetic productivity by fertilization. In large parts of the world, such as many African nations, land-based photosynthesis in the form of crop production is still limited by the lack of fertilizers. Nitrogen (in the form of ammonium, NH_4^+) is often the most-needed fertilizer since it is an essential substrate for synthesis of all amino acids (thus proteins), chlorophylls (thus photosynthetic reaction centers), and many membrane lipid molecules. All are important components of the photosynthetic membranes. An increase in the use of fertilization could dramatically enhance photosynthetic activity by synthesizing more of the "green machinery," resulting in the capture of more sunlight energy and the fixation of more CO_2. On nitrogen-deficient lands, fertilization could probably increase crop (biomass) production hundreds of percents. An increase in agricultural productivity per unit area (land) could make it possible for some of the farm lands to return to forests, which can be a positive contribution to global CO_2 sequestration. Another important contribution could come from fertilization of forests. Urea fertilizer is being increasingly used in forest areas, resulting in dramatic increases in tree growth[4, 5] and sometimes in an increase in carbon content of the soil.[6] Oceans are also "big photosynthetic bioreactors." At the present time, the primary productivity throughout most of the world oceans is limited by the availability of inorganic fixed nitrogen.[7] When technologies are sufficiently advanced to inexpensively produce large quantities of environmentally friendly fertilizers, development of sea farming in a controllable and ecologically well-managed way with advanced oceanographic technologies may be possible. This could be implemented probably near the end of this century and become a vital alternative to sequester CO_2 and support the world's growing human population.

Currently, agricultural products and nitrogen fertilizers are still clearly in demand in many African nations; a large part of Asia, such as India and China; and parts of Europe, including a large area of the Former Soviet Union. The large market for fertilizers and agricultural products could serve as a natural economic force for the global enhancement of photosynthesis by fertilization.

Proposed strategy

The strategy is to effectively convert CO_2, NO_x and SO_x emissions into valuable fertilizers—mainly, NH_4HCO_3 and $(NH_2)_2CO$—that could enhance sequestration of CO_2 into soil and subsoil terrain, reduce the problem of NO_3^- runoff, and stimulate photosynthetic fixation of CO_2 from the atmosphere. This is a systematic concept that consists of four key components, described as follows.

(1). Integration of combustion facilities with NH_4HCO_3 and $(NH_2)_2CO$ production reactions for CO_2 solidification. As mentioned before, a sufficient supply of nitrogen fertilizers is important to enhance the global photosynthetic CO_2 fixation. Development of an environmentally compatible, cost-effective, and efficient nitrogen-fertilizer production technology is essential to the success of the mission. As illustrated in Fig. 2, when the chemical process for production of NH_4HCO_3 and $(NH_2)_2CO$ is coupled to a CO_2 emission source such as a fossil fuel–fired power plant or a steelmaking factory, the process can convert flue gas (CO_2, N_2) into fertilizers using water and renewable H_2. The production of NH_4HCO_3 and $(NH_2)_2CO$ is summarized in reactions (1) and (2):

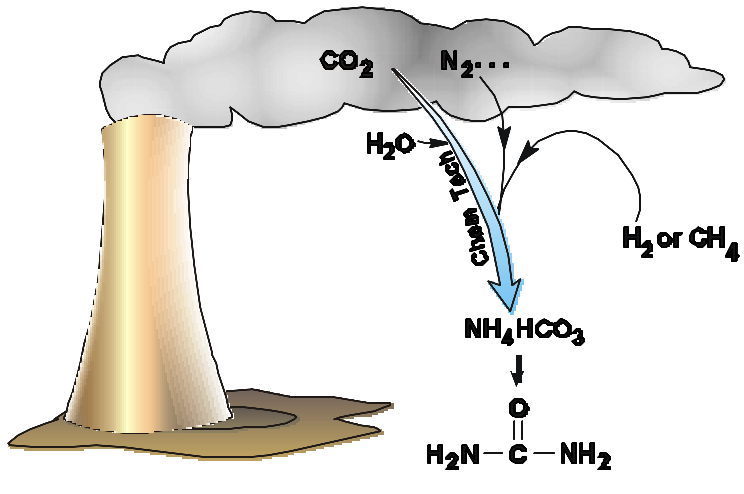

Fig. 2. A proposed CO_2-solidifying technology for fossil fuel–fired power plants.

$$2CO_2 + N_2 + 3H_2 + 2H_2O \rightarrow 2NH_4HCO_3\downarrow \qquad \Delta_r G^o = -86.18 \text{ kJ/mol} \qquad (1)$$

$$CO_2 + N_2 + 3H_2 \rightarrow (NH_2)_2CO\downarrow + H_2O \qquad \Delta_r G^o = -31.34 \text{ kJ/mol} \qquad (2)$$

Calculations using published thermodynamic data[8,9] showed that the standard free energy change ($\Delta_r G^o$) is –86.18 and –31.34 kJ/mol for reactions 1 and 2, respectively. Since both reactions have a negative value for $\Delta_r G^o$, thermodynamically these reactions should be able to occur spontaneously at ambient temperature and pressure. By high-tech catalysis and use of waste heat from flue gas, these reactions should be able to occur very rapidly.

The NH_4HCO_3 production reaction (1) indicates that the use of three H_2 molecules can fix one N_2 molecule and solidify two CO_2 molecules, producing two molecules of the fertilizer. The use of three H_2 in the urea production reaction (2) can fix one N_2 and one CO_2. Therefore, CO_2 solidification by NH_4HCO_3 production is twice as effective as that of urea production. Hydrogen, which has been commonly regarded as an important source of energy for the future,[10,11] could be generated by photosynthetic and solar photovoltaic water splitting.[12,13] Therefore, this concept of CO_2 solidification by innovative application of the NH_4HCO_3 and $(NH_2)_2CO$ reactions (1) and (2) could have long-term strategic importance. Based on our analysis, this chemical process has the potential to remove as much as 90% of the CO_2 from flue gas.

Currently, the most cost-effective means of H_2 production is by gas-reforming reactions of natural gas (CH_4).[14] Therefore, natural gas can also be used to produce CO_2-containing fertilizers such as the following NH_4HCO_3 production:

$$5CO_2 + 4N_2 + 14H_2O + 3CH_4 \rightarrow 8NH_4HCO_3\downarrow \qquad \Delta_r G^o = -5.44 \text{ kJ/mol} \qquad (3)$$

This reaction is more environmentally sound than the current ammonium nitrate production process which emits 3 molecules of CO_2 for the same amount of nitrogen-valued fertilizer:

$$3CH_4 + 4N_2 + 2H_2O + 8O_2 \div 4NH_4NO_3 + 3CO_2 8 \quad (4)$$

By comparison, you can see that the two fertilizer production reactions use the same amount of natural gas ($3CH_4$) and produce the same nitrogen-fertilizer value (each has 8 N atoms). However, the result on carbon is very different. The NH_4HCO_3 production reaction (3) does *not* emit any CO_2. Instead, it can solidify 5 net CO_2 molecules and thus has the potential to be used as an effective CO_2 removal process (3).

The United States has an abundant supply of natural gas (CH_4). Therefore, this CO_2-solidifying technology could enter the market immediately after its development. In 2000, the industrial price of quality natural gas (containing over 90% CH_4) was \$3.47/1000 ft^3 in the United States. Production of 1000 kg NH_4HCO_3 requires only \$15.81 of natural gas. Currently, nitrogen fertilizer is sold at about \$500/1000 kg N, and NH_4HCO_3 contains 17.7% N by weight. For the value of nitrogen alone, 1000 kg NH_4HCO_3 could be sold for at least \$88.50, in addition to providing the benefits of CO_2 emission removal and reduction of NO_3^- runoff since this technology essentially does not produce nitrate (NO_3^-) (see detailed discussion later). Clearly, this CO_2-solidifying technology could be profitable to the power plants and beneficial to the farmers and our environment.

Furthermore, CH_4 is also a form of renewable energy that can be produced through anaerobic biomass fermentation by methanogen.[15,16] In some parts of the world, such as India and China, CH_4 has already been produced in significantly large quantity from biomass fermentation and sewage treatment and has served as an important source of renewable energy for many homes. Therefore, development of the CO_2-solidifying technology based on reaction (3) has both immediate and long-term importance.

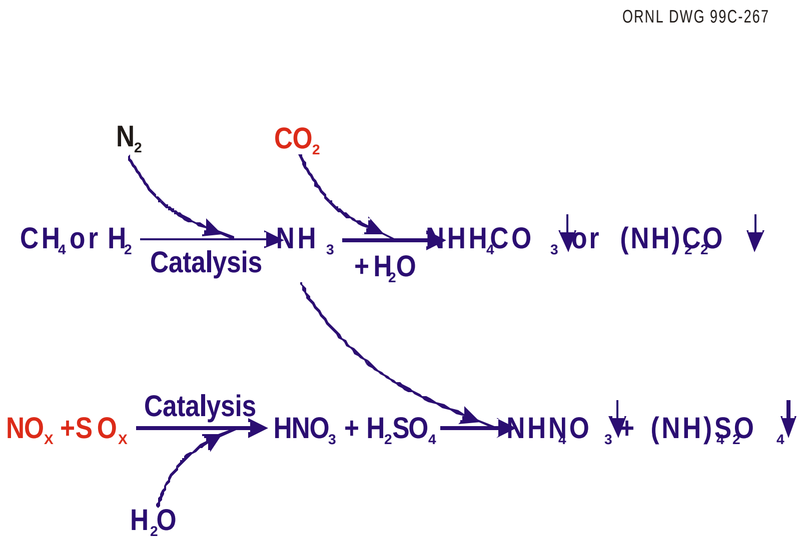

Fig. 3. Simultaneous removal of major CO_2 and the ppm levels of NO_x and SO_x emissions by innovative application of the fertilizer production reactions

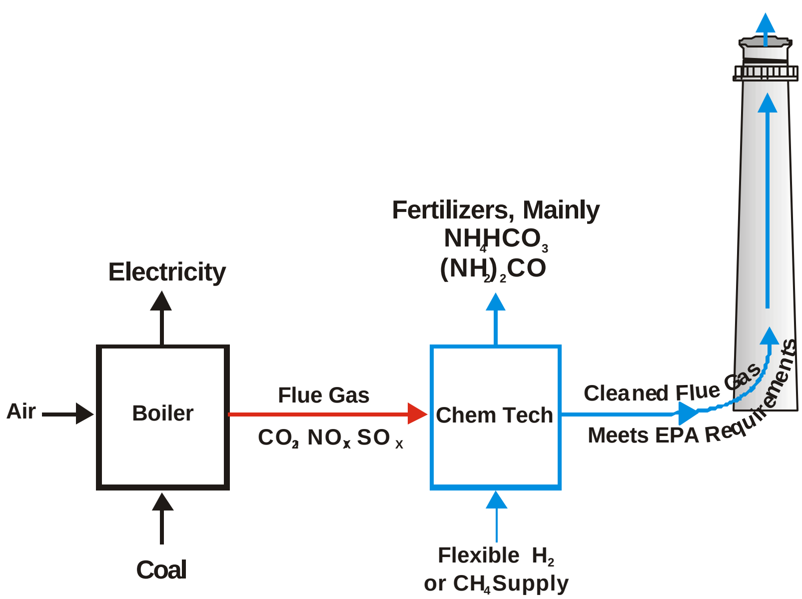

Fig. 4. Development of clean energy systems by integration of existing combustion power systems with the proposed chemical technology to convert major CO_2 and the ppm levels of NO_x and SO_x emissions into fertilizers.

(2). Simultaneous and/or selective removal of NO_x, SO_x, and CO_2 emissions by conversion to fertilizers. Flue gas of combustion facilities such as fossil fuel–fired power plants also contains significant amounts of NO_x and SO_x emissions at ppm levels, which could contribute to acid rain and

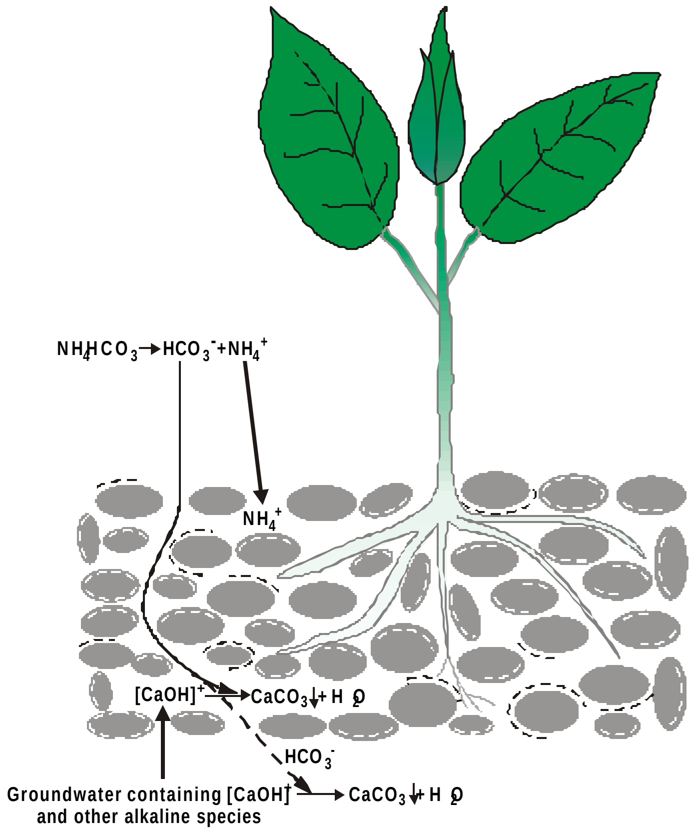

Fig. 5A. Sequestration of CO_2 into soil and subsoil earth layers by enhanced carbonation of earth minerals and groundwater using CO_2-containing fertilizers. Bicarbonate (HCO_3^-) from NH_4HCO_3 can neutralize alkaline species and result in permanent sequestration of CO_2 and reduction of salt content by forming stable and harmless species like water and calcium bicarbonate ($CaCO_3$).

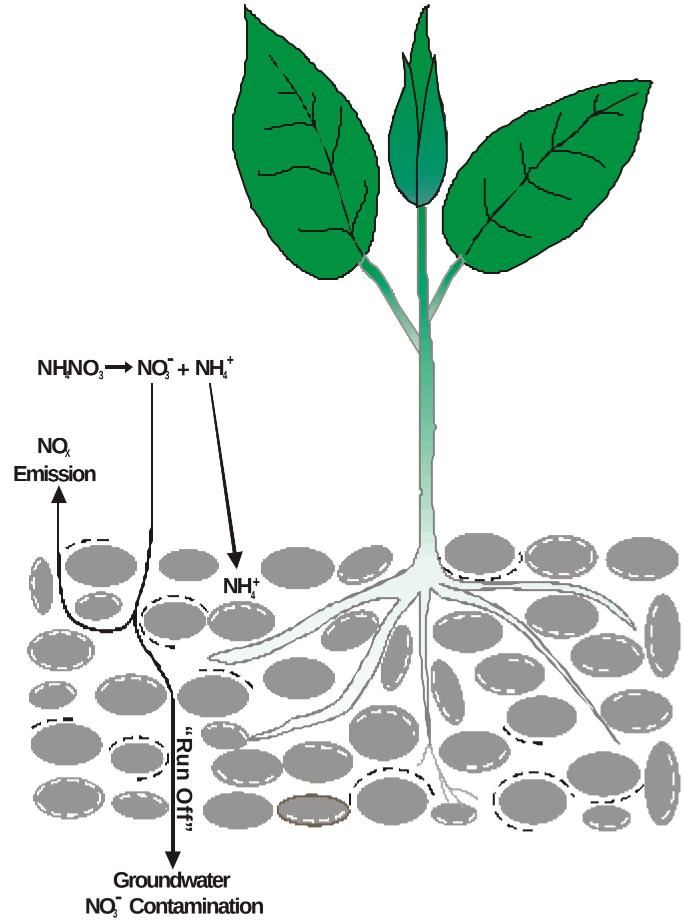

Fig. 5B. Groundwater NO_3^- contamination and NO_x emission caused by the current use of ammonium nitrate (NH_4NO_3). Neither NH_4HCO_3 nor $(NH_2)_2CO$ causes such environmental problems (see Figs. 5A and 5B). Therefore, use of the invention can also help to solve these nitrate (NO_3^-**)** problems.

cause environmental damage. By use of proper catalysts such as platinum and nickel, NO_x and SO_x can be converted into HNO_3 and H_2SO_4 (Fig. 3). These acid species can then be removed by an acid-base reaction with NH_3, an intermediate of the proposed NH_4HCO_3 and $(NH_2)_2CO$ production process, to form additional fertilizer species, NH_4NO_3 and $(NH_4)_2SO_4$. Therefore, the proposed technology can be further advanced to achieve simultaneous removal of major CO_2, the ppm level of NO_x and SO_x emissions from flue gas and produce useful fertilizers (Fig. 4). It could contribute significantly to global CO_2 mitigation and clean air protection.

(3). Reducing the problem of NO_3^- runoff and enhancing sequestration of CO_2 into soil and subsoil earth layers by innovative use of NH_4HCO_3 and $(NH_2)_2CO$. It is known that carbonates can react with alkaline earth minerals such as calcium and magnesium and be deposited as carbonated minerals. For an example, in alkaline soils such as those in the western United States, which may contain high levels of alkaline minerals such as Ca^{2+}, typically from the rising or cumulative use of groundwater, the bicarbonate HCO_3^- from NH_4HCO_3 can neutralize alkaline species and reduce salt content by forming stable species like water and calcium carbonate:

$$HCO_3^- + Ca^{2+} + OH^- \rightarrow H_2O + CaCO_3\downarrow \qquad (5)$$

Solid products like $CaCO_3$ are a perfectly stable form of sequestered CO_2 (Fig. 5A). Furthermore, soils could potentially serve as a "smart" screening material that will retain NH_4^+ but allow HCO_3^- to percolate with natural rainfall and/or irrigation down into groundwater, which is often rich in alkaline mineral species such as Ca^{2+}. Therefore, the carbonates could potentially react with the alkaline species in groundwater and be deposited as carbonated minerals in the subsoil earth layers (Fig. 5A). The reason that soils commonly have much higher retaining affinity for positively charged ions such as NH_4^+ than for negatively charged species such as HCO_3^- is that soil particles carry mostly negative surface charges, which attract positively charged ions but repel negatively charged species.

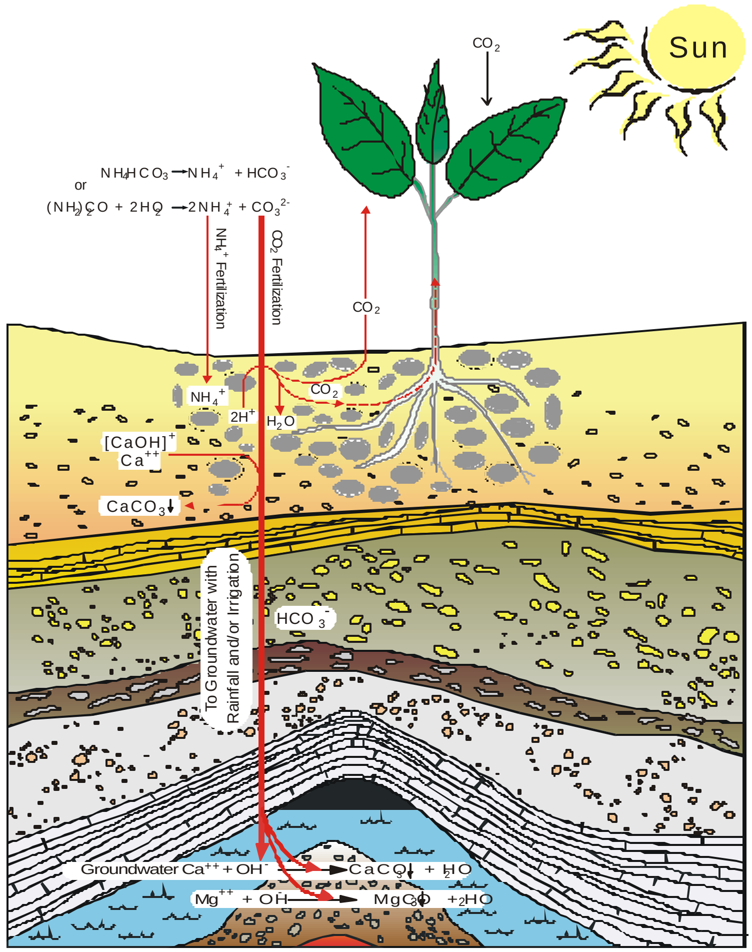

Fig. 6. Sequestration of CO_2 into soil and the subsurface by enhanced carbonation of earth minerals and groundwater using carbonate-containing fertilizers.

For this reason, when NH_4NO_3 is used as a fertilizer, its NO_3^- can easily "run off" with water from soils, resulting in not only the loss of the fertilizer but also the NO_3^- contamination of groundwater (Fig. 5B). However, if NH_4HCO_3 and $(NH_2)_2CO$ are used as fertilizers, the result can be very different—and highly beneficial. Unlike NO_3^-, carbonates (e.g., CO_3^{2-} and HCO_3–) are harmless species, and carbonated groundwater would not cause health problems. Furthermore, movement of groundwater can carry carbonates further down to the earth subsurface as deep as 500 to over 1000 meters, where they can be deposited by the carbonation reaction with minerals (Fig. 6). More importantly, in many geological areas, the residence time of groundwater could be on the order of hundreds—even thousands—of years.[17] Once the carbonates from the fertilizers enter this type of groundwater, they would not return to the atmosphere for hundreds of years even if they are not deposited as carbonated minerals and remain as free carbonates in the groundwater. Therefore, this groundwater-mediated CO_2 sequestration (Fig. 6) could potentially occur in many land areas, as long as the carbonates can effectively percolate from soil with rainfalls and/or irrigation down into groundwater and the earth subsurface.

(4). Enhancing global photosynthetic fixation of CO_2 from the atmosphere through the technology-driven production of NH_4HCO_3 and $(NH_2)_2CO$. Both NH_4HCO_3 and $(NH_2)_2CO$ are water soluble and can provide nitrogen (NH_4^+) and CO_2 fertilization for plant photosynthesis. When NH_4HCO_3 is dissolved in water, it forms ammonium ion and bicarbonate. Both are perfect plant foods that are immediately available for utilization:

$$NH_4HCO_3 \div NH_4^+ + HCO_3^- \qquad (7)$$

When $(NH_2)_2CO$ is applied to soils, soil microorganisms will convert it into ammonium ion and carbonate:

$$(NH_2)_2CO + 2H_2O \div 2NH_4^+ + CO_3^{2-} \qquad (8)$$

Soils commonly have strong binding affinity for ammonium ion (NH_4^+), which prevents its loss. At the same time, NH_4^+ can be absorbed directly by plants, primarily through their root system, for synthesis of amino acids, chlorophylls, etc. Since nitrogen fertilizer generally allows photosynthetic organisms to synthesize more "green machines" (photosynthetic reaction centers and enzymes), supplying NH_4HCO_3 and $(NH_2)_2CO$ to crops not only sends the solidified CO_2 into the field where it is supposed to be but also "catalyzes" plant photosynthesis to fix many additional molecules of CO_2 from the atmosphere (Figs. 1, 5A, and 6). Use of nitrogen fertilizer can typically produce about 50 kg dry biomass/1 kg N through herbaceous plant photosynthesis.[18] For the nitrogen value of NH_4HCO_3 alone, this is equivalent to 23.3 molecules of CO_2 sequestered in biomass per molecule of NH_4HCO_3 used. Production of one molecule of NH_4HCO_3 requires only 3/8 molecule of CH_4. Therefore, input of one CH_4 molecule could result in fixation of 62 molecules of CO_2 by herbaceous biomass production. Much higher efficiency of CO_2 sequestration could come from fertilization of woody plants. Wood has a C:N ratio of about 140:1 and is a more stable form of biomass. With a moderate fertilization efficiency (e.g. 60%), input of one CH_4 molecule through this technology could result in sequestration of 224 molecules of CO_2 into wood. Therefore, to sequester 1000 kg of CO_2 into wood by this combined chemical and photosynthetic technology requires only \$0.34 of CH_4 (Table 1).

In addition to the enhancement of CO_2 sequestration in soils, both NH_4HCO_3 and $(NH_2)_2CO$ have the potential to provide CO_2 fertilization for crop production. Cells of many photosynthetic organisms such as green algae can directly absorb and photoassimilate essentially all forms of CO_2 including bicarbonates (HCO_3^- and CO_3^{2-}). Higher plants absorb CO_2 mostly through their leaves. However, roots of certain crops such as rice plants and *Phaseulus vulgaris* can also absorb CO_2.[19,20] Studies have demonstrated that the yield of photosynthetic CO_2 fixation can be improved by an increase in the supply of CO_2.[21,22] As a result of CO_2-enhanced photosynthesis, the C/N ratio of plant biomass can increase significantly. This phenomenon is known as the "CO_2-fertilization effect."[23] Because NH_4HCO_3 and $(NH_2)_2CO$ contain not only NH_4^+ but also CO_2, use of these fertilizers can provide both nitrogen and CO_2 fertilization for crop production and/or aquatic photosynthesis (Fig. 1).

Therefore, an increase in global use of NH_4HCO_3 and $(NH_2)_2CO$ could significantly enhance the sequestration of atmospheric CO_2 into the biomass, resulting in a richer steady-state volume of biomass. As long as the sequestration is maintained as an enhanced carbon storage (such as $CaCO_3$) in soil and subsoil earth layers (Figs. 5A and 6) and/or as an increase in the steady-state volume of the global biomass (Fig. 1), the CO_2 problem can be solved.

Table 1. Economics of CO_2 Sequestration by the Proposed Technology*

	The Chemical Process Alone	Chemical and Photosynthetic Processes Together
Maximum Efficiency	$\frac{8}{3}$ NH_4HCO_3 / 1 CH_4 Input	224 CO_2 Sequestered into Wood / 1 CH_4 Input
	1000 kg CO_2 Solidified (1800 kg NH_4HCO_3) / \$28.38 CH_4	1000 kg CO_2 Sequestered into Wood / \$0.34 CH_4
Possible Capacity	282 Million Tons of CO_2 per year	3960 Million Tons of CO_2 per year
	16.6% Reduction of CO_2 Emissions from Fossil Fuel-Fired Power Plants in U.S.A. (461 MtC)	18% Reduction of CO_2 Emissions from Worldwide Fossil Fuel Use (6 GtC)

*The economic analysis is based on the 1997 industrial price of quality natural gas (\$3.47/1000 ft^3) and C:N ratio of 140:1 for wood and 60% fertilization efficiency.

Unique features and benefits

The chemical CO_2-solidifying process generates no waste but yields valuable products, using primarily components from air and water. The chemical CO_2-conversion reactions (1–3) clearly show that no toxic materials and no mineral substrates are required for this technology. The production reaction occurs mainly in the gas phase, using principally components from air and water, which are inexpensive and inexhaustible. This is important since global CO_2 is such a massive problem. If minerals such as NaOH (or magnesium) were used as a substrate to solidify CO_2, it would soon exhaust the mineral resource and generate mountains of waste, making the problem probably even worse. Both CH_4 and H_2, which are proposed for use in this technology, can be generated from renewable solar and biotechnology sources (Fig. 1). The proposed chemical technology can use waste heat from the flue gas (Fig. 4). The energy input from H_2 or CH_4 is largely conserved in the formation of NH_3 through nitrogen fixation (Fig. 3). The CO_2 solidification is achieved by a smart acid (HCO_3^-) and base (NH_4^+) reaction, which requires little energy. The products of this CO_2-solidifying process are useful fertilizers—NH_4HCO_3 and $(NH_2)_2CO$—with a market that already exists. Therefore, the cost of this CO_2 capture will be much lower than that offered by any currently existing technology. Use of this technology can be profitable to the fossil energy industry. Effectively, this technology can transform the two industrial greenhouse-gas emitters (the fossil energy system and the present fertilizer industry) into an environmentally remedying, economic, and productive industrial system (Fig. 7).

Because NH_4HCO_3 and $(NH_2)_2CO$ are physiologically effective, environmentally friendly, and socially acceptable fertilizers, they are suitable for large-scale production. In addition to the CO_2-sequestering capability of the proposed technology, there are other reasons that NH_4HCO_3 and $(NH_2)_2CO$ will be preferred to NH_4NO_3. First, NH_4^+ is a better form of nitrogen fertilizer than NO_3^-. What green plants need for synthesis of amino acids and chlorophylls to make enzymes and photosynthetic reaction centers is NH_4^+, which NH_4HCO_3 and $(NH_2)_2CO$ can both supply. If NO_3^- is supplied, as in NH_4NO_3, plants have to use hydrogen (energy) to reduce NO_3^- to NH_4^+ before it can be used in the synthesis of amino acids. This is an unnecessary physiological burden to the plants. Second, NH_4HCO_3

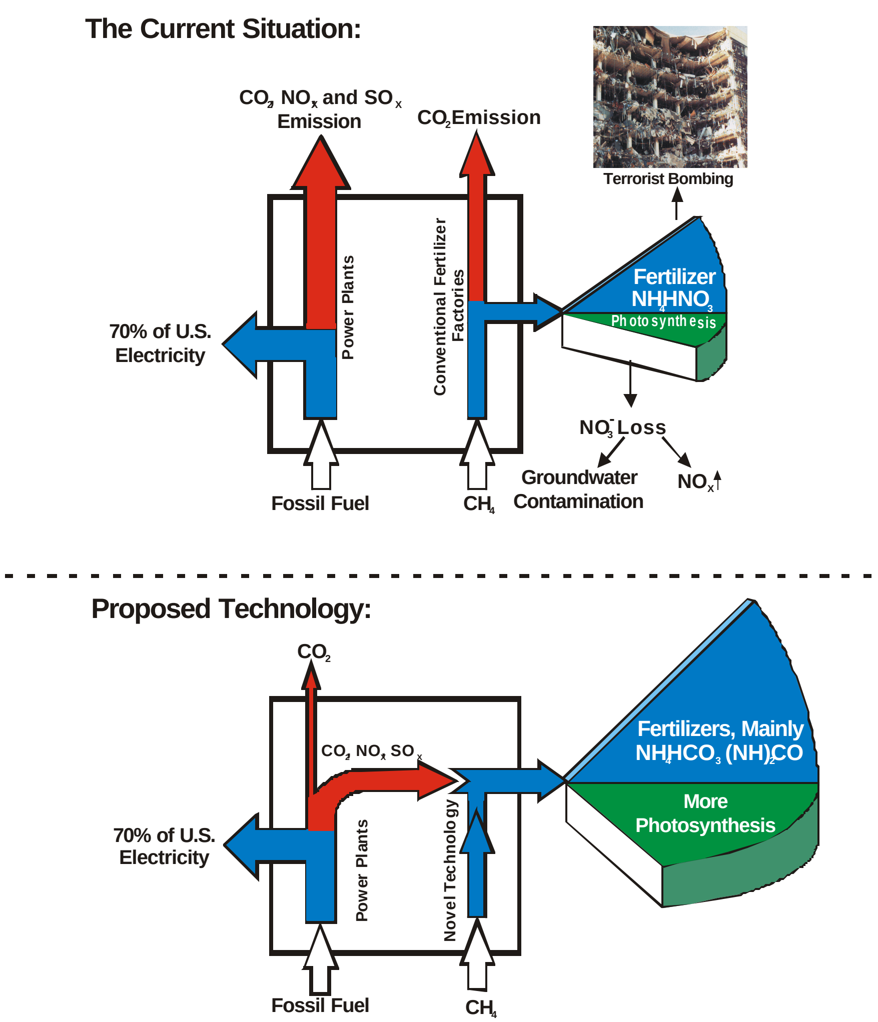

Fig. 7. Comparison of the current situation and the proposed technology, showing that application of the invention can transform the two industrial greenhouse-gas emitters into an environmentally remedying and productive system. The technology can also reduce the problems associated with NH_4NO_3**:** $NO_3^{!}$ loss and groundwater contamination.

and $(NH_2)_2CO$ can also supply CO_2, which is the substrate for plant photosynthesis. Therefore, as discussed before, they can provide "CO_2 fertilization" for crop production and/or aquatic photosynthesis, in addition to their NH_4^+-fertilization effect. Third, soils commonly have much higher retaining affinity for NH_4^+ than for NO_3^-. When NH_4NO_3 is used, its NO_3^- could easily "run off" with water from soil. This results in not only the loss of the fertilizer but also the NO_3^- contamination of groundwater (Fig. 5B). Fourth, if NH_4NO_3 is used in anaerobic soil and/or in a water environment such as rice paddy fields, its NO_3^- could be lost by denitrification as NO_x emissions into the atmosphere (Fig. 5B). Finally, NH_4NO_3 is explosive, whereas both NH_4HCO_3 and $(NH_2)_2CO$ are completely safe (nonexplosive). Because NH_4NO_3 is currently marketed as fertilizer, it is practically impossible to prevent terrorists from having access to it.[24] Had NH_4NO_3 not been marketed as fertilizer in this country, the horrible 1995 Oklahoma City bombing would not likely have happened (Fig. 8). Therefore, NH_4HCO_3 and $(NH_2)_2CO$ should be physiologically, environmentally, economically, and socially preferred to NH_4NO_3.

As illustrated in Figs. 7 and 8, the proposed technology will not only transform the two industrial greenhouse-gas emitters into an environmentally remedying, economic, and productive industrial system but also reduce and/or eliminate the problems of terrorist bombing, NO_3^- loss, and groundwater contamination that have been caused by the current use of NH_4NO_3 as a fertilizer.

A new mechanism for CO_2 sequestration by enhanced carbonation of soil and subsoil earth layers using carbonate-containing fertilizers. The proposed strategy makes effective use of social economics and natural forces such as rainfall and the soil's selective screening effect to send the carbonates of the CO_2-containing fertilizers into groundwater and the earth subsurface—a new mechanism for CO_2 sequestration. As illustrated in Figs. 4, 7, and 8, use of the CO_2-solidifying technology will enable the combustion power systems to remove greenhouse-gas emissions (to satisfy EPA requirements) and produce valuable products that can be sold to farmers. As shown in Table 1, use of \$28.38 CH_4 can convert 1000 kg CO_2 to 1800 kg NH_4HCO_3. For its nitrogen value alone, 1800 kg of NH_4HCO_3 should sell for at least \$159.30. Farmers need fertilizers to grow crops, and the growing world population needs agricultural products. Therefore, the application of this technology—from solidification of CO_2 into fertilizers at the combustion power plants to the use of the CO_2-containing fertilizers to enhance sequestration of CO_2 into soil and the earth subsurface and stimulate photosynthetic fixation of CO_2 from the atmosphere—can occur spontaneously with its natural social economic force. That is, once this systematic technology is developed, its operation does not require tax dollars. Therefore, this invention is better than the alternatives such as injection of CO_2 into the bottom of oceans, a concept that would require tax dollars to implement even if such a technology could be developed.

When farmers use the carbonate-containing fertilizers, they essentially disperse the carbonates in a diluted fashion (at mM concentration levels) into soil. Natural rainfall and/or irrigation could then bring the carbonates down into the subsoil terrain—a potentially huge underground reservoir for CO_2 sequestration. Since this carbon deposition is in a diluted fashion and over a vast land area, the underground reservoir probably will not be saturated by this carbonation process for the next hundreds of years. That is, this technology (CO_2-solidifying fertilizer production and its product application with soil-groundwater-mediated sequestration of CO_2) should be able to be used for the next hundreds of years. Currently, the world consumes about 75 million tons of nitrogen fertilizer annually.[25] One may assume a moderate (e.g. 20%) increase in the use of nitrogen fertilizer (from 75 to 90 million tons per year) when the proposed CO_2-solidifying NH_4HCO_3 production technology is in worldwide use because of its high efficiency and the carbon credit. Since NH_4HCO_3 contains 55.7% CO_2 and 17.7% N by weight, consumption of 90 million tons of nitrogen fertilizer from smokestacks could translate into 282 million tons of CO_2 per year (equal to16.6% of the CO_2 emissions from fossil fuel–fired power plants in the United States) being placed into soil by the use of this technology (Table 1).

The technology can also convert NO_x and SO_x emissions into fertilizers to achieve clean air. As illustrated in Figs. 3 and 4, the integrated technology can simultaneously and/or selectively remove CO_2, NO_x, and SO_x emissions from flue gas and produce useful fertilizers. Therefore, use of this technology will enable fossil fuel–fired facilities such as the combustion power industry to satisfy both the foreseeable regulation on CO_2 emissions and the existing U.S. Environmental Protection Agency (EPA) requirement on reduction of NO_x and SO_x emissions.

The conventional postcombustion technology for removal of NO_x emission is largely based on selective catalytic reduction with ammonia (e.g., $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$).[26 27] Since the conventional technology has to consume NH_3 (an expensive feedstock) and produces nothing valuable ($N_2 + H_2O$), its operation is a financial burden on the power industry. Our proposed technology (Figs. 3 and 4), however, can deal with the same emission problem in a positive and productive way by converting NO_x, SO_x, and CO_2 emissions into valuable commercial products—NH_4NO_3, $(NH_4)SO_4$, and NH_4HCO_3—which can be sold to a worldwide market. The sales of these products could make the use of this air-cleaning technology profitable. Therefore, this technology can lift the financial burden and provide new product opportunity for the power industry. The capability of removing SO_x emissions by this technology (Figs. 3 and 4) will also enable the power industry to use high-sulfur coal—a significant energy resource in the United States.

Furthermore, application of this technology does not have to be limited to fossil fuel–fired power plants. It could be applied to any fossil fuel– and/or biomass-fired industrial facilities. For an example, the iron and steelmaking industry, which also needs to remove CO_2, NO_x, and SO_x emissions, already has a H_2-rich flue gas known as the blast furnace gas which contains about 40% CO and 6% H_2 that are perfect to be used as a H_2 source by this technology. Therefore, this technology can have a wide application and contribute significantly to global CO_2 sequestration and clean air protection.

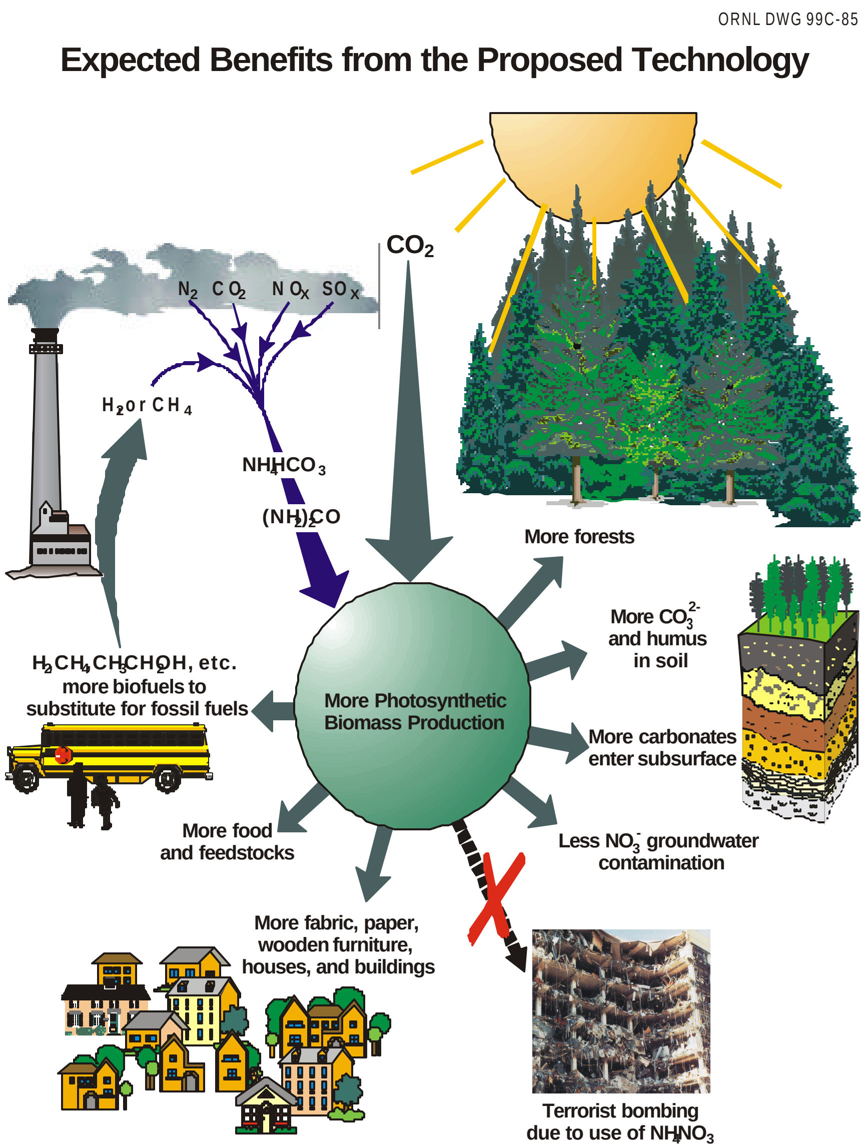

Fig. 8. A systematic strategy that can convert CO_2, NO_x, and SO_x emissions into fertilizers that can enhance sequestration of CO_2 into soil/earth subsurface and stimulate photosynthetic fixation of CO_2 from the atmosphere.

The fertilizer-enhanced agricultural productivity could provide more renewable biomass energy to substitute for fossil fuels. A fertilizer-enhanced agriculture could obviously produce more biomass, mainly in the forms of grains, plant stalks, roots, and leaves. As illustrated in Fig. 8, biomass can have many useful applications. Plant stalks and straws, for examples, are important cellulose materials for the paper industry. With the current biochemical engineering and technology, sugar and/or grain starch such as cornstarch can easily be converted to ethanol. In Brazil, ethanol produced from sugarcane has now replaced one-half of the gasoline used by automobiles (about 200,000 barrels of ethanol per day).[28] All plant materials including stalks, straws, roots, and leaves can be fermented to produce methane, an important gaseous fuel and feedstock, which is proposed for use in this technology. The residue of the biomass fermentation is largely humus, which is a stable organic carbon material that can be used as a valuable additive to improve soil quality. Since humus is much less digestible by microorganisms, its lifetime is much longer than that of other biomass in soil. Addition of humus not only improves soil quality (such as the ability to retain water and nutrients) but also serves as a carbon storage for global CO_2 sequestration (Fig. 8). Therefore, with proper biomass management, a fertilizer-enhanced agriculture can provide more alternative fuels to reduce the consumption of fossil fuels and, at the same time, benefit the soil and the environment.

This technology could lead to a reduction of deforestation and/or an increase in reforestation. Afforestation or reduction of deforestation can also contribute significantly to global sequestration of CO_2. Each year, 1.6 Gt C in the form of CO_2 is discharged into the atmosphere due to the deforestation of land.[19] Because of limited agricultural productivity with insufficient fertilization in large parts of the world, forests have been cut down to create more agricultural lands to support the increasing human populations. A higher agricultural productivity per unit area (land) accomplished by better fertilization could reduce the need of creating more agricultural lands to support the human population. This would also make it possible to have more spare lands for woody crops[29] and/or reforestation (Fig. 8). Therefore, an increase in agricultural productivity per unit area could lead to the return of some agricultural land back to forest. In fact, this has already happened in the United States. Because of the improved agricultural productivity owing to the "green revolution" (including biotechnology, use of fertilizers, and etc.), many active farm lands half century ago in many parts of the United States (such as New York, New Hampshire, Massachusetts, New Jersey, and Tennessee) have now become forest areas. Proper enhancement and /or extension of this type of success to the rest of the world could have positive contribution to global CO_2 management. More contribution could come from fertilization of forest. If the increased N fertilizer (90 – 75 = 15 million tons per year) from the worldwide use of this CO_2-solidifying chemical technology is used to fertilize trees in forest with moderate fertilization efficiency (e.g. 60%), 15 million tons of N could translate into 1080 million tons of carbon being sequestered into wood (C:N = 140:1), which is equivalent to a 18% reduction of CO_2 emissions from the current world use of all fossil fuels (Table 1). Therefore, the $NH_4HCO_3/(NH_2)_2CO$–enhanced agricultural and forest productivity could contribute importantly to global CO_2 sequestration.[30] [31]

The technology could also lead to increased U.S. export of fertilizers and agricultural products and, consequently, a better U.S. economy. Thus far, little research has been conducted concerning flue CO_2 sequestration by NH_4HCO_3 and $(NH_2)_2CO$ formation reactions (1–3). The current U.S. fertilizer industry produces mostly ammonium nitrate (NH_4NO_3).[32] Certainly, the NH_4NO_3 production process[33] cannot sequester any CO_2. Instead, it emits CO_2, with intensive energy consumption (reaction 4). Therefore, such a fertilizer-manufacturing practice is not the best for the environment. Our proposed technology will provide the industry a better way to produce large quantities of fertilizers in harmony with the environment (Fig. 4). Application of this technology could then lead to more U.S. export of fertilizers and agricultural products, benefitting the U.S. economy (Fig. 1).

This invention can also help the developing nations to comply with the reduction of greenhouse-gas emissions. The third-world countries, such as African nations, India, and China, cannot currently afford expensive processes for reduction of greenhouse-gas emissions. However, these countries could readily use this technology to remove the emissions, since it can generate useful products and create a profit (Table 1). Greenhouse gas is a global problem, and sequestration of 1 ton of CO_2 in Africa or India is the same as sequestration of 1 ton of CO_2 in the United States. In fact, if the United States can take the leadership to fully develop this technology, she may be able to sell this technology to the developing countries for carbon credit.

Use of the technology would not only reduce CO_2 emission but also improve agricultural productivity and the quality of human life worldwide. Better fertilization obviously improves agricultural productivity. A richer volume of global biomass also means a richer society worldwide—more foods and feedstocks; more milk and animals; more cotton and silk for clothing; and more paper and woody products including wooden furniture, houses, and buildings. All of these are perfectly sequestered forms of CO_2 and free of the greenhouse effect. Some of them, such as cotton and silk clothing, papers, wooden furniture, houses, and other structures, can remain for tens and even hundreds of years, maintaining their useful functions for human society (Fig. 8). Therefore, this strategy also takes advantage of the potential for biosystems (photosynthesis) to benefit social economics.

Future Activities

This systematic technology concept for global CO_2 sequestration and clean air protection was developed by the authors at Oak Ridge National Laboratory during the last several years. Our latest analysis showed that with the current technologies of CH_4-steam reforming and NH_3 synthesis, it is already possible to run the CO_2-solidifying NH_4HCO_3 production process from flue-gas CO_2, N_2, H_2O, and natural gas with nearly 60% efficiency of the ideal reaction (3). That is, if a coal-fired power plant is integrated with the current technologies of CH_4-steam reforming and NH_3 synthesis for solidification of CO_2 by NH_4HCO_3 production, it can surely achieve net removal of CO_2 emissions from the smokestacks as a result of the overall chemical engineering process. Therefore, this technology concept for integration of industrial combustion facilities with CO_2 sequestration is proved valid. An U.S. patent application has recently been filed to protect this comprehensive technology concept.

With a team of seven students and Professor Robert Counce at the University of Tennessee, Knoxville, we have now completed a computer modeling and economic study on industrial CO_2 removal for coal-fired power plants. The study showed that this concept of CO_2 sequestration is technically possible and economically attractive.[34] Some independent and preliminary research in Asia has now also demonstrated the correctness and potential of this concept.[35] Thus far, however, the United States has not provided significant funding support to explore this new concept. We hope, the U.S. Department of Energy and/or the Environmental Protection Agency can provide some significant funding support for us to further explore this new technology concept at ORNL. We need to demonstrate both the chemical engineering and the soil/biogeological aspects of this technology concept. The success of this project can have a significant impact on carbon management and clean air protection worldwide.

Acknowledgment

We gratefully acknowledge the stimulating discussions with our colleagues and friends at ORNL, DOE, and elsewhere, with particular appreciation to R. Wright, J. Shang, V. K. Der, E. Khan, E. M. Toline, A. C. Bose, R. T. Jubin, J. R. Trabalka, J. Young, E. Hagaman, R. Counce, R. Luxmoore, E. Greenbaum, C. Tsouris, W. Steele, D. DePaoli, B. H. Davison, B. R. Evans, R. Cushman, G. Marland, R. Judkins, M. Farrell, M. A. Brown, and T. J. Wilbanks. We also thank M. K. Savage and D. P. Stevens for editorial assistance, C. D. King and V. W. Purdue for technical illustration. This research was supported in part by the U.S. Department of Energy, Office of Fossil Energy. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

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