Korean J. Chem. Eng., 38(9), 1757-1767 (2021)
DOI: 10.1007/s11814-021-0840-2

pISSN: 0256-1115
eISSN: 1975-7220

INVITED REVIEW PAPER

Techno-economic and environmental feasibility of mineral carbonation technology for carbon neutrality: A Perspective

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(*Received 2 March 2021 • Revised 12 April 2021 • Accepted 10 May 2021*)

Abstract−Although various CO_2 capture and utilization (CCU) technologies are being researched and developed intensively for the purpose of lowering greenhouse gas emissions, most current technologies remain at low technology readiness levels for industrial use and are less economical compared to conventional processes. Mineral carbonation is a CO_2 utilization technology with low net CO_2 emissions and high CO_2 reduction potential, and various commercialization studies are underway around the world. This manuscript reviews the potential of mineral carbonation as a general CCU technology and the techno-economic and environmental feasibility of a representative technology, which produces sodium bicarbonate through the saline water electrolysis and carbonation steps, and examines the potential CO_2 reduction derived from the application of this technology. The future implementation of mineral carbonation technology in ocean alkalinity enhancement for sequestrating atmospheric CO_2 or the production of abandoned mine backfill materials is also discussed in order to deploy the technology at much larger scales for a meaningful contribution to the reduction of greenhouse gas emissions.

Keywords: Carbon Capture and Utilization, Mineral Carbonation, CO_2 Reduction, Economic Evaluation

INTRODUCTION

Mineral carbonation technology can store CO_2 in a highly stable form via a carbonation reaction with alkaline earth oxides to form carbonates. The raw materials used in the mineral carbonation reaction include natural minerals, such as olivine (Mg_2SiO_4), serpentine ($Mg_3Si_2O_5(OH)_4$), wollastonite ($CaSiO_3$), as well as waste products or byproducts generated in the industry, e.g., waste concrete/cement, steel slag, nickel slag and fly ash [1].

Mineral carbonation has several advantages over other CO_2 utilization technologies, the most important of which is the lower Gibbs free energy of the carbonates compared to CO_2 (as shown in Fig. 1) [2]. This is in contrast with other fuel or chemical products, such as methanol, being considered for CO_2 utilization and implies a potentially lower energy requirement for the chemical conversion and the stability of the carbonation product over geologic periods of time.

When developing mineral carbonation technology, the most important factors to consider include techno-economic feasibility and the amount of CO_2 reduction that can ultimately be achieved. Various studies have reported findings and results regarding these factors. According to the Global CCS Institute (GCCSI) that conducted life cycle assessments (LCA) of eleven different CO_2 utilization technologies, mineral carbonation technology produces the lowest amount of CO_2 per unit of product among the analyzed CO_2 utilization technologies [3]. Methods involving methanol and polymer production using CO_2, which have been thoroughly studied in recent years, generate 1.7-5.5 tons of net CO_2 emissions per ton of CO_2 used in the process. In contrast, carbonate mineralization technology results in significantly lower CO_2 emissions of 0.32 ton per ton of CO_2 used. Also, from the perspective of the scale of potential CO_2 reduction, carbonate mineral technologies are considered to have the potential to achieve several million tons of CO_2 reduction with the current market and much more with future market development.

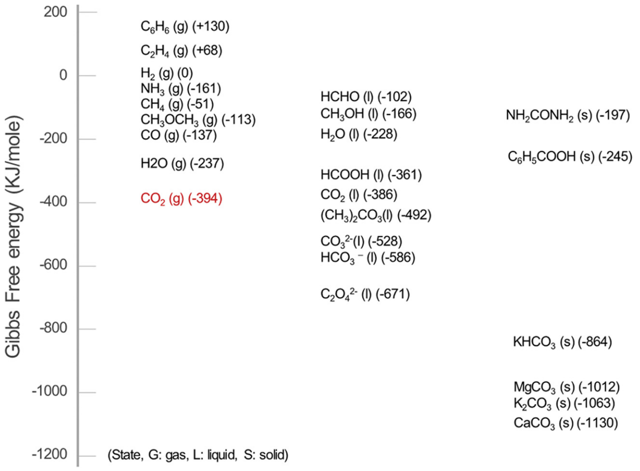

Fig. 1. Thermodynamic considerations in CO_2 utilization (modified from C. Song, 2006 [2]).

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Many research institutes around the world are conducting research regarding the commercialization of mineral carbonation technology. As an exemplary technology with a high technology readiness level (TRL) compared to other technologies, the U.S. company Calera developed a technology that reacts caustic soda (NaOH) produced from an electrolysis process named ABLE (Alkalinity Based on Low Energy) with calcium and magnesium cations obtained from seawater to produce a low-carbon cement product. The production of calcium carbonate and magnesium carbonate via mineral carbonation has been reported to produce 90% less carbon emissions compared to the production of conventional Portland cement [4].

The Australian company Alcoa developed a technology that reacts alkaline mother liquor with alkali metal or alkaline earth metal ions, which can be found in bauxite residue slurry produced in the aluminum production process, with CO_2 emitted from a nearby refinery to produce precipitated calcium carbonate (PCC) and other salts. Since 2007, Alcoa has operated a mineralization plant in Kwinawa, Australia, which is capable of processing 70,000 tons of CO_2 each year [5]. In addition, the U.S. company Skyonic developed a mineral carbonation plant as a part of the SkyMine project supported by the U.S. Department of Energy (DOE). The plant produces commercial products, such as sodium bicarbonate (baking soda), hydrogen gas, and chlorine gas, using 83,000 tons of CO_2 obtained annually from the cement plant [6].

Although various studies have contributed to the growing techno-economic feasibility of mineral carbonation technology [7-9], many of the proposed technologies offer only minor CO_2 reduction due to the large use of energy compared to conventional processes. Furthermore, unlike certain CO_2 utilization technologies (e.g., methanol production) with large market sizes, mineral carbonation technology is constrained by a relatively small market size at current time, meaning there are limitations in expanding the greenhouse gas reduction to meaningful scales. Therefore, in addition to ensuring the techno-economic feasibility of mineral carbonation technology, various new business models should be developed to propose the application of the technology in a wider array of industrial fields. In addition to industrial uses, it will be important to explore large-scale deployments of mineral carbonation technology as a storage option.

As such, this study reviews the techno-economic and environmental feasibility of a representative carbonation technology that utilizes CO_2 to produce sodium bicarbonate through the saline water electrolysis and carbonation steps. The potential CO_2 reduction derived from the application of this technology is calculated and perspectives are provided. Furthermore, this study proposes the feasibility of implementing mineral carbonation technology in ocean storage or in the production of abandoned mine backfill materials to further expand the scale of its contribution to greenhouse gas reduction.

DESCRIPTION

1. Background

Mineral carbonation technology can be divided into direct carbonation that directly reacts to target materials and CO_2 and indirect carbonation that extracts and carbonates alkali ions from the raw materials [10].

Development of indirect carbonation technology is progressing at higher TRLs compared to direct mineralization technology, which typically requires severe operating conditions. Most indirect CO_2 carbonation technologies comprise two steps: an electrolysis step where alkali ions are extracted from industrial byproducts, seawater, or brine; and a carbonation step in which the obtained alkali ions are reacted with CO_2 generated from emission sources to produce minerals [4,6,9]. Certain cases directly use alkali ions from natural minerals [1] or obtain intermediate substances that are involved in the carbonation reaction from external sources [11,12].

2. Mineral Carbonation Technology

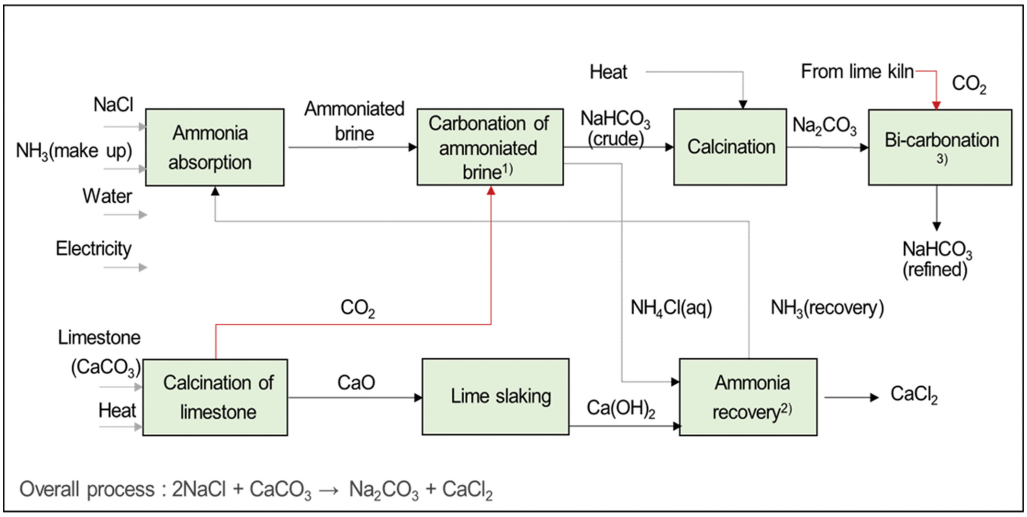
As a representative indirect mineral carbonation technology, we review a technology similar to that of Calera and Skyonic Corp, recently proposed by Lee et al. [9]. They show high techno-economic and environmental feasibility of the technology based on bench-scale performance tests and process simulations. The key results including process improvement are expected to have significant implications for the development of similar technologies.

Carbonation technology produces sodium bicarbonate ($NaHCO_3$) by utilizing CO_2 generated in large-scale emission sources, such as coal-fired power plants or cement production plants, and consists of two steps: a saline water electrolysis (SWE) and a CO_2 carbonation step. The conventional methods of producing sodium bicarbonate include the Solvay process, the trona and nahcolite-based processes, the nepheline synthesis process, and the carbonation processes using caustic soda [13]. The most notable of these is the Solvay process, also known as the ammonia soda process (as shown in Fig. 2). According to a European soda ash producers association report in 2004, the Solvay process accounted for 59% of all sodium carbonate production in 2000 [14]. The greatest advantage of the Solvay process is that it can produce sodium carbonate (Na_2CO_3) and sodium bicarbonate – both widely used industrial products – using raw materials that are commonly distributed around the world (NaCl, $CaCO_3$). However, the process has environmental problems such as ammonia loss and thermal pollution, along with increased CO_2 emissions from the large amounts of energy use [13].

Therefore, if the Solvay process could be replaced with a mineral carbonation technology, it could potentially reduce the CO_2 emission by a significant amount. However, the Solvay process has been in commercial operation since the 19th century and is the most well-proven option in terms of technical stability and economic feasibility. As such, for a mineral carbonation technology to replace the Solvay process, it will be necessary to verify the techno-economic feasibility of the technology at meaningful scales and carry out detailed LCA analyses based on the results. In the following, the overall scheme of the CO_2-utilizing sodium bicarbonate production technology based on mineral carbonation is introduced and the economic feasibility and CO_2 reduction results as analyzed via bench-scale performance tests and process simulations are summarized. In terms of the mineral carbonation technology, the following two different process options are considered.

2-1. (Case 1) Sodium Bicarbonate Production via Saline Water Electrolysis and Carbonation Step

The mineral carbonation process of Case 1 is comprised of



[1] Carbonation of ammoniated brine : $NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3(s) + NH_4Cl(aq)$

[2] Ammonia recovery : $Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2H_2O + 2NH_3$

[3] Bi-carbonation reaction : $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

Fig. 2. Simplified process flow diagram of the Solvay process (modified from Lee et al. [9]).

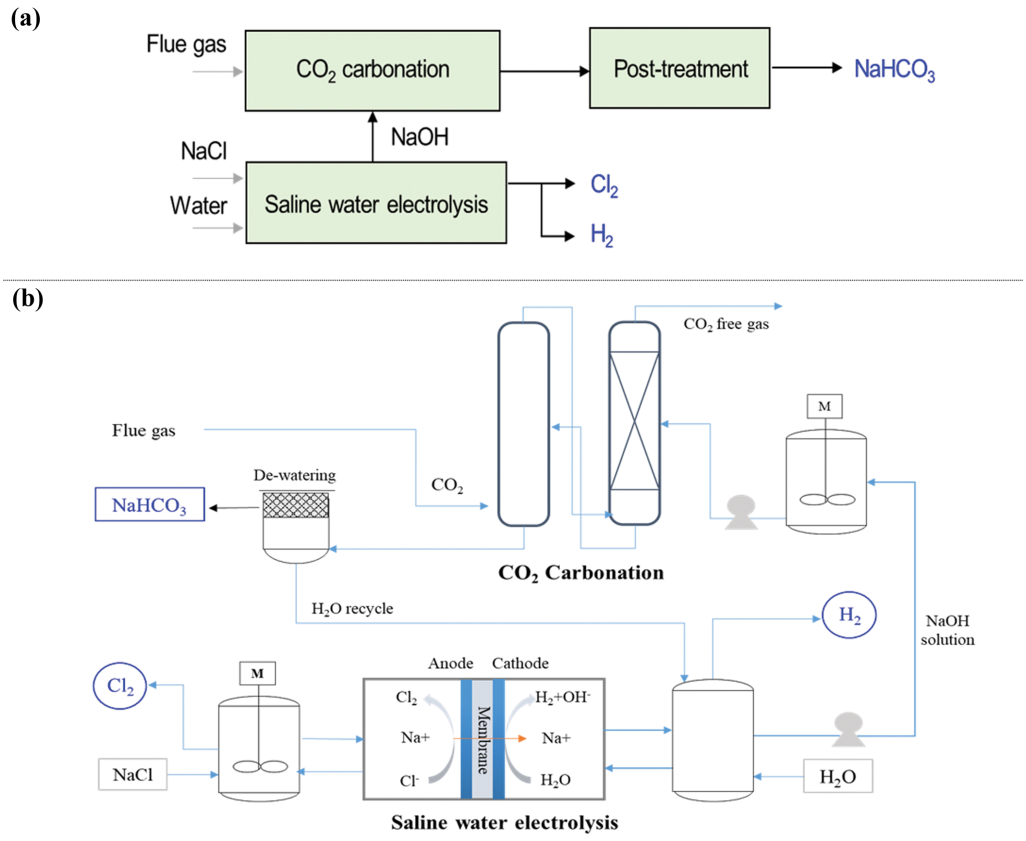


Fig. 3. Sodium bicarbonate production via saline water electrolysis: (a) System boundary, (b) simplified process flow diagram (modified from Lee et al. [9]).

SWE, CO_2 carbonation, and post-treatment steps (Fig. 3). The CO_2 and caustic soda produced from the SWE step become the reactants of the carbonation reaction, producing sodium bicarbonate. The CO_2 from various sources such as power plants and cement factories could be utilized in the process.

The CO_2 in the flue gas and the caustic soda from the SWE step undergo the carbonation reaction (Eq. (1)) and bicarbonation reaction (Eq. (2)) illustrated below to form sodium bicarbonate. For the SWE process, concentrated or saturated sodium chloride solution is subjected to the SWE step to produce chlorine (Cl_2) at the anode and caustic soda and hydrogen at the cathode.

$$\text{Carbonation: } 2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad (1)$$

$$\text{Bicarbonation: } Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3 \quad (2)$$

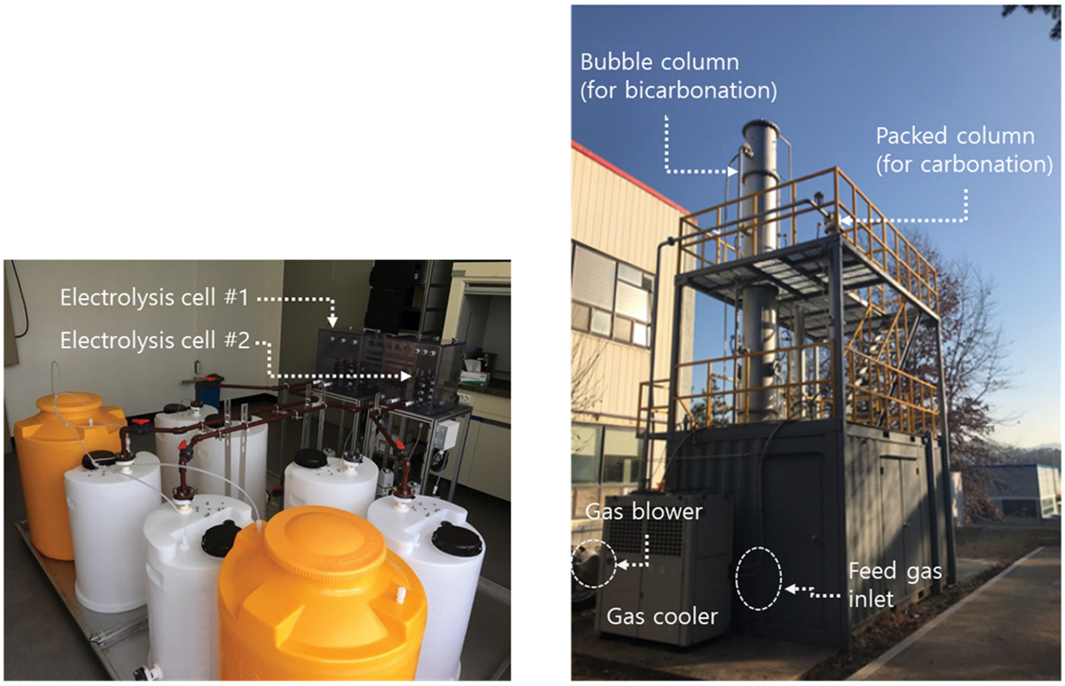
Lee et al. [9] conducted bench-scale performance tests for the mineral carbonation process (flue gas processing capacity: 2 Nm^3/hr) and achieved a CO_2 conversion rate of 95%. In addition, the final product (sodium bicarbonate) has purity levels of 97% or higher, indicating that the product is adequate for industrial usage [9]. Furthermore, a proprietary high-ion conductive membrane was applied to the SWE step, the process with the highest energy consumption in the mineral carbonation plant, to reduce the electrolysis energy consumption by at least 8% [15].

Based on the bench-scale unit performance tests, a pilot-scale mineral carbonation plant was constructed, where follow-up process optimization and improvement studies are in progress. The mineral carbonation plant has a daily CO_2 processing capacity of 200 kg and is capable of producing approximately 300 kg of sodium bicarbonate per day (as shown in Fig. 4). For the SWE step, which produces caustic soda, hydrogen, and chlorine, relative performance comparisons (electrolysis energy consumption, membrane durability, etc.) are conducted between the proprietary high-ion conductive membrane and a commercial membrane (Aciplex-F$^{\circledR}$, Asahi Kasei, Japan) by connecting two electrolysis cells with identical designs (10 cell×100 cm^2) in parallel.

The feed gas used in the carbonation step is the flue gas produced from the burning of LNG fuels. The flue gas is fed into the carbonation column at the optimum operating temperature (35-40 ^{o}C). Furthermore, high-purity CO_2 is mixed with the feed gas being fed into the carbonation column, which enables control of the CO_2 concentration within the desired range (9-14 vol% CO_2). In addition, the pilot-scale carbonation unit was designed to be mobile for the application at various CO_2 sources. Presently, with the basic performance test results as a basis, long-term continuous operation performance tests and process improvement research are in progress.

2-2. (Case 2) Sodium Bicarbonate Production from Carbonation of Sodium Carbonate

The SWE process is likely to serve as a hindrance to near-term commercialization of the Case 1 technology due to the significant costs as well as the numerous safety/environmental issues involved with the large-scale processing of hydrogen or chlorine. As an alternative option, the SWE process could be removed and sodium carbonate could instead be purchased from external sources to directly produce sodium bicarbonate through the CO_2 bicarbonation reaction. This process is comprised of just the bicarbonation and post-treatment steps, with the latter including the dewatering and drying processes (Fig. 5). The bicarbonation reaction involves the sodium carbonate solution and CO_2 in the flue gas. As shown in Eq. (2), one mole of sodium carbonate is used to produce two moles of sodium bicarbonate through the bicarbonation reaction. This indicates that it is possible to produce 1.6 tons of sodium bicarbonate using 1 ton of sodium carbonate and 0.4 tons of CO_2 [11].



(a) Saline water electrolysis process

(b) (Mobile) CO_2 carbonation process

Fig. 4. Photograph of the pilot-scale mineral carbonation plant.

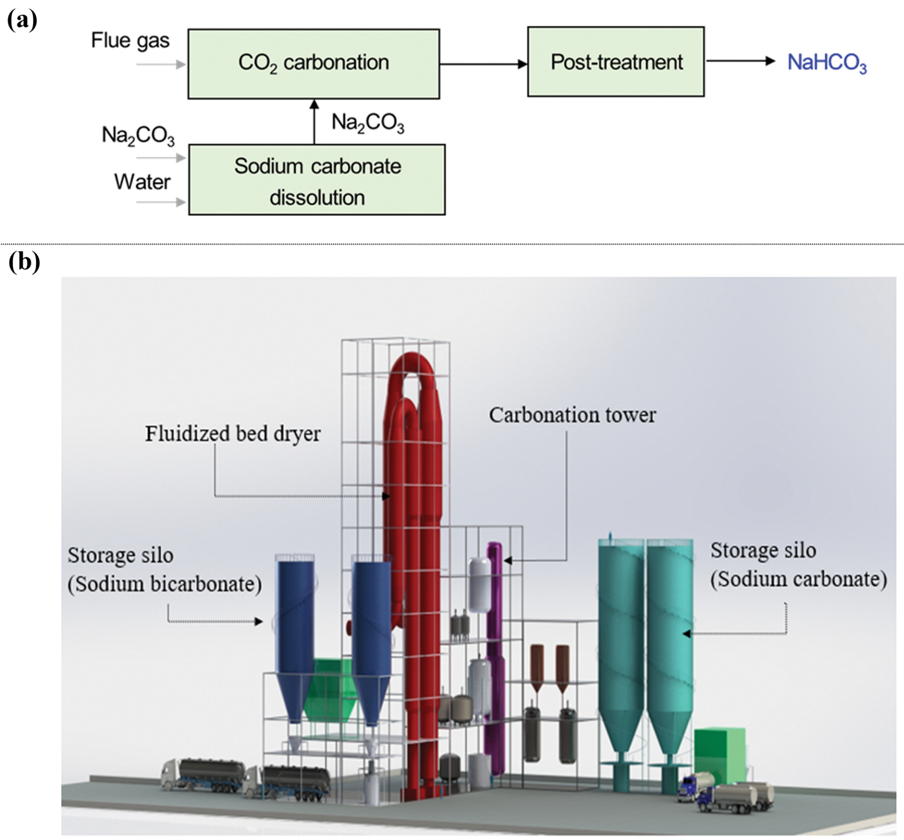


Fig. 5. Sodium bicarbonate production from carbonation of sodium carbonate: (a) System boundary, (b) schematic diagram of a commercial carbonate mineralization plant.

Compared to the mineral carbonation technology that includes the SWE process (Case 1), this option involves relatively simpler processes and requires less capital investment. As such, it is promising as a technology for short-term commercialization with the potential to derive economic profit. Notably, steel mills/biomass power plants require significant amounts of sodium bicarbonate for the removal of the large amounts of acidic gas (SOx, HCl, etc.) emitted from the process. By applying the proposed technology to such plants, the CO_2 that is generated in the plant could be utilized to produce sodium bicarbonate, which in turn is consumed on-site, leading to significant reductions in plant operating cost. Fig. 5 shows a schematic diagram of the process as well as a schematic diagram of a commercial carbonate mineralization plant capable of producing approximately 30,000 tons of sodium bicarbonate per year.

3. Process Improvements

The carbonation process has a slow reaction rate, which increases the volume of carbonation column needed to achieve a high CO_2 conversion rate, further increasing costs. As such, it is vital to maximize the efficiency of the carbonation reaction. Furthermore, the SWE step, which produces alkaline earth oxides, is the most energy-intensive part of the overall mineral carbonation process; thus, it is a crucial factor that determines the economic feasibility of the overall mineral carbonation process. Numerous studies are in progress to improve the techno-economic feasibility of the mineral carbonation process as shown below.

3-1. Carbonation Process

In the case of the carbonation process, various research studies are underway to develop highly efficient catalysts and reactors to increase the relatively low carbonation reaction rate. Regarding the catalyst research, the most notable example involves the use of carbonic anhydrase (CA) enzyme as catalyst for the carbonation process. Carbonic anhydrases catalyze the reversible hydration of CO_2 to HCO_3^- with very high rates [16]. However, despite the excellent CO_2 absorption and catalytic capability of CA, actual application of the catalyst to the commercial plant is hindered by decreased catalyst activation and durability, prohibiting its long-term use. Additionally, there are issues such as the potential loss of the CA during operation and high production costs. As such, various studies are aiming to resolve these issue [17,18].

In addition to the application of CA, various process improvements are being considered. For example, Hwang et al. [19] proposed a technology that utilizes hollow fiber modules based on an ultra-permeable membrane to directly utilize CO_2 from the flue gas, which is expected to decrease capital investments by at least 30% [19]. In addition, Lee [20] developed a column with a new internal structure design that increases the CO_2 conversion rate and minimizes fouling within the bubble column. The developed

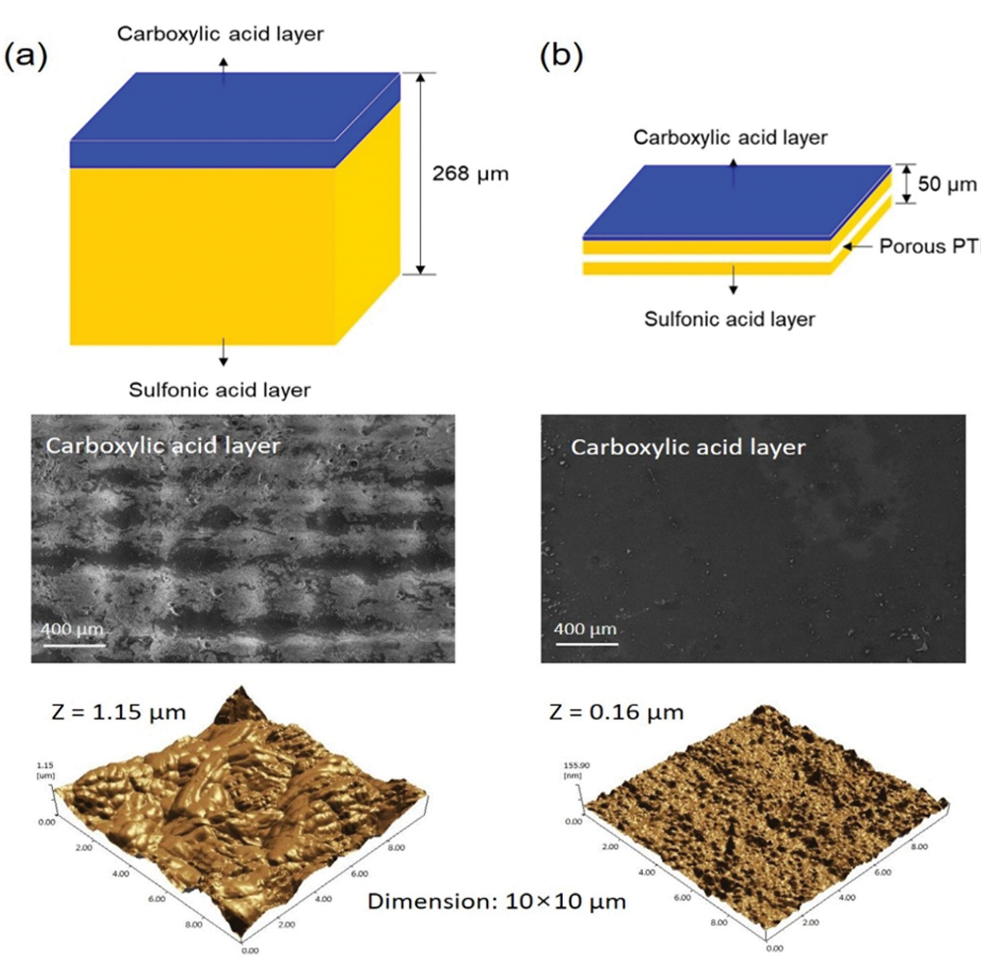


Fig. 6. SWE membranes ((a) Aciplex-F®, and (b) proprietary membranes) with cross-sectional differences (top), and surface morphologies (middle) and atomic force microscopic images (bottom) [15].

anti-fouling tray takes the form of an internal tray with several interconnected caret (Λ)-shaped structures. Continuous operation performance tests with the anti-fouling tray showed a 15% increase in the CO_2 conversion rate with identical feed gas conditions [20].

In addition to improvements to individual processes, the processes can be operated in conjunction with other technologies to improve the economic feasibility of the overall mineral carbonation plant. For example, reject brine (Na concentration: 6-7 wt%) from desalination processes, which would have to be processed at cost, could be used as feed material for the SWE process, further improving the overall economics [21].

3-2. SWE Process

To build an economically feasible mineral carbonation process, it is necessary to develop a low-energy consumption SWE system. SWE is known as an energy-intensive process. For instance, the SWE process of the Skyonic CO_2 utilization plant consumed around 18.4 MW, which is 87% of the total energy used to operate the whole plant [15].

To date, there have been a wide array of approaches to reduce the SWE energy consumption. These efforts include an SWE cell that uses a fuel cell configuration [22], a zero-gap method which minimizes interfacial resistances between SWE cell components, and the use of porous electrodes which activates the generation and emission of product gases [23]. Another suggested approach employs oxygen depolarized cathodes, which can lower energy consumption but with some sacrifices in H_2 evolution [24,25]. A low-energy SWE step that applies a high ion conductivity membrane has also been proposed [15]. This technology utilizes a reinforced composite membrane that is impregnated with an ionomer material with high cation (Na+) conductivity and superior chemical stability and is placed in a polytetrafluoroethylene (PTFE) porous support with high chemical resistance (Fig. 6). The thickness of developed proprietary membrane (50 μm) is approximately one-fifth of commercial membrane (268 μm), which also decreases its intrinsic resistance. According to continuous operation performance tests that are conducted using the developed membrane, the energy consumption decreases by 8.8% compared to commercial membrane Aciplex-$^{®}$F (Asahi Kasei, Japan) [15].

EVALUATION

1. Environmental Evaluation

ISO defines greenhouse gas projects as "activity or activities that alter the conditions of a greenhouse gas baseline and which cause greenhouse gas emission reductions or greenhouse gas removal enhancements" (ISO14064-2, 2019 [26]). A baseline scenario is when there are no reduction activities being intentionally carried out for greenhouse gas reduction projects and the potential for greenhouse gas generation is the highest. A reduction in greenhouse gases due to reduction projects is defined as the difference in greenhouse gas emissions generated under the baseline scenario without any reduction activities and scenarios with reduction activities.

$$CO_2 \text{ reduction=baseline emissions} - \text{project emissions} - \text{leakage} \quad (3)$$

Although various CO_2 utilization technologies are being introduced, it is often the case that the technologies generate more CO_2 compared to baseline emissions from a net CO_2 emission standpoint. This is because CO_2 is thermodynamically stable, which means subsequent reactions require substantial amounts of energy to convert CO_2 into other products of higher energy levels. As shown by the CO_2-utilizing methanol production technology in Table 1, the methanol production process emits 1.7 tons of CO_2 utilizing 1 ton of CO_2. Considering the baseline emissions of methanol (CO_2 emission by conventional manufacturing which is 0.5-1 ton/ton of MeOH), the overall CO_2 savings turn out to be minor or even negative. As such, even with well-developed technology and economic feasibility, such solutions deviate from the original goal of CO_2 reduction.

In contrast, mineral carbonation technology as developed and analyzed by Lee [20] is shown to lower the net CO_2 emissions significantly compared to conventional processes [20]. For sodium bicarbonate production via saline water electrolysis and carbonation step (Case 1), the net CO_2 emission quantities of the plants are evaluated as 0.65 ton CO_2 for the baseline mineral carbonation plant and 0.51 ton CO_2 for the improved process with the low-energy consumption SWE process. In contrast, the net CO_2 emission index of conventional sodium bicarbonate producing plants is analyzed as 2.74 tons, which is due to the excess energy required for the calcination of limestone (2.5 GJ/tonNa_2CO_3) and other parts of the Solvay process. This indicates that the CO_2 mineralization process of this study is capable of achieving CO_2 reduction of 2.09-

Table 1. LCA case study description and results [3]

CO_2 reuse application (case study)	TCO_2-E emitted in the act of reuse of 1 ton of CO_2	Product/Output
Enhanced Oil Recovery (USA)	0.51	Oil
Bauxite Residue Carbonation (West Australia)	0.53	Residue slurry
Urea Synthesis (China)	2.27	Urea product
Enhanced Geothermal Systems (East Australia)	0.58	Electricity
Enhanced Coal Bed Methane (Iceland)	0.44	Methane
Renewable Methanol (Iceland)	1.71	Methanol
Formic acid production (South Korea)	3.96	Formic acid
CO_2 Concrete Curing (Canada)	2.20	Cured concrete product
Algae Cultivation (East Australia)	0.42	Algae cake
Carbonate mineralization (East Australia)	0.32	Freshwater
Polymers (USA)	5.52	Polypropylene carbonate

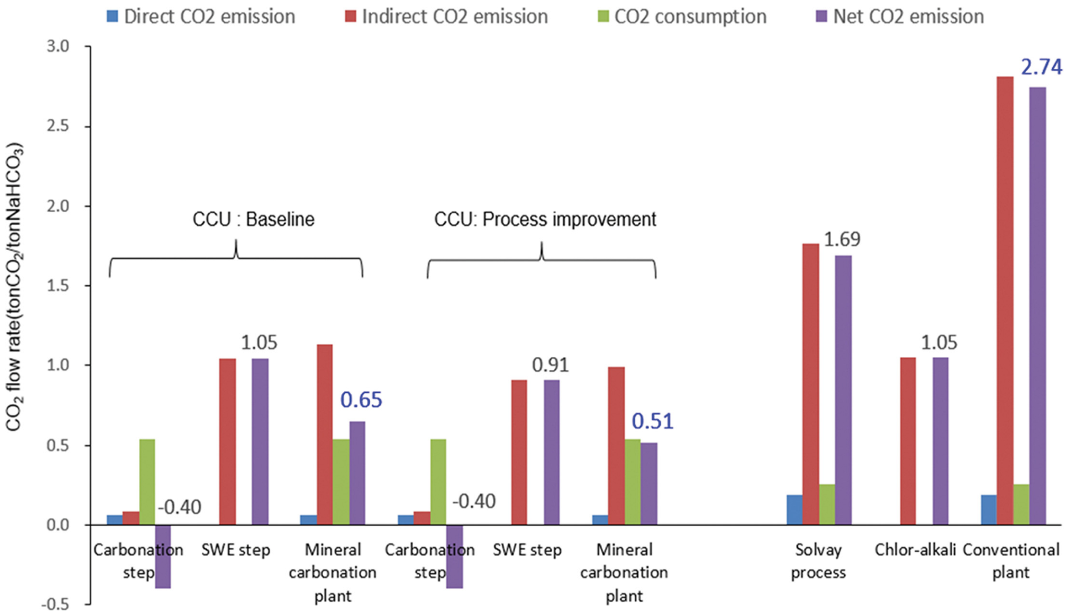


Fig. 7. CO_2 flow in the mineral carbonation plant (Case 1) with respect to the conventional plant (modified from Lee [20]).

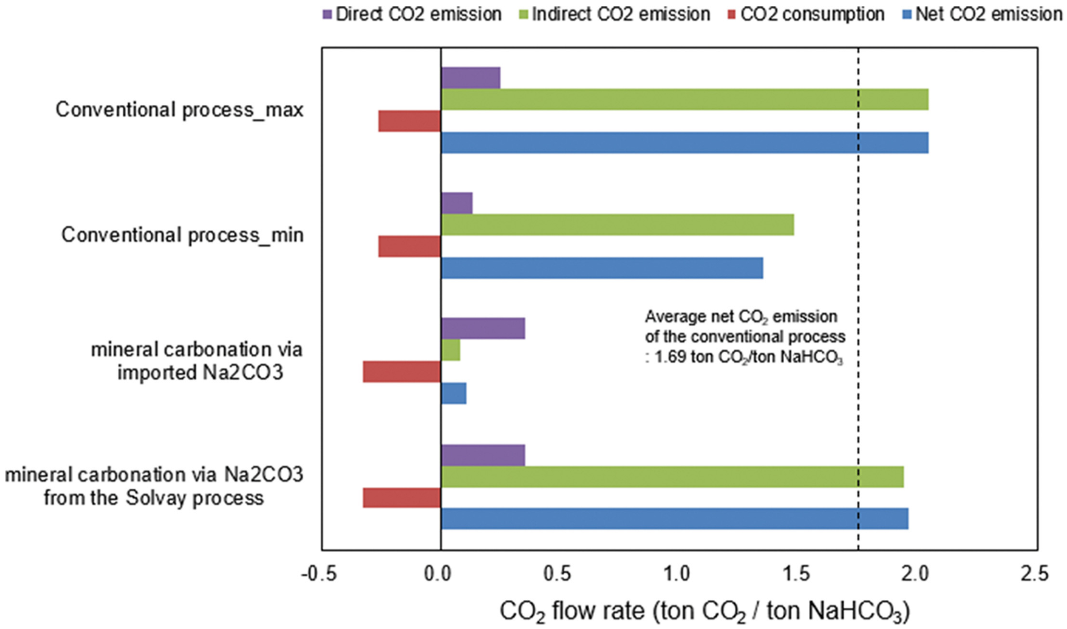


Fig. 8. CO_2 flow in the mineral carbonation plant (Case 2) with respect to the conventional plant (modified from Lee et al. [11]).

2.23 tons per ton of the product compared to conventional processes (refer to Fig. 7).

In the case of the alternative process of obtaining sodium carbonate from external sources to produce sodium bicarbonate (Case 2), net CO_2 emission levels are approximately 0.27 tons higher than the average value of the conventional process for the production of 1 ton of sodium bicarbonate (refer to Fig. 8). However, this number depends on how the raw material is obtained and evaluated, and is subject to change and reinterpretation. For example,

Table 2. Lifecycle CO_2 equivalent of various electricity generation sources [11]

Generation	Lifecycle CO_2 equivalent (kgCO_2/MWh)
Coal (baseline case)	820
Natural gas	480
Korean grid mix	500
Solar photovoltaics	48
Wind offshore	12

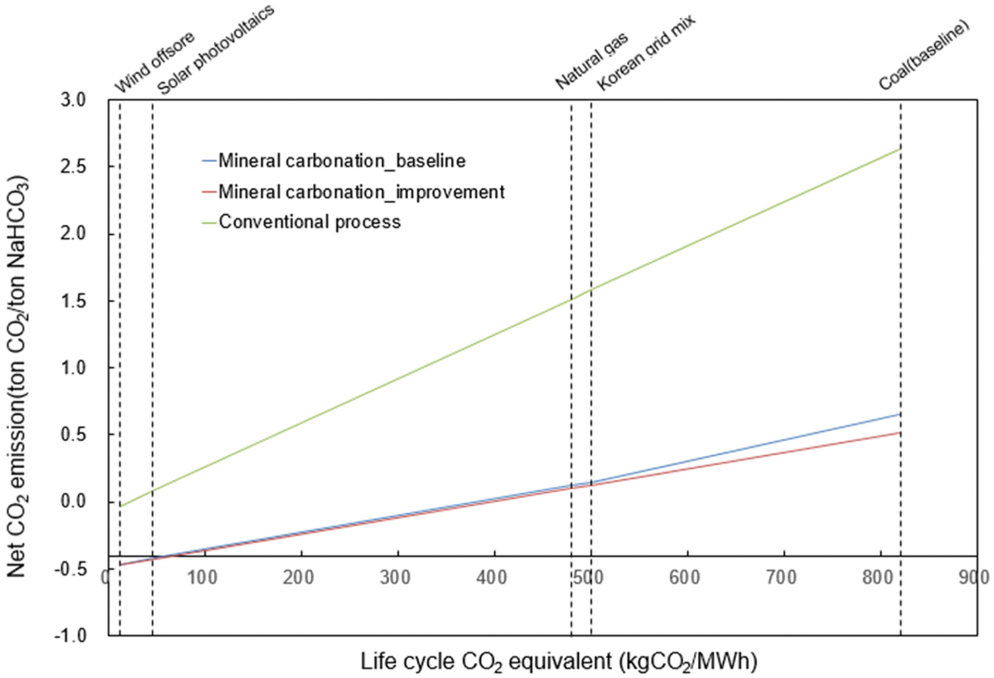


Fig. 9. CO_2 flow in the mineral carbonation plant with respect to various energy resources (Case 1) (modified from Lee [20]).

Table 3. Economic evaluation results of the mineral carbonation process [20]

Specifications	Case	Key results		
		BCR	IRR(%)	NPV(kUSD)
Mineral carbonation plant (Case 1)	Baseline	1.13	10.43	2,351
	Process Improvement	1.16	11.63	2,947

according to the current clean development mechanism (CDM), if the raw material is imported the footprint may not be charged to the country that consumes the material to manufacture another product. As such, the net emission value drops to 0.10 ton per ton of product if the footprint of sodium carbonate is excluded [11].

To investigate the changes according to the carbon emission factors of various electricity sources, changes in the CO_2 reduction potential can also be analyzed for the five cases of electrical energy source, as shown in Table 2.

The evaluation results are shown in Fig. 9. As shown, net CO_2 emission depends linearly on the carbon emission factors for various electricity generation sources [20].

2. Economic Evaluation

According to the economic feasibility analysis results of the aforementioned commercial-scale mineral carbonation plant by Lee [20], the cost of producing 1 ton of sodium bicarbonate for the Case 1 process of this study is 233 USD/t$NaHCO_3$ and 126 USD/t$NaHCO_3$ for the Case 2 process. It is noteworthy that carbon credit from the direct CO_2 utilization within the process (Case 1: 0.6 tonCO_2/t$NaHCO_3$, Case 2: 0.33 ton CO_2/t$NaHCO_3$), only accounts for a small proportion of the total revenue with values of approximately 3.3 (Case 2) - 8.9 USD/t$NaHCO_3$ (Case 1) based on the CO_2 credit figure in 2020. However, this value could increase substantially in the future, with future increases in carbon credit prices and/or with the recognition of the reduction in CO_2 compared to baseline emissions as carbon credits. For example, whereas the Case 1 process uses approximately 0.6 tons of CO_2 to produce 1 ton of sodium bicarbonate, it achieves a reduction in net CO_2 emissions of 2.23 tonCO_2/t$NaHCO_3$ compared to the baseline case. If this reduction is recognized, additional CO_2 credits could be secured.

Furthermore, economic feasibility could be increased through CAPEX and OPEX reductions through improvements to the mineral carbonation process. For example, Lee [20] compared the economic feasibility of the baseline case (case 1) with the case that applied the low-energy SWE process and presented the economic evaluation results shown in Table 3 [20]. For the mineral carbonation plant of Case 1 process, the B/C ratio (Benefit-Cost ratio), IRR (Internal Rate of Return), and NPV (Net Present Value) are 1.13, 10.43% and 2,351 kUSD, respectively. On the other hand, the mineral carbonation plant of Case 1 with the process improvements produces a B/C ratio, IRR, and NPV of 1.63, 11.63% and 2,947 kUSD, which is due to the decrease in O&M costs resulting from the lower electricity consumption in the SWE step.

OPPORTUNITIES

Carbon capture and utilization (CCU) is thought to be in its infancy in terms of technological development, market size, and policy development. As such, the IEA proposed the following key points of consideration for the potential of the CCU market: market scalability, price competitiveness, and climate benefits, which could be expressed as greenhouse gas reduction potential [10].

Among the various CCU technologies, the mineral carbonation technology proposed in this study is evaluated to be a competitive option in terms of net CO_2 emissions. However, compared to technologies that utilize CO_2 to produce fuels, the proposed technology is limited from a market scalability standpoint. For example, if we consider a baseline scenario where the proposed mineral carbonation process is used to produce the entire amount of sodium bicarbonate that is used in Korea (approximately 230,000 tons per year as of 2020), the resulting annual CO_2 reduction is estimated as 138,000 tons. This represents only about 4.6% of the annual CO_2 emissions from a 500 MW coal-fired power plants (approximately 3 million tons).

Therefore, mineral carbonation technologies require further development in terms of techno-economic feasibility as well as the potential to achieve large-scale greenhouse gas reduction. For example, the produced minerals could be used as backfill materials for abandoned mines, or large quantities of them could be used for sequestrating atmospheric CO_2 by increasing ocean alkalinity. The key details of these solutions are as follows.

In the 1980s, proposals were raised regarding the method of storing minerals that are produced by the mineral carbonation process in coal beds and seams or abandoned mines, as well as the application of these minerals as construction materials. To date, several application cases have been reported. For example, the Next Generation Carbon Upcycling Project (NCUP) in Korea is currently developing a technology that uses minerals produced through mineral carbonation as backfill materials. Specifically, calcium carbonate ($CaCO_3$) is produced through mineral carbonation of coal ash (as shown in Eq. (3)-(4)) generated from circulating fluidized bed combustion (CFBC) boilers and is used as controlled low strength materials (CLSM) for mine backfilling [27].

$$CaO+H_2O \rightarrow Ca(OH)_2 \tag{3}$$

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O \tag{4}$$

Coal ash generated from the CFBC boilers is useful for producing calcium carbonate because it is rich in free CaO content (e.g., the free CaO content of fly ash from the CFBC boiler: 1.96-10.8%. [28]) due to the limestone injected during the desulfurization process [29].

Most notably, this research team utilized the product as mine backfill materials to fill underground voids, which allowed the mining of the mine pillars in order to increase the mining capacity.

Furthermore, the dispersion of pressure by the pillars not only increased the lifespan of the mines but also could potentially lead to the securing of CO_2 reduction credits and decrease the cost of processing coal ash [30].

According to an economic feasibility analysis conducted by the group, which also included the cost of constructing a factory that could produce the backfill material for land subsidence prevention at an abandoned mine with an area of 30,000 m^3, the project was evaluated to be economically feasible with a B/C ratio of 1.1-1.5 [30]. In Korea, there are more than 5,000 mines, among which more than 2,000 are estimated to be with underground cavities [29]. Based on this estimate, the scalability of mineral carbonation-based mine backfilling technology is very promising.

An alternative solution involves the application of the geoengineering option to increase the alkalinity of the ocean, thereby improving the ocean storage of the atmospheric CO_2. This concept was first proposed by Kheshgi [31]. Some of the naturally occurring minerals and anthropogenically produced minerals would readily dissolve in the sea water and sequester CO_2. As an example, dissolution products of soda ash (Na_2CO_3) result in two mole equivalents of alkalinity per mole of Na_2CO_3. In net, there would be 0.79 mole of CO_2 uptake per mole Na_2CO_3 dissolved as shown in Eq. (5) [32]).

$$Na_2CO_3+0.79\ CO_2+0.79\ H_2O \rightarrow 2\ Na^+ +1.62\ HCO_3^- +0.17\ CO_3^{2-} \quad (5)$$

Regarding this, a range of techniques have been proposed. Rau suggested the dissolution of carbonate materials (e.g., $CaCO_3$) exposed to flue gas CO_2 and sea water as a means for ocean alkalinity enhancement known as accelerated weathering of limestone (AWL) [31]. Reports have claimed that this technology has the potential to reduce the total CO_2 emissions of major emission sources in the U.S. by approximately 10-20% [33].

In addition, Lee et al., proposed a technology in which CaO is first reacted with excess sea water for conversion into $Mg(OH)_2$, which is then treated with CO_2 to maximize the concentration of dissolved inorganic carbon. While the AWL process proposed by Rau et al. has a CO_2 uptake of just 0.1 kg per ton of sea water, this technology can store about 13 kg of CO_2 per ton of sea water [34]. Through the application of the technology, the concentration of dissolved inorganic carbon is maximized, and when discharged below the mixed layer of the coast, the water mass sinks due to the density differences, minimizing the release of CO_2 into the atmosphere, thus enabling stable CO_2 storage [34].

However, the substances discharged by such ocean-based mineral emission technologies must be approved by the regulatory agency according to the International Maritime Organization (IMO). Furthermore, the technology must be approved as greenhouse gas reduction measure by the Clean Development Mechanism (CDM). As such, additional research will be required to resolve these issues.

However, for the mineral carbonation-based large-scale CO_2 processing technology proposed in this study to achieve similar levels of CO_2 processing as CCS (carbon capture and storage) plants – processing several hundreds of thousands of CO_2 each year – it will be imperative to confirm the techno-economic feasibility of the technology and achieve lower or similar CO_2 avoidance cost as the CCS technology. According to some cost analysis studies of key CCS technologies, the avoidance cost per ton of CO_2 due to the implementation of CCS technology is calculated as approximately 44-86 USD/tCO_2 (excluding CO_2 transport and storage costs) [35,36]. For the mineral carbonation technology of this study, the unit production cost for the production of 1 ton of sodium bicarbonate with the Case 1 process under baseline conditions is evaluated as approximately 233 USD/t$NaHCO_3$. This value becomes 390 USD/tCO_2 when converted to cost per ton of CO_2, and thus it is not a feasible substitute for CCS from a cost standpoint. Therefore, for the proposed mineral carbonation technology to be used for large-scale greenhouse gas reduction purposes via ocean or underground storage, it will be imperative to lower the mineral carbonation technology by an order of magnitude or so. However, as a short-term solution, techno-economic feasibility could be achieved under certain circumstances by utilizing the minerals produced via mineral carbonation as abandoned mine backfill materials. Additional research is required to explore methodology application conditions, the designation of project boundaries, baseline methodologies, reduction calculation formulas, and monitoring methodologies.

CONCLUSIONS

Among the various CO_2 utilization solutions for reducing greenhouse gases, mineral carbonation has high potential to be deployed at large scale while meeting the requisite techno-economic and environmental feasibility. If limited to the currently existing market, however, the potential reduction amount would not be that significant. For example, even if mineral carbonation technology is used to produce the entire amount of sodium bicarbonate imported into Korea in 2020 (approximately 230,000 tons), the resulting reduction in CO_2 emissions compared to a baseline plant would equate to only about 510,000 tons, a meager number compared to the targeted total reduction amount. Looking ahead, the following major implications can be drawn. From a developmental perspective, research should be undertaken to develop various mineral carbonation technologies that can produce other products, such as calcium carbonate ($CaCO_3$) or magnesium carbonate ($MgCO_3$), to expand the application of mineral carbonation technology for large-scale greenhouse gas reduction. Furthermore, processes should be improved to reduce the involved costs, as much as by an order of magnitude. From a policy standpoint, various business models involving mineral carbonation technology should be developed to encourage early participation into the CCU market. Policy-based support will also be necessary, such as the development of greenhouse gas project methodologies to secure credits.

ACKNOWLEDGEMENT

This works was supported by the Carbon-to-X (C2X) R&D project (project no. 2020M3H7A1096361) sponsored by the National Research Foundation (NRF) of the Ministry of Science and ICT.

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