

Scientific and Engineering Progress in CO₂ Mineralization Using Industrial Waste and Natural Minerals

Heping Xie^{1,2*}, Hairong Yue³, Jiahua Zhu³, Bin Liang^{1,3}, Chun Li³, Yufei Wang^{1,2}, Lingzhi Xie¹, Xiangge Zhou⁴

ABSTRACT The issues of reducing CO₂ levels in the atmosphere, sustainably utilizing natural mineral resources, and dealing with industrial waste offer challenging opportunities for sustainable development in energy and the environment. The latest advances in CO₂ mineralization technology involving natural minerals and industrial waste are summarized in this paper, with great emphasis on the advancement of fundamental science, economic evaluation, and engineering applications. We discuss several leading large-scale CO₂ mineralization methodologies from a technical and engineering-science perspective. For each technology option, we give an overview of the technical parameters, reaction pathway, reactivity, procedural scheme, and laboratorial and pilot devices. Furthermore, we present a discussion of each technology based on experimental results and the literature. Finally, current gaps in knowledge are identified in the conclusion, and an overview of the challenges and opportunities for future research in this field is provided.

KEYWORDS CO₂ mineralization, natural mineral, industrial waste, science and engineering

1 Introduction

Carbon dioxide (CO₂) is the primary greenhouse gas emitted by human activities [1]. According to the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report of Climate Change 2013 (AR5), the atmospheric concentration of CO₂ rose to $3.91 \times 10^8 \mu\text{mol} \cdot \text{mol}^{-1}$ in 2011—more than 40% higher than the pre-industrial level. A significant share of the total CO₂ sequestration required for climate change mitigation (about 25% of the total in International Energy Agency (IEA) and IPCC scenarios) is expected to result from carbon capture and storage (CCS). CCS has been intensively inves-

tigated in the past couple of decades [2–4]. Potential storage methods include geological storage (storage in oil and gas fields, deep saline formations, or in un-minable coal beds) and ocean storage [5–9]. Current CCS methods are still far from commercialization, due to their high cost and high energy consumption. The storage of CO₂ in the subsurface may involve risks such as leakage, contamination of underground water, or even geological disasters [10, 11].

CO₂ capture and utilization (CCU) methodology is currently more attractive than CCS as the currently available technology for climate change mitigation. Because CCU produces high-value chemical products, it can be used to reduce CO₂ emissions with relatively low overall cost and energy expenditure. However, CO₂ is considered one of the most stable chemical compounds in the carbon family. Although many publications and much research concern the utilization of CO₂ to produce chemicals, mineralization is one of the most efficient methodologies, since it is thermodynamically favorable (Figure 1) [12]. Other methods, such as the conversion of CO₂ to fuel and organic chemicals, require more energy than they produce and theoretically generate more CO₂.

CO₂ mineralization can store CO₂ in a more stable form for thousands of years via reaction with alkaline earth oxides to form carbonates. Some minerals, such as those in volcanic ash and industrial waste, contain basic alkaline earth compounds, which can be reacted with CO₂. In recent years, natural minerals such as serpentine and olivine have been extensively investigated for their ability to fix CO₂ by mineralization [13], and MgO- or CaO-containing silicate ores have been thermally activated and reacted with CO₂. However, activation and mineralization by these methods require a high energy input and have a high cost, and these factors are the major obstacles for the commercialization of these technologies.

¹ Center of CCUS and CO₂ Mineralization and Utilization, Sichuan University, Chengdu 610065, China; ² College of Water Resources & Hydropower, Sichuan University, Chengdu 610065, China; ³ College of Chemical Engineering, Sichuan University, Chengdu 610065, China; ⁴ School of Chemistry, Sichuan University, Chengdu 610065, China

* Correspondence author. E-mail: Xiehp@scu.edu.cn

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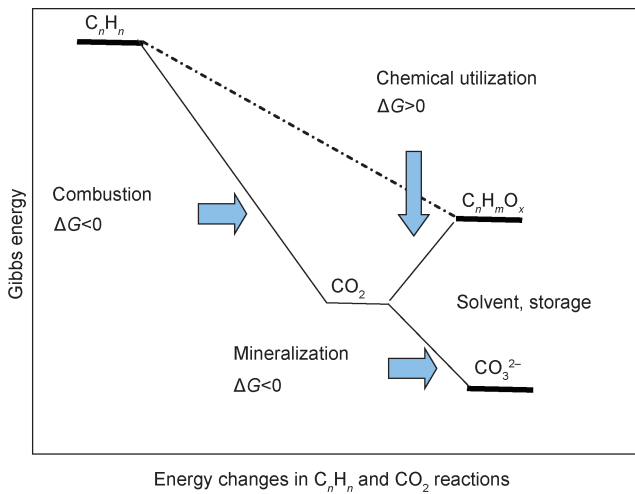


Figure 1. Energy changes in CO_2 reactions.

Sichuan University has developed a series of technologies to sequester and utilize CO_2 by mineralization. These technologies have low energy input and are economically viable. Theoretically, the carbonation of CO_2 with CaO- or MgO-containing minerals releases energy, which can be recovered. In addition, this process utilizes CO_2 to produce valuable chemicals. Energy can be recovered during the mineralization of CO_2 , and used to produce desired chemicals using their chemical potentials.

Figure 2 shows material fluxes and process steps for CO_2 mineralization. This process is coupled with industrial waste conversion, mineral processing, and energy recovery. Phosphogypsum (PG) is a large-scale industrial waste from the production of wet phosphoric acid [14]. The phosphoric acid industry in China deposits about 5×10^7 t of PG every year, resulting in a severe environmental challenge. CO_2 mineralization was used to convert the PG to $CaCO_3$ and $(NH_4)_2SO_4$, which can be used as a construction material and a fertilizer, respectively. Steel slag containing CaO or portlandite ($Ca(OH)_2$) is an industrial waste from steel plants. This material is a toxic deposit due to the leachable CaO. Steel slag is used to produce construction material, and can be used to generate power by CO_2 mineralization (converting CaO to $CaCO_3$). CO_2 mineralization was also applied to potassium extraction from K-feldspar ore. In this process, the K^+ ions were first exchanged with the Ca^{2+} ions and then the Ca^{2+} ions were fixed by reacting it with CO_2 [15]. In addition, an electrolytic method was proposed to intensify the mineralization of CO_2 with earth-abundant natural magnesium chloride from salt lakes in order to recover valuable magnesium carbonate. This method can potentially mineralize as much as several billion tons of CO_2 [16].

In this work, we describe several representative CO_2 -mineralization routes in which natural minerals and industrial waste were used as reaction feedstock/components to produce useful chemicals. We summarize various intensification methodologies, such as the electrochemical method [18], thermal activation [15, 19], and the use of additives to enhance the CO_2 -mineralization reactions [16], with emphasis on scientific progress, engineering

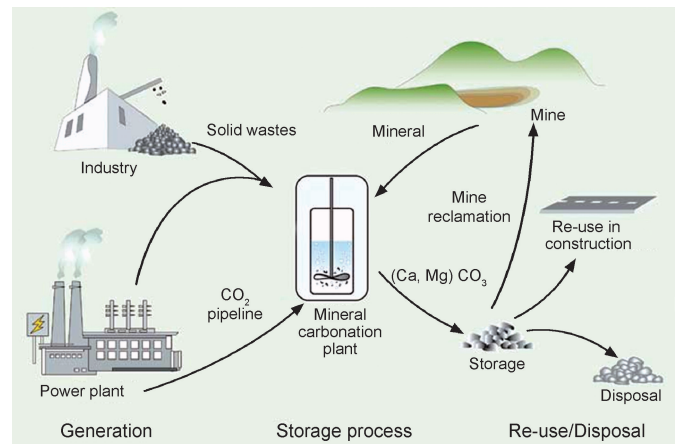


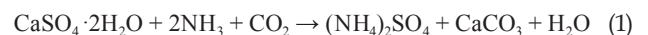
Figure 2. Material fluxes and process steps associated with the CO_2 mineralization of natural rocks or industrial residues. (Adapted with permission from Ref. [17]. Copyright 2005 Cambridge University Press)

applications, and an economic evaluation of these alternative technologies.

2 CO_2 mineralization using industrial waste

2.1 CO_2 mineralization with PG for fertilizer production

PG is a waste deposit from the wet-process phosphoric acid industry. China is the largest manufacturer of phosphorous fertilizer and produces 5×10^7 t PG per year [14]. However, only 15% of this material is used as a set retarder of cement or to make gypsum plaster and bricks [14, 20]. The rest—a huge quantity of PG—is mostly discarded in large stockpiles without proper disposal, resulting in land occupation and environmental pollution, particularly to water resources. PG can be converted into a nitrogen fertilizer through the following chemical reaction, which can be used in CCU:



The CO_2 contained in flue gas was captured and converted by ammonium-saturated PG slurry to produce $(NH_4)_2SO_4$ and $CaCO_3$ as per Eq. (1). As mentioned earlier, $(NH_4)_2SO_4$ is a fertilizer containing both the nutritious elements for plants, nitrogen (N) and sulfur (S), and $CaCO_3$ is a feedstock of cement. This new mineralization approach converted an industrial waste and CO_2 into two useful products. It is a thermody-

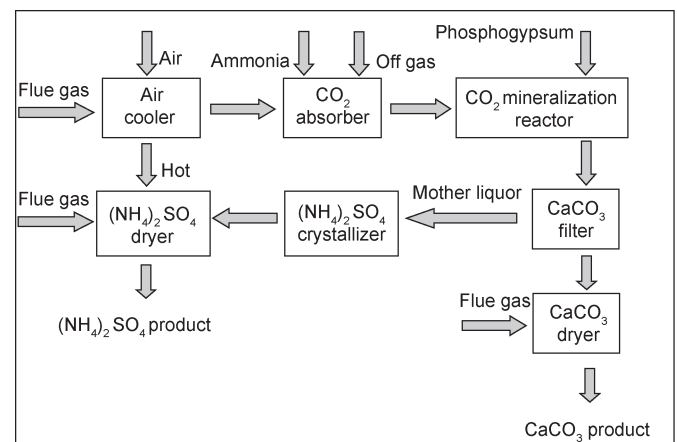


Figure 3. Schematic pilot process for the mineralization of CO_2 using PG.

namically favorable process [12]. Figure 3 shows a schematic for the pilot process for CO₂ mineralization using PG.

In this process, flue gas was scrubbed with ammonium-saturated PG slurry, and the CO₂ contained in the flue gas was captured for conversion into CaCO₃ and NH₄HCO₃. 75% of the CO₂ in the scrubber was converted as the flue gas, and the flue gas was scrubbed with acidic PG slurry to reduce the ammonium slip. The ammonium concentration of the exhaust gas was controlled to less than $1.0 \times 10^{-7} \mu\text{mol}\cdot\text{mol}^{-1}$, which is below the Chinese Emission Controlling Standard (GB 14554—93). The CO₂-rich slurry was then pumped into a three-phase reactor, where it was further reacted with fresh PG to form CaCO₃ and (NH₄)₂SO₄. The formed CaCO₃ in the reactor was filtered, washed, and dried to serve as a building material. Meanwhile, the (NH₄)₂SO₄ in solution was concentrated in a three-effect evaporation system (see the process flow diagram in Figure 4). (NH₄)₂SO₄ was then crystallized and separated as a fertilizer product.

A 100 Nm³·h⁻¹ pilot-scale device was successfully operated at the Puguang natural gas purification plant (the pilot device is shown in Figure 5). The main operation parameters were as follows: The flue gas was cooled with circulating water to a temperature of 50 °C and absorbed with ammonia to reduce the concentration of CO₂ from 15% to 4.5%. The absorption liquid was mineralized with PG (conversion of 90%) at 75 °C

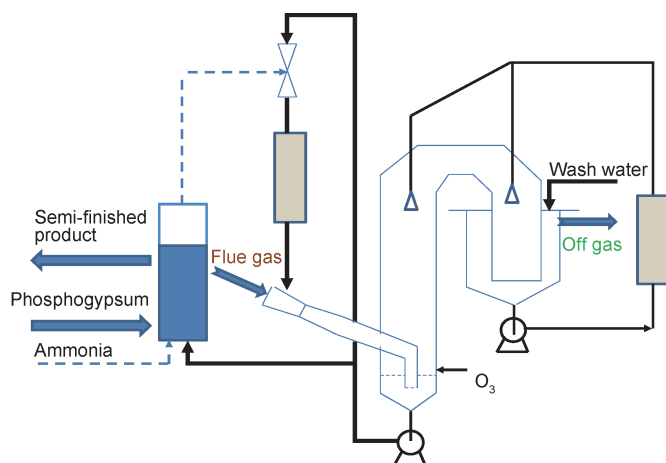


Figure 4. Illustration of the “one-step” method for the mineralization of CO₂ in flue gas using PG.



Figure 5. The pilot device at Puguang for the mineralization of flue-gas CO₂ using PG.

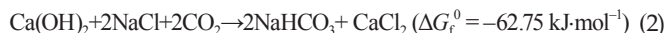
for 6 h to produce CaCO₃, which was washed with water, filtered, and then dried using flue gas at 250 °C. Subsequently, the residual solution was evaporated, achieving a 45% concentration of (NH₄)₂SO₄, which was then crystallized to produce a granular (NH₄)₂SO₄ fertilizer. The evaluated income for the conversion per ton of CO₂ is about \$17 USD [12].

This process integrated CO₂ capture, PG conversion, and fertilizer production. It effectively utilized mineralization as a means of waste processing, and it is both environmental friendly and economically viable. The pilot project has introduced the following technological advances:

- (1) The direct capture of CO₂ from flue gas using mineralization;
- (2) A new method of producing valuable (NH₄)₂SO₄ fertilizer;
- (3) The use of industrial waste, PG, as a raw material;
- (4) A economical way to integrate CCU as part of a routine process.

2.2 Mineralization with portlandite for power generation

Portlandite is one of the main by-products in industrial alkaline wastes, including carbide slag, steel slag, paper mill waste, kiln dust, and coal fly ashes. Portlandite can easily be reacted with CO₂ to yield CaCO₃, which is naturally abundant but cheap. On the other hand, sodium bicarbonate (NaHCO₃), a rare chemical compound in nature, is an important industrial feedstock for the production of soda ash, baking soda, magnesium carbonate, and so on. With this in mind, NaCl was introduced into this reaction in order to mineralize portlandite to obtain NaHCO₃ instead of CaCO₃ as the end product. The following carbonation reaction was conceived as a prototype reaction:



The benefit of this reaction is that it uses two industrial pollutants (CO₂ and Ca(OH)₂) to produce two valuable products (NaHCO₃ and energy) concomitantly. This carbonation reaction is theoretically an energy-releasing process, which converts CO₂ ($\Delta G_f^0 = -394 \text{ kJ}\cdot\text{mol}^{-1}$) into CO₃²⁻ ($\Delta G_f^0 = -528 \text{ kJ}\cdot\text{mol}^{-1}$) [21]. It is essential to use an approach that efficiently harnesses this energy.

Recently, we used reaction (2) to realize an energy-output strategy by harvesting the released energy from the reaction in the form of electricity via a CO₂-mineralized fuel-cell (CMFC) system (Figure 6) [22]. This CMFC system consists of a hydrogen-diffusion anode coated with a Pt/C catalyst, a conventional Pt cathode, three chambers separated by an anion-exchange membrane (AEM) and a cation-exchange membrane (CEM), and three buffer tanks to supply the reactants to the individual chambers. The cathode and anode are connected through an external circuit.

The key factor for the generation of electricity from this carbonation reaction is to promote electron transfer, since the acid-base carbonation reaction entails no electron-transfer process, which is required to generate electricity directly. Because the electricity can be generated in an opposite direction, we used membrane electrolysis to produce acids and bases from salts using electricity. The reversed electrolysis

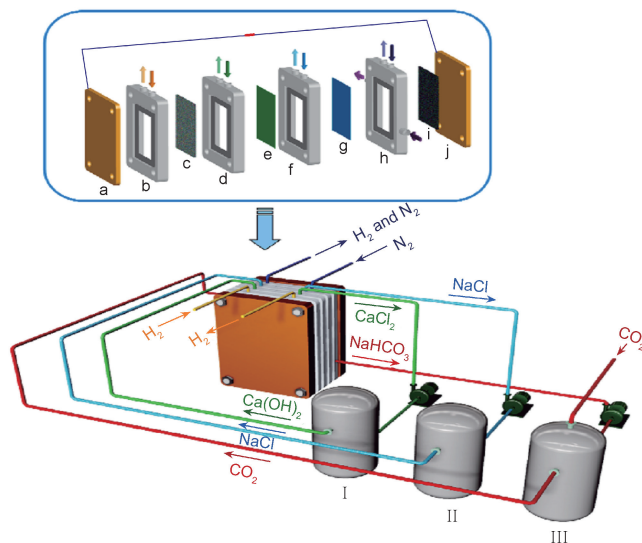


Figure 6. Schematic diagram of the CMFC system and the inner structure of a single CMFC. (a) Anode current collector; (b) anode gas chamber frame; (c) hydrogen-diffusion anode; (d) anode liquid chamber frame; (e) AEM; (f) salt chamber frame; (g) CEM; (h) cathode chamber frame; (i) cathode; (j) cathode current collector. (I) Anode buffer tank. (II) Salt buffer tank. (III) Cathode buffer tank. (Reproduced with permission from Ref. [22]. Copyright 2014 Science China Press)

process in the CO₂-mineralized fuel cell was chosen to enhance the CO₂ utilization.

In this system, the highly valuable product, industrial NaHCO₃, was produced concomitantly during electricity generation. The highest power density of this system was 5.5 W·m⁻², higher than that of many microbial fuel cells. The maximum open-circuit voltage was 0.452 V. Moreover, this system was demonstrated to be viable for low concentrations of CO₂ (10%) and for other carbonation processes. Therefore, this new strategy is an energy-generating and environmentally friendly approach to utilize CO₂, and could be used as a supplement to current CO₂-emission scenarios.

3 CO₂ mineralization using natural minerals

3.1 Electrolytic CO₂ mineralization with MgCl₂ to produce MgCO₃

Magnesium chloride (MgCl₂) is an abundant natural resource that is widely distributed in seawater, salt lakes, and ore minerals. The average concentration of magnesium ions in seawater is about 0.13%, which can potentially mineralize as much as 3.34 × 10⁹ t of CO₂ (111 years' worth of global CO₂ emissions). The prospective reserves of magnesium chloride salt in the four major saline lakes in China are estimated to be as high as several billion tons.

An electrolytic method was proposed to intensify the mineralization reaction of flue-gas CO₂ with magnesium chloride (0.1 mol·L⁻¹) to recover valuable magnesium carbonate (MgCO₃) (Figure 7) [18]. First, magnesium chloride was converted into magnesium hydroxide and hydrochloric acid by electrolysis. Next, the resulting magnesium hydroxide was reacted with CO₂ to produce a magnesium bicarbonate solution. The magnesium carbonate product was finally obtained by calcination of the Mg(HCO₃)₂.

In the electrolysis cell, H₂ is oxidized to form H⁺ ions with the help of a special nickel-foil anode. The H⁺ ions react with

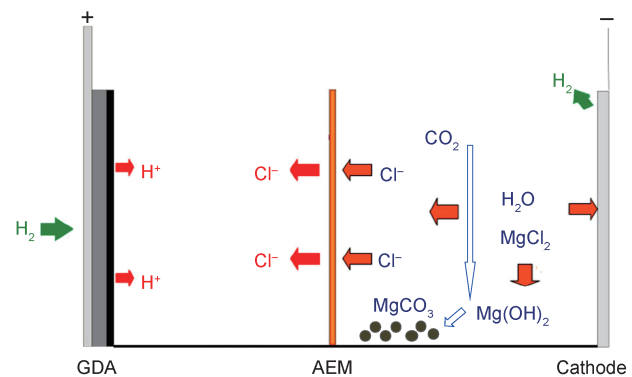


Figure 7. Illustration of an electrolysis cell and the process for the conversion of magnesium chloride to magnesium carbonate. (Reproduced with permission from Ref. [18]. Copyright 2014 Springer)

the Cl⁻ ions diffusing through the AEM membrane from the cathode side of the cell to form HCl. Water is electrolyzed on the cathode and transformed into H₂, which is recycled to the anode. CO₂ mineralization occurs on the cathode side, where the Mg(OH)₂ reacts with CO₂ to form MgCO₃.

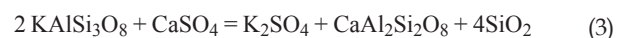
Both pure and diluted CO₂ gas can be used directly in this mineralization process. CO₂ concentration can be reduced to below 20%, which is a normal concentration for industrial flue gas. This mineralization method avoids the high-energy-consuming process of CO₂ purification and greatly reduces the energy consumption of CO₂ mineralization. About 871 kWh (about \$70 USD according to the price of electricity on March 16, 2015) of electricity at a cell voltage of 0.7 V is required to mineralize 1 t of CO₂ and produce 3.16 t of MgCO₃. According to the market price of magnesium carbonate (\$480 USD·t⁻¹, according to the price from the CHEMinfo website (<http://www.cheminfo.cn/>) on March 10, 2015), CO₂ mineralization by means of magnesium chloride is an efficient (net effect of 50%–70%) and economical way to reduce CO₂ emissions.

3.2 CO₂ mineralization with natural K-feldspar to produce potash fertilizer

Soluble potassium resources are scarce in many parts of the world (< 1% of global potassium storage), including China. On the other hand, K-feldspar (KAlSi₃O₈) is an abundant and stable insoluble potash ore with reserves of more than 1.0 × 10¹⁰ t; therefore, the production of potash fertilizer from K-feldspar is crucial in order to reduce the consumption of soluble potassium resources [23].

3.2.1 K-feldspar-phosphogypsum co-activation and mineralization process

A coupling process (Figure 8) comprising the activation of K-feldspar with PG at high temperature was investigated as a method of extracting K₂SO₄ and mineralizing CO₂. The main reactions in this activation and mineralization process are:



This process extracts potassium from natural K-feldspar ore and simultaneously deals with PG waste [15]. The K-extraction and CO₂-mineralization rates were significantly affected by activation parameters. Under specific activating

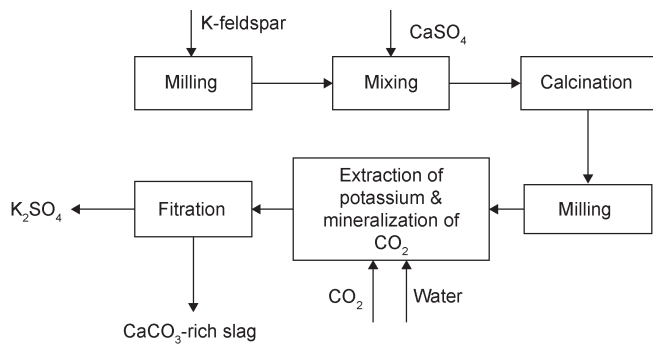


Figure 8. Schematic diagram of the thermal activation of K-feldspar and PG for CO₂ mineralization. (Reproduced with permission from Ref. [15]. Copyright 2014 American Chemical Society)

conditions—1200 °C for 2 h with an ore/CaSO₄ mass ratio of 1 : 2, and mineralizing at 100 °C with an initial CO₂ pressure of 4 MPa—the K-extraction and CO₂-mineralization yields exceeded 87% and 7.7%, respectively.

This potassium-extraction process follows an ion exchange reaction of Ca²⁺ from CaSO₄ with K⁺ from K-feldspar, in which CO₂ reacts with CaAl₂Si₂O₈. The K⁺ ions exchange with Ca²⁺ ions to form K₂SO₄, and the remaining molecular skeleton after this ion exchange forms an electrical neutral phase CaAl₂Si₂O₈. The CaAl₂Si₂O₈ is then dissolved by H⁺, which results from the ionization of H₂CO₃, and Ca²⁺ is released. Finally, the Ca²⁺ is reacted with HCO₃⁻ to form CaCO₃ [24].

The reaction activation temperature of 1200 °C is much lower than that of the decomposition temperature of K-feldspar (1500 °C), which significantly reduces the energy consumption of this process. The reaction temperature is expected to be in the range between the particle surface melting (half-melting) and the melting point, in order to maintain the fluidity of the reactants in commercial production. The co-activation of K-feldspar with PG facilitates the formation of a molten phase in the calcination reaction, which enhances the mass transfer and reaction rate and reduces the reaction temperature. Therefore, this process is a viable alternative approach for the application of natural K-feldspar and industrial solid waste, with a relatively low energy consumption.

To evaluate the economic efficiency of this co-activation and mineralization process, the primary balance of the materials and energy needed for the mineralization of one ton of CO₂ was calculated based on the experimental data (Figure 9, *y* denotes the amount of CO₂ mineralized by K-feldspar). The results showed that the primary cost is the input of ore and the energy consumption, while the primary income is the production of K₂SO₄. According to the CHEMinfo website, the present market value of K₂SO₄ is about \$600 USD · t⁻¹, so the net profit for this mineralization technology is \$200 USD · t⁻¹ of CO₂. Therefore, this coupled activation and mineralization process is an economically feasible method to reduce CO₂ emissions.

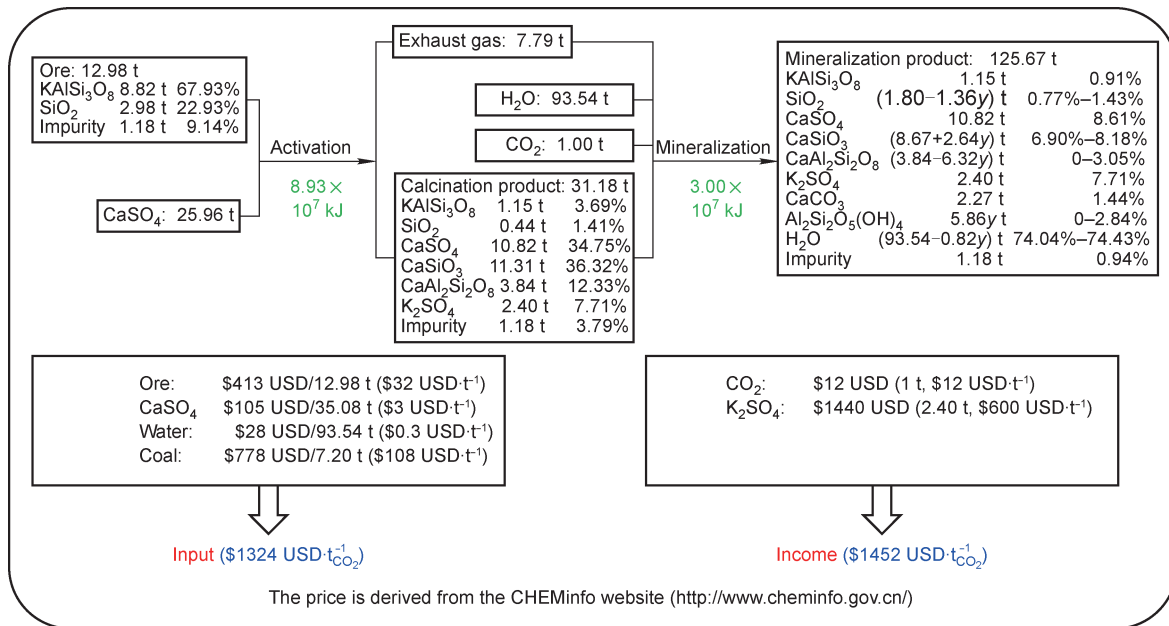


Figure 9. An economic analysis of the K-feldspar-phosphogypsum co-activation and mineralization process, based on the mineralization of 1 t of CO₂.

3.2.2 K-feldspar-CaCl₂ co-activation and mineralization process

In order to further reduce the activation temperature and the energy consumption, a compound with a lower melting point, CaCl₂ (ca. 782 °C), was used as the promoter for the thermal activation of K-feldspar and mineralization of CO₂ to extract soluble potassium [19]. CaCl₂ is an industrial waste with limited practical use, deposited by the Solvay process of soda-ash production. Therefore, this new process is environ-

mentally friendly, due to its consumption of the CaCl₂ waste.

Activation temperature, reaction time, and the K-feldspar/CaCl₂ ratio are the important factors in this K-extraction and CO₂-mineralization system. A fairly high K-extraction ratio (over 90%) and CO₂-mineralization ratio (0.12 g_{CO₂}/g_{K-feldspar}) were obtained at an activation temperature of 908.3 °C—a much lower temperature than that of the PG co-activation system. As shown in the reaction model (Figure 10) the use of an appropriate temperature and CaCl₂ content fa-

cilitates the exchange of Ca^{2+} with K^+ and the formation of $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{Ca}_3\text{Si}_3\text{O}_9$, and CaSiO_3 , due to the hydrolysis of CaCl_2 and the collapse of the K-feldspar framework. CO_2 is fixed by reactions with $\text{Ca}_3\text{Si}_3\text{O}_9$ and CaSiO_3 , resulting in the mineralization product, CaCO_3 . The results also showed that the pH of the solution was a significant factor for CO_2 mineralization. Low pH accelerates the leach of Ca^{2+} but restrains the absorption of CO_2 , while high pH increases the concentration of CO_3^{2-} . Therefore, an appropriate pH, CO_3^{2-} concentration, and Ca^{2+} concentration are key factors for the precipitation of CaCO_3 in this mineralization reaction.

The results indicate that this alternative technology utilizing insoluble K-

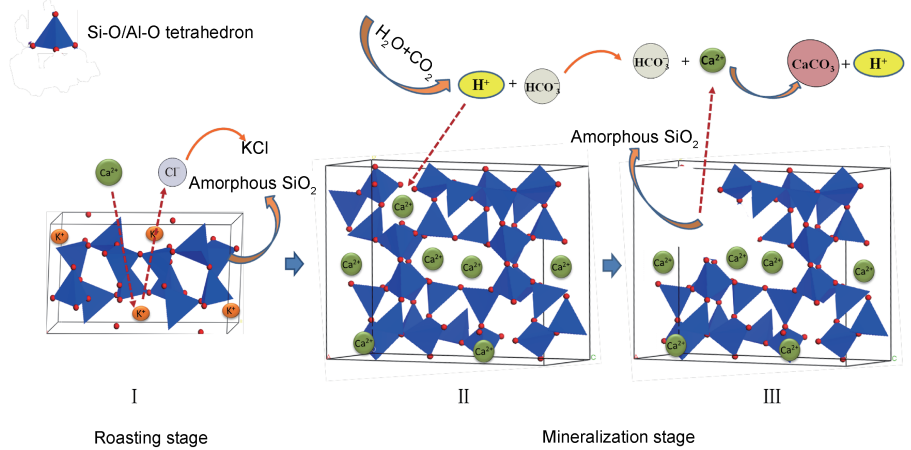
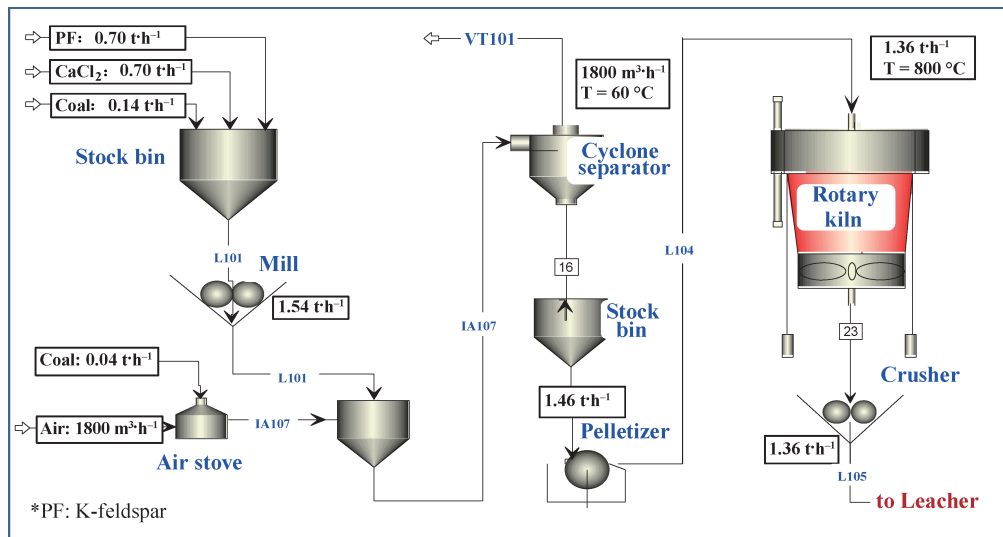
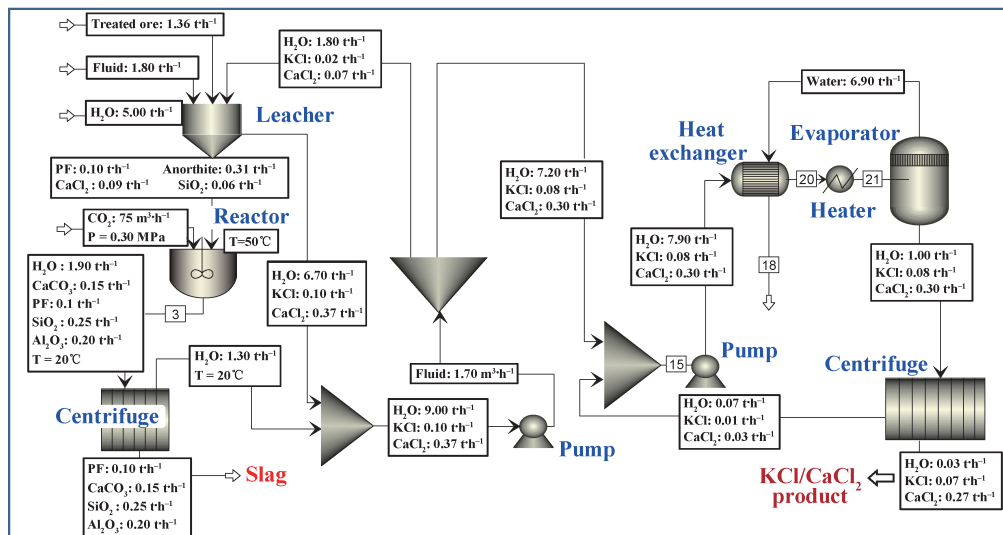


Figure 10. Schematic diagram of the mechanism of the activation and mineralization stage. (Reproduced with permission from Ref. [19]. Copyright 2014 American Chemical Society)

feldspar, CaCl_2 industrial waste, and CO_2 mineralization is a promising process with the potential to produce potash fertilizer and reduce CO_2 emissions.



(a)



(b)

Figure 11. The technological process for mineralization of 500 t a^{-1} CO_2 with K-feldspar. (a) Pretreatment and activation section; (b) leaching and mineralization section.

3.2.3 The technological process for mineralization of 500 t·a⁻¹ CO₂ with K-feldspar

To evaluate the potential of this mineralization technology for industrial application, a scale-up pilot plant was designed on the basis of the experimental results with a mineralization ability of 500 t of CO₂ per year. Figure 11 shows the principal process.

This process involves four main steps: pretreatment, activation, leaching, and mineralization. K-feldspar, CaCl₂, and coal were first mixed and milled to a particle size below 150 μm, and then shaped and activated at an appropriate temperature (e.g., 800–900 °C) in order to exchange K⁺ with Ca²⁺ ions from anhydrous calcium chloride. The activated slag was leached with hot deionized water (at a temperature of ca. 80 °C) to extract potassium, and then CO₂ was bubbled in the suspension of the residue at 0.3 MPa and 50 °C for 2 h, for mineralization of CO₂ to occur. The slag was centrifuged and filtered after mineralization, and the filtrate and washing solutions were concentrated to obtain the KCl and CaCl₂ products. This pilot plant has been designed and is currently under construction. At this plant, the technological parameters of the process will

be investigated systematically, to develop further understanding and to pave the way for industrial applications.

4 Conclusions and future scope

In recent years, Sichuan University has made remarkable progress in the development of CO₂-mineralization technologies with high efficiency, low cost, and low energy consumption. We summarize the reactions, relative reactivity, and economic viability for the representative CO₂-mineralization technologies in Table 1. Based on the cost analysis of these performed processes, the presented CCU techniques exhibit excellent economic viability and potential for application. In this context, we anticipate that research in CO₂ mineralization will become even more widespread in the near future, particularly for the coupled technologies of natural resource exploitation and industrial waste treatment. The technologies described in this paper have the potential to process large quantities of CO₂ and industrial waste, while producing high-value chemicals.

CO₂ mineralization using natural minerals and industrial

Table 1. Comparison of the reactions, relative reactivity and the economic viability for the processes.

	Reactions	K-extraction ratio (%)	CO ₂ mineralization	Economic viability
Phosphogypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NH}_3 + \text{CO}_2 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3 + \text{H}_2\text{O}$	—	75%	Income \$17 USD · t _{CO₂} ⁻¹
K-feldspar & Phosphogypsum	$\text{KAlSi}_3\text{O}_8 + \text{CaSO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{SiO}_2$ $\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	87%	7.7%	Income \$200 USD · t _{CO₂} ⁻¹
K-feldspar & industrial CaCl ₂	$2\text{KAlSi}_3\text{O}_8 + \text{CaCl}_2 \rightarrow 2\text{KCl} + \text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{SiO}_2$ $\text{CaCl}_2(\text{s or l}) + \text{SiO}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CaSiO}_3(\text{s}) + 2\text{HCl}$ $\text{CaSiO}_3(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{SiO}_2(\text{s})$	Over 90%	0.12 g _{CO₂} /g _{K-feldspar}	—
Magnesium chloride	$\text{MgCl}_2 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{MgCO}_3 + 2\text{HCl}$ (In electrolysis cell)	—	—	Income \$70 USD · t _{CO₂} ⁻¹
Portlandite	$\text{Ca}(\text{OH})_2 + 2\text{NaCl} + 2\text{CO}_2 \rightarrow \text{NaHCO}_3 + \text{CaCl}_2$	—	—	5.5 W·m ⁻²

Notes (components of the natural K-feldspar and the industrial wastes)

Phosphogypsum: CaO (28.98%), (9.84%), Al₂O₃ (0.08%), Fe₂O₃ (0.08%), MgO (0.05%), SO₃ (41.5%), Na₂O (0.05%), K₂O (0.97%), F (0.14%), P₂O₅ (0.79%).

K-feldspar: K₂O (8.29%), Al₂O₃ (18.25%), SiO₂ (58.52%), CaO (1.78%), Na₂O (2.46%), Fe₂O₃ (2.23%), others (8.47%).

Portlandite: CaO (68.99%), (2.84%), Al₂O₃ (2.16%), Fe₂O₃ (0.15%), MgO (0.12%), SO₃ (0.76%), Na₂O (0.03%), H₂O (24.85%).

Industrial CaCl₂: NaCl (3.2%), CaCl₂ (60.1%), CaO (14.9%), Fe₂O₃ (1.55%), MgO (10.2%), Al₂O₃ (4.25%), SiO₂ (8.5%).

wastes has recognized and well-documented advantages, such as very large capacity, no requirement for post-storage monitoring, and overall exothermic processes. However, a number of significant challenges still exist, and must be faced and addressed. Potential exists for breakthroughs in the development of more efficient technologies and optimal systems that allow for the practical mineralization and utilization of CO₂. Future research should be encouraged in the following areas.

- (1) At present, these processes are still somewhat expensive and are not fully economically favorable. Efforts should be made to assess large-scale technical feasibility and corresponding energy requirements, and to develop simple and cheap methodologies for CO₂ storage.
- (2) Expanding the advertisement to increase public understanding and support is crucial. Public acceptance might be enhanced by the fact that this storage method is highly verifiable and unquestionably permanent.
- (3) Integration of power generation, mining, the carbon-

ation reaction, the carbonates' disposal, and the associated transport of materials must occur to enable energy needs to be optimized in a site-specific manner.

- (4) Future work in mineral carbonation requires the development of a series of demonstration plants in order to enable a deeper understanding of the mineralization processes for industrial applications.

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Compliance with ethics guidelines

Heping Xie, Hairong Yue, Jiahua Zhu, Bin Liang, Chun Li, Yufei Wang, Lingzhi Xie, and Xiangge Zhou declare that they

have no conflict of interest or financial conflicts to disclose.

References

1. C. Y. Tai, W. R. Chen, S. M. Shih. Factors affecting wollastonite carbonation under CO₂ supercritical conditions. *AIChE J.*, 2006, 52(1): 292-299
2. W. Wang, X. Liu, P. Wang, Y. Zheng, M. Wang. Enhancement of CO₂ mineralization in Ca²⁺-/Mg²⁺-rich aqueous solutions using insoluble amine. *Ind. Eng. Chem. Res.*, 2013, 52(23): 8028-8033
3. V. Materic, S. I. Smedley. High temperature carbonation of Ca(OH)₂. *Ind. Eng. Chem. Res.*, 2011, 50(10): 5927-5932
4. G. Grasa, J. C. Abanades, E. J. Anthony. Effect of partial carbonation on the cyclic CaO carbonation reaction. *Ind. Eng. Chem. Res.*, 2009, 48(20): 9090-9096
5. D. Tong, J. P. M. Trusler, D. Vega-Maza. Solubility of CO₂ in aqueous solutions of CaCl₂ or MgCl₂ and in a synthetic formation brine at temperatures up to 423 K and pressures up to 40 MPa. *J. Chem. Eng. Data*, 2013, 58(7): 2116-2124
6. K. K. Godishala, J. S. Sangwai, N. A. Sami, K. Das. Phase stability of semi-clathrate hydrates of carbon dioxide in synthetic sea water. *J. Chem. Eng. Data*, 2013, 58(4): 1062-1067
7. X. Li, E. S. Boek, G. C. Maitland, J. P. M. Trusler. Interfacial tension of (brines + CO₂): CaCl₂(aq), MgCl₂(aq), and Na₂SO₄(aq) at temperatures between (343 and 423) K, pressures between (2 and 50) MPa, and molalities of (0.5 to 5) mol·kg⁻¹. *J. Chem. Eng. Data*, 2012, 57(5): 1369-1375
8. Z. Sun, M. Fan, M. Argyle. Supported monoethanolamine for CO₂ separation. *Ind. Eng. Chem. Res.*, 2011, 50(19): 11343-11349
9. W. Chaikittisilp, R. Khunsupat, T. T. Chen, C. W. Jones. Poly (allylamine)-mesoporous silica composite materials for CO₂ capture from simulated flue gas or ambient air. *Ind. Eng. Chem. Res.*, 2011, 50(24): 14203-14210
10. S. Holloway, J. M. Pearce, V. L. Hards, T. Ohsumi, J. Gale. Natural emissions of CO₂ from the geosphere and their bearing on the geological storage of carbon dioxide. *Energy*, 2007, 32(7): 1194-1201
11. H. Hassanzadeh, M. Pooladi-Darvish, D. W. Keith. Accelerating CO₂ dissolution in saline aquifers for geological storage — Mechanistic and sensitivity studies. *Energy Fuels*, 2009, 23(6): 3328-3336
12. J. Zhu, et al. Thermodynamics cognizance of CCS and CCU routes for CO₂ Emission Reduction. *J. Sichuan Uni. (Eng. Sci. Ed)*, 2013, 45(5): 1-7 (in Chinese)
13. M. Verduyn, H. Geerlings, G. Mossel, S. Vijayakumari. Review of the various CO₂ mineralization product forms. *Energy Procedia*, 2011, 4: 2885-2892
14. H. Tayibi, M. Choura, F. A. López, F. J. Alguacil, A. López-Delgado. Environmental impact and management of phosphogypsum. *J. Environ. Manage.*, 2009, 90(8): 2377-2386
15. C. Wang, H. Yue, C. Li, B. Liang, J. Zhu, H. Xie. Mineralization of CO₂ using natural K-feldspar and industrial solid waste to produce soluble potassium. *Ind. Eng. Chem. Res.*, 2014, 53(19): 7971-7978
16. H. Xie, et al. Simultaneous mineralization of CO₂ and recovery of soluble potassium using earth-abundant potassium feldspar. *Chin. Sci. Bull.*, 2013, 58(1): 128-132
17. B. Metz, O. Davidson, H. C. de Coninck, M. Loos, L. A. Meyer, eds. *IPCC Special Report on Carbon Dioxide Capture and Storage*. Cambridge: Cambridge University Press, 2005
18. H. Xie, Y. Wang, W. Chu, Y. Ju. Mineralization of flue gas CO₂ with coproduction of valuable magnesium carbonate by means of magnesium chloride. *Chin. Sci. Bull.*, 2014, 59(23): 2882-2889
19. L. Ye, et al. CO₂ mineralization of activated K-feldspar + CaCl₂ slag to fix carbon and produce soluble potash salt. *Ind. Eng. Chem. Res.*, 2014, 53(26): 10557-10565
20. İ. Akin Altun, Y. Sert. Utilization of weathered phosphogypsum as set retarder in Portland cement. *Cement Concr. Res.*, 2004, 34(4): 677-680
21. H. V. M. Hamelers, O. Schaetzle, J. M. Paz-García, P. M. Biesheuvel, C. J. N. Buisman. Harvesting energy from CO₂ emissions. *Environ. Sci. Technol. Lett.*, 2013, 1(1): 31-35
22. H. Xie, et al. Generation of electricity from CO₂ mineralization: Principle and realization, *Sci. China Technol. Sc.*, 2014, 57(12): 2335-2346.
23. K. Huang, X. Meng, G. Wang. Research progress of extracting potassium from potassium feldspar. *Phosphate & Compound Fertilizer*, 2011, 26(5): 16-19
24. I. A. Munz, et al. Mechanisms and rates of plagioclase carbonation reactions. *Geochim. Cosmochim. Acta*, 2012, 77: 27-51