The technology of CO₂ sequestration by mineral carbonation: Current status and future prospects

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Abstract
Mineral carbonation (MC) has been extensively researched all over the world since it was found as a natural exothermic process to permanently and safely sequester CO₂. In order to accelerate the natural process, various methods for carbonation of Mg-/Ca-silicate minerals and other industrial wastes have been studied. It has been found that the MC efficiency will increase with an increase of CO₂ pressure, retention time, temperature, mass ratio of Mg or Ca to Si in minerals, specific surface area, and the slurry concentration in a specific range, and with the introduction of effective catalysts, for example, 1M NaCl and 0.64M NaHCO₃ or carbonic anhydrase. However, there still is not a successful industrial application because of high economic cost and slow reaction rate. It is not economic to exploit Mg- and Ca- silicate minerals deposits or tailings to sequester CO₂ by MC, due to the cost of grinding and heat pre-treatment and in some cases the whole sequestration process may result in more CO₂ emissions than the amount of CO₂ sequestered due to the requirements of energy inputs. The process however, may be profitable as a whole (with carbon credits). It is suggested to combine MC with recovery of valuable metals from ore deposits in order to reduce the cost for MC by cost sharing for mineral recovery.

Keywords: CO₂ sequestration; Cost sharing; Metal recovery; Mg silicate minerals; Mineral carbonation

Introduction
According to the reports of the International Panel on Climate Change (IPCC)¹, it is postulated that the global climate is warming. Many of changes which have been observed include the rising of global average sea level, the decreasing of global ice thickness, and the acidification of ocean. All these changes have the potential to affect human health and welfare. As a result of these changes and potential impacts, it may be desirable to control or decrease the CO₂ concentration in atmosphere. Among the available methods, CO₂ removal by sequestration by mineral carbonation is considered as the promising permanent method²³.
In fact, mineral carbonation (MC) is a natural and exothermic process, which has been observed all over the world\textsuperscript{4-8}. Furthermore, scientists found that Mars also has been experiencing the MC process, through which the CO\textsubscript{2} concentration has been decreased dramatically\textsuperscript{9}. In essence, MC process transforms divalent metal oxide or silicate minerals into carbonates. More importantly, the formed carbonates are stable and will not be affected by acid rain\textsuperscript{5,10}. Theoretically, the carbonates can go through the geological period. However, divalent metal oxide is very rare in nature whereas the magnesium- or calcium- silicate minerals are abundant on earth\textsuperscript{11}. Therefore, the main materials for MC are Mg- or Ca-silicate minerals\textsuperscript{6}, which in the form of peridotite globally has the carbonation capacity of more than 100 trillion tons CO\textsubscript{2}\textsuperscript{8}. The following equations (1-4) are the most important and main MC reactions\textsuperscript{2}.

\[
\begin{align*}
Mg_2SiO_4 + 2CO_2 & \rightarrow 2MgCO_3 + SiO_2 \\
Mg_3Si_2O_5(OH)_4 + 3CO_2 & \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \\
CaSiO_3 + CO_2 & \rightarrow CaCO_3 + SiO_2 \\
Fe_2SiO_4 + 2CO_2 & \rightarrow 2FeCO_3 + SiO_2
\end{align*}
\]

However, these natural processes are kinetically unfavourable under atmospheric and pressure conditions though they are thermodynamically favoured\textsuperscript{6}. They usually need to take hundreds of years to millennia\textsuperscript{12}. Since the 1990s\textsuperscript{2,3,6}, the current MC research mainly focuses on how to accelerate this process to an effective and acceptable extent, in order to sequester CO\textsubscript{2}. From the originally direct gas-solid MC to current several branches of MC, for example, in-situ gas-aqueous-solid route, ex-situ direct gas-aqueous-solid route, researchers have obtained many significant breakthrough\textsuperscript{2,4-6,12-18}. However, the assignment of CO\textsubscript{2} sequestration by MC is still very urgent. Therefore, it is meaningful to summarize the development of MC and to point out the future directions. It has been certified that direct gas-
solid MC route is extremely slow and cannot be applied effectively\textsuperscript{19–21} while addition of water can considerably enhance the MC rate\textsuperscript{5,20,22,23}. Thus, gas-solid MC routes are excluded in this literature review. By contrast, this review concludes the development, current status and prospects the future of the gas-aqueous-solid MC routes.

**MC by Mg- and Ca- silicate minerals**

**In-situ MC**

The Mg- and Ca- silicate minerals which are available for MC are mainly in basalts and peridotite\textsuperscript{8}. They are called mafic and ultramafic rocks respectively according to their content of SiO\textsubscript{2}, 45-52\% and <45\% respectively. Both groups of silicate minerals are being researched.

**Basalts**

Basalts form the top igneous layer in the oceanic crust and occur in large continental provinces, shown in Figure 1. Generally, basalts are more abundant than peridotite\textsuperscript{8}.

Thus far, the most successful and the most important in-situ MC by basalts is the CarbFix pilot project in Iceland. This project is a cooperation between Iceland and the United Kingdom (UK), the United States of America (USA), France, Netherlands, Australia and Denmark\textsuperscript{25–27}. A CO\textsubscript{2}-H\textsubscript{2}S gas mixture was injected into a 2000-m-deep well and monitored the MC situation by 8 monitoring wells ranging in depth from 150 to 1300m, as shown in Figure 2\textsuperscript{25}. During the in-situ MC, the water temperature and pH are in the range from 20\degree C to 33\degree C and from 8.4 to 9.4 without oxygen respectively\textsuperscript{28}. Furthermore, in order to prevent the CO\textsubscript{2} gas leakage during injection, they developed a novel CO\textsubscript{2} injection system, dissolving the gas mixture into down-flowing water into the well and keeping the CO\textsubscript{2} concentration below its solubility at these conditions\textsuperscript{29}. Isotopic analysis method is applied to
monitor the MC process. Their study for the first time successfully, thus far, demonstrates that permanently CO\textsubscript{2} sequestration into carbonates through in-situ MC by basaltic rocks is possible and reasonable. They found that 95\% CO\textsubscript{2} injected into CarbFix site has been mineralized in just less than 2 years\textsuperscript{25}, rather than hundreds to thousands of years thought before, under these conditions: 20°-33°C, pH=8.4-9.4 with water but without O\textsubscript{2}, up to almost 200 bars CO\textsubscript{2} pressure. Thus far, the CarbFix project has successfully sequestered the 175 tons of pure CO\textsubscript{2} and 73 tons of a CO\textsubscript{2}-H\textsubscript{2}S gas mixture\textsuperscript{25}. Lu et al. also verified that O\textsubscript{2} (up to 3.5\% of the mixture gas) has no detrimental effect on MC process\textsuperscript{30}, which means it is unnecessary to use pure CO\textsubscript{2} gas. Based on CarbFix’s success, another in-situ MC pilot project, Big Sky Regional Partnership is conducting in Columbia River Basalt in the USA, with the support of CarbFix team (https://www.or.is/english/carbfix-project).

However, Hang et al.\textsuperscript{31} had different opinions when they studied a natural CO\textsubscript{2} analogue reservoir (CO\textsubscript{2} gas injected into depleted oil reservoirs\textsuperscript{32}). They found that there were no obvious MC reaction and carbonates from CO\textsubscript{2} gas were rather limited.

\textit{Peridotite}

Peridotite has a higher divalent metals content with lower silica content. Theoretically, it has great capacity to permanently store CO\textsubscript{2} and is more suitable for MC than basalts. Peridotite occurs on almost every continent\textsuperscript{8,33}. It is clear that there are a lot of peridotite deposits along the east and west coast of North America. Furthermore, peridotite is more reactive than basalts theoretically\textsuperscript{34}. However, both porosity and permeability of peridotite are very low\textsuperscript{8}. These hinder the in-situ MC development and thus the research of in-situ MC by peridotite is still in the infancy stage.

At present, there has been less active in-situ MC by peridotite research\textsuperscript{35}. In fact, in-situ MC by peridotite research still mainly concentrates on passive MC. Kelemen and
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Matter\textsuperscript{8,36} have evaluated that MC capacity of Oman site alone is over 30 trillion tons CO\textsubscript{2} and by near Oman surface approximately $\sim10^3$ tons of CO\textsubscript{2} km\textsuperscript{3}/year are consumed by passive peridotite carbonation. In addition, many researchers\textsuperscript{7} have researched the passive MC on mining tailings and the results are also promising. Lechat et al.\textsuperscript{37} simulated the in-situ MC for ultramafic milling wastes by laboratory scale experiment. They supposed that the diffusion of CO\textsubscript{2} was the dominant transport mechanism and the MC reaction close to the surface was the most active. In fact, this process should belong to ex-situ MC because the milling wastes are the tailings which had been through previous pulverization and other processing process, rather than the original ores underground.

It is interesting that Schaef et al.\textsuperscript{38} newly developed in-situ High Pressure X-Ray Diffraction (HXRD) and in-situ Infrared Spectroscopy (IP) and applied them to in-situ MC studies. With the help of these innovative in-situ analysis methods, the generated nesquehonite, magnesite and calcite due to MC reactions have been identified under the CO\textsubscript{2} pressure (90-160 bars) and temperature (35-70°C). In addition, they observed that carbonation extents of peridotite were correlated to the thicknesses of mineral surface’s water-film by in-situ IR and enstatite (MgSiO\textsubscript{3}) was the least reactive by in-situ HXRD.

However, as a whole, there is still no successful in-situ (underground) MC project report thus far. The limits are mainly the decrease of permeability due to clogging or porosity from precipitates and the passivation layers from generated silica. The former limits the practical scale of MC and the latter prevents the further carbonation reaction. Zhang and Liu\textsuperscript{39} made a review of porosity-permeability relationships in modeling salt precipitation during in-situ MC. According to their review, there is no unequivocal conclusion about whether the permeability or porosity will decrease due to the precipitation of carbonates. Therefore, the in-situ MC way is promising but there are still work which need to be done.
Especially, the success of CarbFix project makes the in-situ MC more promising and more attractive.

**Ex-situ direct MC**

Thus far, the majority of mineral carbonation technology development still focuses on the ex-situ ways. Since 1990s\(^3,13,40–44\), scientists have started the fundamental research on MC by peridotite, in order to accelerate the natural process. At present, the fundamental characteristics of MC have been discovered. It is hard to accelerate the process except for strict conditions, high temperature, high CO\(_2\) pressure and small particle size\(^{13,23,40,42,44–47}\). If the materials are serpentine, heat pre-treatment will be also needed\(^{40,48}\). The reasons why so strict conditions are needed are from three main rate-limiting steps\(^2\). The first and the most rate-limiting step is the CO\(_2\) dissolution into solution from gas\(^2,49,50\), followed by the dissolution of Mg- or Ca- silicate minerals into solution. However, whether the former or the latter limits the extent of MC still remains in controversy\(^51,52\). But there is no doubt that both of them are the main difficulties. The less important step is the product layer diffusion, for example the generated MgCO\(_3\) and SiO\(_2\) layers.

Based on the rate-limiting mechanisms, the strict conditions requirement for MC can be easily explained. Firstly, particle size determines the specific surface area which affects the contact between minerals and solution, which controls the dissolution of minerals. So generally, with the particle size increasing, the MC efficiency also increases. Temperature affects the dissolution of both minerals and gas CO\(_2\) into solution. But the influence on them is different. The dissolution of minerals increases with the increasing temperature\(^53\) while the dissolution of CO\(_2\) gas decreases\(^54\). In order to address the conflicts between them, high CO\(_2\) pressure is needed. High CO\(_2\) pressure can improve the dissolution of the CO\(_2\) itself to balance the detrimental effects of high temperature, but also facilitate to increase temperature
over 100°C and enhance the dissolution of minerals\textsuperscript{53}. Furthermore, with MC reaction going, the more and more solid product of carbonates and silica will be produced and cover the surface of unreacted minerals, which hinders the MC reaction from continuing further. Therefore, continuous agitation and high but suitable liquid/solid (L/S) ratio is helpful. They can help remove the passivation layers immediately by attrition function when MC reaction is happening. If the mineral target is serpentine, because serpentine is more stable than olivine as serpentine is weathered from olivine\textsuperscript{48}, heat pre-treatment can help remove the –OH group and disintegrate the crystal structure of serpentine and then facilitate to dissolve serpentine into solution.

Typically, the American Albany Research Center (ARC) discovered an effective but economical catalyst, the mixture of NaHCO\textsubscript{3} and NaCl\textsuperscript{13,40,42,44}. The mechanism of catalyst can be presented as the equations (5-7). Bicarbonate ion can react with the Mg- or Ca- silicate minerals to form more insoluble carbonates and hydroxyl ions. In return, the hydroxyl ions can immediately absorb CO\textsubscript{2} gas to form bicarbonate ions again. Furthermore, the chloride ions can form complex ions with magnesium cations, which can facilitate the dissolution of magnesium silicate minerals by increasing the solubility of magnesium. In principle, the additives will not be consumed. In addition, the discovery promotes MC development in basic conditions. Historically the main approach has been to dissolve silicate minerals in acid conditions\textsuperscript{55,56}. The slurry of Mg- or Ca- silicate minerals is weak basic in essence. So the discovery is a great breakthrough for MC. In fact, almost most all later MC researchers are based on or referred to their work including the catalyst.

\[
\begin{align*}
Mg_2SiO_4 + 2HCO_3^- & \rightarrow 2MgCO_3 + SiO_2 + 2OH^- \\
OH^- + CO_2 & \rightarrow HCO_3^- \\
Mg^{2+} + nCl^- & \rightarrow [MgCl_n]^{2-n}
\end{align*}
\]
All these fundamental research not only promotes the development of ex-situ MC but also in-situ MC. However, it is also clear that intensive energy is needed for acceptable MC efficiency and rate, which results in very high costs. It is because of this that there is still no successful ex-situ MC practical application yet. ARC tried to combine ex-situ direct MC with in-situ MC by injecting mineral slurry and CO$_2$ gas into underground because the ex-situ direct process is too energy-intensive$^{41}$. This approach may be promising.

Furthermore, in order to enhance the MC efficiency under mild conditions, lower pressure and lower temperature, considering that grinding by mills is used to not only increase specific surface area of minerals and also disintegrate the structures of minerals to some extent$^{57-65}$, some researchers started to develop a similar in-situ grinding MC concept which means MC happens during grinding stage. The mechanism of in-situ grinding MC can be explained by Figure 3. Park and Fan$^{66}$ found that in-situ grinding can help remove SiO$_2$ passivation layers instantly and improve the dissolution of serpentine, especially when there is Mg-leaching solvent in this system. They did the research in a 5 cm diameter fluidized bed reactor, which can be shown in the schematic diagram of Figure 4. Verduyn et al.$^{18}$ also presented their idea to make flue gas containing CO$_2$ start to contact with minerals slurry during grinding stage because of the fact that MC efficiency is much slower by directly using flue gas due to the lower CO$_2$ pressure than using pure CO$_2$ gas. They wanted to do this to counteract the negative influence of directly using flue gas (with about 10% CO$_2$). Turianicová et al.$^{57,58,64,67}$ used a planetary ball mill to do the in-situ grinding MC of vermiculites without additives and verified that this way can indeed enhance the structural breakdown of minerals. However, most of them did not continue to do the in-situ grinding MC research because there are specific requirements for milling equipment, for instance, sealed and higher pressure than atmosphere. These may not only increase investment on
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equipment but also risk the whole process because of the importance and high energy consumption of ball mill in a plant. But in-situ grinding MC may be still worth researching.

Particularly, Santos et al.\textsuperscript{68} did an interesting and meaningful research that ex-situ direct MC was used as a pre-treatment to enhance nickel extraction from pure olivine. The olivine they adopted has the nickel content of 0.27%. The majority of nickel exists in this olivine by replacing magnesium in the Mg-silicate structure as the isomorphous Mg-Ni silicate \((\text{Mg},\text{Ni})_2\text{SiO}_4\) and is dispersed in the materials. Fully carbonation efficiency has been acquired under the conditions: 35 bars CO\textsubscript{2} pressures, 200°C, 20(wt)% slurry concentration, 86% <80μm of particle size, 0.64M NaHCO\textsubscript{3}+1M NaCl for 72 hours. They compared the leaching behaviour of nickel between fresh olivine and full carbonated olivine and found that the leaching efficiency was increased dramatically at the same conditions by HCl acid or HNO\textsubscript{3}. This shows that carbonation made nickel leaching easier. In fact, after the complete carbonation, nickel was found to be more dispersed by EPMA analysis. This research, for the first time, connects MC tightly with valuable metals. However, after the carbonation, they just leached all the solids. Therefore, CO\textsubscript{2} in the whole process can be shown as CO\textsubscript{2}g→MgCO\textsubscript{3}s→CO\textsubscript{2}g. There is no CO\textsubscript{2} which has been carbonated. That is to say, in terms of CO\textsubscript{2} sequestration, this process is meaningless. But it points out a new idea that it will be more valuable if ex-situ MC could be tightly connected with valuable metal recovery.

Furthermore, many researchers\textsuperscript{6,14,52} believe that the Energy Reactor\textsuperscript{©} invented by Innovation Concepts may be the most promising ex-situ direct MC method, as shown in Figure 5(a). Its specialties are that it not only transforms the high CO\textsubscript{2} pressure requirement into gravity itself but also utilizes the heat released from MC reaction itself. The former can decrease the requirements of equipment and reduce the costs considerably. And the latter can make full use of the exothermic characteristic of MC reactions and decrease the requirement
of massive energy input which is limiting the economics of MC. In addition, due to high speed of slurry during the Energy Reactor®, particles will be attrited, which can remove the passivation layers of silica and facilitate the successive MC reaction. According to the report of Innovation Concepts, the temperature and pressure can be up to 200°C and 90 bars (http://www.innovationconcepts.eu/CO₂EnergyReactor.htm). However, this process is hard to simulate in a laboratory scale. In the year 2016, there is cooperation between Canada and Netherlands to do lab-scale CO₂ Energy Reactor experiments, as shown in Figure 5(b). Though they believed that the MC through this apparatus was good but it still did not make full use of the specialities of Energy Reactor itself. However, they gave interesting ideas that it is not advisable to obtain maximal MC efficiency by increasing the processing costs and in contrast, the main impetus of MC is the value of products.

In addition, some researchers are trying to find a more efficient catalyst than NaHCO₃+NaCl. One of the catalysts is Carbonic Anhydrase (CA). It is a kind of metalloenzyme, E·ZnH₂O. The mechanism that it enhances MC can be shown in equations (8-12). Compared to the buffer of NaHCO₃+NaCl, it can enhance not only the dissolution of silicate minerals but also the dissolution of CO₂ gas, both of which are the main rate-limiting steps. Power et al.⁴⁹,⁵⁰,⁶⁹ used it to accelerate the MC by brucite and verified that CA can help address the rate-limiting step of CO₂ dissolution. However, the price of CA is too expensive, approximately $800 per 500mg Bovine CA (No. C3934). Therefore, some researchers believed it was impossible to adopt so expensive CA to sequester CO₂², and it is also the main reason why there is almost no research on MC of olivine enhanced by CA. But if the price of CA could be much cheaper and more suitable, for example, artificial CA, MC would have great development.

\[
E \cdot ZnH₂O \rightarrow E \cdot ZnOH^- + H^+ \quad (8)
\]

\[
E \cdot ZnOH^- + CO₂ \rightarrow E \cdot ZnHCO₃^- \quad (9)
\]
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\[
E \cdot ZnHCO_3^- + H_2O \rightarrow E \cdot ZnH_2O + HCO_3^- \quad (10)
\]

\[
Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + SiO_2 + 2H_2O \quad (11)
\]

\[
Mg^{2+} + 2HCO_3^- \rightarrow MgCO_3 + 2H^+ \quad (12)
\]

**Ex-situ indirect MC**

Ex-situ indirect MC, in fact, dates from the ex-situ direct MC. In order to accelerate the MC rate and address the rate-limiting step of dissolution of minerals, as well as to make MC process profitable by increasing the value of products, some researchers tried to separate the carbonation reaction from the dissolution of Mg-silicate minerals as different stages, though some others believed pressurized reactors are the highest investment costs\(^70\). At present, the majority of indirect MC is two-stage MC: dissolution of silicate minerals followed by carbonation reaction\(^71\). The mechanism of indirect MC is based on that minerals are dissolved or precipitated on different pH values or different temperatures. But it should be noticed that ex-situ indirect MC does not bypass the requirement of pre-treatments, for example, fine-grinding with/without heat-treat, which mainly result in non-profitable direct MC processes\(^72\)–\(^74\).

Azdarpour et al.\(^75\) made a review on indirect MC through pH-swing process. Firstly, silicate minerals are dissolved in low-pH solution (with or without ammonium salts), and after L/S separation, carbonates are acquired by raising the solution’s pH value\(^73\). Compared to direct MC, it is easier to acquire relatively high carbonation efficiency by pH-swing ways. In addition, the carbonates product with high purity also can be acquired, which can considerably increase the value of products. However, MC by pH swing, in general, still cost too much because the minerals prior to dissolution also need to be ground which is the main costs of MC. Furthermore, massive additives will be consumed and it is hard to recycle them. More importantly, this method cannot use the exothermic characteristics of MC.
The representative of institutions who use temperature change to reach the dissolution and carbonation is the Åbo Akademi University in Finland\textsuperscript{5,22,76}. They previously researched the direct gas-solid MC and have done a lot of significant works\textsuperscript{4,5}. Recently, they\textsuperscript{10,12,16,22,76,77} invented the ÅA route which has 3 stages and can be shown in Figure 6. The original idea of this technology is to utilize the exothermic heat from MC. So in the first stage, direct solid-solid reaction between ammonia sulphate and Mg-silicate minerals happens under 400–440°C to generate solids containing MgSO\textsubscript{4}. Then in near ambient aqueous solution, precipitation Mg(OH)\textsubscript{2} is acquired and subsequently enters a pressurized fluidized bed under conditions of over 20 bars of CO\textsubscript{2} pressure and 450–500°C to carbonate CO\textsubscript{2}. The chemical reactions can be shown in equations (13-15). Generally, the whole process does not need to consume additional energy. But in fact, it is still hard to recover the additive of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and it is very complicated to reach the heat balance including hot-cold-hot alterations. Because of these, they recently changed the final stage (under about 500°C) into aqueous condition (under less than 100°C)\textsuperscript{22}. However, the main two disadvantages still exist.

\[
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3(\text{NH}_4)_2\text{SO}_4 \xrightarrow{400-440°C} 3\text{MgSO}_4 + 2\text{SiO}_2 + 2\text{H}_2\text{O} + 2\text{NH}_3 \quad (13)
\]

\[
\text{MgSO}_4 + 2\text{H}_2\text{O} + 2\text{NH}_3 \xrightarrow{\text{near room temperature}} \text{Mg(OH)}_2 + (\text{NH}_4)_2\text{SO}_4 \quad (14)
\]

\[
\text{Mg(OH)}_2 + \text{CO}_2 \xrightarrow{450-500°C} \text{MgCO}_3 + \text{H}_2\text{O} \quad (15)
\]

There is one of interesting ex-situ indirect MC research\textsuperscript{78} it adopted mining wastes for indirect MC through crushing, grinding, transportation, heat-treatment, dissolution and precipitation. Finally, two valuable products can be obtained: magnetic products containing magnetite, and pure carbonates. Through economic evaluation, they believed that the whole process is profitable with carbon credits, and through technical evaluation, they concluded that the whole process needs 1.8252 GJ energy input for sequestering 234 Kg CO\textsubscript{2} by 1 ton rocks. However, if the input energy is from coal combustion, according to the average energy
production value, 6150 kWh/t coal\textsuperscript{79}, then the whole process will equivalently produce 260 Kg CO\textsubscript{2} (assuming 85% content of C in coal), which is more than the amount of CO\textsubscript{2} sequestered. According to the emission factor for electricity produced using coal from IPCC report, 760 g CO\textsubscript{2}/kWh\textsuperscript{78}, the whole MC process will release 385 Kg CO\textsubscript{2}, which is still more than the amount of CO\textsubscript{2} it has sequestered. Therefore, though this process may be profitable, it may still be meaningless in terms of CO\textsubscript{2} sequestration.

**MC by industrial wastes**

Mineral carbonation by industrial wastes is still a significant part of MC to mitigate global warming, though its capacity is much smaller than by natural silicate minerals\textsuperscript{2,6}. Industrial wastes containing divalent metal usually have higher chemical reactivity and their corresponding MC can therefore achieve an acceptable rate of CO\textsubscript{2} conversion under milder conditions\textsuperscript{6,80}. Furthermore, industrials wastes can come from various resources, for example, the coal fly ash (FA)\textsuperscript{20,81–85}, metallurgical slag\textsuperscript{86–89}. Meanwhile, the applied technology is the same as that of MC by silicate minerals.

Mayoral et al.\textsuperscript{81} used direct MC route by lime-rich coal ashes. 78% carbonation efficiency can be achieved for coal ash and coal waste under 75°C, pH=11.5, 60mL solution/g ash for only 1 h. Nyambura et al.\textsuperscript{83} adopted brine and coal FA to sequester CO\textsubscript{2} and found that fractionated coal FA, especially 20-150μm particle size, had the best carbonation efficiency (71.84 kg CO\textsubscript{2}/t FA) while larger or smaller size cannot achieve that. Furthermore, brine had the better effect on MC than pure water. Dananjayan et al.\textsuperscript{20} compared the direct gas-solid MC with direct aqueous MC (L/S ratio of 15) under room temperature, 4 bars for 2h, and found that the dry route is much slower process. By contrast, the aqueous route can obtain the capacity of 50.3 Kg CO\textsubscript{2}/t coal FA. Hosseini et al.\textsuperscript{82} adopted indirect MC route to sequester CO\textsubscript{2}. In the first stage, coal FC was leached by NH\textsubscript{4}Cl solution.
The leachate which containing Mg\textsuperscript{2+} and Ca\textsuperscript{2+} then was used to carbonation by injecting flue gas containing CO\textsubscript{2} to acquire carbonate product which can be sold as a product. The leaching residue also can be sold as a cement additive. During this process, ammonia chloride can be recycled. Theoretically, this process is profitable. Han et al.\textsuperscript{84} also use coal FA to do indirect MC research under room temperature and pressure and found the capacity was up to 31.1 Kg CO\textsubscript{2}/t coal FA. Bertos et al.\textsuperscript{90} also used direct MC route by municipal solid waste (MSW) incinerator ashes not only to sequester CO\textsubscript{2} but also to treat hazardous wastes.

Santos et al.\textsuperscript{87} researched the direct MC by steel slags which were intensified by ultrasound. They also showed that sonication can facilitate the MC reaction by removing the passivation layers of generated carbonates and silica as well as reduce the particle size obviously. Araiz et al.\textsuperscript{91} have done the research that the direct MC by three kinds of alkaline waste residues, air pollution control residues, cement bypass dust and ladle slag, were enhanced by ultrasound. They verified that the application of ultrasound can considerably promote the carbonation efficiency but needed the help of high L/S ratios (50-100). Huijgen et al.\textsuperscript{80} also believed that steel slag was suitable for MC. Kasina et al.\textsuperscript{86} tried to use blast furnace and steel making slags to sequester CO\textsubscript{2} through direct MC route. They discovered that steel making slag was much easier to sequester CO\textsubscript{2} into carbonates than blast furnace slag. Su et al.\textsuperscript{88} utilized basic-oxygen furnace (BOF) slag to sequester CO\textsubscript{2} by direct MC as well. However, they acclaimed that BOF slag was a better CO\textsubscript{2} storage medium. Meanwhile, the valuable vanadium and chromium metals were released into solution during MC. Polettini et al.\textsuperscript{89} analyzed in details the effects of particle size on the MC by BOF slag. They found the effect was considerable. Particularly, the carbonation efficiency difference between the particle size of D\textsubscript{50}=44\mu m and D\textsubscript{50}=88\mu m was over 60\% (approximately 72\% and 8\% respectively) at the same conditions whereas when D\textsubscript{50}=17\mu m, the carbonation efficiency
decreased to only 44% again. They have the consistent conclusions with Nyambura et al. in terms of the important of particle size.

Song et al.\textsuperscript{92,93} applied flue gas desulfurization (FGD) gypsum for indirect MC to not only sequester CO\textsubscript{2} but gain pure carbonate crystals. Furthermore, Xuan et al.\textsuperscript{94} adopted direct MC to produce eco-friendly concrete blocks by recycling concrete aggregates. They discovered that these concrete blocks got higher strength than normal blocks and CO\textsubscript{2} pressure of 5 bars and retention time of 24 h were enough for the blocks. By comparing the MC between by waste concrete and by anorthosite tailings, Ghacham et al.\textsuperscript{19} further showed that MC by waste concrete is much easier than by anorthosite tailings because calcium was locked by the framework structure of anorthosite.

**Future prospects**

In summary, in the last 30 years, the technology of CO\textsubscript{2} sequestration by mineral carbonation has been developed considerably. Firstly, the fundamental characteristics of MC have been discovered. To acquire high MC efficiency during short period, strict conditions are necessary: high temperature, high CO\textsubscript{2} pressure, fine particle size and catalyst (such as sodium bicarbonate). Otherwise, MC still needs to take long time. Secondly, there has been successful in-situ MC pilot, CarbFix project in basalts in Iceland. It has been verified the possibility of in-situ MC and found that the in-situ MC of basalts only needs to take less than 2 years without any additives rather than hundreds of years. This is a great encouragement for MC further development. Furthermore, in-situ HXRD and in-situ IR technology has been developed and can be used to monitor the practical in-situ MC. In addition, there are also great developments in terms of ex-situ MC: invention of Energy Reactor\textsuperscript{©}, in-situ grinding MC conception as well as the idea that ex-situ MC can tightly associate with valuable metal recovery.
In the near future, it has been believed that MC technology will undergo rapid development. There will be more in-situ MC of basalts pilots and application in the model function. Whether in-situ MC will be challenged by the decrease of porosity and permeability due to the precipitation of carbonates will also be discovered with the help of in-situ analysis tools and more in-situ pilot research. In-situ active MC of peridotite research will also be promoted.

Ex-situ MC will continue to mainly focus on direct routes but can share the costs with the main flow sheet of valuable metals recovery. Through this way, it will be unnecessary for MC to particularly decrease the particle size of minerals because the valuable metals recovery needs to liberate or expose minerals by grinding as well. Then the majority of costs of ex-situ MC will be decreased dramatically but the profits of the whole process will be increased considerably due to the carbon credits and probable increase of metals recovery. However, it also means that it is not economic to exploit Mg- and Ca-silicate minerals deposits or tailings to only sequester CO₂ by MC⁴⁴, due to the cost of grinding and heat pre-treatment and especially in some cases the whole sequestration process may result in more CO₂ emissions than the amount of CO₂ sequestered due to the requirements of energy inputs though the process may be profitable as a whole (with carbon credits). It is suggested indeed to combine MC with recovery of valuable metals from ore deposits which contain high content of divalent metals. Energy Reactor will play a vital important role in the successful application of ex-situ direct MC owing to its two outstanding advantages: transforming high pressure requirement into gravity and utilizing exothermic heats of MC. In-situ grinding MC may also have positive influence on success of ex-situ MC if the mill equipment which can operate at higher pressure than atmosphere can be made economically. In addition to the mixture of NaHCO₃ and NaCl, more efficient but economical catalysts need to be discovered or manufactured, such as artificial CA. Furthermore, though the capacity of MC by industrial
wastes is much less than by silicate minerals, it is still important, especially if they can make high-value by-products or accompany metals recovery.

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Figure 1. Locations of continental basalts that could serve as in-situ mineral carbonation sites.\textsuperscript{24}
Figure 2. Geological cross-section of the CarbFix injection site²⁵
Figure 3. Mechanism depiction of in-situ grinding direct aqueous mineral carbonation
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Figure 4. Schematic diagram of the internal grinding system.
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Figure 5. (a) Schematic representation of the CO\textsubscript{2} Energy Reactor\textsuperscript{6,6} and (b) Lab-scale Energy Reactor: “rocking autoclave” at ~45° position\textsuperscript{52}
Figure 6. Schematic representation of the typical ÅA route (AS: (NH$_4$)$_2$SO$_4$)