

Carbon Mineralization by Reaction with Steel-Making Waste: A Review

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Keywords: steel slag, steel-making waste, CO₂ sequestration, Carbon Capture

Abstract:

Carbon capture and sequestration (CCS) is taking the lead as a means for mitigating climate change. It is considered a crucial bridging technology, enabling carbon dioxide (CO₂) emissions from fossil fuels to be reduced while the energy transition to renewable sources is taking place. CCS includes a portfolio of technologies that can possibly capture vast amounts of CO₂ per year. Mineral carbonation is evolving as a possible candidate to sequester CO₂ from medium-sized emissions point sources. It is the only recognized form of permanent CO₂ storage with no concerns regarding CO₂ leakage. It is based on the principles of natural rock weathering, where the CO₂ dissolved in rainwater reacts with alkaline rocks to form carbonate minerals. The active alkaline elements (Ca/Mg) are the fundamental reactants for mineral carbonation reaction. Although the reaction is thermodynamically favored, it takes place over a large time scale. The challenge of mineral carbonation is to offset this limitation by accelerating the carbonation reaction with minimal energy and feedstock consumption. Calcium and magnesium silicates are generally selected for carbonation due to their abundance in nature. Industrial waste residues emerge as an alternative source of carbonation minerals that have higher reactivity than natural minerals; they are also inexpensive and readily available in proximity to CO₂ emitters. In addition, the environmental stability of the industrial waste is often enhanced as they undergo carbonation. Recently, direct mineral carbonation has been investigated significantly due to its applicability to CO₂ capture and storage. This review outlines the main research work carried out over the last few years on direct mineral carbonation process utilizing steel-making waste, with emphasis on recent research achievements and potentials for future research.

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Review

Carbon Mineralization by Reaction with Steel-Making Waste: A Review

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Abstract: Carbon capture and sequestration (CCS) is taking the lead as a means for mitigating climate change. It is considered a crucial bridging technology, enabling carbon dioxide (CO₂) emissions from fossil fuels to be reduced while the energy transition to renewable sources is taking place. CCS includes a portfolio of technologies that can possibly capture vast amounts of CO₂ per year. Mineral carbonation is evolving as a possible candidate to sequester CO₂ from medium-sized emissions point sources. It is the only recognized form of permanent CO₂ storage with no concerns regarding CO₂ leakage. It is based on the principles of natural rock weathering, where the CO₂ dissolved in rainwater reacts with alkaline rocks to form carbonate minerals. The active alkaline elements (Ca/Mg) are the fundamental reactants for mineral carbonation reaction. Although the reaction is thermodynamically favored, it takes place over a large time scale. The challenge of mineral carbonation is to offset this limitation by accelerating the carbonation reaction with minimal energy and feedstock consumption. Calcium and magnesium silicates are generally selected for carbonation due to their abundance in nature. Industrial waste residues emerge as an alternative source of carbonation minerals that have higher reactivity than natural minerals; they are also inexpensive and readily available in proximity to CO₂ emitters. In addition, the environmental stability of the industrial waste is often enhanced as they undergo carbonation. Recently, direct mineral carbonation has been investigated significantly due to its applicability to CO₂ capture and storage. This review outlines the main research work carried out over the last few years on direct mineral carbonation process utilizing steel-making waste, with emphasis on recent research achievements and potentials for future research.

Keywords: carbon capture; CO₂ sequestration; steel-making waste; steel slag

1. Introduction

Fossil fuels are used as the main source of energy globally, and now they supply over 80% of the world energy demand [1]. Fossil fuels are expected to remain the most used energy source for years to come. This is due to the ever-increasing demand for energy created by the thriving economies around the globe. International Energy Agency reported a total energy demand of 574 exajoules globally in 2014 [2]. Although there are multiple sources for atmospheric CO₂, human activities, such as transportation and electricity generation, which directly burn several kinds of fossil fuels

(including coal, oil, and natural gas), release more CO₂ into the atmosphere. This leads to increases in the earth temperature and in turn causes global warming. Hence, mitigating CO₂ emissions is a key to decrease global warming and sustain a better future for humanity [3]. Carbon capture and storage serves as the main technology for mitigating carbon emissions. Numerous conventional CO₂ capture technologies based on a post-combustion approach are being used in the industry. Separation based methods, such as absorption, adsorption, and membrane separation, are the most utilized separation technologies available [4–7]. Mineral carbonation is one of few technologies that work as both capture and storage technologies [8]. It is based on the principles of natural rock weathering, where the CO₂ dissolved in rainwater reacts with alkaline rocks to form carbonate minerals. The active alkaline elements (Ca/Mg) are the fundamental reactants for mineral carbonation reaction. Although the reaction is thermodynamically favored, it takes place over a large time scale. The challenge of mineral carbonation is to offset this limitation by accelerating the carbonation reaction with minimal energy and feedstock consumption. Calcium and magnesium silicates are generally selected for carbonation due to their abundance in nature. Industrial waste residues emerge as an alternative source of carbonation minerals that have higher reactivity than natural minerals; they are also inexpensive and readily available in proximity to CO₂ emitters. In addition, the environmental stability of the industrial waste is often enhanced as they undergo carbonation. Recently, mineral carbonation has been investigated significantly, due to its applicability to CO₂ capture and storage. Despite the growing interest in mineral carbonation research, there have not been any focused reviews that assess the status of CO₂ sequestration using steel-making waste. In this review, mineral carbonation using steel-making waste is reviewed in the light of different process parameters and their effect on CO₂ uptake. Potentials for future research in the area are highlighted.

1.1. CO₂ Storage

Several storage techniques are used to store CO₂, and the most feasible option to do so is geological sequestration [1]. Literature work investigating geological CO₂ storage has seen a substantial increase in the last decade [2]. Practically, over 1 million ton CO₂ is being sequestered in 14 individual different locations around the globe [3]. Estimates of CO₂ storage capacity varies depending on the region at which the study has been conducted. Nonetheless, the capacity is in the range of 100–20,000 giga ton CO₂ worldwide [4]. One of the mature CO₂ storage techniques is to inject it into depleted gas or oil reservoirs. Carbon dioxide is used to increase reservoirs pressure to produce enough driving force to push the gas/oil out of it. In other words, it enhances oil recovery in active wells by extracting the residual oil left. Additionally, CO₂ can be used to recover natural gas (methane, CH₄) trapped in coal beds. The main premise behind the idea is that CH₄ can be quickly displaced from coal by carbon dioxide injection, allowing CO₂ to be stored in the porous structure of the coal bed [5]. Injecting CO₂ into saline aquifers is also a viable option that commercially exists with an acceptable capacity [6,7]. Carbon dioxide is usually injected in its supercritical conditions [8]. At these conditions, CO₂ is buoyant relative to porous rocks and saline aquifers. Thus, there is always a possibility that buoyant CO₂ could leak to the surface and cause catastrophic environmental impacts. Most critically, monitoring programs for post-injection are limited and do not provide long-term detectability of the gas that can potentially escape from the storage medium [9]. Hence, these approaches cannot be taken for granted and considered as permanent and safe CO₂ storage solutions. Mineral carbonation is one approach that can provide long-term storage solution in addition to being CO₂ leak-free. This is due to the fact that carbonates are in a lower energy state than CO₂ [10]. More importantly, it possesses extremely large sequestration capacity compared to other geological storage options, as indicated in Table 1.

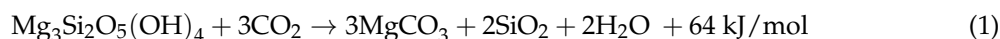
Table 1. Storage capacities for several geological storage options [11].

Reservoir Type	Estimated Range of Storage Capacity (GtCO ₂)
Mineral carbonation	Very large (>10,000) ^a
Saline aquifers	1000–10,000
Oil and gas fields	675–900 ^b
Coal beds	3–200

^a No specific number can be given, however, massive potential to sequester CO₂ exists. ^b Including fields that are not economically viable to inject carbon dioxide into.

1.2. Mineral Carbon Sequestration

Mineral carbon sequestration is based on the principles of the natural carbonation process of natural rocks, where the CO₂ dissolved in rainwater forms a weak carbonic acid. Consequently, alkali and alkaline earth metals (i.e., Ca and Mg) neutralize the acid to form insoluble carbonate minerals [12,13]. Sequestration happens in several alkaline minerals, such as calcite (CaCO₃), dolomite (Ca/Mg(CO₃)₂), magnesite (MgCO₃), siderite (FeCO₃), and serpentine (Mg₃Si₂O₅(OH)₄) [14]. For mineral carbonation, having a sufficient amount of a certain natural mineral is an essential factor. Hence, magnesium-based silicates are utilized since they are available in considerable amounts globally [11]. However, increasing CO₂ levels led to more CO₂ absorption by the oceans, hence increasing its acidity by 30% since the industrial era started [15]. Hence, this limits the natural carbonation process. The formed carbonates are in solid form resulting from exothermic reaction (Equation (1)) and a certain amount of heat is released, depending on the type of metal oxide reacting.



Carbonates require a high amount of energy to decompose back into CO₂. Hence, carbonates can be considered as thermodynamically stable CO₂ sink [16]. CO₂ will be fixed permanently without further monitoring to check its stability [17]. Table 2 shows the composition of different minerals rocks and the mass of CO₂ that can be sequestered by a unit mineral mass (mass CO₂/mass mineral). This ratio is based on the theoretical basis and considered as the maximum potential carbonation capacity for the specific mineral. Different minerals have different ratios according to their alkali metal content. Whether or not the maximum capacity can be reached, it is subject to the carbonation process and different operating parameters.

Table 2. Carbonation potential for different naturally occurring minerals [18].

Mineral/Formula	U (mass CO ₂ /mass mineral)
Serpentine (Mg ₃ Si ₂ O ₅ (OH) ₄)	0.40
Serpentine ((Mg,Fe) ₃ Si ₂ O ₅ (OH) ₄)	0.48
Wollastonite (CaSiO ₃)	0.36
Olivine (Fe ₂ SiO ₄)	0.36
Olivine (Mg ₂ SiO ₄)	0.56

Mineral sequestration technique was first proposed by Seiftritz [19]. The proposed idea suggested introducing high purity CO₂ to accelerate the carbonation process. This ensured that carbonation time can be shortened from geological time scale to hours or minutes. Since then, the literature work has expanded greatly. However, it is clear that the research progress is facing challenges in enhancing the carbonation process to be viable to deploy on a large scale, as shall be demonstrated in the following sections. Nonetheless, the technique possesses several advantages over other sequestration techniques such as ocean and geologic sequestration, due to concerns over long term carbon leakage, as described previously [20]. Mineral carbonation produces more stable products that have the potential to be profitable and usually produced in fewer steps than other techniques. Additionally, the heat of the reaction can be further utilized as a source of energy.

Mineral sequestration techniques are often divided into in situ or ex situ manner. In situ sequestration requires injecting CO₂ into underground reservoirs to start a reaction with the existing underground minerals to form carbonates. Ex situ sequestration is related to carbonation process above the ground, where the raw natural mineral needs to be mined and treated before it undergoes the carbonation process. The scope of this work focuses on ex situ mineral carbonation and its related mechanisms and applications.

Although naturally occurring minerals have the potential to sequester huge amounts of CO₂ due to their abundance, it is not practically feasible due to the cost of extracting and pretreatment of the minerals and the impacts associated with it [21]. In addition to numerous process challenges in terms of carbonation efficiency and energy intensity (temperature and pressure). Alkaline industrial waste rich with Mg²⁺ and Ca²⁺ is an attractive alternative for CO₂ sequestration. It can be used to imitate mineral carbonation without the additional mining cost associated with natural rocks. Even so, alkaline waste is available in less amounts than natural minerals. It is available at lower cost, higher reactivity, and uptake capacity, and less pretreatment is required. Table 3 summarizes the most studied industrial alkaline waste and their alkali earth metal composition (Mg and Ca), in addition to their production rate per year and CO₂ emissions associated with their production. Examples of the industrial wastes include fly ash, such as coal and shale oil ashes, cement industry waste dust, and steel slag.

Table 3. Alkaline solids studied in the literature, their composition and global production per year and the CO₂ emission.

Alkaline Solid Waste	Production Per Year (t)	CO ₂ Emissions Per Year (t) ^a	Examples	Composition (wt.%)	Ref.
Steel slags	315–420 ^a	171 ^a	Basic Oxygen Furnace (BOF) Electric Arc Furnace (EAF) Blast Furnace Slag (BFS)	Ca: 45–55, Mg: 2–5 Ca: 40–46, Mg: 1–6.5 Ca: 35–43, Mg: 4–7	[17,22–24]
Waste cement	1100 ^a	62 ^a	Cement kiln dust	Ca: 35–50, Mg: 0–2	[25]
Fly ash	600 ^a	12,000 ^a	Coal fly ash Oil shale ash	Ca: 35–53, Mg: 0–3 Ca: 10–25	[26–34]
Air pollution control (APC) residues	1.2 ^b	N/A	Waste incineration plant residues	Ca: 35–38, Mg: 0–1	[35,36]
Red mud	1.25 ^a	3.6 ^a	Red gypsum	Ca: 1–6, Mg: 1–5	[37]

^a Retrieved from [10]; ^b Retrieved from [38].

Globally, cement industries account for 5% of the total CO₂ emissions [39,40]. Furthermore, the steel industry accounts for 7% of CO₂ emissions globally [41]. There are four main types of steelmaking slags, including blast furnace (BF), basic oxygen furnace (BOF), electric arc furnace (EAF), and ladle furnace (LF) slags. The slags consist of several oxides, primarily calcium, iron, and magnesium oxides that are present in different phases. On average, manufacturing 1 ton of steel produces approximately 420 kg of BOF and 180 kg of EAF [42]. There are two main approaches for ex situ alkaline waste carbonation: direct and indirect; each one has several sub-classifications based on the carbonation technique.

Direct carbonation technique implies that the carbonation process happens in one single step. On the other hand, indirect carbonation has more than one step (two or more) that usually involves pre-treatment of used minerals. Typically, mineral ores undergo a pre-treatment process where the reactive chemical components (i.e., alkali earth metals) in the rocks are separated for the mineral core. Pre-treatment usually involves mining, grinding, and activation of the rock minerals (Table 4). The end product of the pre-treatment process is almost pure carbonate form of the mineral. Then, the mineral carbonate is reacted with carbon dioxide in a separate step [12]. Table 5 shows the CO₂ uptake capacity using natural rocks. It lists numerous studies that investigated the carbonation efficiency of minerals using natural minerals (i.e., olivine and serpentine) by dry and aqueous carbonation routes. The table includes details about the process parameters and carbonation conversion.

Table 4. Description of pretreatment process.

Pre-Treatment Method	Description	Advantages/Disadvantages	Ref.
Grinding (reduction in size)	Rock minerals undergo grinding process to reduce particle size of the minerals to less than 63 μm (smaller particles size, more surface area available)	Advantages: <ul style="list-style-type: none"> • Surface area increase • Carbonation efficiency increase Disadvantages: <ul style="list-style-type: none"> • Energy intensive (releases additional CO_2 emissions) 	[43,44]
Heat (thermal) activation	Naturally occurring minerals contains water molecules bounded to its chemical structure i.e., up to 13% of serpentine is water. By heating the mineral up to 600 $^\circ\text{C}$ water is removed and more mineral is available for carbonation	Advantages: <ul style="list-style-type: none"> • Specific surface area of mineral is increased by removal of water molecules Disadvantages: <ul style="list-style-type: none"> • Economically not feasible 	[45,46]
Surface activation	Increasing the mineral surface area by treating it with steam or extraction acids	Advantages: <ul style="list-style-type: none"> • Specific surface area of mineral is increased Disadvantages: <ul style="list-style-type: none"> • Increasing CO_2 capture cost • Some of alkali earth metal elements can be reduced due to leaching 	[47]
Magnetic separation	The presence of iron element in mineral rocks can decrease the carbonation efficiency due to the formation iron oxides layers on the surface of the mineral. Separating iron compounds magnetically before carbonation can solve this issue	Advantages: <ul style="list-style-type: none"> • Increases carbonation capacity • Separating iron bearing compounds as marketable products Disadvantages: <ul style="list-style-type: none"> • Increasing CO_2 capture cost 	[48]
Sonication (ultrasound)	Ultrasound waves are used with extraction acid in conjunction to enhance the rate of mineral dissolution in the acid. The waves forms bubbles in the liquid that can enhance the mass transfer and the mineral dissolution rate.	Advantages: <ul style="list-style-type: none"> • Increases carbonation capacity by enhancing the dissolution rate Disadvantages: <ul style="list-style-type: none"> • Only tested on lab scale studies 	[49]

1.3. Indirect Carbonation

The term indirect mineral carbonation refers to the carbonation process that happens in two or more stages. Extraction of the reactive elements (Mg and Ca) from the mineral solid matrix is an essential step in indirect carbonation. Typically, strong acids are used as extracting agents. The extracted mineral then undergoes the carbonation process by reacting with CO_2 . One of the main advantages of using extraction is that it allows the production of almost pure mineral, as other impurities available in the natural mineral core can be removed after the reactive metal is extracted [50]. Numerous methods exist that can achieve mineral extraction, such as using acids, molten salts, caustic soda, and bioleaching. Table 6 lists all extraction methods studied in the literature with their associated extraction reactions. Every extraction technique possesses its intrinsic advantage and disadvantages. For example, using HCl produces pure alkali earth metal; however, it is significantly energy intensive if the recovery of HCl is required. Inversely, molten salts are less energy intensive in terms of regeneration. Nonetheless, molten salts are more corrosive compared to HCl [12]. Another approach of indirect carbonation is pH swing. pH swing refers to the extraction of mineral carbonate from the solid matrix at low pH condition in the first stage. In a second stage, the pH of the extraction solution is raised to improve carbonate formation [51]. Although acids are able to extract significant amounts of calcium and magnesium ions from the feedstock, as explained previously, pH plays a great

role in the precipitation of calcium and magnesium carbonates. Therefore, increasing the solution pH to approximately 10 in the second stage of mineral extracting helps to increase the rate of carbonate precipitation [10]. Hence, due to the added cost of implementing a second process step and the extensive use of extraction agents, direct carbonation is a more practical mineral carbonation option. In this review, direct aqueous carbonation using steel-making waste is being reviewed.

Table 5. Mineral carbonation studies for natural minerals.

Material	Carbonation Method	Composition (wt.%)	Maximum CO ₂ Uptake %	Reactor Type	Conditions/Remarks	Ref.
Serpentine	Direct aqueous carbonation	MgO: 40	30%	Batch	Temperature: 300 °C CO ₂ Partial pressure: 335.4 atm	[52]
Olivine	Direct aqueous carbonation	CaO: 0.07 SiO ₂ : 41.4 MgO: 49.7 Al ₂ O ₃ : 0.21 Fe ₂ O ₃ : 2.7	91%	CSTR	Temperature: 155 °C Process pressure: 185 atm	[53]
Serpentine	Indirect using pH swing	-	42%	Batch	Temperature: 70 °C Process pressure: 1 atm	[51]
Serpentine	Direct aqueous carbonation	CaO: 0.15 SiO ₂ : 39.5 MgO: 38.7 Al ₂ O ₃ : 0.35 Fe ₂ O ₃ : 4.86	7%	Batch	Temperature: 25 °C Process pressure: 125 atm	[46]
Wollastonite CaSiO ₃	Direct aqueous carbonation	-	69%	Batch	Temperature: 200 °C Process pressure: 20 bar Particle size: <38 μm L/S: 2	[54]
Serpentinite	Dry carbonation	-	50%	Fluidized bed	Temperature: 500 °C Process pressure: 20 bar	[55]
Wollastonite CaSiO ₃	Direct aqueous carbonation	-	83.5%	Batch	Temperature: 150 °C Process pressure: 40 bar Particle size: <30 μm	[56]
Serpentinite	Dry carbonation	MgO: 35.3	0.0075 gCO ₂ /g serpentinite	Fluidized bed	Temperature: 90 °C Moist CO ₂ Process pressure: 1 bar	[57]

Table 6. Description of different indirect carbonation methods.

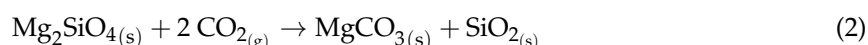
Indirect Carbonation	Description/Reactions	Ref.
Acid extraction	<p>Numerous acids are investigated in the literature as an extraction agent. Examples of these acids are: acetic acid, nitric acid, formic acid and hydrochloric acid. Acid extraction is achieved through multiple routes. The most straightforward extraction method includes mixing the mineral and the extracting agent in a stirred reactor or vessel at a certain temperature and pressure to extract the minerals, followed by carbonation process of the extracted mineral according to the following reactions:</p> $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 6\text{HCl}_{\text{aq}} + \text{H}_2\text{O} \xrightarrow{100^\circ\text{C}} 3\text{MgCl}_2\cdot 6\text{H}_2\text{O}_{\text{aq}} + 2\text{SiO}_{2(s)}$ $\text{MgCl}_2\cdot 6\text{H}_2\text{O}_{\text{aq}} \xrightarrow{250^\circ\text{C}} \text{MgCl}(\text{OH})_{\text{(aq)}} + \text{HCl}_{\text{aq}} + 5\text{H}_2\text{O}$ $2\text{MgCl}(\text{OH})_{\text{(aq)}} \xrightarrow{\text{Cooling}} \text{Mg}(\text{OH})_{2(s)} + \text{MgCl}_{2(\text{aq})}$	[46]
Molten salt	<p>The molten salt process is aimed to reduce energy requirements resulting from HCl extraction. It shares many similarities with HCl extraction except the molten salt, $3\text{MgCl}_2\cdot 3.5\text{H}_2\text{O}_{\text{(aq)}}$, is being used as an extracting agent.</p> $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_{4(s)} + 3\text{MgCl}_2\cdot 3.5\text{H}_2\text{O}_{\text{(aq)}} \xrightarrow{200^\circ\text{C}} 6\text{Mg}(\text{OH})\text{Cl} + 2\text{SiO}_{2(s)} + 9.5\text{H}_2\text{O}$	[12]
Ammonia	<p>Using NH_4Cl as extraction agent according to the following reaction:</p> $4\text{NH}_4\text{Cl}_{\text{aq}} + 2\text{CaO}\cdot\text{SiO}_2 \rightarrow 2\text{CaCl}_{2(\text{aq})} + 2\text{SiO}_2 + 4\text{NH}_3 + 2\text{H}_2\text{O}$ $2\text{CaCl}_{2(\text{aq})} + 2\text{CO}_{2(\text{g})} + 4\text{NH}_{3(\text{aq})} + 2\text{H}_2\text{O} \rightarrow 2\text{CaCO}_{3(s)} + 4\text{NH}_4\text{Cl}_{\text{aq}}$	[51]
Caustic soda	<p>Using sodium hydroxide as an extracting agent:</p> $\text{CaSiO}_{3(s)} + \text{NaOH}_{\text{aq}} \xrightarrow{200^\circ\text{C}} \text{NaCaSiO}_3(\text{OH})_s$ $2\text{NaOH}_{\text{aq}} + \text{CO}_{2(\text{aq})} \xrightarrow{200^\circ\text{C}} \text{Na}_2\text{CO}_{3(\text{aq})} + \text{H}_2\text{O}$ $\text{Na}_2\text{CO}_{3(\text{aq})} + 3\text{NaCaSiO}_3(\text{OH})_s + \text{H}_2\text{O} \xrightarrow{200^\circ\text{C}} 4\text{NaOH}_{\text{aq}} + \text{CaCO}_3 + \text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})_s$	[12]
Bioleaching	<p>Bioleaching is defined as the process of using bacteria to extract minerals from natural rocks, can be applied for the extraction of Ca & Mg oxides from silicates.</p>	[58]

2. Direct Carbonation

Direct carbonation includes the reaction of CO₂ with a suitable feedstock or Calcium/Magnesium rich solid residue in a single step. It is relatively easier to implement compared to indirect carbonation. Hence, it has the potential to be used in industrial scale. The following sections explain the working principles of direct carbonation, discussing the operational parameters that have the most impact on the carbonation capacity.

2.1. Gas-Solid Carbonation

The reaction of gaseous CO₂ with solid minerals is the most basic and straightforward approach of direct carbonation, first studied by Lackner et al [52]. In the case of olivine carbonation:



The reaction suffers from very slow reaction rates. Hence, it is usually carried over an elevated temperature and pressure. However, due to thermodynamics limitations, the temperature is restricted between 170–400 °C for most natural minerals, as equilibrium shifts to the reactant side with increasing temperature [52]. Hence, the maximum carbonation temperature is a function of CO₂ partial pressure and the specific mineral used (Table 7). The process high temperature requirement can be further utilized to generate steam that will be used to produce electricity [12]. Nevertheless, the process slow kinetics is still the main obstacle hindering further progress even at high temperature and pressure.

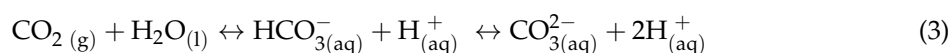
Table 7. Maximum carbonation temperature for several minerals at CO₂ partial pressure of 1 bar [59].

Mineral	Maximum Carbonation Temperature (°C)
Olivine (Mg ₂ SiO ₄)	241
Wollastonite (CaSiO ₃)	280
Calcium oxide (CaO)/Calcium hydroxide (Ca(OH) ₂)	887
Magnesium oxide (MgO)/Magnesium hydroxide (Mg(OH) ₂)	406

Thus, the experimentally obtained carbonation rate of direct dry rock minerals carbonation is insignificant, even at elevated temperature and pressure [12]. Kwon et al. [60] reported that introducing moisture to the flue gas in dry carbonation process can increase the carbonation rate significantly. However, due to low CO₂ sequestering efficiency, 8 tons of olivine would be required to capture 1 ton of CO₂. This renders the process practically not viable and reduces its wide scale applicability. Hence, focus shifted on dry carbonation of pure magnesium and calcium oxides [52]. Nevertheless, the limited availability of the used minerals hindered the research progress. However, alkali earth metals can be extracted from the mineral rocks and industrial wastes. This adds another process step (extraction) to the overall process scheme. Hence, the process becomes an indirect carbonation process, which is discussed previously.

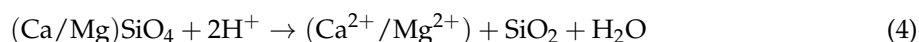
2.2. Direct Aqueous Carbonation

As explained in the introduction section, natural carbonation occurs when CO₂ is dissolved in rain water according the following equation:

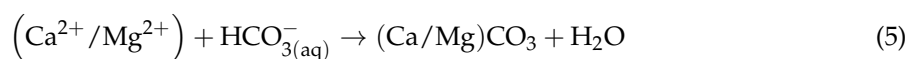


The aqueous solution becomes more acidic due to the presence of protons (H_(aq)⁺) resulting from CO₂ solubility in water. Hence, by imitating natural carbonation, carbonation of natural minerals could take place in aqueous media in a single stage process. When the rock mineral is placed in aqueous

solution, calcium or magnesium element in the solid matrix leaches from mineral ore according to Equation (4):



Eventually, mineral carbonate is formed when the mineral reacts with dissolved CO₂ (bicarbonate proton)



When studying direct aqueous carbonation, a good practice is to study the process parameters, such as temperature, pressure, and solution medium, that can maximize CO₂ uptake capacity. For aqueous carbonation specifically, increasing process pressure enhances CO₂ solubility in the aqueous medium. Therefore, according to Equation (5), the reaction will shift towards the products side, which is highly desirable. On the other hand, increasing the reaction rates can be enhanced by elevating temperature. However, this applies to a certain extent due to the decline in CO₂ solubility in the solution with increasing temperature. In other words, CO₂ solubility in a certain solution dictates the upper limit at which the process temperature can be elevated. Carbonation conversion is a way to measure the carbonation efficiency and is defined according to the following equation:

$$\eta_{(\text{Carbonation})} \% = \frac{\text{Quantity of Mg or Ca converted to carbonate}}{\text{Quantity of Mg or Ca available in mineral}} \times 100 \quad (6)$$

Hence, the efficiency is reported on the basis of magnesium and calcium content of the mineral, not the total quantity of the used mineral.

Studies investigating direct aqueous carbonation reaction mechanism revealed that aqueous carbonation proceeds in two distinct steps, as opposed to 1 step in dry carbonation [61]:

- (1) Dissolution of alkali earth element into the solution (leaching step).
- (2) Formation of mineral carbonate (carbonation step).

Typically, leaching of alkali metal into aqueous solution is the rate limiting step. Nonetheless, altering the process parameters, such as temperature and pressure, can make the carbonation step the rate limiting step [62]. This is explained by the formation of the carbonation products on the surface of the minerals that will increase the mass transfer resistance between the dissolved CO₂ and mineral core. Hence, controlling the dissolution rate and finding the best process parameters is a must to ensure sufficient carbonation efficiency. Different minerals have different dissolution rates [63]. The rate depends on the morphology of the mineral (surface area and structure) [64]. Thus, pre-treatment techniques stated in Table 4 can be used to enhance the dissolution rate, hence, the carbonation efficiency.

3. Steelmaking Waste Mineral Carbonation

Solid industrial wastes are generally alkaline and rich in Ca/Mg and can therefore be applied as an additional feedstock for mineral CO₂ sequestration. The main advantages of industrial waste are that they are available at low to no costs in proximity to industrial emitters, almost no pre-treatment is needed, and they are more reactive in less energy intensive conditions. In addition, the end product of the sequestration can be used in several applications, i.e., as a construction material and in fertilizers. The fundamental working principles for mineral CO₂ sequestration apply for industrial waste in the same way. In fact, the major elements of e.g., steel slag (Mg, Ca, Si, and Fe) are present in a comparable concentration as in natural rocks. However, trace metals and soluble salt concentrations are available in more quantities compared to the average composition of natural rocks. Thus, steel industry waste can undergo the same direct and indirect carbonation techniques previously explained. Presently, the research is going towards optimizing the uptake capacity of CO₂ by modifying the

operating parameters including pressure, temperature, liquid-to-solid ratio, CO₂ gas flowrate, solid particle size, and pretreatment. Table 8 presents a summary of steel making waste which have been tested as mineral carbonation in terms of feedstocks; feed composition, the experimental CO₂ capture capacity, and the different process conditions were investigated. The mineral carbonation uptake is a function of process temperature, CO₂ partial pressure, and steel waste surface area, which affect the carbon dioxide dissolution rate, the diffusion rate of ions through the reaction with steel slag. The pH value is an additional essential parameter in mineral carbonation process. Optimum pH for aqueous carbonation is achieved at pH of 10 [65]. pH of the process influences the carbonation reaction, as the reaction is more favorable in alkaline mediums. In addition, the pH decreases continuously as carbonation, due to CO₂ being dissociated into the solution. Eventually, the pH value remains unchanged at around 7 after the carbonation process ends. This signifies that the mineral carbonation process will not proceed in acidic mediums. Figure 1 summarizes the different aspects that affect the ex-situ mineral carbonation process, such as different reactor types and process parameters.

3.1. Temperature and Particle Size

Huijgen et al. [21] were among the first to utilize steel slag as feed stock for mineral carbonation. The authors studied parameters that could affect the carbonation rate, which include reaction temperature and steel slag particle size. An autoclave reactor was used to carry out the reactor, and a 450 mL of the slurry was used with a liquid to solid ratio of 20 kg/kg. A maximum conversion of 70% of the calcium in the feed stock was carbonated at a pressure of 19 bar and temperature of 100 °C was achieved. The authors reported that at higher temperatures leaching of calcium from steel slag components will proceed faster, hence increasing the reaction rate, but the solubility of CO₂ in the solution decreases. This was also observed by Han et al. [65]. To achieve this carbonation percentage, the particle size was reduced from <2 mm to <38 µm. Reducing the particle size will produce more surface area for the carbonation reaction to occur, hence increasing the conversion. Particle size and specific surface area are among the most important factors affecting the dissolution kinetics of any kind of material. Mineral particle size determines its reactive surface area in addition to its leaching mechanisms. Typically, grinding is used to achieve a specific particle size. However, it is an energy intensive process. Hence, determining the optimal particles size will help in reducing the process cost in addition to increasing its efficiency. Baciocchi et al. [43] reported that the parameter that most affected the CO₂ uptake of the slag was particle size, especially the specific surface of the particles. An increase in temperature also had a positive effect, achieving a maximum uptake of 130 g CO₂/kg slag. The authors reported that an average particle size of less than 150 micrometers is considered as optimum.

3.2. Liquid to Solid Ratio

Liquid to solid ratio is defined by the amount of steel slag that is being utilized in a certain amount of aqueous medium (mass/mass). Revathy et al. reported that the carbonation efficiency increased when the S/L ratio decreased. The results indicate that when L/S is increased from 5 to 10 g/g, the carbonation degree of steel slag also increases. A further L/S increase causes a decrease in the carbonation degree of steel slag. This is caused due to the presence of extra liquid that leads to dilution of calcium ion concentration in the aqueous medium [66]. In a similar manner, the sequestration capacity of slag water slurry increased with the L/S ratio from 2 to 10, after which it decreased. This is due to the fact that a high amount of water inside the reactor causes blocking in the diffusion of gas molecules in the slurry [67].

Table 8. Summary of the tested steel slag for mineral carbonation in terms of CO₂ capture capacity, feedstock composition and process parameters.

Material	Carbonation Method	Composition (wt.%)	Maximum CO ₂ Uptake	Reactor Type	Conditions/Remarks	Year	Ref
Steel Slag	Direct aqueous carbonation	Fe ₂ O ₃ : 35.5 CaO: 31.7 SiO ₂ : 9.1 MgO: 6.0	74% of Ca content	Batch	CO ₂ pressure: 19 bar Temperature: 100 °C Particle size: <38 µm Reaction time: 30 min	2005	[21]
BSF	Indirect aqueous carbonation: (extraction) using acetic acid	CaO: 40.6 SiO ₂ : 34.1 MgO: 10.7 Al ₂ O ₃ : 9.4	0.23 g CO ₂ /g CaO	Stirred batch	3.6 liters of Acetic acid was used to produce carbonates by leaching	2008	[50]
Steel slag	Indirect carbonation	CaO: 32.1 SiO ₂ : 19.4 MgO: 9.4 Al ₂ O ₃ : 8.6 Fe ₂ O ₃ : 26.4	30%	Batch	Slag was leached in deionized water Ambient temperature and pressure. Increasing the leachate temperature from 60 °C enhanced the Ca-leaching	2008	[70]
LFS	Indirect aqueous carbonation	CaO: 58.1 SiO ₂ : 26.4 MgO: 6.2 Al ₂ O ₃ : 4.6 FeO: 4.30	0.247 g CO ₂ /g CaO	Stirred batch	L/S: 10 Temperature: 20 °C Process pressure: 1 bar CO ₂ : 15 vol.% CO ₂ flowrate: 5 mL/min Rotational speed: 200 rpm	2008	[71]
Steel slag	Indirect aqueous using pH swing using NH ₄ Cl	CaO: 44.5 SiO ₂ : 9.28 MgO: 7.6 Fe ₂ O ₃ : 19.1 Al ₂ O ₃ : 2.3	70% of Ca content	Stirred batch	CO ₂ : 13 vol.% Temperature: 80 °C Pressure: 1 atm Rotational speed: 300 rpm	2008	[72]
APC	Direct aqueous carbonation	CaO: 35 SiO ₂ : 1.01 Al ₂ O ₃ : 0.21 MgO: 0.84	0.25 g CO ₂ /g CaO	Batch	CO ₂ : 100 vol.% L/S: 0.2 Temperature: 30 °C Process pressure: 3 bar	2009	[36]
EAF Slag	Indirect aqueous carbonation (extraction) using nitric acid	CaO: 41.6 SiO ₂ : 18.8 MgO: 8.0 Al ₂ O ₃ : 3.4	0.359 g CO ₂ /g CaO & MgO	Batch	L/S: 0.2 Temperature: 22 °C	2010	[73]
Industrial wastes from acetylene production	Carbonation by atmospheric CO ₂	CaO: 41.6 SiO ₂ : 18.8	0.476 g CO ₂ /g waste	N/A	L/S: 0.33	2010	[74]

Table 8. Cont.

Material	Carbonation Method	Composition (wt.%)	Maximum CO ₂ Uptake	Reactor Type	Conditions/Remarks	Year	Ref
BFS	Indirect carbonation (extraction) using nitric acid	CaO: 51.1 SiO ₂ : 11.5 MgO: 4.2 Al ₂ O ₃ : 1.5 Fe ₂ O ₃ : 24.1	0.27 g CO ₂ /g CaO	Slurry	L/S: 10 Temperature: 70 °C CO ₂ Partial pressure: 101.3 kPa CO ₂ flowrate: 0.1 L/min Particles size: <44 µm	2011	[75]
Steel slag	Direct aqueous carbonation	CaO: 38.84 MgO: 10.36 Al ₂ O ₃ : 3.91 Fe ₂ O ₃ : 32.8	93% based on CaO content	high-gravity rotating packed bed	Rotational speed: 750 rpm Temperature: 65 °C Process pressure: 1 bar L/S: 20	2012	[76]
BOFS	Direct aqueous carbonation	CaO: 36.37 MgO: 7 Al ₂ O ₃ : 1.89 Fe ₂ O ₃ : 10.36	99% based on CaO content	Rotating packed bed	Rotational speed: 1000 rpm Temperature: 25 °C L/S: 20 mg/L Process pressure: 1 bar CO ₂ : 30 vol.% CO ₂ flowrate: 1.8 L/min	2013	[77]
BOFS	Direct aqueous carbonation	CaO: 41.15 SiO ₂ : 10.59 MgO: 9.21 Al ₂ O ₃ : 2.24 Fe ₂ O ₃ : 24.41 MnO: 2.75	89.4%	Slurry reactor	Temperature: 25 °C L/S: 20 CO ₂ pressure: 1 bar CO ₂ flowrate: 1 L/min Slurry volume: 350 mL	2013	[78]
BSF	Indirect aqueous carbonation (extraction) using EDTA	CaO: 47.15 SiO ₂ : 31.08 MgO: 3.34 Al ₂ O ₃ : 13.81 Fe ₂ O ₃ : 0.378 MnO: 0.71	0.09 g CO ₂ /g slag	Batch	Temperature: 25 °C Process pressure: 1 bar CO ₂ flowrate: 1.5 L/min	2013	[17]
Steel slag	Dry carbonation	-	0.0449 g CO ₂ /g slag	Batch	Temperature: 600 °C CO ₂ %: 10 vol.% CO ₂ flowrate: 1.5 L/min	2014	[79]
BOFS	Direct aqueous carbonation	CaO: 43 SiO ₂ : 12.9 Fe ₂ O ₃ : 28.7	0.16 g CO ₂ /g CaO	rotating packed bed	Rotational speed: 541 rpm Temperature: 25 °C L/S: 10 Process pressure: 1 bar	2014	[80]

Table 8. Cont.

Material	Carbonation Method	Composition (wt.%)	Maximum CO ₂ Uptake	Reactor Type	Conditions/Remarks	Year	Ref
Steel slag	Indirect aqueous carbonation (extraction) using NH ₄ SO ₄	CaO: 38.98 SiO ₂ : 12.13 MgO: 8.96 Al ₂ O ₃ : 2.74 Fe ₂ O ₃ : 22.53 MnO: 3.58	74%	Batch	Temperature: 65 °C L/S: 15 g/L Process pressure: 1 bar	2014	[24]
Steel slag	Direct aqueous carbonation	CaO: 41.3 SiO ₂ : 20.9 MgO: 6.2 Al ₂ O ₃ : 2.3 Fe ₂ O ₃ : 20.7	0.264 g CO ₂ /g CaO	Batch	Temperature: 60 °C L/S: 10 CO ₂ flowrate: 0.6 L/min Process pressure: 10 bar CO ₂ %: 100 vol. %	2015	[66]
BOFS	Direct aqueous carbonation	CaO: 23 SiO ₂ : 6 MgO: 3.8 Al ₂ O ₃ : 1.1 Fe ₂ O ₃ : 25	0.403 g CO ₂ /g CaO	Batch	Temperature: 100 °C L/S: 5 L/kg CO ₂ : 100 vol. % Process pressure: 10 bar Particle size: <150 µm	2015	[81]
EAFS	Dry carbonation	CaO: 42.8 SiO ₂ : 4.49 MgO: 4.96 Al ₂ O ₃ : 0.28 Fe ₂ O ₃ : 42.8	0.657 g/g CaO	Slurry		2015	[82]
BOFS	Direct aqueous carbonation	CaO: 51.1 SiO ₂ : 11.2 MgO: 4.2 Al ₂ O ₃ : 1.2 Fe ₂ O ₃ : 24	57%	Batch	Temperature: 50 °C L/S: 20 mL/g CO ₂ flowrate: 0.1 L/min Process pressure: 1 bar	2016	[83]
Steel slag	Dry carbonation	CaO: 28.27 SiO ₂ : 15.4 MgO: 7.88 Al ₂ O ₃ : 1.01 Fe ₂ O ₃ : 24.25	0.011 g CO ₂ /g slag	Batch	Temperature: 50 °C CO ₂ : 100 vol. %	2016	[67]
EAF	-	CaO: 33.19 SiO ₂ : 16.71 MgO: 9.43 Al ₂ O ₃ : 6.73 Fe ₂ O ₃ : 38.19	0.052 g CO ₂ /g slag	Batch	Temperature: 25 °C Process pressure: 10.68 bar L/S: 10	2016	[68]

Table 8. Cont.

Material	Carbonation Method	Composition (wt.%)	Maximum CO ₂ Uptake	Reactor Type	Conditions/Remarks	Year	Ref
BOF	Direct aqueous carbonation	CaO: 31 SiO ₂ : 5.1 MgO: 7.5 Fe ₂ O ₃ : 27	0.536 g CO ₂ /g slag	Batch	Temperature: 83.7 °C Process pressure: 5.9 bar L/S: 5 L/kg CO ₂ : 60.6 vol.%	2016	[84]
BFS	Direct aqueous carbonation	CaO: 42.5 SiO ₂ : 31.9 MgO: 4.81 Al ₂ O ₃ : 13 Fe ₂ O ₃ : 0.34	0.0295 g CO ₂ /g slag	Batch	Temperature: 50 °C Process pressure: 5 bar L/S: 3 CO ₂ : 100 vol.%	2017	[69]

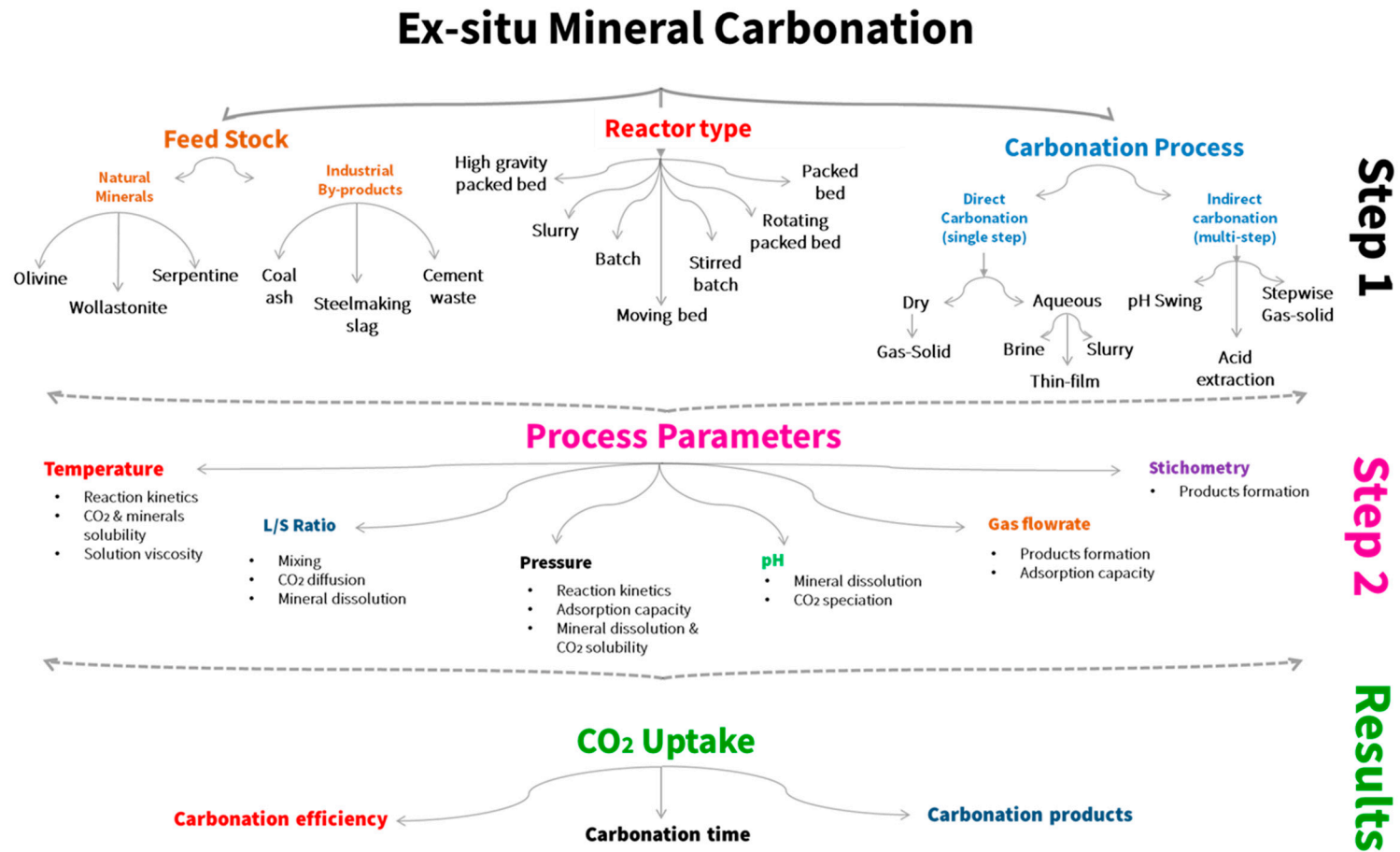


Figure 1. Ex-situ mineral carbonation literature summary.

3.3. Pressure

At constant temperature, CO₂ gas solubility increases along with pressure according to Henry's law. Hence, CO₂ molecules that are involved in the carbonation process will be more as the pressure is elevated. The effect of pressure on CO₂ uptake was tested at 10, 50, 100, and 150 bar under the same condition (50 °C, L/S = 1) by Han et al. [65]. The carbonation conversion was found to be 21% and 50.2% for 10 and 150 bar, respectively. Similarly, Ghacham et al. [68] reported that a higher CO₂ partial pressure caused more CO₂ to be soluble in aqueous medium, forming carbonic acid and consequently increasing the bicarbonate ions formation. Therefore, more bicarbonates will react with calcium ions. Hence, higher CO₂ uptake. Fagerlund et al. [55] reported that the carbonation rate and degree might increase exponentially with time, as long as a high enough CO₂ pressure could be maintained. Additionally, high pressure will cause the reaction time to be shorter, hence, having lower carbonation time. Similarly, Eloneva et al. [69] reported shorter reaction times as the partial pressure of CO₂ is increased.

4. Summary and Future Prospective

Carbon capture and sequestration can be achieved through different techniques that have the potential to capture substantial amounts of CO₂ and help reduce its emissions. Mineral carbonation is evolving as a possible candidate to sequester CO₂ from medium-sized emissions point sources. The process of natural carbonation forms the basis of mineral carbonation process. Active alkaline elements (Ca and Mg) are the fundamental reactants for mineral carbonation reaction. Industrial alkaline wastes, such as steel-making waste, are rich with these alkaline compounds, especially calcium and magnesium oxides. Hence, they are studied in the literature as a possible mineral carbonation process feedstock. Several parameters govern the carbonation process, including process temperature, pressure, and liquid to solid ratio. There is still a room for improvement by targeting higher CO₂ uptake value. This can be achieved by using a different aqueous medium to carry out the carbonation process, i.e., reject brine and the development of reactor systems that minimize mass transfer limitations. Optimizing the interactions between process parameters, such as the interplay between temperature, pressure, and the degree of mixing, will contribute to the carbonation process. In addition, studying the adsorption behavior of CO₂ on other elements, such as iron oxide, will give more insights into increasing CO₂ uptake.

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