Accelerated Carbonation of Ca- and Mg-Bearing Minerals and Industrial Wastes Using CO_2

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CHAPTER OUTLINE

8.1 Introduction

One of the options for permanently storing CO_2 is to convert calcium- and magnesium-bearing minerals and alkaline industrial wastes into environmentally benign, insoluble and thermodynamically stable solid magnesium and calcium carbonates.[1] The conversion of CO_2 into solid carbonates is known as carbon mineralization. This process is thermodynamically favoured, but is kinetically challenging in nature. Thus, most of the research in the area of carbon mineralization has been focused on accelerating mineral dissolution and carbonation. The reaction between

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injected high-pressure CO_2 and geologic formations in the carbon storage site is also known as in situ carbon mineralization. While the rate of in situ carbon mineralization is still slow, its implications on the long-term stability of the geologically stored CO_2 are important. Alternatively, the minerals can be mined, mechanically ground and reacted with CO_2 in highly engineered processes, also known as ex situ carbon mineralization. Minerals with significant amounts of reactive components, such as calcium and magnesium, are preferred for the ex situ approach in order to minimize the reactor size. In addition to abundant silicate minerals, industrial wastes with high alkalinity can also react with CO_2, and generally the carbonation of industrial wastes such as fly ash and steel slags are relatively fast. The reaction of industrial wastes with CO_2 renders them safe for landfill disposal via neutralization.

The availability of Ca- and Mg-bearing minerals and alkaline industrial wastes for carbonation are presented in Figures 8.1 and 8.2. The most abundant non-carbonated minerals on earth containing significant Ca and Mg are silicate minerals such as olivine $[(Mg,Fe)_2SiO_4]$ and serpentine $[(Mg,Fe)_3(OH)_4(Si_3O_5)]$, and a smaller quantity of wollastonite $(CaSiO_3)$. In addition to these minerals with high Ca and Mg contents, there are rocks, such as basalt and labradorite, as well as asbestos, which can react with CO_2. These have a potential for in situ carbon mineralization. Compared to Ca- and Mg-bearing minerals, the quantity of alkaline industrial wastes (e.g. stainless steel slag, fly ash and cement kiln dust) available for CO_2 fixation is relatively limited but they are generally more reactive. Including in situ carbon mineralization, more than $10,000-1,000,000$ Gt of total carbon can be stored via mineral carbonation compared to only about $200-300$ Mt of CO_2 that can be stored in alkaline industrial wastes annually.[23] The annual production rates of fly

▲ Basalt　　■ Labradorite　　● Magnesium-based Ultramafic Rocks (e.g., serpentine, olivine)　　● Asbestos
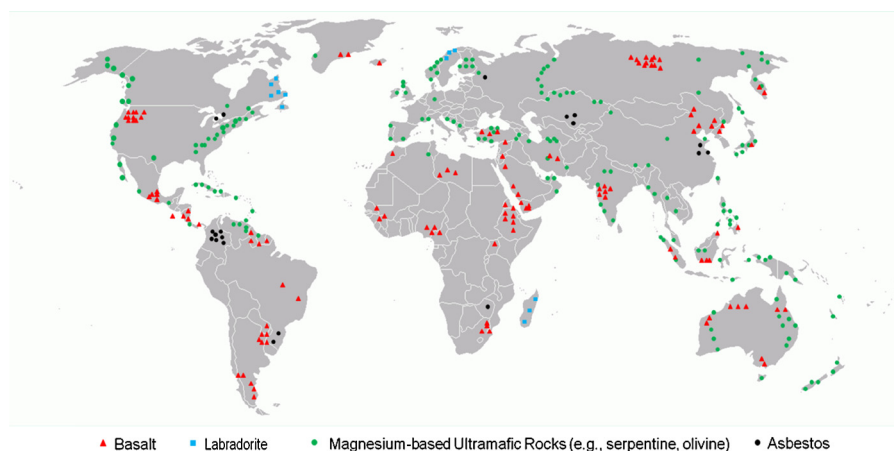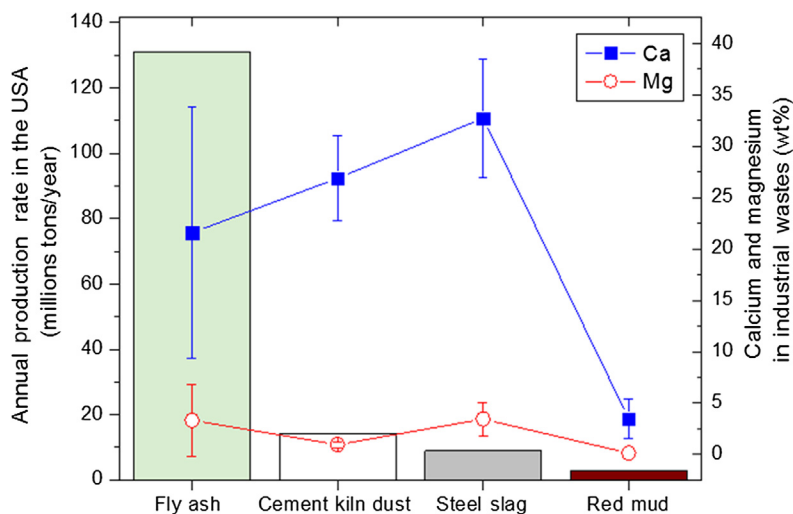
FIGURE 8.1

Worldwide distribution of minerals and rocks with CO_2 storage capabilities (although asbestos belongs to the serpentine group, it is displayed separately because of its hazardous character).

FIGURE 8.2

Annual production rate in the United States and average calcium and magnesium concentrations in fly ash,[2–9] cement kiln dust,[10,11] steel slag[12–20] and red mud[21,22] based on studies reported in Table 8.2.

ash,[24] cement kiln dust,[25] steel slag[26] and red mud[27] in the United States alone are of the order of less than 200 Mt. There is a considerable variability in the amount of Ca and Mg in the alkaline industrial wastes, as represented in Figure 8.2.

In terms of the cost of carbon mineralization processes, in situ carbon mineralization tends to be low in initial cost compared to the ex situ carbonation of silicate minerals and industrial wastes. On the other hand, ex situ carbon mineralization has unique benefits of faster reaction, straightforward quantification of stored carbon, avoidance of long-term monitoring and potential generation of value-added products. Studies have showed that about 4600 Gt of materials can be produced via carbon mineralization to offset 20% of global CO_2 emissions over 100 years.[23] Of these, 1240 Gt include carbonates, silica and iron oxides while about 3400 Gt may need to be disposed or used for low-value applications.[23] Some of the applications of carbonates include utilisation in filler materials, coatings, CO_2 sorbents, construction materials, liming agents to neutralize soil acidity, land reclamation, hazardous waste reclassification and remediation of contaminated lands. Iron oxide is used in iron and steel manufacturing and in pigments such as paints and ceramics, while silica is used in semi-conductors, glass, construction and refractory materials and ceramics. Carbonated industrial wastes such as steel slags, fly ash, bottom ash and cement kiln dust can also be used as construction aggregates.[2,10,11,23,28]

In order to optimize the carbon mineralization technology, particularly ex situ schemes, various reaction parameters have been investigated ranging from particle size, porosity, reaction temperature and CO_2 pressure, solvent pH and chemical

additives (e.g. chelating agents to enhance dissolution, or catalysts such as carbonic anhydrase to enhance CO_2 hydration).[29−34] To achieve sufficient dissolution and carbonation rates, minerals and rocks, in some cases even industrial wastes, need to be ground to the order of $10-100$ s μm, which can be energy intensive. The addition of bicarbonate and Mg-targeting chelating agent has been found to be effective at accelerating the mineral carbonation, while higher reaction temperatures ($>150\,°C$) allow the production of anhydrous magnesium carbonates, rather than nesquehonite or hydromagnesite.[35−38] Once carbonated, the carbonates and other solid by-products such as high surface area silica and iron oxide can be characterized for their chemical and physical properties (e.g. the composition and mineralogy, the particle size and distribution, pore size and distribution, surface area, crystal structure and microstructure of the solids) in order to identify their potential uses. If the carbonated materials would be landfilled, a regulated leaching test should be performed. The CO_2 storage and utilisation potential via the carbonation of minerals and industrial wastes are compared in Table 8.1.

The use of the value-added products including mineral carbonates would offset the cost of carbon sequestration and avoid the carbon emission associated with those products. However, it should also be noted that the amount of anthropogenic CO_2 emission is orders of magnitude larger than the product (e.g. carbonate) markets. Thus, in order not to flood the market, the use of only a small fraction ($<5\%$) of value-added products should be considered and additional disposal considerations need to be taken into account for the overall carbon mineralization scheme. The

Table 8.1 CO_2 Storage and Utilisation Potential of Silicate Minerals and Industrial Wastes

Ca- and Mg-bearing Minerals	Industrial Wastes
CO_2 storage capacity is in the order of thousands of Gt of carbon.[23]	About 200–300 Mt of industrial wastes are produced annually. [23]
Crystalline structure may hinder reactivity.	Disordered surfaces and lack of a definite composition or crystal structure facilitate faster reactivity.
Requires preprocessing such as mining, crushing and grinding.	Mining is not required for the production of industrial wastes.
After mining, CO_2 and/or minerals need to be transported to the processing site for treatment.	In some cases, when industrial wastes are generated along with CO_2, the carbonation process can be carried out on the site of generation.
Depending on the type of mineral, higher temperatures and highly concentrated solvents may be required to achieve high conversions.	Most industrial wastes are highly reactive and can generally react with the CO_2 to form neutral salts at ambient conditions (exceptions include asbestos that contains chrysotile fibres).

carbon mineralization schemes for the engineered weathering of silicate minerals and carbonation of alkaline industrial wastes are discussed in the following sections.

8.2 **Engineered weathering of silicate minerals**

Minerals such as olivine [$(Mg,Fe)_2SiO_4$] and serpentine [$(Mg,Fe)_3(OH)_4(Si_3O_5)$] are abundant on earth, far exceeding the global coal reservoir, and comprise more than 35 wt% MgO. These minerals need to be mined and ground for ex situ carbon mineralization. The mass of ore that needs to be mined to store a unit mass of CO_2 was defined as the carbonation potential, R_{CO_2}.[39,40] Higher $1/R_{CO_2}$ values indicate higher carbonation potential. Compared to Mg-silicate minerals, Ca-silicate minerals such as wollastonite ($CaSiO_3$) are more reactive and form calcium carbonates. Unfortunately, wollastonite is not as abundant as olivine and serpentine. Thus, the carbonation of wollastonite is considered only in limited locations, for example, New York state. The mass of CO_2 that is trapped per unit mass of the mineral, $1/R_{CO_2}$ of another less available mineral, brucite ($Mg(OH)_2$), is 0.77 kg of CO_2/kg of mineral, which is higher than that of olivine and serpentine, whose $1/R_{CO_2}$ values are in the range of 0.56–0.63 and 0.40–0.53, respectively (Table 8.2). This is because the MgO content in brucite is 69%, while it is lower than 50% in olivine and serpentine.

Since in ex situ carbon storage, the minerals are mined and reacted with CO_2 in engineered processes and in situ carbon storage, CO_2 is directly injected into the mineral formations, the selection of suitable minerals for each case depends on the CO_2 storage capacity. Minerals with high carbonation efficiency or high $1/R_{CO_2}$ (e.g. olivine and serpentine) are suitable for ex situ carbon storage and utilisation. The geologic formations rich in minerals and rocks including aluminosilicates, such as labradorite [$(Ca, Na)(Al, Si)_4O_8$], and basalt (mixture of various Ca and Mg-bearing minerals), that have lower $1/R_{CO_2}$ values, are selected for in situ carbon mineralization. The content of CaO or MgO in these aluminosilicates is lower than 25%, which may not make it economical to mine and convert these minerals to carbonates via ex situ carbon mineralization.

While mining of Ca- and Mg-rich minerals would be necessary for large scale ex situ mineral carbonation, a significant amount of these minerals are also available as industrial wastes such as mining tailings as a low hanging fruit for carbon mineralization. Serpentine has been actively mined for the extraction of nickel (<3.6 wt%)[47] and large deposits of serpentine mine tailings exist across the world. Therefore, these mine tailings would be great candidates for CO_2 storage via carbon mineralization.

8.2.1 **Reaction schemes**

Given the abundance of silicate minerals, there has been a considerable interest over the past 20 years to understand the reaction of CO_2 with minerals. Since
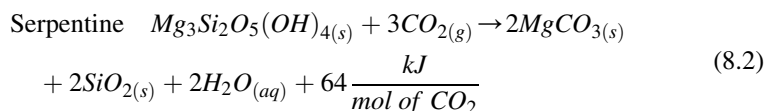
Table 8.2 Summary of Mineral Carbonation Studies

Minerals and Rock	Composition (wt%)	$\frac{1}{R_{CO_2}}$ [a] (kg_{CO_2}/kg_{ore})	Extent of Carbonation (%)	Pretreatment	Reaction Phase	P_{CO_2}, T, Reaction Time	Chemical Additives	References
Brucite, $Mg(OH)_2$	MgO: 68%	0.77	60%	None	Gas–solid	40 bar, 510 °C, 6 h	None	41
Olivine, $(Mg,Fe)_2 SiO_4$	Mg: 30.2%; Fe: 6.5%	0.63	55%	Attrition grinding	Aqueous	152 bar, 185 °C, 1 h	2.5 M $NaHCO_3$	42
	CaO: 0.2%; MgO: 47.3%; FeO: 12.3%	0.59	73%	None	Aqueous	141 bar, 185 °C, 3 h	1.0 M NaCl + 0.64 M $NaHCO_3$	43
	Ca: 0.1%; Mg: 27.9%; Fe: 6.1%;	0.56	38%	Attrition grinding	Aqueous	152 bar, 185 °C, 1 h	1.0 M NaCl + 0.64 M $NaHCO_3$	39
Serpentine, $(Mg,Fe)_3 (OH)_4 Si_3O_5$	Mg: 27.1%; Fe: 4.3%	0.53	65%	Aqueous with pH swing	Aqueous	1 bar, 70 °C, 1 h	Orthophosphoric acid (1 vol%) + oxalic acid (0.9 wt%) + EDTA (0.1 wt%)	30
			42%	Aqueous with pH swing	Aqueous	1 bar, 70 °C, 1 h	1.4 M $(NH_4)_2SO_4$	30
	Mg: 24.6%; Fe: 2.4%; ([a]Antigorite)	0.48	43%	Attrition grinding (−38 μm) + heat treatment (630 °C, 2 h)	Aqueous	152 bar, 185 °C, 1 h	1.0 M NaCl + 0.64 M $NaHCO_3$	30
	CaO: 0.1%; MgO: 38.7%; Fe_2O_3: 4.9%	0.48	60%	Magnetic separation + steam activation	Aqueous	128 bar, 155 °C, 1 h	1.0 M NaCl + 0.64 M $NaHCO_3$	44
	MgO: ~40%	0.43	30%	No	Gas–solid	340 bar, 300 °C	None	41
	Ca: 0.1%; Mg: 27.9%; Fe: 6.1% ([a]Lizardite)	0.40	41%	Attrition grinding (−38 μm) + heat treatment (630 °C, 2 h)	Aqueous	152 bar, 185 °C, 1 h	1.0 M NaCl + 0.64 M $NaHCO_3$	45

Mineral	Composition	$\frac{1}{R_{CO_2}}$[a]	Conversion	Pretreatment	Medium	Conditions	Solution	Ref
Wollastonite, $CaSiO_3$	Ca: 31.6%, Mg: 0.3%; Fe: 0.5%	0.38	82%	Attrition grinding	Aqueous	152 bar, 185 °C, 1 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	39
			100%	Attrition grinding	Aqueous	40.5 bar, 100 °C, 1 h	No	39
Fayalite, Fe_2SiO_4	Ca: 0.6%; Mg: 0.3%; Fe: 44.3%	0.36	66%	Attrition grinding	Aqueous	152 bar, 185 °C, 6 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	45
Talc, $Mg_3Si_4O_{10}(OH)_2$	Ca: 2.2%; Mg: 15.7%; Fe: 9.2%	0.36	15%	Attrition grinding	Aqueous	152 bar, 185 °C, 0.5 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	45
Anorthite, $CaAl_2Si_2O_8$	Ca: 10.3%; Mg: 4.8%; Fe: 3.0%	0.23	9%	Attrition grinding	Aqueous	152 bar, 185 °C, 6 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	45
Magnetite, Fe_3O_4	Ca: 0.6%; Mg: 0.3%; Fe: 21.9%	0.13	8%	Attrition grinding	Aqueous	152 bar, 155 °C, 6 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	45
Labradorite, $((Ca, Na)(Al, Si)_4O_8)$	CaO: 10.2%; MgO: 0.2%; FeO: 1.0%	0.09	33%	None	Aqueous	141 bar, 185 °C, 3 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	46
Anorthosite, Mixed rock	CaO: 14.1%; MgO: 8.7%; FeO: 8.7%	0.26	17%	None	Aqueous	141 bar, 185 °C, 3 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	46
Basalt, Mixed rock	Ca: 6.7%; Mg: 4.3%; Fe: 6.7%	0.20	15%	Attrition grinding	Aqueous	152 bar, 185 °C, 1 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	45
Basalt from Columbia River, Mixed rock	CaO: 8.1%; MgO: 4.8%; FeO: 11.3%	0.19	5%	None	Aqueous	141 bar, 185 °C, 3 h	1.0 M $NaCl$ + 0.64 M $NaHCO_3$	46

[a] $\frac{1}{R_{CO_2}}$ represents the CO_2 storage potential and is the mass of CO_2 that can be trapped per unit mass of mineral. It is defined as: $\frac{1}{R_{CO_2}} = \left(\frac{y_{Mg}}{MW_{Mg}} + \frac{y_{Ca}}{MW_{Ca}} + \frac{y_{Fe}}{MW_{Fe}} \right) \times MW_{CO_2}$ where y is the mass fraction of the metal that can react with CO_2 to form insoluble carbonates, and MW is the molecular weight of the alkaline metal species.

then, significant advancements in the field of carbon mineralization have been made. The process of mineral carbonation is exothermic and thermodynamically favoured as CO_2 is converted into carbonates, as represented by the following reactions.

$$\text{Olivine} \quad Mg_2SiO_{4(s)} + 2CO_{2(g)} \rightarrow 2MgCO_{3(s)} + SiO_2 + 89\frac{kJ}{mol\ of\ CO_2} \quad (8.1)$$

$$\text{Serpentine} \quad Mg_3Si_2O_5(OH)_{4(s)} + 3CO_{2(g)} \rightarrow 2MgCO_{3(s)}$$
$$+ 2SiO_{2(s)} + 2H_2O_{(aq)} + 64\frac{kJ}{mol\ of\ CO_2} \quad (8.2)$$

$$\text{Wollastonite} \quad CaSiO_{3(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + SiO_{2(s)} + 90\frac{kJ}{mol\ of\ CO_2} \quad (8.3)$$

Unfortunately, the process of carbon mineralization is often kinetically limited, particularly depending on the type of alkaline materials reacting with CO_2. In order to accelerate the process of carbon mineralization, it is important to understand the rates of the involved reactions: for example, in aqueous carbonation, the relative rates of mineral dissolution, CO_2 hydration and carbonate formation need to be considered.

The carbonation of Ca- and Mg-bearing minerals could occur via both gas—solid and aqueous reactions. In gas—solid reactions, the alkaline materials can directly react with gaseous CO_2 to form $CaCO_3$ or $MgCO_3$, but these reactions take place over geologic time scales. Some have reported that in the presence of high pressure steam, the carbonation of $Ca(OH)_2$ or $Mg(OH)_2$ can be significantly improved[48,49] but the use of high pressure steam would increase the overall parasitic energy requirement unless the carbon mineralization process is integrated into processes such as the water—gas shift reaction.[49] Thus, most of ex situ carbon mineralization technologies currently take the aqueous carbonation approach. Aqueous carbonation of minerals and industrial wastes can be performed in single or two-step modes as illustrated in Figure 8.3.

8.2.2 Single-step carbon mineralization

Much of the earlier work in the area of carbon mineralization was focused on the single-step carbonation of olivine, because serpentine is less reactive compared to olivine due to the presence of —OH groups.[39,40,42] For serpentine, a number of pre-treatment options were investigated including heat-treatment at temperatures greater than 630 °C, which resulted in dehydroxylation of the hydrous magnesium silicate (serpentine).[39,40,45,46,50,51] The pretreatment option of attrition grinding[39] where the minerals were ground down to sizes smaller than 2 µm to disrupt the crystal structure and create larger reactive surface area for mineral dissolution and carbonation were also investigated. Steam treatment to increase the porosity of minerals and chemical activation using strong acids or bases was also adapted to accelerate mineral carbonation.[44] Both olivine and serpentine contain a significant amount of
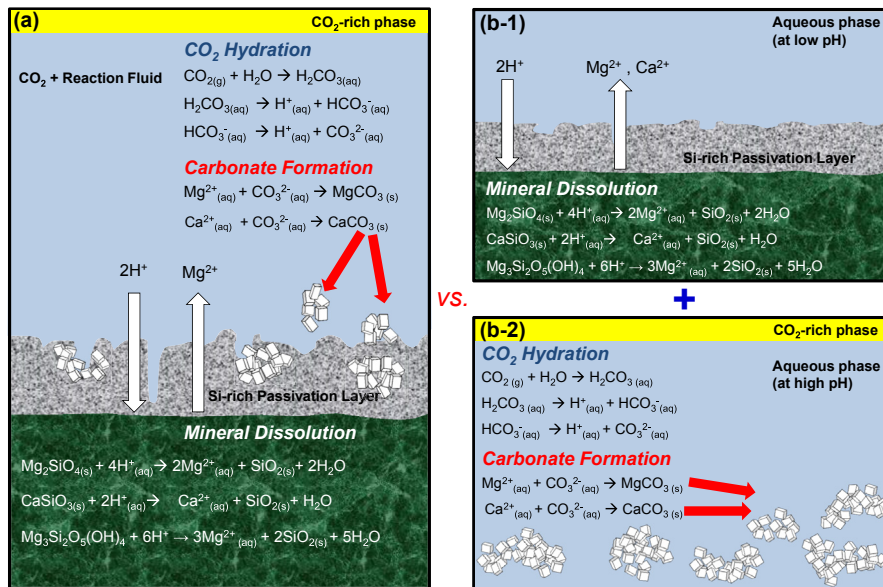
FIGURE 8.3

Schematics of carbon mineralization via (a) direct aqueous carbonation where the interactions of CO_2-mineral-reaction fluid occur in a single process, and (b) two-step aqueous carbonation where the mineral is first dissolved under acidic conditions (top (b-1)), and the subsequent carbonation of dissolved calcium and magnesium to form solid mineral carbonates (bottom (b-2)).

iron in their mineral matrix and the presence of iron oxide often resulted in the formation of an iron-rich passivation layer on the mineral surface, which limited the reactivity of these minerals.[39,43] Thus, magnetic separation of magnetite (Fe_3O_4) from minerals was often carried out prior to the mineral carbonation process. Many of these pretreatment methods significantly improved the extent of mineral carbonation. However, it also increased the parasitic energy consumption of the overall process. Thus, a careful energy balance and life cycle analysis should be carried out to accurately quantify the net carbon storage and utilisation.

In case of a single-step carbon mineralization process, ground and prepared (with the optional pretreatments discussed earlier) minerals are converted into solid carbonates via direct aqueous carbonation. As illustrated in Figure 8.3(a), protons are produced during CO_2 hydration and the lowered pH favours mineral dissolution. As Mg and/or Ca ions are released into the bulk fluid, they react with the carbonate ions and form their respective carbonates. In the single-step direct aqueous carbonation process, the mineral dissolution and carbonate formation occur simultaneously, and thus, the overall reaction rates are quickly complicated by the internal pH swing and the development of a complex passivation layer of carbonates and precipitated silica. The addition of bicarbonates such as $NaHCO_3$, which can

serve as a pH buffer and a source of carbon, has been found to be very effective in increasing the overall extent of silicate mineral carbonation.[39,40,42,43,45] Generally, the single-step carbonation requires high CO_2 pressure and elevated reaction temperatures ($>100\,°C$), and its end product is a mixture of carbonates, silica and unreacted silicate mineral. Thus, the carbonated materials have limited applications as low-grade construction materials. Representative mineral carbonation studies are summarized in Table 8.2.

8.2.3 Two-step carbon mineralization

In order to individually optimize mineral dissolution and carbonate formation reactions, the decoupling of reactions was suggested and the two-step carbon mineralization process was developed. This decoupling was based on the differences in the pH that favour mineral dissolution (acidic) and carbonation (basic). As the individual reaction steps were accelerated, it was plausible to form mineral carbonates at lower reaction temperatures.[23,29,30,52] Furthermore, the production of high purity materials was achieved by adding a separation step between mineral dissolution and carbonation reactors. The two-step approach also allowed for an in-depth investigation of the reactions involved during the carbonation of various minerals.[29,30,33]

First, the mineral preparation and pretreatment methods described for the single-step carbon mineralization process can also be used to enhance the two-step carbon mineralization process. The overall scheme, also known as a pH swing process, is represented in Figure 8.3(b).[23,29,30,52] Once the silicate mineral is digested at a low pH ~ 2 (Figure 8.3(b-1)). The subsequent precipitation of various solid phases from the filtrate can be achieved by carefully increasing the system pH (Figure 8.3(b-2)). For example, iron oxide would precipitate out from the filtrate as the pH is raised to ~ 8.6.[23,29,30,52] Once all other dissolved components such as Fe are removed, the aqueous solution rich in Mg and/or Ca is transferred to the carbonation reactor. Here, pure $MgCO_3$ or $CaCO_3$ can be synthesized by further increasing the pH (~ 9.5) and bubbling CO_2 through the solution containing Mg and/or Ca.[23,29,30,52] The process of carbonate formation is presented in Figure 8.3(b-2).

The formation of mineral carbonates is favoured at high pH (>9.5) because carbonate ions dominate in that pH range as dissolved CO_2 speciates in water. Therefore, these consecutive changes in pH result in the precipitation of high purity products such as silica, iron oxide and $MgCO_3$ or $CaCO_3$. Variations to this pH swing scheme include using $(NH_4)_2SO_4$[52] or NH_4Cl[53] as the base, such that the chloride or sulfate salts of Ca or Mg that are formed can be readily converted to carbonates of Ca or Mg, while regenerating the original NH_4Cl or $(NH_4)_2SO_4$ reagents, which is suggested to improve the overall economics of the carbon mineralization process. The data given in Table 8.2 illustrates the differences between single-step and two-step carbon mineralization processes. As summarized in Table 8.2, a number of chemical and biological catalytic enhancement schemes for mineral dissolution and carbonate formation have also been developed in recent years. These schemes are discussed in the following sections.

8.2.4 **Accelerated mineral dissolution**

During the early stage of the development of carbon mineralization technologies, the mineral dissolution step was considered to be the rate-limiting step.[29,30] The most important factor influencing the rate of mineral dissolution is pH. However, the mineral dissolution kinetics are also accelerated in the presence of chelating agents, which preferentially bind to the Mg and Ca in the mineral, destabilize the binding within the mineral matrix and facilitate its dissolution.[30,54−56] While chelating agents that form stronger complexes with Mg and Ca are preferred for faster mineral dissolution, those may also inhibit the subsequent formation of mineral carbonates. For example, while chelating agents such as oxalate may be effective in binding to the Mg in the silicate mineral matrix, at high concentrations of oxalate, the binding may be too strong to prevent the exchange of oxalate with the carbonate species to facilitate the formation of $MgCO_3$.[34] Therefore, it is important to screen for not only the effectiveness of various chelating agents but also for their ability to readily exchange with carbonate ions. Effective chelating agents for preferential dissolution of Mg include citrate and acetate.[30,57]

As rapid leaching of Mg from silicate mineral is achieved, continued mineral dissolution is often challenged by the formation of a silica-rich passivation layer on the surface of the mineral particle. This layer is formed as the cations (Mg and Ca) are progressively leached out over the course of the mineral dissolution process, and high surface area silica remains which acts as a mass transfer limiting layer. The process of mineral dissolution in the presence of H^+ ions which exchange with Mg^{2+} and Ca^{2+} and the resulting formation of a silica-rich layer is graphically illustrated in Figure 8.3(a) and (b-1). In order to achieve greater dissolution of silicate minerals, several means of removing this silica-rich passivation layer have been suggested including in situ physical attrition and chemical activation methods that keep the passivation layer thin or the pores within the passivation layer open, respectively.[29]

8.2.5 **Enhanced hydration of CO_2 and formation of different carbonate phases**

After significantly improving the mineral dissolution rates, some of the carbon mineralization technologies then became limited by the hydration of CO_2. Carbonic anhydrase, an enzyme that catalyzes the formation of bicarbonate species from CO_2, has been proposed to accelerate CO_2 hydration kinetics.[31,32] In addition to the use of carbonic anhydrase, the extent of carbonation can be improved by increasing the partial pressure of CO_2,[39,40,43] adding bicarbonate buffer (e.g. $NaHCO_3$),[39,40,42,43] and adding carbonate seeds to provide surface area for the faster growth of carbonates. The synthesis of high purity products can also be complicated by the formation of different phases, which are reaction temperature−dependent. For example, magnesite ($MgCO_3$) generally forms at temperatures greater than $70\,°C$, while the formation of hydrated phases of magnesium carbonate such as nesquehonite ($MgCO_3.3H_2O$) and hydromagnesite ($Mg_5(CO_3)_4(OH)_24H_2O$) is favoured at lower temperatures.[35−37] These carbonate phases have very different crystal structures.[35−37] While

magnesite has a rhombohedral crystal structure, nesquehonite and hydromagnesite are needle-shaped and rosette-like, respectively. Based on the differences in their chemical and physical properties (i.e. different thermal decomposition behaviours and morphological characteristics such as surface area and particle size distributions), the application of magnesium carbonates can differ. Compared to magnesium carbonate phases, the synthesis of precipitated $CaCO_3$ has been well understood due to a greater market size.[33,54,58−60] Industrial and commercial applications of these carbonates require relatively pure materials with a specific particle size distribution and surface area. Therefore, the customized synthesis of different carbonate phases would be important for their commercial utilisation. For example, the synthesis of precipitated calcium carbonate (PCC) from wollastonite can be performed to mimic commercial grade PCC as represented by Figure 8.4.

8.2.6 Summary of environmental implications and potential benefits

- The carbonation of Ca- and Mg-bearing silicate minerals such as olivine and serpentine leads to the formation of thermally and chemically stable mineral carbonates that can be safely stored over a geologic time scale. It is likely the only carbon storage method that does not require potentially expensive long-term monitoring of stored CO_2.
- CO_2 capture has been considered as the most expensive step of carbon mitigation strategies. Here, CO_2 from flue gas may be directly used as an acid source for mineral dissolution in conjunction with carbonic anhydrase to overcome slow CO_2 hydration kinetics. This scheme would eliminate the cost of capturing and compressing CO_2, reduce the need for acid, and preclude the need for treating the concentrated effluents post-reaction.[62]
- The ex situ mineral carbonation process allows for flexible reaction schemes and the two-step process could be used to produce various products of high value, while the single-step approach would possibly result in low-grade construction materials. The potential value-added materials include calcium and magnesium carbonates and high surface area silica. They can be used as fillers in various applications such as papers, plastics and construction materials. The commercial value of these products may be used to offset the mining and processing costs of minerals for large-scale carbon mineralization.
- Calcium and magnesium minerals may also contain Fe, Ni and Cr, which are commercially useful metals. Thus, the recovery of those materials during carbon mineralization would also improve the overall economics of the process.
- Since the amount of CO_2 to be sequestered would far exceed the market size and demand for the value-added products, it would be important to identify the appropriate production levels of these value-added products considering the costs of preprocessing (e.g. mining and grinding), capital expenditures (e.g. reactor design and other equipment needs) and operating costs (e.g. chemical, labour and transportation needs) using a complete life cycle assessment of the overall process.
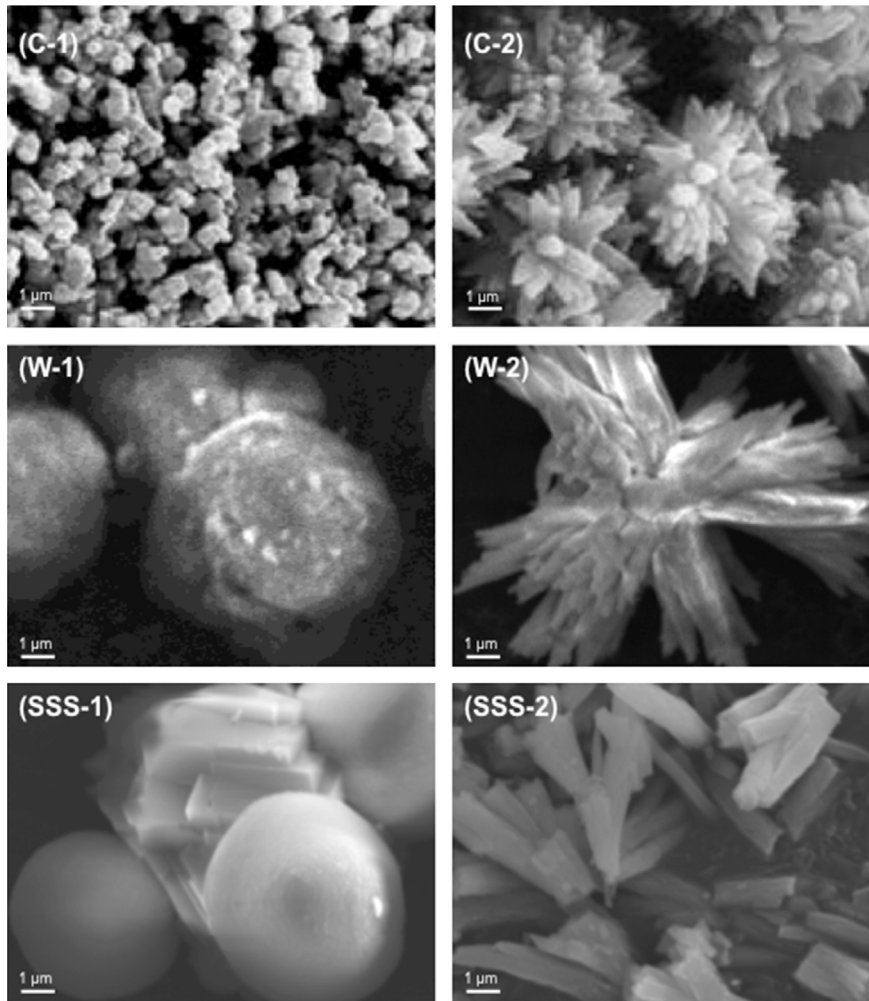
FIGURE 8.4

SEM images of different precipitated calcium carbonates (PCCs): (C-1) and (C-2): Commercial PCC produced by Specialty Mineral,[61] (W-1) and (W-2): PCC derived from wollastonite, and (SSS-1) and (SSS-2): PCC derived from stainless steel slag.

8.3 Carbonation of alkaline industrial wastes

There is an increasing level of interest for utilizing CO_2 to treat alkaline industrial wastes evolved during energy generation, chemical processes and construction projects. Industrial wastes often contain a high content of cations (e.g. Ca, Mg, Al and Fe) that can react with carbonate ions. This makes them particularly attractive for carbon storage. Unlike minerals that are predominantly composed of calcium and

magnesium silicates, these alkaline industrial wastes are primarily composed of oxides and hydroxides which are more reactive. However, the quantity of industrial wastes for carbon mineralization is in orders of magnitude smaller compared to minerals; only about 200−300 Mt of CO_2 can be stored in these wastes annually.[23] Despite the limited carbon storage capacity of industrial wastes, it is important to note that the carbonation of industrial wastes will provide a means to reduce the carbon footprint of each industrial process. Considering the scale of carbon emissions, all the options that can reduce anthropogenic CO_2 emission should be considered and adapted. Thus, the carbonation of industrial wastes can serve the dual purpose of neutralizing these alkaline industrial wastes to render them safe for disposal or for the utilisation as value-added materials, and provide an option for long-term storage of CO_2.

The three major types of alkaline residues can be classified as wastes from (1) power generation (e.g. fly ash, bottom ash, air pollution control (APC) residues and oil shale waste), (2) cement, building material and paper production (e.g. cement kiln dust, asbestos and paper mill waste) and (3) steel and aluminium production (e.g. steel slag and red mud). As represented in Figure 8.2, the availability of fly ash far exceeds that of other industrial wastes. While the overall quantity of each waste is important, the calcium and magnesium contents in these materials should also be considered when developing industrial waste carbonation technology. The compilation of various studies has revealed that there is a considerable variability in the calcium and magnesium contents in these wastes, but the average alkaline content shows the following trend: highest in steel slag[12−20] > cement kiln dust[10,11] > fly ash[2−9] > red mud.[21,22] The magnesium content is reported to be lower than 10% in most of the industrial wastes. Of all the wastes, the availability of red mud in the United States is the lowest, and its calcium and magnesium contents are also the smallest compared to fly ash, cement kiln dust and steel slag (Figure 8.2).

Alkaline industrial wastes are usually more reactive compared to silicate minerals because of their inherent chemical and physical properties: often smaller particle size, greater porosity, relatively disordered structures and higher solubility. Some of the wastes such as asbestos and stainless steel slag can pose serious health and environmental hazards. Asbestos (chrysotile), which is used as building materials, are highly regulated due to their needle-shaped, fibrous structure which can puncture the lung to cause serious respiratory illnesses including lung cancer, and thus their direct landfilling is banned.[63] Unlike regular steel slags, stainless steel slags contain a significant amount of heavy metals, and so they are also classified as hazardous wastes.

The dominant method for treating industrial wastes is by single-step direct aqueous carbonation in which the alkaline wastes directly react with CO_2 in the reaction fluid as presented in Figure 8.3(a). The two-step process for treating industrial wastes is represented in Figure 8.3(b), where dissolution and carbonation are decoupled. This helps increase the yield of the higher purity value-added materials, calcium and/or magnesium carbonates. However, as in the mineral carbonation cases, the two-step approach would be most attractive if the amount of potentially value-added materials produced from industrial waste is high. Another challenge

with the two-step aqueous carbonation process is the consumption of acids and bases during the pH swing process, which could significantly increase the overall operating cost, while the single-step approach of direct carbonation of wastes may require a larger reactor. Thus, based on the reactivity of each industrial waste, the appropriate reaction scheme should be selected.

In alkaline industrial wastes containing hazardous materials such as heavy metals (e.g. Ni and Cr), the fate of those components should be carefully examined before and after the carbonation treatment. As alkaline wastes are processed in aqueous media, this may result in the increased leaching of the heavy metals into the liquid phase. The leached heavy metals may be subsequently immobilized into the carbonate matrix or leached into the liquid phase. Therefore, a new recovery or treatment step may be required downstream of the carbonation reactor for those heavy metals. Carbonation studies of alkaline industrial wastes are summarized in Table 8.3, and the following sections discuss CO_2 utilisation and storage in alkaline industrial wastes for each category of industrial wastes.

8.3.1 Wastes from power generation

A number of studies have focused on the carbonation of industrial wastes from power generation to offset its own CO_2 emissions.[3-9,64] Fly ash is one of the most abundant industrial wastes in the United States as represented in Figure 8.2. Ash is produced during coal combustion and municipal solid waste incineration (MSWI). If the ash generated during combustion or incineration rises with the flue gas, it is called fly ash. The ash that sticks to the walls of the furnace as clinkers during combustion is known as bottom ash. The extents of carbonation have been reported to be as high as 86% with coal fly ash.[3] However, the alkaline composition of fly ash is highly variable from as low as 4.1 wt%[4] of CaO in coal combustion fly ash to 53.02 wt%[5] in MSWI fly ash, and this greatly impacts the carbonation potential of fly ash. Air Pollution Control (APC) residues are very similar to fly ash but unlike fly ash, their quantity is often limited depending on the installation of APC units at each power plant. The APC unit that is installed to capture SOx from the flue gas generates alkaline residues that usually consist of a mixture of $Ca(OH)_2$, CaOHCl and CaO.[65] They are often highly reactive and CO_2 storage capacities of 200−250 kg CO_2/tonne of APC residue have been reported.[65,65] With the recent development of oil shale, the industrial wastes associated with their combustion have been rapidly increasing. For instance, countries likes Estonia generate oil shale ash that contains 30−50% free Ca−Mg oxide and it has been reported that about 167 kg of CO_2 could be stored in 1 tonne of oil shale waste.[67,68]

8.3.2 Wastes from the production of cement, construction material and paper

As shown in Figure 8.2, cement kiln dust in the United States is the second largest source of alkaline industrial wastes. Considering that cement production is one of

Table 8.3 Summary of Carbonation Studies of Alkaline Industrial Wastes

Material Type		Composition (wt%)	CO_2 Storage Capacity (kg_{CO_2}/kg_{waste})	Extent of Carbonation (%)	Reaction Phase	P_{CO_2}, T, Reaction Time	Chemical Additives	References
Fly ash	Coal	CaO: 9.3%	0.07	86%	Aqueous	40 bar, 30 °C, 1 h	NaCl	3
	Coal	CaO: 4.1%	0.03	82%	Aqueous	1 bar, 30 °C, 18 h	None	4
	Coal	CaO: 55.44%, MgO: 1.04%	N/A	81%	Gas–solid	80% vol CO_2, 800 °C, 1 h	None	5
	Coal	CaO: 27.1–31.9%, MgO: 1.4–9.6%	0.158	50–72%	Aqueous	76–116 bar, 155–185 °C, 1 h	$NaHCO_3$ + Na_2CO_3 + NaCl	6
	MSWI	CaO: 36.3%	N/A	N/A	Aqueous	3 bar, 8–42 °C, 3 d	None	7
	MSWI	CaO: 53.02%	N/A	N/A	Aqueous	1 bar, 25 °C, 10 d	None	2
	Lignite	CaO: 15.72–29.28%, MgO: 0.78–4.47%	0.04–0.09	N/A	Aqueous	10 bar, 25 °C, 10 d	None	8
	Lignite	Ca: 28.4%, Mg: 9.2%	0.21	53%	Aqueous	0.15 bar, 25 °C, 2 h	None	9
Bottom ash	MSWI	N/A	N/A	N/A	Gas–solid	1 bar, 50 °C, 3 d	None	28
	MSWI	CaO: 16.3%, MgO: 2.6%	24 L CO_2/kg	N/A	Gas–solid	17 bar, 25 °C, 3 h	None	64
APC residues	APC	Ca: 35%, Mg: 0.0084%	0.25	67%	Aqueous	3 bar, 30 °C, 5 h	None	65
	MSWI APC	Ca: 308,069 mg/kg, Mg: 29.243 mg/kg	0.20	N/A	Aqueous	1 bar, 20 °C, 3 h	None	66
Oil shale waste	Oil shale	CaO: 50.75%, MgO: 15.19%	0.17	N/A	Aqueous	1 bar, 25 °C	None	67
	Oil shale	CaO: 50.16%, CO_2: 1.49%	N/A	N/A	Aqueous	1 bar, 25 °C	None	68

Cement kiln dust	Cement kiln dust	CaO: 34.5%, MgO: 2.1%	0.19	71%	Gas–solid	1 bar, 25 °C, 12 d	None	11
		CaO: 34.5%, MgO: 2.1%	0.20	75%		1 bar, 25 °C, 3.4 d		
		CaO: 34.5%, MgO: 2.1%	0.26	94%		1 bar, 25 °C, 4.9 d		
Asbestos* heat-treated, building materials	Chrysotile (natural mineral)	CaO: 0.5%, MgO: 39.7%	N/A	0.7 mol CO_2/mol Mg	Gas–solid	32 bar, 100–220 °C, 1 h	None	69
	Chrysotile*	CaO: 0.05%, MgO: 38.8%	N/A	53% (alkali) 45% (Water)	Aqueous	30 bar, 260 °C, 1 h	NaOH	70
	Asbestos*	CaO: 35.4%; MgO: 5.12%	0.14–0.18	N/A	Aqueous	55 bar, 22 °C, 1 h	None	71
Paper mill waste	Calcium mud	CaO: 83.2%	0.22	85%	Aqueous	10 bar, 30 °C, 2 h	None	72
Steel slag	Steel slag	CaO: 31.7%, MgO: 6.0%	0.25	74%	Aqueous	19 bar, 100 °C, 0.5 h	None	12
	LF slag	CaO: 58.1%, MgO: 6.2%	0.25	N/A	Aqueous	1 bar (15% vol. CO_2), 25 °C, 40 h	None	13
	Blast furnace slag	CaO: 40.6%, MgO: 10.7%	0.23	90%	Aqueous (pH-swing)	1 bar, 30 °C, 2 h	NaOH + CH_3COOH	14
	Converter slag	N/A	N/A	80%	Aqueous (pH-swing)	0.07 bar (13% vol. CO_2), 40 °C, 1 h	NH_4Cl	15
	Stainless steel slag	Ca: 40–50% Mg: 2.2–4.5%	0.13	N/A	Aqueous	3 bar, 50 °C, 2 h	None	16
	BOF slag	CaO: 38–45%	N/A	90%	Aqueous	80 bar, 150 °C, 1 h	None	17
			N/A	92%	Aqueous	20 bar, 200 °C, 1 h	None	17
	BHC	CaO: 54.2%, MgO: 4.0%	0.19	44%	Aqueous	1 bar, 70 °C, 2 h	None	18

Table 8.3 Summary of Carbonation Studies of Alkaline Industrial Wastes—cont'd

Material Type		Composition (wt%)	CO$_2$ Storage Capacity (kg_{CO_2}/kg_{waste})	Extent of Carbonation (%)	Reaction Conditions			References
					Reaction Phase	P$_{CO_2}$, T, Reaction Time	Chemical Additives	
	BOF slag	CaO: 51.1%, MgO: 4.2%	0.23	57%	Aqueous	1 bar, 70 °C, 2 h	None	18
	BHC	CaO: 52.8%, MgO: 4.7%	0.29	69%	Aqueous	48.3 bar, 160 °C, 12 h	None	19
			0.24	59%	Aqueous	89.6 bar, 160 °C, 1 h	None	19
	BOF slag	CaO: 42.4%, MgO: 9.2%	0.29	93%	Aqueous	1.47 bar, 60 °C, 30 min	None	20
Red mud	Bauxite residue	Ca: 4.8%, Mg: 0.1%	0.02	N/A	Aqueous	1 bar, 30 d	None	21
	Red mud	CaO: 2.99%	0.05	N/A	Aqueous	3.5 bar, 25 °C, 3.5 h	NaOH	22

* refers to heat-treated asbestos. Updated from Pan et al.[10]

the major industrial contributors to the emissions of CO_2, the potential use of cement kiln dust for carbon capture and storage is encouraging. Cement kiln dust is a by-product of cement clinker production, and has about 35 wt% of CaO and 2 wt% of MgO. Therefore, cement kiln dust has a high CO_2 storage capacity between 191 and 256 kg CO_2/tonne of cement kiln dust.[11] Another source of Ca-based industrial waste is the paper industry. Paper mill waste is generated during the calcination of $CaCO_3$ to produce lime for paper production. While each paper mill generates variable compositions of waste, the primary constituents of the paper mill waste have been reported as 55 wt% $Ca(OH)_2$, 33 wt% $CaCO_3$ and 12 wt% $Ca_{10}(PO_4)_6(OH)_2$. This translates to a CO_2 storage capacity of 218 kg CO_2/tonne of paper mill waste.[72]

Another potential application for CO_2 is its utilisation for the remediation of Asbestos Containing Materials (ACMs). Asbestos which is composed of amphibole or chrysotile (a serpentine morph) was used in construction materials and in manufactured goods for many years, due to their high tensile strength and heat resistant properties. However, these materials are now banned, since chrysotile fibres have been found to cause significant health problems including lung cancer and mesothelioma.[63] Therefore, the carbonation of the asbestoid component of ACMs has been proposed to convert the fibres into a different crystal structure, which renders the material safe for disposal or reuse. This morphological change can be achieved by reacting ACMs with CO_2 to form insoluble solid carbonates. A study has reported that at 130 °C, direct carbonation of chrysotile in the presence of steam and high pressure CO_2 resulted in the partial dehydroxylation and carbonation of chrysotile in the amount of 0.7 mol of CO_2 per mole of Mg.[66] Like natural silicate minerals, chrysotile is quite unreactive under ambient temperature and pressure conditions and neutral pH. Therefore, heat-treatment at temperatures up to 750 °C has been investigated to accelerate the ACM carbonation.[70,71] Approximately 53% conversion of heat-treated chrysotile to carbonates was achieved at 260 °C[70] and 13.5−17.7% of CO_2[71] was bound in the heat-treated asbestos cement.

8.3.3 Wastes from steel and aluminium production

In addition to coal-fired power plants, steel and aluminium plants are major emitters of CO_2. They also generate a large quantity of solid industrial wastes that are often hazardous to landfill. A mixture of CaO and MgO are added to the blast furnace to remove impurities such as CO and Si and during this process, steel slag is produced. After separating steel slags from molten steel, they are transferred to holding locations to be shipped for landfill. While most of the steel slags are currently categorized as unhazardous wastes, stainless steel slags that contain Ni and Cr are labelled as hazardous wastes; these cannot be landfilled without further treatment. A large number of research groups have studied the carbonation of steel slags and found promising results, particularly in Europe where the landfill areas are limited.[12−20]

Steel slags are primarily composed of CaO (31.7−58.1 wt%) and MgO (3.97−10.7 wt%).[12−14,18] Their CO_2 capture and storage capacities vary between

130 and 289 kg CO_2 per tonne of steel slag,[16,20] as reported in Table 8.3. Steel slag has the highest alkaline content compared to fly ash, cement kiln dust or red mud (Figure 8.2), although the annual production of steel slag is not as high as that of fly ash in the United States. Given the high Ca content in steel slag, the synthesis of precipitated calcium carbonate (PCC) has been investigated. Studies have shown that PCC with controlled morphological structures can be synthesized from steel slag (Figure 8.4(SSS-1 and SSS-2)) to mimic commercial grade PCC (manufactured by Specialty Minerals[61]) shown in Figure 8.4(C-1 and C-2). They are also compared with PCC prepared from natural minerals such as wollastonite (Figure 8.4(W-1 and W-2)). In all these cases, increasing temperature favoured the formation of scaleno-hedral $CaCO_3$ over spherical $CaCO_3$.

Another alkaline, but highly hazardous, industrial waste is red mud, which is a by-product of aluminium manufacturing.[21,22,73] Red mud is the residue that remains after bauxite (a mixture of aluminium oxides and hydroxides) is dissolved in a strong base such as NaOH. The residue is red due to the presence of iron oxide, and is haz-ardous because of radioactive substances such as radium and thorium.[73] Therefore, red mud cannot be safely disposed without subsequent treatment. While it is impor-tant to treat red mud to reduce the environmental impact of the aluminium produc-tion process, the overall CO_2 utilisation potential of red mud in the United States is limited due to its small production rate and the lowest CaO and MgO contents compared to other industrial wastes.[21,22] The reported CO_2 storage capacities are in the order of 21−53 kg CO_2 per tonne of red mud (Table 8.3).[21,22]

8.3.4 Summary of environmental implications and potential benefits

- Anthropogenic CO_2 can be used to treat alkaline industrial wastes and make them safe for subsequent disposal or reuse. Furthermore, this scheme can serve as a permanent sink for CO_2 by fixing gaseous CO_2 into a solid matrix. Thus, there would be carbon storage potential associated with the carbonation of alkaline industrial wastes. Although the annual carbon storage potential of in-dustrial wastes is only about 1% of the total CO_2 emissions due to the limited availability of these wastes,[23] some wastes containing high concentrations of Ca and Mg, such as fly ash and steel slag, can certainly be used to offset the CO_2 emissions of various industrial processes.
- Usually, the generation locations of these alkaline industrial materials are within the CO_2 emission sites: power plants, steel plants and cement plants. As a result, these wastes can be reacted with CO_2 at the site of generation, which eliminates CO_2 and/or waste transportation expenses.
- Carbon mineralization can also be used to treat asbestos-bearing materials that are considered to be health hazard.
- Due to the heterogeneity of the industrial wastes, consistent production of a specific grade of material may be challenging.
- If the demand for heavy metals such as Ni and Cr further increases, the extraction and use of these trace metals from industrial wastes may also offset the overall

cost of waste treatment with CO_2. Studies have reported that heavy metals can be mobilized or immobilized via the carbonation of industrial wastes depending on the operating conditions. Therefore, for each developed technology the fate of heavy metals during the treatment of alkaline industrial wastes should be carefully investigated and complete leaching tests should be performed to verify the environmental safety of the treated industrial wastes.

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