



Review

## An Innovative Approach to Integrated Carbon Mineralization and Waste Utilization: A Review

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### ABSTRACT

Carbon dioxide (CO<sub>2</sub>) emission reduction in industry should be a portfolio option; for example, the carbon capture and utilization by mineralization (CCUM) process is a feasible and proven technology where both CO<sub>2</sub> capture and alkaline waste treatment occur simultaneously through an integrated approach. In this study, the challengeable barriers and significant breakthroughs of CCUM via *ex-situ* carbonation were reviewed from both theoretical and practical perspectives. Recent progress on the performance of various carbonation processes for different types of alkaline solid wastes was also evaluated based on CO<sub>2</sub> capture capacity and carbonation efficiency. Moreover, several process intensification concepts such as reactor integration and co-utilization with wastewater or brine solution were reviewed and summarized. In addition, the utilization of carbonated products from CCUM as green materials including cement, aggregate and precipitate calcium carbonate were investigated. Furthermore, the current status of worldwide CCUM demonstration projects within the iron- and steelmaking industries was illustrated. The energy consumption and cost analyses of CCUM were also evaluated.

**Keywords:** CO<sub>2</sub> capture; Accelerated carbonation; Green cement; Cost evaluation; Energy consumption.

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### INTRODUCTION

#### *Carbon Capture and Utilization by Mineralization (CCUM)*

Carbon capture and utilization by mineralization (CCUM) is a promising and feasible technology because the CO<sub>2</sub> generated from combustion of fossil fuels or carbon-related chemicals can be directly fixed as mineral carbonates. As shown in Fig. 1, since the carbonates are naturally occurring minerals and possess the lowest free energy of formation, the carbonation product is safe and stable over geologic periods of time, resulting in negligible release of CO<sub>2</sub> to the environment. The theoretical consideration of CCUM is based on the so-called “accelerated carbonation” process, whereby the gaseous CO<sub>2</sub> is reacted with alkaline-earth metal-oxide (e.g., CaO and MgO) and converted into carbonate precipitates in the presence of aqueous environments. Appropriate feedstock sources for carbonation reaction include (1) natural ores such as serpentine and

wollastonite and (2) alkaline solid wastes such as iron- and steelmaking slag and municipal solid waste incineration fly ash (MSWI-FA) (Eloneva *et al.*, 2012; Teir *et al.*, 2009; Huntzinger *et al.*, 2009; Renforth *et al.*, 2011; Sanna *et al.*, 2012a; Nduagu *et al.*, 2013; Olajire, 2013; Said *et al.*, 2013; Pan *et al.*, 2014). However, accelerated carbonation using natural ores creates its own environmental legacy because of the massive mineral requirements and associated scale of mining (Gerdemann *et al.*, 2007). Therefore, the size of the mining operation is believed to comprise the most significant economic and environmental barrier to be overcome if any large-scale process is implemented.

Accelerated carbonation can be accomplished either *in-situ* (underground in geologic formation) or *ex-situ* (aboveground in a chemical processing plant) (Pan *et al.*, 2012; International Energy Agency (IEA), 2013a; Sanna *et al.*, 2014). In the case of *in-situ* carbonation, CO<sub>2</sub> is transported to underground igneous rocks, typically basalt, and is permanently fixed within the hosting rocks as solid carbonates (Kelemen and Matter, 2008; Muriithi *et al.*, 2013). In the case of *ex-situ* carbonation, a source of calcium-silicate feedstock (e.g., natural ores and alkaline wastes) is carbonated aboveground; for instance, carbonation at industrial sites, biologically mediated carbonation, and carbon mineralization in industrial reactors (Gerdemann *et al.*, 2007; Pan *et al.*, 2013a).

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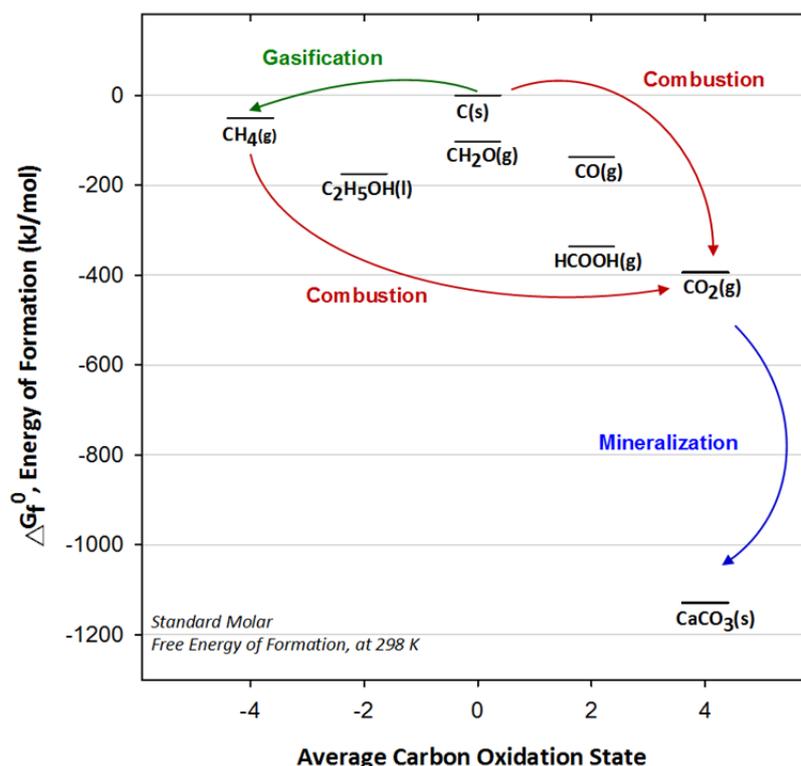


Fig. 1. Standard molar free energy of formation for several carbon-related substance at 298 K.

#### Integrated Ex-situ Carbonation for Alkaline Wastes

In the *ex-situ* carbonation approach, two branches have been developed: direct carbonation and indirect carbonation. Basically, direct carbonation occurs in one single step, while for indirect carbonation the mineral has to first be refined, and then the refined mineral is carbonated. Although *ex-situ* carbonation is not economically viable so far, relevant research is still active and attractive, since the raw materials required for carbonation are globally abundant.

In this study, an innovative approach to *ex-situ* carbonation using industrial wastes including waste  $\text{CO}_2$  gas, alkaline solid wastes and wastewater was proposed, as shown in Fig. 2. Through the carbonation process, the gaseous  $\text{CO}_2$  in flue gas was fixed as solid carbonates, while the wastewater was neutralized to a pH value of 6–7. In addition, the physicochemical properties of carbonated solid waste can be upgraded, which makes it suitable to be utilized as green cementitious materials (Fernandez Bertos *et al.*, 2004a). Carbonation could also act positively in the immobilization of heavy metals, such as Cd, Pb, and Cr, leaching from the alkaline solid waste by sorption in the newly formed products. The leaching of Pb, Zn, Cr, Cu, and Mo is markedly reduced upon carbonation for both APC and BA (Fernandez Bertos *et al.*, 2004a; Arickx *et al.*, 2006; Cappai *et al.*, 2012; Santos *et al.*, 2013b). Cd and Pb have a strong affinity with calcium carbonate and also form complexes with Fe and Al (hydroxides) (Rendek *et al.*, 2006). Immobilization of Sb could also be achieved by combining with other processes (e.g., sorbent adding) during carbonation reaction (Cappai *et al.*, 2012). Furthermore, carbonation has recently proved to be an effective way to improve the durability of concrete because

relatively insoluble  $\text{CaCO}_3$  is formed from the soluble  $\text{Ca}(\text{OH})_2$  in the concrete (Tsuyoshi *et al.*, 2010). Therefore, improvements in the chemical and physical characteristics of treated residues after carbonation can facilitate its reuse in a variety of applications, such as construction materials.

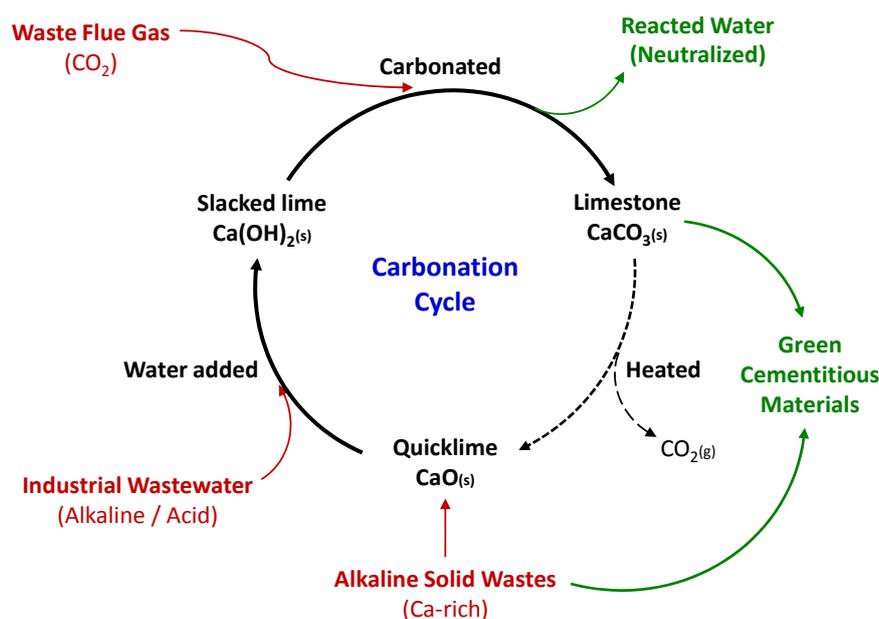
#### Objectives

In this paper, the challenging barriers and significant breakthroughs of CCUM were reviewed from the perspective of both theoretical and practical considerations. Recent progress on the performance of various carbonation processes for different types of alkaline solid wastes was evaluated based on  $\text{CO}_2$  capture capacity and carbonation efficiency. Moreover, several process intensification concepts such as physicochemical activations, co-utilization with wastewater or brine solution, and integration of novel reactors were discussed and summarized. In addition, the utilization of carbonated products as green materials including cement, aggregate, and precipitate calcium carbonate (PCC) were reviewed. Furthermore, the current status of CCUM demonstration projects within the iron- and steelmaking industries in the U.S., France, Australia and Taiwan were illustrated. The energy consumption and cost analyses of CCUM were also evaluated.

#### ACCELERATED CARBONATION USING ALKALINE WASTES

##### Properties of Alkaline Wastes

Alkaline wastes are suitable and can be used as alternative reactants in carbonation to natural ores because



**Fig. 2.** Integrated carbon mineralization and waste utilization through accelerated carbonation: an innovative CCUM process.

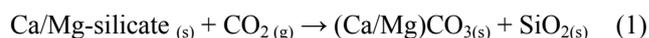
they are abundant, cheap and usually generated from nearby CO<sub>2</sub> emission points in many industries. However, it is difficult to directly compare different wastes for mineral CO<sub>2</sub> sequestration because each waste has its own unique set of advantages and disadvantages, and different capacity results are proposed and published in a variety of forms. Fig. 3 shows the relationship of CO<sub>2</sub> capture capacity (in terms of CaO and MgO contents) and hardness (in terms of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> contents) for different types of solid wastes. In general, the contents of CaO and MgO in iron- and steelmaking slags were relatively higher than those in fly ash (FA) or bottom ash (BA). However, some steelmaking slag such as basic oxygen furnace slag (BOFS) is hard (due to high contents of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) and requires energy-intensive processing, which makes it challenging as viable sinks of CO<sub>2</sub>. Conversely, FA is relatively more promising, since it is a fine powder and already close at hand, which means the costs for transportation, extraction and crushing are minimal. The amounts of CaO and SiO<sub>2</sub> contents in BOFS increase remarkably with the decrease of particle size, while the Fe<sub>2</sub>O<sub>3</sub> fraction decreases significantly (Zhang et al., 2011; Pan et al., 2013b).

In addition, wastewater or brine, which is a saline-based waste solution (total dissolved solid is generally more than 10,000 mg/L) produced from some industrial procedures such as oil and natural gas extraction (known as oil-field brines), could be used as the liquid agents in the carbonation reaction (Druckenmiller and Maroto-Valer, 2005; Uibu and Kuusik, 2009; Liu and Mercedes Maroto-Valer, 2011, 2012). Most wastewater treatments use chemicals as a neutralizing agent to adjust pH and enhance metal precipitation. However, the use of chemicals carries with it a high economic and environmental cost because it is a “resource” and not a “residue.” Under the appropriate conditions, CO<sub>2</sub> would dissolve in the brine solution to initiate a series of reactions that ultimately lead to the bonding of carbonate ions to

various metal cations inherent in brine to form carbonate precipitates such as calcite (CaCO<sub>3</sub>), magnesite (MgCO<sub>3</sub>), and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>).

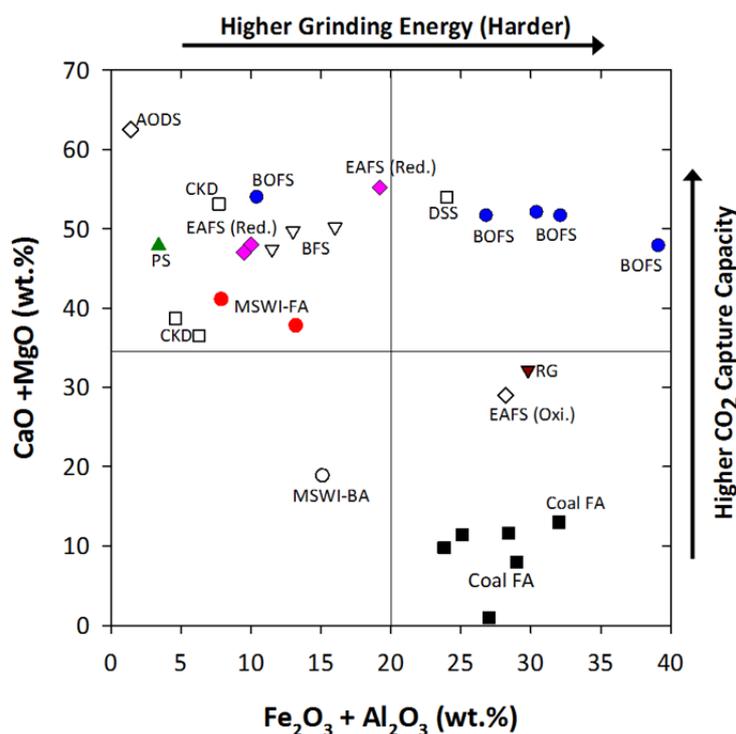
#### Types of Carbonation Processes

There are two approaches to *ex-situ* carbonation: direct and indirect carbonation. Direct carbonation can be conducted in two ways, i.e., a dry gas-solid reaction or an aqueous reaction (gas-liquid-solid). The gas-solid carbonation, as described in Eq. (1), is the simplest method to mineralization.



However, the reaction kinetics of the dry gas-solid reaction at ambient pressure and temperature is far too slow to be effective in CCUM on a wide-scale basis. The reaction can be slightly accelerated by either pre-treating feedstock (such as grinding process and thermal activation) to increase the reactive surface area, or possessing carbonation up to 500°C (Pan et al., 2012). Nevertheless, those treatments and processes are very energy intensive; therefore, the environmental benefits of carbonation might be easily offset. Moreover, the low capture efficiency is not currently viable on the industrial scale.

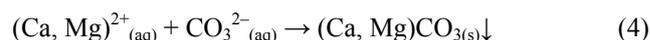
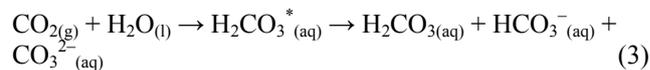
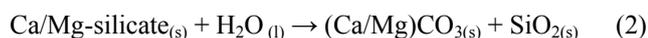
The addition of water to the direct carbonation process (i.e., aqueous carbonation) can significantly increase the reaction kinetics because of the mobilization of ions in the reaction of carbonic acid with alkaline materials. Fig. 4(a) shows a schematic diagram of direct aqueous carbonation for CO<sub>2</sub> fixation and construction material production. The carbonation of alkaline solid waste was carried out with the direct contact of flue gas from a stack, in the presence of a liquid phase, typically using tap water. The wastewater generated in the same industries also can be introduced for the carbonation process to avoid the use of freshwater resources. After carbonation, the slurry is separated into



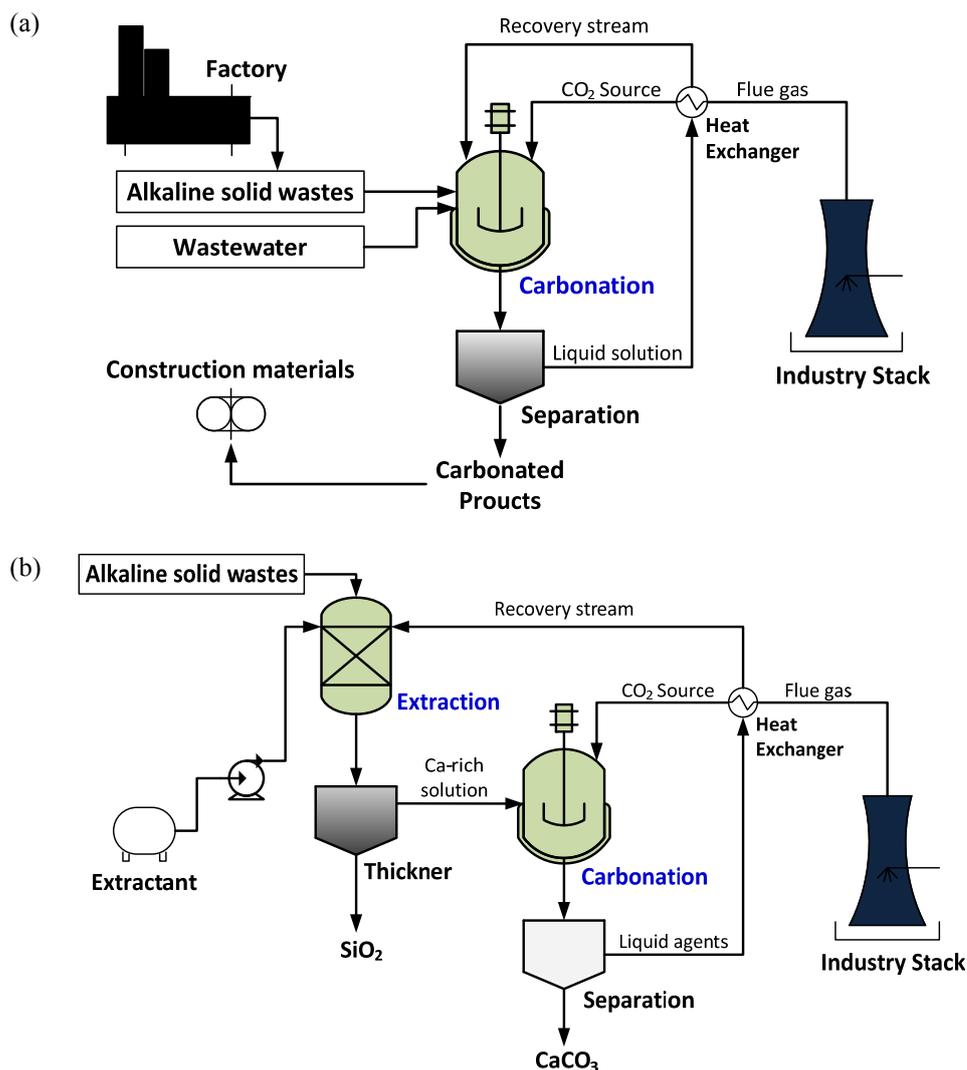
**Fig. 3.** Relationship of CO<sub>2</sub> capture capacity (in terms of CaO and MgO contents) and hardness (in terms of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> contents) for different types of solid wastes. Note: Basic oxygen furnace slag (BOFS); Electrical arc furnace slag (EAFS); Argon oxygen decarburization slag (AODS); Victorian brown coal fly ash (VBC-FA); Municipal solid wastes incinerator (MSWI); Fly ash (FA); Cement kiln dust (CKD); Blast furnace slag (BFS), phosphorus slag (PS); steel slag (SS); RG (Red gypsum); DSS (Desulfurized Slag) (Teir *et al.*, 2007; Reddy *et al.*, 2010; Sanna *et al.*, 2012a; Abo-El-Enein *et al.*, 2013; Dri *et al.*, 2013; Hekal *et al.*, 2013; Muriithi *et al.*, 2013; Santos *et al.*, 2013b, c; Dri *et al.*, 2014; Jo *et al.*, 2014; Reynolds *et al.*, 2014; Salman *et al.*, 2014; Santos *et al.*, 2014; Ukwattage *et al.*, 2014).

carbonated solid wastes and liquid solution. The separated liquid solution can be heated by a heat exchanger with relatively hotter flue gas, and recirculated into the reactor for the next carbonation. It was noted that no excessive heat was required in aqueous carbonation for enhancing the reaction; however, the solution can be moderately heated to 60–80°C to achieve a higher carbonation conversion of solid wastes compared to that at ambient temperature (Chang *et al.*, 2012a, 2013a).

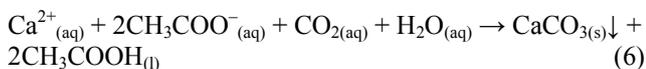
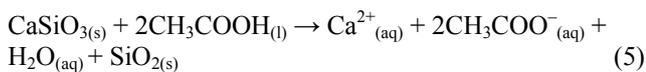
The process chemistry of aqueous carbonation can be simply separated into three pathways but occurs spontaneously: (1) leaching of calcium/magnesium ions from a solid matrix of alkaline materials into solution, (2) dissolution of gaseous CO<sub>2</sub> into solution, and (3) precipitation of calcium/magnesium carbonates, as shown in Eqs. (2)–(4), respectively. Aqueous carbonation has been extensively studied in the literature. The previous studies were focused on different subjects relating to carbonation including reaction kinetics modeling (Chang *et al.*, 2011a, 2013a; Pan *et al.*, 2014; Ukwattage *et al.*, 2014), process evaluation (Chang *et al.*, 2011b, 2012b; Xiao *et al.*, 2014), process optimization (Pan *et al.*, 2014), multi-feedstock development (Chang *et al.*, 2013a, b), and novel reactor design (Chang *et al.*, 2012a; Pan *et al.*, 2013a; Santos *et al.*, 2013a, d).



On the other hand, indirect carbonation, as shown in Fig. 4(b), involves several steps: (1) extraction of metal ions from alkaline solid wastes, (2) liquid-solid separation, and (3) carbonation of the filter solution. Eq. (5) shows the first step of indirect carbonation (i.e., so-called extraction), where calcium ions are extracted for example using acetic acid (CH<sub>3</sub>COOH) from mineral crystals of CaSiO<sub>3</sub>. The extracted solution is filtered through a fiber membrane to separate the mother solution (i.e., rich in calcium ion) and extracted solids (i.e., calcium-depleted SiO<sub>2</sub> particles). After that, the filtered solution is carbonated with a CO<sub>2</sub> source where the precipitation reaction occurs, as shown in Eq. (6). Several effective extractants such as acetic acid and ammonium salts (e.g., CH<sub>3</sub>COONH<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>SO<sub>4</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) are commonly used in the extraction stage (Kakizawa *et al.*, 2001; Dri *et al.*, 2013; Jo *et al.*, 2014; Santos *et al.*, 2014). After carbonation, the end product is usually a pure carbonate (i.e., CaCO<sub>3</sub> and MgCO<sub>3</sub>) because most of the oxides and hydroxides from the material have been extracted, and followed by direct carbonation of the oxides and hydroxides with the CO<sub>2</sub>.



**Fig. 4.** Schematic diagram of (a) ex-situ direct aqueous carbonation (one-step carbonation) for CO<sub>2</sub> fixation and construction material production; (b) ex-situ indirect carbonation (multi-step carbonation) for CO<sub>2</sub> fixation and CaCO<sub>3</sub> production.



Multistep indirect carbonation in the presence of additives can reach high carbonation efficiency under mild operating conditions within a short residence time (Jung *et al.*, 2014a; Sanna *et al.*, 2014). It was observed that high-purity spherical carbonates (e.g., vaterite) can be obtained by indirect carbonation (Jo *et al.*, 2014). However, the requirement of an energy-intensive process for chemical regeneration is still a limiting factor for large-scale deployment. Research has indicated that energy and chemical costs could be reduced by carrying out the reaction between hydroxide and CO<sub>2</sub> at high pressure and temperature (i.e., 25 bar and 450°C), potentially making the hydroxide route technically achievable on an industrial scale (Nduagu *et al.*, 2012).

Table 1 presents the various approaches to *ex-situ* direct

or indirect carbonation using alkaline solid wastes as reported in the literature. The overall CO<sub>2</sub> capture capacity of steelmaking slag such as BOFS, CODS and CCS was relatively higher than that of other solid wastes such as FA. However, it was noted that the energy requirement for crushing, heating, and stirring needs to be offset by the carbonation process exotherm to make the process economically viable in an industrial context (Huijgen *et al.*, 2006, 2007, International Energy Agency (IEA), 2013a; Pan *et al.*, 2013b). Since the reaction temperature would affect not only the leaching rate of calcium ions from solid wastes but also the rates of CO<sub>2</sub> dissolution and carbonate precipitation, it was observed that the appropriate temperature for overall CO<sub>2</sub> capture performance should be set at around 60–80°C in the cases of aqueous carbonation using SS and FA (Chang *et al.*, 2012a, b; Ukwattage *et al.*, 2014). In addition, utilization of the reacted materials should be implemented to couple the CO<sub>2</sub> reduction and waste utilization in industries (Pan *et al.*, 2012). Although the CO<sub>2</sub> capture efficiency using direct carbonation was found

**Table 1.** Performance evaluation of *ex-situ* carbonation using alkaline solid wastes in the literature.

Types of wastes	Methods	Reactor	Process Characteristics	Performance <sup>a</sup>	Reference
CKD	Indirect carbonation	Batch flask	• Extraction by $\text{NH}_4\text{NO}_3/\text{CH}_3\text{COONH}_4$ (1 M)	• CC = 180 kg $\text{CO}_2$ /t-waste	(Jo et al., 2014)
			• Without adjusting pH during carbonation	• 420 kg $\text{CaCO}_3$ /t-waste	
			• S/L ratio = 50 g/L, $\text{CO}_2$ flow rate = 200 mL/min	• Vaterite purity > 98% (Spherical)	
CKD, SDA, and CDSA	Indirect carbonation	Batch flask	• Solvent leaching by $\text{NaHCO}_3$ (0.5 M) for 24 h	• CC = 101–123 kg $\text{CO}_2$ /t-waste	(Noack et al., 2014)
			• Primarily amorphous $\text{CaCO}_3$ formation	• CE = 77–93%	
FA (MSWI)	Indirect carbonation	Batch flask	• Two step carbonation using ammonia	• $\text{CO}_2$ Uptake = 58.6%	(Jung et al., 2014)
			• pH of solution reached 6.95 within 5 min	• CE = 56.9%	
			• Formation of $\text{CaCO}_3$ , $\text{NaCl}$ , $\text{CaSO}_4$ precipitates		
SS, PS, and BFS	Indirect carbonation (pH swing)	Batch flask	• Dissolution using $\text{NH}_4\text{SO}_4$ at pH 8.2–8.3	• CE of SS/PS = 74%/67%	(Dri et al., 2013, 2014)
			• Particle size fraction of 75–150 $\mu\text{m}$	• CE of BFS = 59%	
			• Optimal S/L ratio = 15 g/L for 1 h at 65°C	• $E_a$ = 42.0 kJ/mol	
			• Mixed with $\text{NH}_4\text{OH}$ (1 M) for 5 mL/g-waste	• CE = 41.1%	
RG	Direct gas-solid carbonation	Autoclave reactor	• Production of both $\text{CaCO}_3$ and $\text{FeCO}_3$	• $\text{CaCO}_3$ purity = 24.5%	(Azdarpour et al., 2014)
			• Operated at 70 bar with a particle size < 45 $\mu\text{m}$	• $\text{FeCO}_3$ purity = 19.0%	
AODS	Direct aqueous carbonation	Autoclave reactor	• Operated at 30 bar and 180°C for 120 min	• CC = 260 kg $\text{CO}_2$ /t-waste	(Santos et al., 2013)
			• Optimum S/L ratio = 25–250 g/L for $D_p$ of 46 $\mu\text{m}$	• CC = 310 kg $\text{CO}_2$ /t-waste	
Coal FA (Victorian brown coal)	Direct aqueous carbonation	Autoclave reactor	• Reduction of basicity and heavy metal leaching		(Ukwattage et al., 2014)
			• Operated at 40°C and 3 MPa with 60-rpm stirring	• CC = 27.1 kg $\text{CO}_2$ /t-waste	
			• Optimum L/S ratios = 0.2–0.3 (w/w)	• CE = 13.9%	
			• Increase of heat for faster rate of $\text{CO}_2$ transfer	• $E_a$ = 34.5 kJ/mol	
BOFS	Direct aqueous carbonation	Rotating packed bed	• Integrated with metalworking wastewater	• CC = 277–290 kg $\text{CO}_2$ /t-waste	(Chang et al., 2013)
			• Optimum L/S ratio = 20 mL/g at 65°C for 30 min	• CE = 91–94%	
			• $\text{CaO}_F$ and $\text{Ca}(\text{OH})_2$ in BOFS was eliminated		

Note: <sup>a</sup> SDA: spray dryer absorber ash; CDSA: circulating dry scrubber ash; CCS: Continuous casting slag; RG: Red gypsum; <sup>b</sup> CC:  $\text{CO}_2$  capture capacity (kg  $\text{CO}_2$  per ton of waste); CE: Carbonation efficiency (%);  $E_a$ : Activated energy.

to be superior to that using indirect carbonation, the purity of the produced  $\text{CaCO}_3$  precipitate using indirect carbonation was higher than that using direct carbonation.

### Process Intensification: Principles and Practices

One of the challenges of CCUM using alkaline waste is to accelerate the reaction and exploit the heat of reaction to minimize energy and material losses. In recent years, the *ex-situ* direct aqueous carbonation has aggressively developed, with several novel process intensification concepts as shown in Fig. 5: (1) thermal heat activation (Maroto-Valer *et al.*, 2005; Li *et al.*, 2009); (2) chemical activation using solvents, acids and bases (Maroto-Valer *et al.*, 2005; Rao *et al.*, 2008); (3) co-utilization with wastewater (or brine solution) (Druckenmiller and Maroto-Valer, 2005; Chang *et al.*, 2013a, b); (4) biological enhancement using enzymes and microorganisms; (5) centrifugal force (Pan *et al.*, 2013a, 2014); (6) ultrasonic vibration (Rao *et al.*, 2008; Santos *et al.*, 2012, 2013a); and (7) electrolysis treatment (Li *et al.*, 2009).

#### 1. Thermal Heat Activation (Pre-treatment)

Thermal heat activation is commonly used as a pre-treatment for solid wastes to remove chemically bound water. Especially for serpentines containing up to 13% of chemically bound water, the crystalline features are changed to amorphous ones following the decomposition of hydroxyl groups after heating to 600–650°C (Park and Fan, 2004; Li *et al.*, 2009). It was also observed that the porosity and surface area of solid wastes increase, and the structural instability was created after thermal heat treatment, thereby promoting the rate of carbonation afterward (Park and Fan, 2004; Li *et al.*, 2009). The drawback is that huge amounts of energy are required to achieve the high temperatures, which makes it impractical for use as a large-scale treatment. Another new approach is utilizing the exothermic reaction that comes from mineral carbonation,

which has been proved to be self-sufficient in terms of energy (Moazzem *et al.*, 2013).

#### 2. Chemical Activation Using Acids and Bases

Chemical activation utilizes the solvent, acid or base agents to weaken the Mg-bonds in an Mg-silicate structure. This allows the improvement of dissolution kinetics, thereby increasing the carbonation efficiency. Many chemical solutions such as ammonia, acetone and HCl have been evaluated in the literature (Maroto-Valer *et al.*, 2005; Power *et al.*, 2013; Jung *et al.*, 2014b). Another approach is the “pH-swing” process used in indirect carbonation (Park and Fan, 2004). This process allows silicates to be dissolved at a low pH and precipitates carbonates at a higher pH, resulting in more control of the carbonation process. However, it is much more expensive than traditional carbonation.

#### 3. Co-utilization with Wastewater or Brine Solution

Another approach is utilizing the wastewater (or brine solution) to enhance the rate of calcium ion leaching from solid wastes or gaseous  $\text{CO}_2$  dissolution into the liquid phase. The carbonation conversion was found to be higher in the wastewater (brine)/solid residue system than in the water/solid (Nyambura *et al.*, 2011; Chang *et al.*, 2013b; Pan *et al.*, 2013b). The leaching rate and capacity of calcium ions from steelmaking slag in metal-working wastewater was greater than that in tap water. Both organic and inorganic (non-acid) ionic species in wastewater (e.g., sodium and/or chloride ions) can promote the dissolution of silicate minerals (Beard *et al.*, 2004; O' Connor *et al.*, 2005; Krevor and Lackner, 2011; Jo *et al.*, 2012; Chang *et al.*, 2013a; Pan *et al.*, 2013b). The findings reported by Jo *et al.* (2012) show that a greater reactivity of the calcium-bearing complex towards chloride than other ions could thereby result in greater rates of mineral dissolution in the presence of chloride. The selection criteria of wastewater (or brine) for

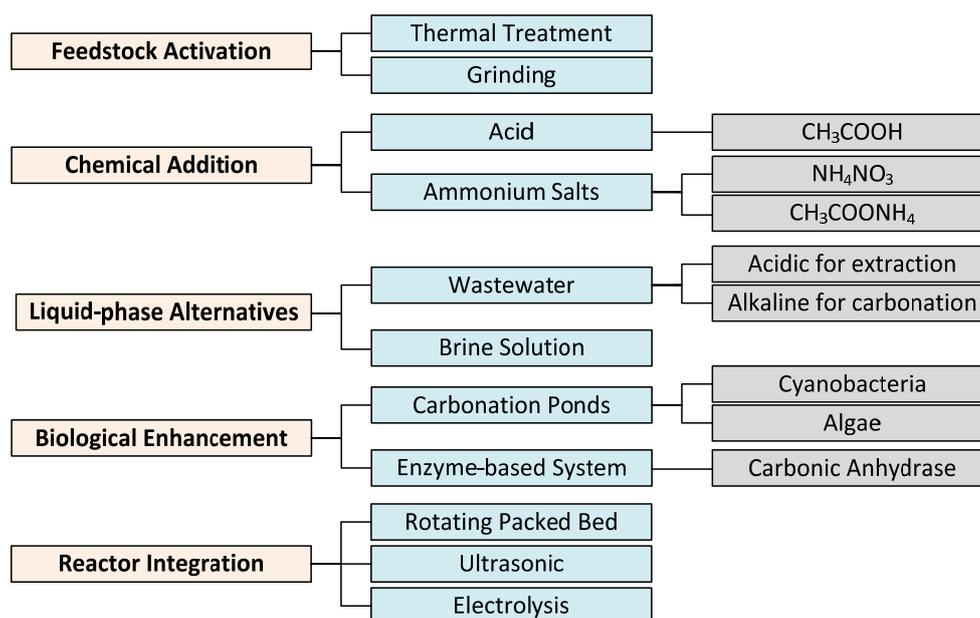


Fig. 5. Different approaches to process enhancement of *ex-situ* direct carbonation for alkaline solid wastes.

carbonation were as follows: first, the pH of the solution should be over 9.0 where  $\text{CO}_3^{2-}$  dominates because the precipitation of carbonate is favored under a basic condition. Second, the selected solution should contain neither bicarbonate nor carbonate ions (Druckenmiller and Maroto-Valer, 2005; Liu and Maroto-Valer, 2012).

#### 4. Biological Enhancement (Bio-Carbonation)

Microorganisms, e.g., anaerobic and aerobic bacteria, can positively affect carbonation by directly or indirectly enhancing the solubility and dissolution of minerals (Huang and Tan, 2014). Another approach is to utilize algae and cyanobacteria to perform photosynthesis in the presence of sunlight as energy to convert gaseous  $\text{CO}_2$  (Huang and Tan, 2014, McCutcheon *et al.*, 2014). The absorption of cations by a net negative cell wall increases the cation concentration within the cell, which can be used to facilitate mineral precipitation. Specially designed “carbonation ponds” or “basins” with a high alkalinity would have to be made using a natural cyanobacteria-dominated consortium in order for the photoautotrophs to thrive and precipitate carbonates (McCutcheon *et al.*, 2014). In addition, this process can serve as silicon sinks by the formation of mineralized cell walls (i.e., frustule) from  $[\text{SiO}_2 \cdot n\text{H}_2\text{O}]$  in the bioreactor.

Furthermore, “enzymatic carbonation” relying on carbonic anhydrase (CA) can be effective, especially when the supply of  $\text{CO}_2$  is limiting the rate of carbonation, even in an industrial environment, or utilized in an open-air environment. In addition, the CA enzyme enhances the carbonation of Ca- and Mg-bearing materials (Li *et al.*, 2013a, b). A CA enzyme-based system has been developed inside a membrane that was able to remove 90% of the  $\text{CO}_2$  supplied (Figuerola *et al.*, 2008). However, the instability and very high costs of CA may be the challenges for practical applications (Sanna *et al.*, 2014).

#### 5. Combination with Novel Processes

Since the aqueous carbonation of alkaline solid wastes was believed to be a diffusion-controlled reaction, intensification of mass transfer efficiency among phases was essential to improve  $\text{CO}_2$  capture capacity and reduce energy consumption and operating costs. A slurry reactor incorporated with ultrasound vibration has been introduced to accelerate the precipitation rate of calcium carbonate via ultrasonic irradiation (Rao *et al.*, 2007, 2008; Santos *et al.*, 2012, Santos *et al.*, 2013a). The results indicate that the efficiency of physical mixing, particle breakdown and removal of passivation layers increased with sound waves with frequencies in the range of 16–100 kHz. Therefore, a better conversion can be achieved in a shorter time compared to that without ultrasound; for instance, the carbonation conversion of combustion ashes increased from 27% to 83% with ultrasound for 40 min (Rao *et al.*, 2007).

Another approach is using a rotating packed bed (RPB) reactor, which has been successfully introduced for carbonation of solid wastes (Chang *et al.*, 2012a, 2013a; Pan *et al.*, 2013a, b, 2014), as a so-called “high-gravity carbonation process.” RPB can provide a mean acceleration of up to 1,000 times greater than the force of gravity,

thereby leading to the formation of thin liquid films and micro- or nano-droplets. (Chen *et al.*, 2004, Chen *et al.*, 2010, Cheng and Tan, 2011, Kelleher and Fair, 1996, Lin and Chen, 2008, Wang, 2004, Yu *et al.*, 2012). Both the  $\text{CO}_2$  removal efficiency and carbonation conversion of steelmaking slag in an RPB were observed to be greater than those in an autoclave or a slurry reactor (Chang *et al.*, 2012b; Pan *et al.*, 2013a, b). High  $\text{CO}_2$  removal efficiency can be achieved with a retention time of less than 1 min under ambient temperature and pressure conditions (Pan *et al.*, 2013a).

#### Summary

In this section, the principles and applications of several novel processes were illustrated, as summarized in Table 2. Alkaline wastes including wastewater (e.g., cold-rolling mill wastewater) and solid wastes (e.g., steelmaking slag) from steel manufacturing plants could be used to sequester meaningful quantities of  $\text{CO}_2$ , especially if the wastes are generated near a point source of  $\text{CO}_2$  emission, although the  $\text{CO}_2$  sequestration potential remains marginal on a global scale of  $\text{CO}_2$  emission. In other words, the integrated waste treatment, i.e.,  $\text{CO}_2$ , wastewater, and steelmaking slag, for sustainable development should be promoted and implemented in industries. It was observed that mineralization of  $\text{CO}_2$  by accelerated carbonation of alkaline wastes has the potential to not only sequester  $\text{CO}_2$  but also upgrade the physicochemical properties of waste streams.

### CARBONATED PRODUCT UTILIZATION AS GREEN MATERIALS

#### Cement in Concrete

Concrete is made of roughly 80% aggregate (sand and gravel), 10–15% cement, and 5–10% additives, water, and air. The worldwide cement industry is increasingly turning to the use of alkaline solid wastes, such as blast furnace slag (BFS) and FA, as supplementary cementitious materials (SCM) because of increasing petroleum prices and government regulations, as well as a lack of raw materials and increasing demand for concrete and cement. Processes using fresh fine BFS or fly ash as alternative binders in place of Portland cement in concrete have been developed and widely used, especially in the U.S., to reduce the energy consumption and  $\text{CO}_2$  emission associated with concrete production. However, the challenges resulting from the negative effects of this substitution, which are mainly related to early strength development, remain.

Engineering experience shows that with 50% clinker replacement with fresh FA, the early strength of concrete is reduced dramatically (Crow, 2008). Despite the fact that FA usually replaces no more than 25% of the Portland cement in concrete, research conducted at Montana State University successfully demonstrated the use of 100% fly ash concrete with glass aggregate to construct a building (Hasanbeigi *et al.*, 2012). Furthermore, not every alkaline solid waste can be successfully utilized in concrete directly. Several types of alkaline solid wastes like BOFS typically containing 3–10% free-CaO and 1–5% free-MgO would lead to fatal

**Table 2.** Process intensification of *ex-situ* carbonation using alkaline solid wastes in the literature.

Methods	Process Descriptions	Improvements on Leaching and Carbonation	Performance Evaluation	Reference
Thermal activation	Pretreatment on feedstock to remove chemically bound water	<ul style="list-style-type: none"> <li>Decomposition of hydroxyl groups after heating to 600–650°C</li> </ul>	<ul style="list-style-type: none"> <li>Increases of porosity and surface area of solid wastes</li> <li>Creation of structural instability</li> </ul>	(Park and Fan, 2004; Li et al., 2009)
Chemical additives	Use of CH <sub>3</sub> COONH <sub>4</sub> and NH <sub>4</sub> NO <sub>3</sub> solutions (or pH-swings)	<ul style="list-style-type: none"> <li>Weakening Mg-bonds in Mg-silicate structure</li> </ul>	<ul style="list-style-type: none"> <li>Silicates dissolved at a low pH</li> <li>Precipitates at a higher pH</li> <li>High Ca<sup>2+</sup> extraction efficiency = ~70%</li> </ul>	(Jo et al., 2014)
Co-utilization with wastewater (brine)	Alkaline metalworking wastewater as liquid phase for carbonation	<ul style="list-style-type: none"> <li>Enhanced leaching of various metal ions (e.g., Ca)</li> <li>Carbonation of Ca-Fe-Al-O, C<sub>2</sub>-S-H, and C<sub>1</sub>S phases in BOFS were enhanced</li> </ul>	<ul style="list-style-type: none"> <li>Ca<sup>2+</sup> concn. = 1,700 mg/L (in tap water)</li> <li>Ca<sup>2+</sup> concn. = 2,700 mg/L (in wastewater)</li> <li>Ca<sup>2+</sup> leaching rate increases by 45%</li> </ul>	(Pan et al., 2013)
Carbonic anhydrase (CA) enzyme	Bio-catalytic CaCO <sub>3</sub> precipitation via gaseous diffusion system	<ul style="list-style-type: none"> <li>CA concentrations of 0.2–2.0 U/mL were beneficial to carbonation</li> </ul>	<ul style="list-style-type: none"> <li>100% Ca<sup>2+</sup> concentration</li> <li>Precipitation rate increases 10.52 times</li> </ul>	(Li et al., 2013)
	Atmospheric CO <sub>2</sub> Uptake for Mg-carbonates	<ul style="list-style-type: none"> <li>Solutions reach chemical and isotopic equilibrium more rapidly</li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> uptake increases by up to 600%</li> </ul>	(Power et al., 2013)
	Combined with synthesized silica nanoparticles	<ul style="list-style-type: none"> <li>Surface area and activity of CA were improved</li> <li>Lifespan of the CA was also increased</li> </ul>	<ul style="list-style-type: none"> <li>SCA enzymes were immobilized and not carbonated</li> </ul>	(Zhang et al., 2013)
Rotating packed bed	Operated with a retention time of 1 min at 25°C and 1 atm at 800 rpm	<ul style="list-style-type: none"> <li>Alkaline wastewater was introduced to enhance Ca<sup>2+</sup> leaching capacity</li> <li>Faster mass transfer between gas and liquid phases</li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> removal efficiency = 96–99%</li> <li>Wastewater was neutralized to pH 7–8</li> <li>Lime and Ca(OH)<sub>2</sub> in BOFS were eliminated</li> </ul>	(Pan et al., 2013)
Ultrasonic process	Ultrasonic horn in the range of 16–100 kHz	<ul style="list-style-type: none"> <li>Higher mixing and particle breakdown efficiencies</li> <li>Removal of passivation layers increases</li> </ul>	<ul style="list-style-type: none"> <li>Conversion increases from 27% to 83% with ultrasound for 40 min</li> </ul>	(Santos et al., 2013)

expansion of hardened cement-BOFS paste (Zhang *et al.*, 2011), which has limited its application as aggregates or cements during the past.

The carbonation process is capable of permanently mineralizing carbon in the form of either fine or coarse aggregates or an SCM to meet the growing green product market as a carbon-negative material. In other words, when alkaline solid wastes are carbonated via direct carbonation, the products can also be used for a broad range of applications such as construction aggregate (large particles) and cement (fine particles), without the potential presence of free-CaO and free-MgO. Accelerated carbonation of alkaline wastes could be a potential commercialization route where the produced carbonates can be used as a substitute for components of cement (International Energy Agency (IEA), 2013b). The suitability of the calcareous material as a partial replacement for cement clinker in cement has been documented in some non-structural applications in the U.S., but the suitability of the calcareous material as a cement ingredient in concrete applications (Zaelke *et al.*, 2011) has not yet been demonstrated publicly. It was also reported that CKD and FA have been successfully used to produce a green Portland ash (Shah, 2004; Zaelke *et al.*, 2011). Currently, the challenges in the application of this process include (1) the effect of impurities on performance, (2) acceptance of the product by the cement industry, (3) the ability to capture large amounts of CO<sub>2</sub>, (4) energy requirements, (5) finding an appropriate water source, (6) production of alkalinity, and (7) having sufficient demand for the end product.

### **Aggregate in Concrete**

In addition to the “green” cement, the carbonated alkaline solid waste can function as construction aggregate to partially replace sand, gravel, and crushed stone. Many industrial waste materials can potentially be used as economical and environmentally friendly sand substitutes for cementitious building products. There are two types of aggregate: (1) coarse aggregate (generally ranging from 9.5 mm to 37.5 mm) including gravel and crushed stone, and (2) fine aggregate (usually smaller than 9.5 mm) including sand and crushed stone. Most construction aggregate is used to strengthen composite materials, such as concrete and asphalt concrete, for a myriad of uses ranging from railroad bases to housing foundations.

Monkman *et al.* (2009) evaluated the use of carbonated ladle slag as a fine aggregate in zero-slump press-formed compact mortar samples and compared them to similar samples containing control river sand. The 28-day strengths of the mortars made with the carbonated slag sand were comparable to the strengths of the normal river sand mortars (Monkman *et al.*, 2009), which clearly indicates the successful use of carbonated ladle slag as fine aggregates to prepare mortar samples simulating its applications in precast products, such as masonry units, paving stones, and hollow core slabs, which could be further treated by carbonation curing. Moreover, the carbonated particles became coarser due to agglomeration, which should be beneficial for use in aggregate manufacturing (Fernandez Bertos *et al.*, 2004b).

In addition, recycled concrete aggregate (RCA), collected from old roads and buildings, has shown promise as an alternative to natural aggregate (NA). Table 3 presents the various properties of RCA for replacement of NA in construction concrete. While RCA and NA have similar gradation, RCA particles are more rounded in shape and have more fine particles broken off in L.A. abrasion and crushing tests (McNeil and Kang, 2013). This suggests that the use of RCA as a structural concrete should be viable because the performance of RCA concrete beams was still within standard specifications (Sagoe-Crensil *et al.*, 2001; Shayan and Xu, 2004; McNeil and Kang, 2013; Behera *et al.*, 2014). Furthermore, creep can be minimized by incorporating FA as either an additive or a replacement in concrete in the case of RCA utilization (Behera *et al.*, 2014).

### **Precipitate Calcium Carbonate (PCC)**

Precipitate calcium carbonate (PCC) is a product from indirect carbonation. Different crystal morphologies and shapes of PCC can be produced and utilized in various applications in the construction, oil, plastics, paper, and pharmaceutical industries (Teir, 2008; Eloneva *et al.*, 2010, 2012). Approximately 75% of the produced PCC is expected to be used in the paper industry (Teir *et al.*, 2005, Zevenhoven *et al.*, 2008), where PCC can serve as a replacement for more expensive pulp fiber and optical brightening agents to improve the quality and printing characteristics of paper (e.g., smoothness, gloss, whiteness, opacity, brightness, and color).

PCC also can be used to replace some of the cellulose as fillers and coating pigments in plastics, rubbers, paints, and papers (Eloneva *et al.*, 2009, 2010). For these applications, several physicochemical properties of PCC play an important role, including particle size distribution, specific surface area, morphology, polymorphism and purity (Sanna *et al.*, 2012b). In addition, PCC can be utilized as an additive and filler in construction materials. Companies in North America, the EU, and Australia are working on developing a similar process, which involves CO<sub>2</sub> capture by bubbling flue gases through saline water to produce solid carbonates as an aggregate material in cement (International Energy Agency (IEA), 2013b).

### **Summary**

Application of fresh steelmaking slag as an alternative to standard materials has been known for a number of years around the world. It was used most often in asphalt mixtures, other layers of pavement structure, unbound base courses and embankments. Nonetheless, the use of alkaline solid wastes must comply with strict regulations, consisting of civil-technical and environmental requirements. Several barriers including volume expansion of blended materials (e.g., in the case of fresh BOFS) and concerns about environmental impacts and social acceptance have been encountered. It has been proved that the CaO<sub>f</sub> and Ca(OH)<sub>2</sub> in steelmaking slags can be eliminated after carbonation, thereby preventing the expansion problem of the blended materials. In addition, several studies concluded that the mechanical properties of mortar blended with carbonated

**Table 3.** Various properties of recycled concrete aggregate for natural aggregate replacement (Sagoe-Crensil *et al.*, 2001; Shayan and Xu, 2004; McNeil and Kang, 2013; Behera *et al.*, 2014).

Properties	Unit	Performance of RCA replacement <sup>a</sup>				Remarks
		RCA 100%	RCA 50%	RCA 30%	RCA 15%	
Density	kg/m <sup>3</sup>	2,394	n.r.	n.r.	n.r.	2,890 • RCA is approximately 7–9% lower than NA
Porosity and water absorption	%	4.0–5.2	n.r.	n.r.	n.r.	0.5–2.5 • NA has low water absorption due to low porosity • RCA has greater water absorption due to greater porosity • In a saturated surface dry condition, up to a 4.2% difference
Crushing test	%	23–24	n.r.	n.r.	n.r.	13–16 • Higher values for RCA was observed
L.A. abrasion test	%	32	n.r.	n.r.	n.r.	11 • Impacted and crushed by steel balls to determine amount of fine particles that break down • Higher values for RCA was observed
Compressive strength	MPa	n.r.	29	31.7	32.7	38.6 • Decreases compressive strength • Greater midspan deflections under service load
Tensile strength (splitting)	MPa	n.r.	2.7	2.7	3.0	3.3 • Concrete with RCA has comparable splitting tensile strength
Modulus of rupture (MOR)	MPa	n.r.	8.9	9.0	9.7	10.2 • MOR of RCA was slightly less than that of conventional concrete
Modulus of elasticity	MPa	15–28	n.r.	n.r.	n.r.	26–33 • Modulus of elasticity of RCA (28-d) is lower up to 45% than NA concrete
Drying Shrinkage	Micro strain	540–790	n.r.	n.r.	n.r.	275–590 • Creep can be minimized by incorporating fly ash whether as addition or replacement (in the case of RCA)

Note: <sup>a</sup> RCA (Recycled Concrete Aggregate); NA (Natural Aggregate); n.r. (Not report).

solid wastes were superior to those with fresh solid wastes. At the same time, the carbonated materials can meet the standards of construction engineering, providing positive benefits for practical applications.

## CASE STUDIES

### *Pilot Study/Demonstration Project*

Scale-up of the CO<sub>2</sub> post-combustion process is possible without significant developments or costs (International Energy Agency (IEA), 2013b). However, process performance should be further improved by process integration, thereby reducing the energy requirement for the capture process. An integrated steelmaking process is composed of numerous facilities from the entire life-cycle of iron ore to steel products including raw material preparation (e.g., coke production, ore agglomerating plant and lime production), ironmaking (e.g., blast furnace, hot metal desulphurization), steelmaking (e.g., basic oxygen furnace, ladle metallurgy), casting and finishing mills. Therefore, deployment of the CCS process in steelmaking mills is challenging, since the CO<sub>2</sub> emissions come from multiple sources. The largest part of direct CO<sub>2</sub> emissions in steelmaking mills is from power plants which are around 48% in total CO<sub>2</sub> emissions, followed by blast furnaces at around 30% in total CO<sub>2</sub> emissions (Santos, 2013). In addition, the source of the CO<sub>2</sub> may not be the emitter of the CO<sub>2</sub>. In other words, the emissions also strongly depend on management of the use of byproduct gases, as well as on the definition of boundary limits.

Table 4 summarizes the pilot studies and demonstration projects of CCUM using alkaline wastes. At Rocks, Wyoming, in the U.S., accelerated carbonation has been demonstrated in a 2,120 MW coal-fired power plant using FA since 2007 (Reynolds *et al.*, 2014). Another pilot study in the U.S. has been developed by Calera Corp. The Calera technology can capture CO<sub>2</sub> (approximately 30,000 t/y) from fossil fuel power plants and other industrial sources and sequester it in geologically stable substances suitable for disposal, storage, and/or use as building materials. In the summer of 2009, Calera identified what was believed at the time to be an ideal demonstration site at a brown-coal power plant in the Latrobe Valley, Victoria, Australia (Zaelke *et al.*, 2011).

In France, the Carmex project was initiated in 2007 to carbonate various materials such as harzburgite, wehrlite, iherzolite, slags, and olivine through direct carbonation with and without organic ligand or mechanical exfoliation. The highlight of this project is that the accessible alkaline wastes are matched to large CO<sub>2</sub> emitters through a dedicated geographical information system (GIS). A high carbonation conversion, 70–90%, can be achieved without heat activation of feedstock. The Carmex experiences indicate that the use of mineral carbonation is feasible for industries (Bodénan *et al.*, 2014).

Recently in Australia, the MCI project has been carried out to transform CO<sub>2</sub> into carbonates for use in future building products like bricks, pavers and plasterboard replacements that are non-fired products (Mineral Carbonation International, 2013). Similarly, the China Steel Corporation (CSC) project

in Taiwan was launched in 2013 by introducing the high-gravity carbonation process (i.e., RPB reactor) for small-scale carbonation of BOFS and alkaline wastewater. The CO<sub>2</sub> removal efficiency of hot-stove gas from the blast furnace was greater than 95%, with total elimination of CaO<sub>F</sub> and Ca(OH)<sub>2</sub> content in the BOFS. The carbonated BOFS was further used as green cement with different substitution ratios in mortar. As presented in Fig. 6, an integrated approach to applying the high-gravity carbonation process (so-called HiGCarb process) was proposed for CO<sub>2</sub> capture in flue gas and solid product utilization within a steelmaking plant. It was noted that the CO<sub>2</sub> removal rate by the high-gravity process can meet the time scale in industrial plants.

The world's first commercialized carbon mineralization plant (Capitol SkyMine®) is under construction by Skyonic at the Capitol Aggregates, Ltd., cement plant in San Antonio, Texas, U.S. and scheduled for completion by 2014. This plant is expected to directly remove CO<sub>2</sub> (~75,000 t/y) from industrial waste streams through co-generation of carbonate and/or bicarbonate materials (~143,000 t/y) for use in bio-algae applications to become a profitable process. In addition to capturing and mineralizing CO<sub>2</sub>, the SkyMine® process can remove SO<sub>x</sub>, NO<sub>2</sub> and heavy metals such as mercury from existing power plants and industrial plants that can be retrofitted with SkyMine®.

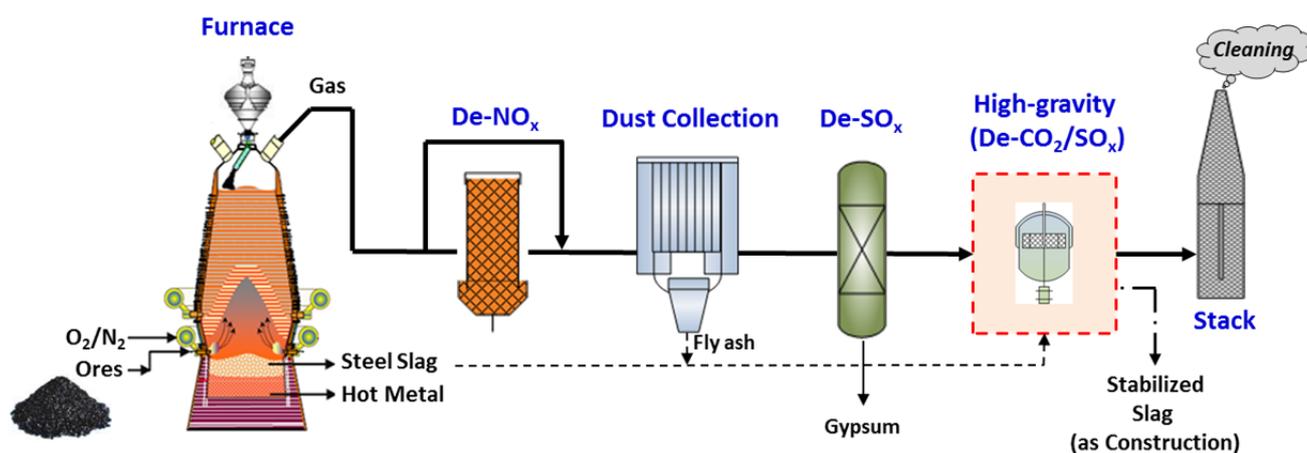
### *Cost Evaluation and Energy Consumption*

CCUM is definitely an important part to the reduction of CO<sub>2</sub> from the industrial sector and the use of industrial wastes as cement replacement. Technology may not be the only barrier to the deployment of CCS in the industrial sector. Market competitiveness and the global nature of some of these industries are important issues that should be addressed. Energy and cost penalties are related to plant scale, operation conditions, and operation modulus such as pre-treatment (e.g., grinding and thermal activation) and/or post-treatment processes (e.g., product separation and disposal) (Pan *et al.*, 2012; Sanna *et al.*, 2012a). However, due to lack of commercialized plant studies, cost estimations of accelerated carbonation are based roughly on pilot- or laboratory-scale operations.

In the case of indirect carbonation using chemical extraction (e.g., HCl, HNO<sub>3</sub>, CH<sub>3</sub>COOH and NaOH) without regeneration of chemicals, a fairly high cost, US\$600–4,500, would be required for capturing one ton of CO<sub>2</sub> (Sanna *et al.*, 2014). In addition, the regeneration of the chemicals would generate more than 2.5 times the amount of CO<sub>2</sub> fixation in the carbonation process (Teir *et al.*, 2009). The operating costs would also depend largely on the purity of the PCC product. An average cost of US\$80 was required per ton of the PCC production from two-stage carbonation using cement wastes at 50°C and 30 bar, where the energy consumption including pulverization, carbonation, CO<sub>2</sub> separation, CO<sub>2</sub> pressurization, and stirring process for both extraction and carbonation were considered at a total of 52.8 MW (Katsuyama *et al.*, 2005). On the other hand, as presented in Table 5, the energy consumption and cost evaluation of direct carbonation were found to be relatively

Table 4. Pilot Studies and Demonstration Projects of accelerated carbonation around the world.

Project	Scale <sup>a</sup>	Since	Feedstock	Description of Features	Performance	Reference
Rocks, Wyoming, the U.S.	Pilot scale	2007	Coal fly ash	<ul style="list-style-type: none"> <li>Conducted at Jim Bridger Power Plant</li> <li>Direct mineralization of CO<sub>2</sub>, SO<sub>2</sub>, and Hg in flue gas</li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> removal efficiency = 90%</li> <li>SO<sub>2</sub> removal efficiency &gt; 85%</li> <li>HgCO<sub>3</sub> formation = 0.4 mg/kg (25–58°C)</li> </ul>	(Reddy et al., 2010; Reynolds et al., 2014)
Calera (Moss Landing, CA, the U.S.)	Pilot scale	2007	Naturally occurring brines, waste materials	<ul style="list-style-type: none"> <li>Stabilize a number of pollutants (e.g., mercury, SO<sub>2</sub>) in addition to CO<sub>2</sub></li> <li>Potentially low energy penalty compared to other carbon capture processes</li> <li>Produces calcareous material and HCl</li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> capture capacity = 30,000 t/y</li> <li>CO<sub>2</sub> capture efficiency &gt; 50%</li> <li>SO<sub>2</sub> removal efficiency &gt; 95%</li> <li>Further improved to replace 40% of clinker in cement production</li> </ul>	(Calera, 2011; Zaelke et al., 2011)
Carmex (New Caledonia, France)	Pilot scale	2009	Mafic wastes (mine tailings)	<ul style="list-style-type: none"> <li>Ex situ mineral carbonation</li> <li>Matching accessible wastes to large CO<sub>2</sub> emitters through dedicated GIS</li> <li>Environmental assessment through LCA</li> </ul>	<ul style="list-style-type: none"> <li>High carbonation yield (70–90%) without heat activation</li> <li>23% of initial Mg was carbonated in Ni-pyrometallurgical slag</li> </ul>	(Bodénan et al., 2014)
MCI (New South Wales, Australia)	Pilot scale	2013	Serpentine	<ul style="list-style-type: none"> <li>Capture CO<sub>2</sub> emissions at its Kooragang Island plant</li> <li>Solid product can be turned into various green products including building materials (bricks and pavers)</li> </ul>	<ul style="list-style-type: none"> <li>Total investment of \$9 million over four years to establish pilot plant at the University of Newcastle</li> <li>Bricks was used as construction materials, acting as physical carbon sinks</li> </ul>	(Mineral Carbonation International, 2013)
CSC (Kaohsiung, Taiwan)	Small scale	2014	BOFS, alkaline wastewater	<ul style="list-style-type: none"> <li>High-gravity carbonation process (RPB)</li> <li>Alkaline wastewater were introduced</li> <li>Carbonated BOFS was utilized as partial replacement of cement</li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> removal efficiency &gt; 95%</li> <li>Alkaline wastewater is neutralized to pH 7</li> <li>Free-CaO and Ca(OH)<sub>2</sub> in BOFS can be eliminated</li> </ul>	(Pan et al., 2013)
Capitol SkyMine (San Antonio, TX, the U.S.)	Toward Business Model (Commerc.)	2014	Brine solution	<ul style="list-style-type: none"> <li>Groundbreaking at September 30, 2013 and completion by 2014</li> <li>Produce green chemicals such as HCl, bleach, Cl, and H<sub>2</sub></li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> capture capacity = 75,000 t/y</li> <li>CO<sub>2</sub> removal anywhere from 10%–99%</li> <li>Remove CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub> from flue gas</li> <li>Removes heavy metals such as mercury</li> </ul>	(Skyonic, 2014)



**Fig. 6.** An integrated approach to applying high-gravity carbonation (HiGCarb) process for CO<sub>2</sub> capture in flue gas and solid product utilization within steelmaking plant.

lower than that of indirect carbonation. In the case of direct carbonation, the energy requirement of the grinding process was the major cost in the overall process (Gerdemann *et al.*, 2007, Pan *et al.*, 2013b). It was observed that the cost of *ex situ* direct carbonation was in the range of US\$54–133 per t-CO<sub>2</sub>, depending on the types of feedstock and operating modulus. Moreover, the handling of solids in the process has the potential to raise the O&M costs when compared to CO<sub>2</sub> absorption using ammonia and amine technologies (Yu *et al.*, 2012).

In contrast, the total cost of *in-situ* carbonation was estimated at US\$72–129 per t-CO<sub>2</sub> (considering an estimated transportation and storage cost of ~US\$17 per t-CO<sub>2</sub> in basaltic rocks (Gislason and Oelkers, 2014)), without taking into account long-term monitoring costs. However, all of those costs are by far greater than the recent European carbon market price of ~US\$7 per t-CO<sub>2</sub> in 2014 (Sanna *et al.*, 2014). It was noted that the CO<sub>2</sub> price may increase to US\$35–90 per t-CO<sub>2</sub> by 2040 (Wilson *et al.*, 2012). In another scenario estimated by the International Panel on Climate Change, the price of carbon credit gives ~US\$55 per t-CO<sub>2</sub> as a lower bound estimate, necessary to meet Kyoto protocol targets.

It has been observed that the carbonated SS can potentially be used as partial cement replacement materials (Liang *et al.*, 2012; Salman *et al.*, 2014). However, in order to make *ex-situ* carbonation more economically feasible, a breakthrough on the use of carbonated solid wastes or products should be sought in the areas of technology, regulation, institution and finance. The global cement market is quite large, with roughly 3.5 billion metric tons used in 2011, and a processing cost of nearly US\$100 per ton (International Energy Agency (IEA), 2013b). The benefits returned from product utilization should be taken into consideration in the fiscal evaluation of the overall carbonation process. From the viewpoint of energy consumption, fine FA is a good candidate for low-cost carbonation because no grinding process is required in advance. In addition, waste-heat integration from manufacturing processes could be implemented instead of electrical heating to reduce the overall energy requirement

and operating cost (Balucan *et al.*, 2013).

#### Life Cycle Assessment (LCA)

Although accelerated carbonation can potentially fix and store CO<sub>2</sub> over a geological time scale, the environmental effects of the process involved need to be considered from the perspective of life cycle assessment (LCA). The LCA of the CCUM process is particularly important, since energy is used in transporting slag, grinding, sieving, pressuring, heating, and operating the reactor (Xiao *et al.*, 2014). CCUM may increase other environmental impacts such as eutrophication or acidification due to the increase in the concentrations of other pollutants. Hence, the effects of CCUM should be weighed and compared carefully according to changes in the environmental impacts.

Steelmaking slag is a solid waste of the steel manufacturing industry characterized by its strongly alkaline nature and significant levels of metal ions, especially calcium. After carbonation, the physicochemical properties of slag can be improved and suitably used as SCM to replace portions of the Portland cement in concrete. Typically, 1.5–1.7 tons of natural resource (e.g., limestone and clay) and 0.11–0.13 ton of coal are used per ton of cement clinker production (Kumar *et al.*, 2006). Moreover, concrete made from Portland cement carries a carbon footprint of approximately 0.73–0.99 ton CO<sub>2</sub> per ton cement, corresponding to roughly 537 pounds of CO<sub>2</sub> per cubic yard of concrete (Hasanbeigi *et al.*, 2012). Therefore, both the natural resource consumption and carbon footprint of concrete can be mitigated through the use of carbonated solid wastes as construction aggregate (large particles) or SCM (fine particles).

The annual world cement production is expected to grow by ~60% and reach 3.7–4.4 Gt by 2050, compared to approximately 2.5 Gt in 2006 (Hasanbeigi *et al.*, 2012). According to Zhang *et al.* (2011), blended cements with 30–60% residual slag product have properties comparable to those of Portland cement (Kumar *et al.*, 2006). Therefore, it can be expected that huge environmental benefits can be obtained, e.g., approximately 1.45–3.89 Gt of limestone,

**Table 5.** Cost evaluation and energy consumption of *ex-situ* direct carbonation using various processes.

Feedstock	Process Descriptions	Evaluation Consideration	Remarks	Energy Consu. (kW/h/t-CO <sub>2</sub> )	Cost <sup>b</sup> (US\$/t-CO <sub>2</sub> )	Reference
Olivine	Pre-treatment (grinding to 38–75 μm and heating to 630°C for 2 h)	<ul style="list-style-type: none"> <li>Totally 7 regions were studied</li> <li>Operation including standard pretreatment, mechanical or thermal treatment, and carbonation reaction</li> </ul>	<ul style="list-style-type: none"> <li>Mineral grade is 70%</li> <li>Mineral (lizardite or antigorite) grade is 100%</li> </ul>	633–653	54–55	(Gerdemann <i>et al.</i> , 2007)
Wollastonite				429	91	
Serpentine	Thermal heat instead of electrical energy	<ul style="list-style-type: none"> <li>Heat activation pretreatment</li> <li>Partial dehydroxylation of lizardite</li> </ul>	<ul style="list-style-type: none"> <li>Up to 63% of decrease in energy requirement due to heat integration</li> </ul>	n.a. <sup>a</sup>	70	(Rayson <i>et al.</i> , 2008)
FA	Pilot scale plant using fluidized bed (70°C for 120 min)	<ul style="list-style-type: none"> <li>Conducted at a 532 MW coal fired power plant</li> <li>No grinding of fly ash was required</li> </ul>	<ul style="list-style-type: none"> <li>CO<sub>2</sub> capture = 90%</li> <li>Mineralization capacity of 207 kg CO<sub>2</sub> per tonne of fly ash</li> </ul>	n.a.	7.4–27.3	(Christensen, 2010; Reddy <i>et al.</i> , 2010)
Mixed waste (SS, concrete)	Lab-scale spraying glass chamber	<ul style="list-style-type: none"> <li>Operating (pumps, reactor, sprayers) and labor costs</li> <li>Cost of water consumption included</li> </ul>	<ul style="list-style-type: none"> <li>Grinding to ~45 μm</li> <li>A 50% of removal efficiency from feed CO<sub>2</sub> gas</li> </ul>	15.6 (power)	8	(Stolaroff <i>et al.</i> , 2005)
Wollastonite	Lab-scale autoclave reactor (20 bar and 200°C)	<ul style="list-style-type: none"> <li>Depreciation of investments</li> <li>Viable (feedstock, electricity, cooling water) and fixed (labor, supervision, maintenance, insurance, laboratory) operating costs</li> </ul>	<ul style="list-style-type: none"> <li>Feedstock costs (US\$70)</li> <li>Grinding (from 100 mm to &lt; 38 μm) and compression costs (US\$34)</li> <li>Fixed operating cost (US\$36)</li> <li>High depreciation cost (US\$30)</li> </ul>	296 (power) –295 (Heat)	133	(Huijgen <i>et al.</i> , 2007)
SS				337 (power) –167 (Heat)	100	
BOFS	Lab-scale rotating packed bed reactor (1 atm and 25°C)	<ul style="list-style-type: none"> <li>Only operating costs of grinding, stirring, pumps and reactor</li> <li>A scale factor of 0.7 was used</li> </ul>	<ul style="list-style-type: none"> <li>Electricity cost of RPB rotating (US\$24.3)</li> <li>Grinding cost (US\$17.7)</li> </ul>	485 (power) 0 (Heat)	57	(Pan <i>et al.</i> , 2013)

<sup>a</sup> n.a.: Not Available; <sup>b</sup> : Assumed EUR€1.0 = US\$1.3.

0.22–0.60 Gt of clay, and 0.12–0.34 Gt of coal would be annually avoided by 2050, with the use of BOFS in blended cement.

Furthermore, to achieve an acceptable reaction rate for industrial applications, alkaline wastes are usually ground down to fine particles (~ 100 µm) prior to use. The effect and toxicity of finely ground particles seems to cause significant health issues related to particulate formation, which is often believed to be a leading cause of respiratory disease (Koorneed and Nieuwlaar, 2009; International Energy Agency (IEA), 2013a; Giannoulakis *et al.*, 2014).

### Summary

Despite the great amount of alkaline waste available for CO<sub>2</sub> capture, the costs of both direct and indirect carbonation are too high for large-scale industrial deployment, suggesting that it may not be a complete solution to carbon capture issues. *Ex-situ* carbonation of alkaline wastes, which combines the treatment of industrial wastes that are readily available near a CO<sub>2</sub> emission point, could be part of an integrated approach to CO<sub>2</sub> mitigation issues for industrial plants. Another interesting issue is the problem of cost-allocation in the case of multiple emission reductions. Although CO<sub>2</sub> emission in an industrial plant was lower than in a power generation plant, the management of a variety of CO<sub>2</sub> sources within a single industrial plant and the selection of appropriate process and technology for CO<sub>2</sub> capture were the main barriers to lowering the industrial capture costs. To promote industrialization of CCUM, future work should be concentrated on the selection of appropriate processes, design and build-up of full-scale equipment, and management of material recycle and residue treatment.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

Since reducing CO<sub>2</sub> emissions is critical to limit global warming to 2°C, CCUS technologies need to be deployed in steelmaking industries. Currently, the technology development is on track; however, the financial benefits are not great, since CCS projects need to demonstrate long-term viability and market support in the form of direct incentives. The proposed integrated CCUM process provides a solution for multiple waste treatments, i.e., reduction of CO<sub>2</sub> in flue gas, neutralization of alkaline wastewater, and stabilization of alkaline solid waste such as steelmaking slag. This could both lower the cost for wastewater treatment and CO<sub>2</sub> capture and enhance the utilization potential for steelmaking slag. Since the CO<sub>2</sub> emitted from the stacks in industries was generally pressurized and purified, it could be applied for accelerated carbonation directly at the source point, thereby reducing the cost for CO<sub>2</sub> capture. Although the use of waste steelmaking slag and metalworking wastewater for CO<sub>2</sub> capture will not lead to significant carbon credits, these wastes are available in large amounts and are near the emission sites, hence eliminating the need for transportation of raw material. The integrated CCUM process seems to be

a viable option for industries because it is capable of the production of a saleable product, multi-pollutant treatments for flue gas and wastewater, and potential process integration for lowering the costs.

### Recommendations

Since industrial waste products are generally produced near places of CO<sub>2</sub> emissions, using the CO<sub>2</sub> that is emitted to carbonate industrial waste offers an improvement over existing methods because it does not require the CO<sub>2</sub> or the industrial waste to be transported, and it allows better monitoring of total emissions. Several recommendations of CCUM were proposed for further investigation:

1. The reduction of CO<sub>2</sub> emissions in industry can be integrated with the waste treatment including alkaline solid wastes and wastewater, and their utilization such as green cement and aggregate in the construction engineering industry.
2. A cost benefit analysis should be systematically carried out based on the consideration of (a) capital and operating costs for carbonation process and (b) profits from CO<sub>2</sub> reduction (e.g., carbon tax or carbon credit) and waste utilization (i.e., high-value products).
3. Carbon footprint and energy consumption of the developed novel processes should be calculated using the LCA to determine the optimal particle size of solid wastes from the viewpoint of both CO<sub>2</sub> capture efficiency and product utilization.

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