CO$_2$ Capture by Accelerated Carbonation of Alkaline Wastes: A Review on Its Principles and Applications

Shu-Yuan Pan[1], E.E. Chang[2], Pen-Chi Chiang[1*]

[1] *Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 10617, Taiwan*
[2] *Department of Biochemistry, Taipei Medical University, Taipei 11031, Taiwan*

ABSTRACT

CO$_2$ capture, utilization, and storage (CCUS) is a promising technology wherein CO$_2$ is captured and stored in solid form for further utilization instead of being released into the atmosphere in high concentrations. Under this framework, a new process called accelerated carbonation has been widely researched and developed. In this process, alkaline materials are reacted with high-purity CO$_2$ in the presence of moisture to accelerate the reaction to a timescale of a few minutes or hours. The feedstock for accelerated carbonation includes natural silicate-minerals (e.g., wollastonite, serpentine, and olivine) and industrial residues (e.g., steelmaking slag, municipal solid waste incinerator (MSWI) ash, and air pollution control (APC) residues). This research article focuses on carbonation technologies that use industrial alkaline wastes, such as steelmaking slags and metalworking wastewater. The carbonation of alkaline solid waste has been shown to be an effective way to capture CO$_2$ and to eliminate the contents of Ca(OH)$_2$ in solid residues, thus improving the durability of concrete blended with the carbonated residues. However, the operating conditions must be further studied for both the economic viability of the technology and the optimal conditions for CO$_2$ reaction.

Keywords: Carbon capture, utilization, and storage; Steelmaking slag; Calcite; Adsorption.

INTRODUCTION

Human activities result in emissions of four long-lived greenhouse gases (GHGs): CO$_2$, CH$_4$, N$_2$O and halocarbons, of which CO$_2$ is the most important anthropogenic GHG because it is responsible for about two-thirds of the enhanced greenhouse effect (Nyambura *et al.*, 2011). The following are possible strategies for reducing CO$_2$ in the atmosphere: (i) reducing the amount of CO$_2$ produced (reducing energy intensity); (ii) using CO$_2$ (or reducing carbon intensity); (iii) capturing and storing CO$_2$; (iv) switching to less carbon-intensive fuels; and (v) increasing the use of renewable energy (IPCC, 2005; Yang *et al.*, 2008; Mikkelsen *et al.*, 2010). The third strategy involves the development of innovative, available and cost-effective carbon capture and storage (CCS) technologies because of a 50-year estimate for the continued widespread burning of fossil fuels, the goal of reaching a 500 ppm atmospheric CO$_2$ concentration plateau, and the lag time needed for the development and implementation of new carbonless sources of energy (Pacala and Socolow, 2004; IPCC, 2005; Figueroa *et al.*, 2008).

CCS technologies can be classified into three categories: pre-combustion capture, post-combustion capture, and oxy-combustion (Figueroa *et al.*, 2008). Table 1 presents the comparison of the post-combustion CO$_2$ capture technologies by absorption process and adsorption process using aqueous absorbents, solid adsorbent, ionic liquid (IL), and metal organic frameworks (MOFs). Other post-combustion capture technologies include membrane separation, enzyme-base system, and bio-algae capture. However, in recent years, extending CCS technology to incorporate "utilization" has received dramatically global attention as a viable option for reducing CO$_2$ emissions. With the newly developed concept, i.e., moving CCS to Carbon Capture, Utilization and Storage (CCUS), Mainland Europe, and in particular Germany, the U.S. and Australia, are well-advanced in research and development of CCUS technologies (CSLF, 2011; Styring *et al.*, 2011). The utilization routes of the captured CO$_2$ include enhanced fuel recovery (i.e., EOR and EGR), biological conversion (i.e., algae), food industry, chemicals (i.e., fertilizer and liquid fuel), refrigerant, inerting agents, fire suppression, plastics, and even mineralization as carbonates (i.e., precipitation calcium carbonates (PCC) and construction materials). CO$_2$ utilization by mineralization as carbonates is related to the accelerated carbonation technology (ACT).

Accelerated carbonation (chemical adsorption) is a feasible and attractive alternative method for the mitigation of CO$_2$ emissions in the coming decades because it involves storing

---

* Corresponding author. Tel.: 886-2-23622510;
  Fax: 886-2-23661642
  E-mail address: pcchiang@ntu.edu.tw

Table 1. Comparison of CO_2 capture process by absorption and adsorption.

Unit Process		Process Description/ Chemical Components	Advantages	Disadvantages	Reference
Absorption	Physical	· Selexol Process · Rectisol Process · Purisol Process	· Low vapor pressure and toxicity (Selexol) · Low corrosion (Rectisol) · Low energy consumption (Purisol)	· Low absorption capacity · Limited refractory life (Selexol) · High capital and operating costs (Rectisol)	Olajire, 2010
	Chemical	· Alkanolamine solution (MEA, DEA, MDEA) · Sterically hindered amine (AMP) · Promoter (PZ, PIP)	· High absorption capacity · Low operating pressure and temperature · Suitable for retrofitting of the existing power plant	· Severe equipment corrosion rate · High energy consumption in regeneration · Large absorber volume required · Amine degradation by SO_2, NO_2, and O_2	Tan and Chen, 2006; Haszeldine, 2009; Yu *et al.*, 2012
		· Ionic liquid (IL)	· Low vapor pressure · Non-toxicity · Good thermal stability · High polarity	· High viscosity · High energy requirement for regeneration · High unit costs	Figueroa *et al.*, 2008
Adsorption	Physical	· Activated carbon (AC) · Zeolite · Mesoporous silica (MS) · Metal-organic frameworks (MOFs)	· Wide availability and low cost · High thermal stability (AC) · Low sensitivity to moisture (AC) · High pore size and tunable pore size (MS and MOFs)	· Low CO_2 adsorption capacity · Low CO_2 selectivity · Slow adsorption kinetics · Thermal, chemical, and mechanical stability in cycling.	Figueroa *et al.*, 2008; Huang *et al.*, 2010
	Chemical	· Amine-based adsorbent · Alkali-earth metal adsorbent · Lithium-based adsorbent	· Exothermal reaction · High adsorption capacity · Low cost in natural minerals	· Deactivation of synthesis adsorbent · Low CO_2 selectivity · Serious diffusion resistance	Huang *et al.*, 2010
		· Alkaline solid waste (steelmaking slag, MSWI, etc)	· Thermodynamically stable product · High availability of wastes · Reuse product in a variety of application · Decreased leaching of heavy metal trace elements from the wastes	· Low CO_2 adsorption capacity · Slow adsorption kinetics and mass transfer · High energy consumption in crushing	Bobicki *et al.*, 2012; Chang *et al.*, 2012

CO_2 as carbonate precipitation, which is environmentally benign. The basic goal of accelerated carbonation is to mimic the natural weathering processes in which CO_2 reacts with metal oxide bearing materials to form stable and insoluble carbonates, with calcium- or magnesium-oxide being the most favourable metal oxide in reacting with CO_2. Besides that, carbonation is an exothermal reaction, so energy consumption and costs may be reduced by its inherent properties (Lackner, 2003; Eloneva *et al.*, 2008a; Baciocchi *et al.*, 2009a). In all cases, carbonation must provide base ions, such as monovalent sodium and potassium, or divalent calcium and magnesium ions to neutralize the carbonic acid (Costa *et al.*, 2007; Gerdemann *et al.*, 2007). Other carbonate-forming elements such as iron carbonates are not practical due to their unique and precious features (Lackner, 2002).

Industrial residues such as steelmaking slags, combustion residues, waste concrete, fly ashes, etc. are alkaline and also appear to be potential raw materials for CO_2 sequestration by accelerated carbonation due to the fact that these materials are generally rich in metal oxides including calcium, magnesium, aluminium, iron, and manganese oxide. The
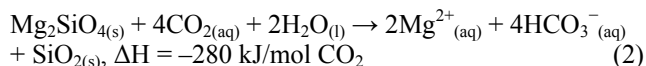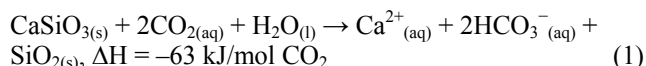
potential advantages of accelerated carbonation of applied industrial alkaline solid wastes include: (a) carbonation is an exothermal reaction and hence energy consumption and costs may be reduced by its inherent properties; (b) carbonation products such as calcium or magnesium carbonates are thermodynamically stable under ambient conditions, that is, in the absence of acidification.; (c) it offers great sequestration capacity due to the high availability of deposits; (d) it does not require transport at sites within steel-works and is therefore cost-effective; (e) products may be beneficially reused in a variety of application, such as construction materials; (f) carbonation eliminates environmental impacts due to decreased leaching of heavy metal trace elements such as Pb, Ni, and Cd from residues and stabilizing of the waste leading to an improvement of environmental quality; and (g) it could neutralise the pH of the solution as carbonate precipitations are formed if alkaline wastewater is used as the liquid agents (Lackner, 2003; Fernandez-Bertos *et al.*, 2004a; Huijgen *et al.*, 2005b, c; Costa *et al.*, 2007; Eloneva *et al.*, 2008a; Bonenfant *et al.*, 2009; Huntzinger *et al.*, 2009a; Gunning *et al.*, 2010; Lim *et al.*, 2010).

This paper focuses on accelerated carbonation of industrial alkaline wastes, e.g., steelmaking slags and metalworking wastewater. The principles of accelerated carbonation, the applications of carbonation of various wastes and the performance evaluations for CO_2 sequestration by carbonation of various alkaline wastes are reviewed to establish the state of the art for this emerging technology.

CARBONATION OF ALKALINE MATERIALS

Natural Carbonation

Carbonation can occur naturally. Natural carbonation is also well known as "weathering", which eventually removes CO_2 from the atmosphere by neutralizing the acid with mineral alkalinity. Natural weathering occurs by the reaction between natural alkaline silicates and atmospheric CO_2, as shown in Eqs. (1) and (2):

$$CaSiO_{3(s)} + 2CO_{2(aq)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2HCO_3^{-}_{(aq)} + SiO_{2(s)}, \Delta H = -63 \text{ kJ/mol } CO_2 \quad (1)$$

$$Mg_2SiO_{4(s)} + 4CO_{2(aq)} + 2H_2O_{(l)} \rightarrow 2Mg^{2+}_{(aq)} + 4HCO_3^{-}_{(aq)} + SiO_{2(s)}, \Delta H = -280 \text{ kJ/mol } CO_2 \quad (2)$$

Atmospheric CO_2 dissolves in rainwater, producing weak carbonic acid, and becomes slightly acidic by nature. Calcium and magnesium silicates are therefore leached from the mineral matrix after coming in contact with the rainwater. Rainwater thus carries the leached calcium and magnesium to rivers and subsequently to the ocean, where calcium and magnesium precipitates and forms solid carbonates (M^{2+} represents alkaline earth metal element) as shown in Eq. (3)

$$M^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow M^{2+}CO_3^{-}_{(aq)} \rightarrow M^{2+}CO_3^{-}_{(s)} \quad (3)$$
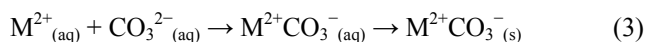
Chemical weathering of natural mineral ores is one of the main mechanisms contributing to the global geochemical carbon cycle. Nature's carbon cycle sequesters CO_2 as mineral carbonates by precipitation from the ocean in a geological timescale (Gerdemann *et al.*, 2007). However, the kinetics of natural carbonation is extremely slow due to the relatively low CO_2 concentration, about 0.03–0.06% (Lackner, 2002; Costa *et al.*, 2007). According to an investigation by Haug *et al.* (2010), the weathering rate of olivine is estimated to be $10^{-8.5}$ mol/(m^{2}s) using the average ground temperature in Norway of 6°C and a pH of 5.6, which corresponds to the acidity of rainwater.
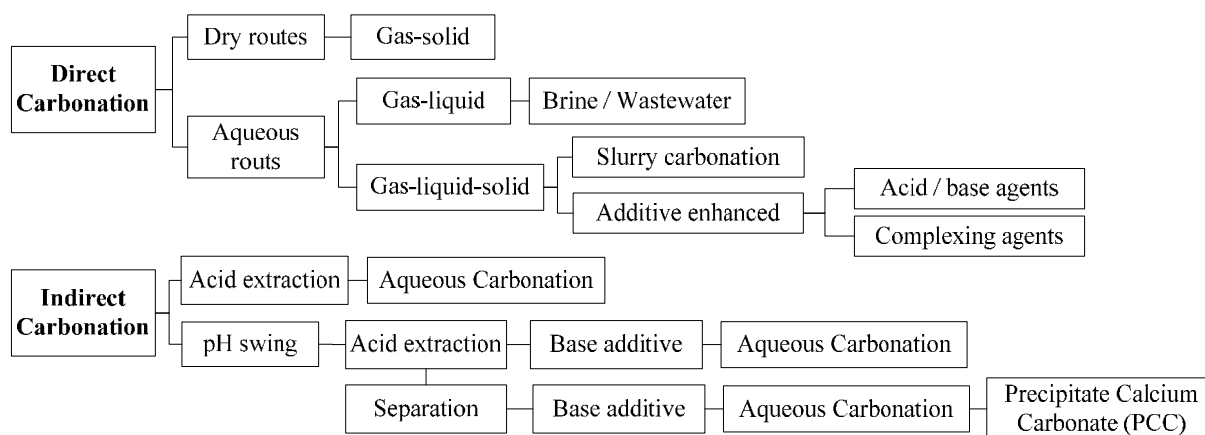
Accelerated Carbonation

First proposed by Seifritz (1990), accelerated carbonation involves alkaline materials reacting with high-purity CO_2 in the presence of moisture to accelerate the reaction to a timescale of a few minutes or hours (Lim *et al.*, 2010). Accelerated carbonation can be classified into two main types: mineral carbonation and alkaline solid waste carbonation. Mineral carbonation can be defined as the reaction between minerals and CO_2 where the product is at least one type of carbonate (Haug *et al.*, 2011). Currently, accelerated carbonation has been primarily investigated through the direct aqueous route (Huijgen and Comans, 2006a; Costa, 2009; Uibu *et al.*, 2009; Chang *et al.*, 2011a). Carbonation can result in lowering of pH, affecting the solubility, and leaching of metals which are mobilized at high pH and fixed at low pH (Costa *et al.*, 2007).

Currently, accelerated carbonation processes have been focused on assessing and maximizing the storage of CO_2 by optimizing the operating conditions including pressure, temperature, liquid-to-solid (L/S) ratio, gas humidity, gas flow rate, liquid flow rate, particle size, and solid pretreatment in numerous experimental investigations (Costa *et al.*, 2007; Huntzinger *et al.*, 2009b; Haug *et al.*, 2010; Chang *et al.*, 2011a, b).

The main process routes for accelerated carbonation of minerals are shown in Fig. 1. They are classified as: *direct processes*, where carbonation occurs in a single process step, and *indirect processes*, where alkaline earth metal is first extracted from the mineral matrix and subsequently carbonated.

The processes via which the carbonation of the minerals or alkaline solid wastes takes place in a single route step are referred to as *direct carbonation.* Usually, these processes can be divided into two types: gas-solid (dry) carbonation and aqueous (wet) carbonation; these processes are generally operated at an L/S ratio of less than 0.2 and more than 5, respectively (Lim *et al.*, 2010). The direct gas-solid carbonation process, first studied by Lackner *et al.* (1995), consists of converting oxide or silicate minerals directly to carbonates using gaseous or supercritical CO_2. Lackner *et al.* (1997) reported that the highest conversion by direct gas-solid carbonation of silicates was found to be 25% by exposing 100-μm serpentine particles to a CO_2 pressure of 340 bar and a temperature of 500°C for 2 h. Drawbacks of the gas-solid process that have prevented its widespread large-scale use to date are (i) the slow kinetics of carbonation chemistry and (ii) the significant energy input requirement (IPCC, 2005). However, the gas-solid process

Fig. 1. Various process routes of accelerated carbonation for CO_2 capture.

is much more economical than wet carbonation using aqueous solutions (Zevenhoven *et al.*, 2008). Zevenhoven *et al.* (2008) investigated the gas-solid process based on MgO-based minerals, and they found that the process for MgO extraction followed by MgO hydration and $Mg(OH)_2$ carbonation, compared with the process for MgO extraction followed by MgO carbonation, is preferable from an exergy point of view. Also the process appeared to show more rapid carbonation kinetics. Therefore, MgO-based mineral carbonation requires a stepwise process, combining the extraction of the MgO from a mineral with carbonation of the MgO, at presumably different temperatures and pressures.

In *indirect carbonation* processes, e.g., pH-swing methods (Park and Fan, 2004; Eloneva *et al.*, 2008a; Kodama *et al.*, 2008; Doucet, 2010; Wang and Maroto-Valer, 2011), reactive alkaline earth metals are first extracted from the solid matrix and then carbonated. Fig. 2 shows the typical indirect carbonation for carbonating minerals using HCl. The drawback of this process is the high energy consumption for evaporation of the aqueous solution and the large variations in free energy resulting from the necessary formation of intermediate products (Teir, 2008). Moreover, Kakizawa *et al.* (2001) suggested the use of acetic acid for the extraction of calcium from a calcium-rich feedstock in two-steps. The general problem of this process is that other elements, such as heavy metals, may also leach out during the extraction step, thus leading to impure carbonate precipitation.
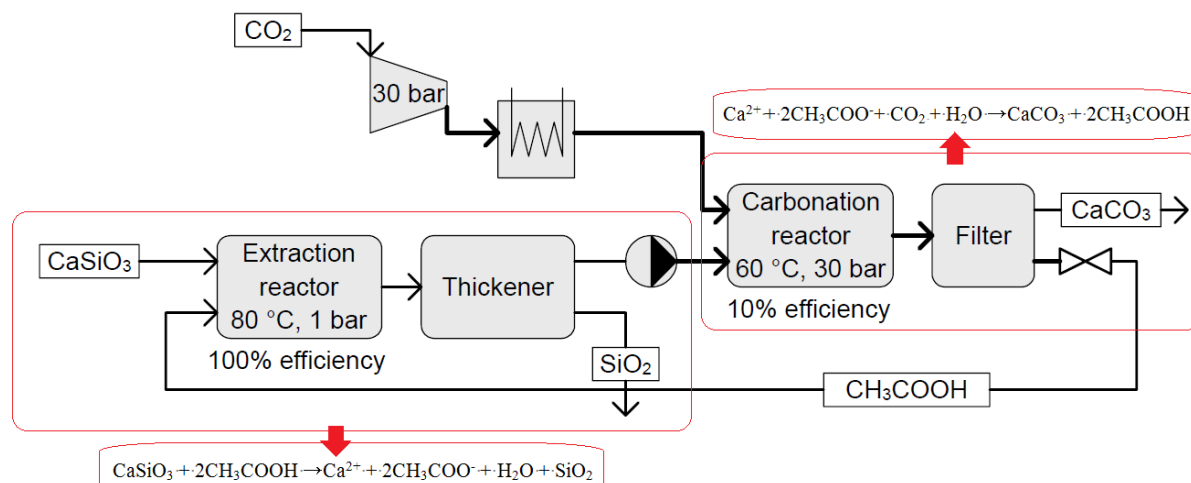
According to a study by Teir (2008), where the Gibbs free energy of the carbonation reactions was calculated using Outokumpu HSC 5.1, the carbonation of calcium ions proceeds at temperatures over 45°C, while the carbonation of magnesium ions should be possible only at temperatures over 144°C. The results also indicated that the dissolution reactions of calcium and magnesium are more exothermic ($\Delta H < 0$), while the carbonation reactions are less endothermic ($\Delta H > 0$), giving an exothermic net reaction. Mineral carbonates are thermodynamically stable and could theoretically store CO_2 permanently under ambient conditions, since they have a lower energy state than their reactants (CO_2 and silicates). Mineral carbonates, however, can be readily dissolved in the presence of strong acids in ambient conditions. Therefore, there is still a small risk

that CO_2 gas could be released into the atmosphere if mineral carbonates make contact with acids, e.g., acid rain (pH 5–7).

Alkaline Wastes as Adsorbents

Both alkali metals (i.e., Na, K, etc.) and alkaline earth metals (i.e., Ca, Mg, etc.) can be carbonated from a chemical elements perspective and a thermodynamic view point (Huijgen and Comans, 2003; 2005a). Alkali (bi)carbonates, however, are soluble in water, which would result in releasing CO_2 back into the atmosphere. This thus suggests that alkali metals are unsuitable for the long-term storage of CO_2. In addition, a number of other metals such as Mn, Fe, Co, Ni, Cu, and Zn could potentially be carbonated, but most of these metals are impractical due to their unique and precious features. To provide significant storage of CO_2, large amounts of raw materials are required as feedstock for carbonation, which must be abundant and cheap (Teir, 2008).

One kind of feedstock for accelerated carbonation is natural silicate minerals, such as wollastonite ($CaSiO_3$), serpentine ($Mg_3Si_2O_5(OH)_4$), olivine (Mg_2SiO_4), talcum ($Mg_3Si_4O_{10}(OH)_2$), pyroxene, and amphibole, which are rich in calcium or magnesium content, or industrial residues, the former being abundant but generally difficult to access and the latter relatively scarcer but easily accessed. The majority of previous research has focused on the aqueous carbonation of naturally occurring silicate minerals such as serpentine (Mckelvy *et al.*, 2004; Alexander *et al.*, 2007; Krevor and Lackner, 2011), olivine (Haug *et al.*, 2010), limestone (Symonds *et al.*, 2009) and wollastonite (Tai *et al.*, 2006; Huijgen *et al.*, 2006c; Daval *et al.*, 2009) due to their high calcium or magnesium content. Although the CO_2 storage capacity of these natural Ca-Mg-silicate minerals is sufficient to fix the CO_2 emitted from the combustion of fossil fuels, the technological carbonation of these minerals is slow and energy demanding. One way to avoid some of these drawbacks is to utilize alkaline waste residues. Table 2 summarizes the example of industrial alkaline solid wastes, e.g., coal- and oil shale-fired power plants (Uibu *et al.*, 2009b; Uibu and Kuusik, 2009a; Uibu *et al.*, 2011), steelmaking slag (Huijgen *et al.*, 2005c; Bonenfant *et al.*, 2008; Eloneva

$$Ca^{2+}+2CH_3COO^-+CO_2+H_2O \rightarrow CaCO_3+2CH_3COOH$$

$$CaSiO_3+2CH_3COOH \rightarrow Ca^{2+}+2CH_3COO^-+H_2O+SiO_2$$

Fig. 2. Indirect carbonation processes for carbonating calcium silicate using acetic acid (proposed by Teir, 2008).

Table 2. Example of alkaline solid wastes in literature.

Types of Alkaline Solid Waste	Examples	Reference
Slag	Steelmaking slag (BOF, EAF) Coal slag Blast furnace slag (UF, FA, BFS)	Huijgen *et al.*, 2005c; Bonenfant *et al.*, 2008; Eloneva *et al.*, 2008b; Kodama *et al.*, 2008; Baciocchi *et al.*, 2009b; Doucet, 2010; Chang *et al.*, 2011a, b
Air pollution control (APC) residue	Municipal solid waste incinerator (MSWI) APC residue Cyclone dust	Costa *et al.*, 2007; Baciocchi *et al.*, 2009a; Montes-Hernandez *et al.*, 2009; Nyambura *et al.*, 2011; Cappai *et al.*, 2012
Fly ash	MSWI fly ash Coal fly ash Oil shale ash	Li *et al.*, 2007; Uibu *et al.*, 2009b; Uibu and Kuusik, 2009a; Wang *et al.*, 2010; Uibu *et al.*, 2011
Bottom ash	MSWI bottom ash	Arickx *et al.*, 2006; Rendek *et al.*, 2006
Cement wastes	Cement kiln dust (CKD) Cement bypass dust (CBD) Construction and demolition waste Cement/Concrete waste Blended hydraulic slag cement (BHC)	Haselbach, 2009; Huntzinger *et al.*, 2009a, b
Mining and mineral processing waste	Asbestos tailings Nickel tailings Red mud (Bauxite)	Khaitan *et al.*, 2009; Yadav *et al.*, 2010
Sludge (incinerator) ash	Sewage sludge incinerator ash (SSA) Steel wastewater sludge (SWS) Paper sludge incinerator ash (PSIA)	Gunning *et al.*, 2010
Paper pulping and mill waste	Paper mill waste (calcium mud) Green sludge dreg Lime mud Lime slaker grits	Bird and Talberth, 2008; Pérez-López *et al.*, 2008

et al., 2008b; Kodama *et al.*, 2008; Baciocchi *et al.*, 2009b; Doucet, 2010; Chang *et al.*, 2011a, b), municipal solid waste incinerator (MSWI) ashes (Arickx *et al.*, 2006; Fernandez-Bertos *et al.*, 2004b; Costa *et al.*, 2007; Li *et al.*, 2007; Wang *et al.*, 2010), air pollution control (APC) residues (Baciocchi *et al.*, 2009c; Montes-Hernandez *et al.*, 2009; Nyambura *et al.*, 2011), cement kiln dust (Huntzinger *et al.*, 2009a, b), red mud (RM) (Khaitan *et al.*, 2009; Yadav *et al.*, 2010), paper mill waste (Pérez-López *et al.*, 2008) and even concrete (Haselbach, 2009), etc., as CO_2 adsorbents.

Fig. 3 shows the relationship of CaO content with the actual CO_2 capture capacity of various alkaline solid wastes in the literature. The CaO contents were significantly high in these wastes, e.g., steelmaking slag (~30–60% wt. CaO), residues from APC (Ca content up to 35%) and bauxite (4.8% Ca), cement kiln dust (~34–50% wt. CaO), oil-shale waste (CaO content up to 50%), and fly ash (53% CaO) from municipal solid waste incinerators (Huijgen *et al.*, 2005b; Bonenfant *et al.*, 2008; Eloneva *et al.*, 2008a; Baciocchi *et al.*, 2009c; Wang *et al.*, 2010; Chang *et al.*,
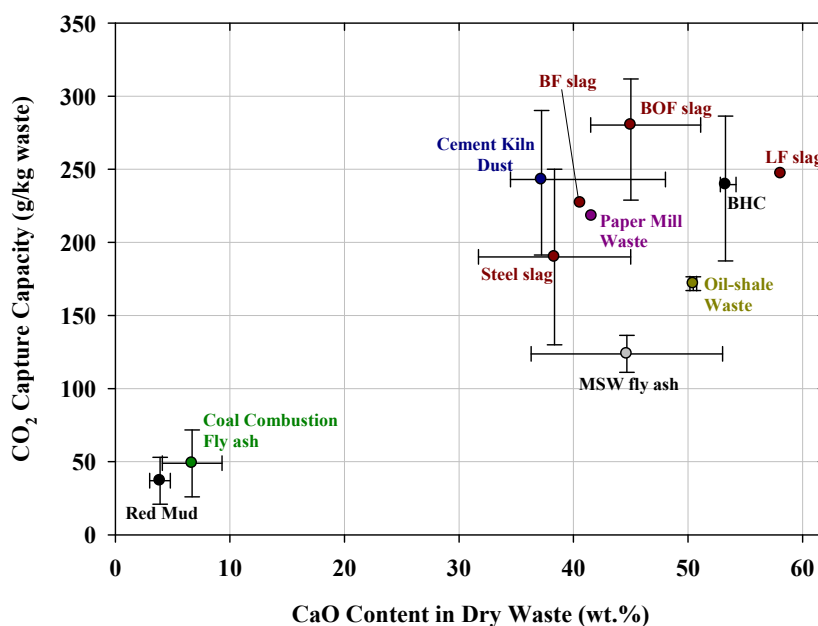
Fig. 3. Comparison of actual CO_2 capture capacity with the CaO content in solid for different types of wastes.

2011a). Industrial alkaline solid wastes such as sources of calcium or magnesium oxide are ideal CO_2 sequestration materials due to their availability and low cost. These materials are generally rich in calcium-content and often associated with CO_2 point source emissions so no mining is needed and the consumption of raw materials is avoidable. In addition, these solid wastes tend to be chemically less stable than geologically derived minerals (Huijgen *et al.*, 2006c). Carbonation of industrial solid waste does not generally require the extraction of reactive ions from the solid matrix due to the alkaline-containing silicates, oxides and hydroxides as the mainly reactive phase (Costa, 2009).

Worldwide, the iron and steel industry accounts for 6–7% of total CO_2 emissions (Doucet, 2010). The industry is moving toward environmental sustainability through careful control of GHG emissions and appropriate management of steel manufacturing residues generated. Within this framework, a combined approach aimed at capturing CO_2 while also improving the environmental and mechanical properties of steelmaking slags, appears to be highly desirable. Therefore, CO_2 capture by carbonating the steelmaking slags could be an interesting option for reducing CO_2 emissions from the steel plant. In recent years, accelerated carbonation of steelmaking slags has been progressively tested to assess the CO_2 capture potential of this material (e.g., Huijgen *et al.*, 2005c; Bonenfant *et al.*, 2008; Teir, 2008; Eloneva *et al.*, 2008a; Kodama *et al.*, 2008; Costa, 2009; Wang and Yan, 2010; Chang *et al.*, 2011a, b; De Windt *et al.*, 2011).

Fig. 4 shows the main chemical composition of various alkaline wastes, e.g., steelmaking slag, cement, and fly ash in the literature. Along with GHG emissions from the steel manufacturing industry, considerable amounts of alkaline solid residues such as fly-ash (FA) slag, ultra-fine (UF) slag, basic oxygen furnace (BOF) slag, and blended hydraulic slag cement (BHC) are generated, which are either used in

various applications or ultimately landfilled. BOF slag is a residue from the basic oxygen converter in the steelmaking process (about 10% of the steel production) and has the potential of capturing 6 to 10% of BOF CO_2 emissions (considering about 519 kg CO_2 production per ton steel produced) (Costa, 2009; Wang and Yan, 2010; De Windt *et al.*, 2011). While global theoretical CO_2 emissions reduction potential of steelmaking slag carbonation is only 170 Mt/year (Eloneva *et al.*, 2009), the reduction could be quite significant for an individual steel industry.

The chemical compositions of BOF slag, primarily in the form of Ca and Mg silicates, are highly variable due to the differing characteristics of the raw materials used and types of manufacturing and smelting processes used in steel production. On the other hand, the physical properties of the slags depend chiefly on the cooling techniques applied. The mineralogical compositions of the steelmaking slags are generally more complex than those of other types of residues such as APC ash (Costa, 2009). Hence, those mineralogical investigations are crucial in order to identify the possible CO_2-reacting phases precisely, as well as the main reaction products contributed by the carbonation process. The physico-chemical properties of various alkaline solid wastes used in studies reported in the literature are presented in Table 3. The CaO content in the BOF slag was higher than that in the UF and BF slag. The typical chemical compositions of BOF slag consist of CaO 38–60%, SiO_2 10–15%, Al_2O_3 1–5%, Fe_2O_3 3–20%, MgO 3–13%, FeO 5–20%, and P_2O_5 1–4% (Shi and Qian, 2000, CSC Group, 2003). The common mineralogy of BOF slag includes olivine, merwinite, C_3S (tricalcium silicates), larnite (C_2S, dicalcium silicates), C_4AF, C_2F, RO phase (CaO – FeO - MgO solid solution), free lime (CaO), and periclase (MgO) (Shi and Qian, 2000; Costa, 2009; Birat, 2009). Free lime (as much as 6% in total) in steelmaking slag comes from two sources: residual free lime from the raw material
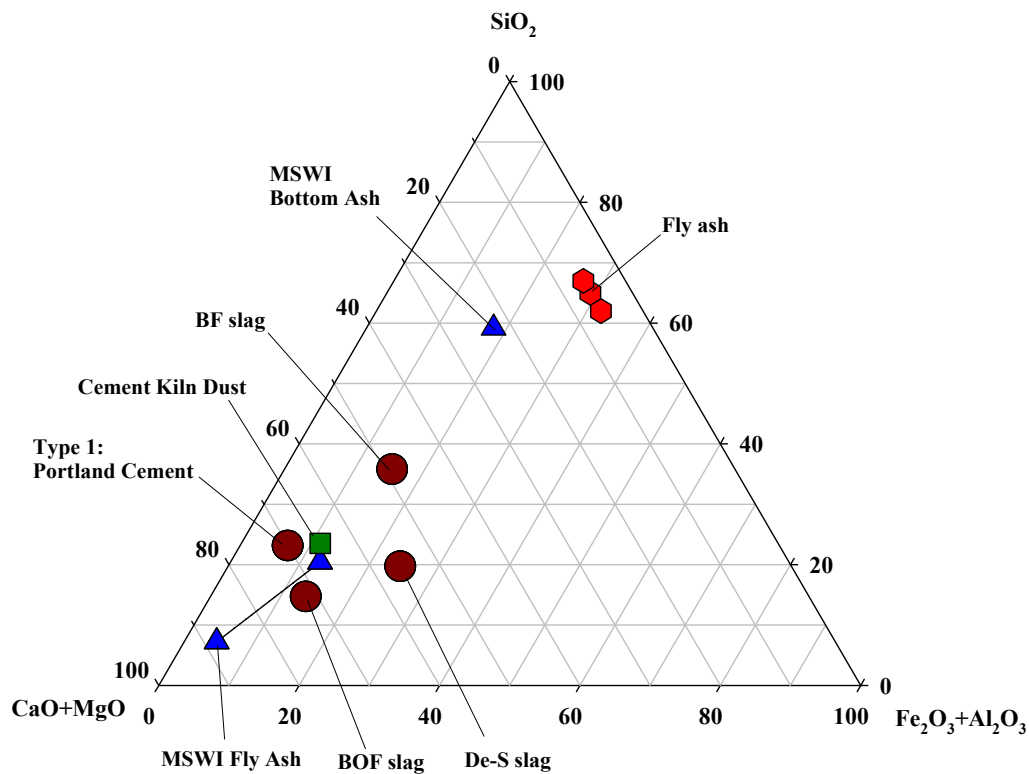
Fig. 4. The normalized $CaO(MgO)$-SiO_2-$Al_2O_3(Fe_2O_3)$ phase diagram of various types of alkaline waste.

Table 3. Physico-chemical properties of ultra fine (UF), fly ash (FA), blast furnace (BF), basic oxygen furnace (BOF) slags, desulfurization (De-S) slag, and blended hydraulic slag cement (BHC) analyzed by China Hi-cement Corporation (CSC group, 2003; Rendek *et al.*, 2006; Li *et al.*, 2007; Huntzinger *et al.*, 2009a; Wang *et al.*, 2010; Chang *et al.*, 2011a, b).

	Parameters	Steelmaking slag					BHC	MSWI		CKD
		UF slag	FA slag	BF slag	BOF slag	De-S slag		FA	BA	
Physical Properties	True Density (g/cm³)	2.89	2.78	2.90	3.51	-	2.94	-	-	-
	Mean Diameter (μm)	11.67	17.35	-	14.98	-	20.63	61.7	-	46
	BET Surface Area (m²/g)	0.15	0.24	-	2.79	-	0.12	0.94	-	-
	Specific Surface Area (m²/cc)	-	-	-	-	-	-	-	-	0.9
Chemical Properties	SiO₂ (%)	30–36	35.5–44.1	33.0–36.7	9.3–12.9	16–19	25–28	4.3–12.6	49.3	11–16
	Al₂O₃ (%)	13.5–15.2	15.8–17.7	13.5–15.5	1.1–2.0	2–4	8.4–9.3	0.9–4.1	7.5	3–6
	Fe₂O₃ (%)	0.3–0.6	2.1–3.8	0.2–0.5	22.7–25.3	10–20	1.5–3.7	1.1–3.8	7.6	1–4
	CaO (%)	40–43	25.4–38.3	38–42	46.3–55.9	43–49	51.4–56.9	36.4–53.0	16.3	38–50
	MgO (%)	4.4–5.7	4.5–6.0	5–8.2	2.1–6.3	1–5	2.5–5.4	2.3	2.6	0–2
	Sulfide Sulfur (%)	0.2–0.7	-	0.3–1.0	-	1.0–1.3	0–0.5	-	0.3	-
	SO₃ (%)	0.5–0.8	0.5–1.1	-	0–0.7	-	1.4–1.6	5.2–8.6	-	2–18
	pH	9–11	9–11	9.0–11.5	11.5–12.4	11.5–12.4		11.1–12.5	11.8–12.4	13.2

and precipitated lime from the molten slag (Costa, 2009; Birat, 2009). The hydrolysis of BOF slag can induce a rapid increase of alkalinity (e.g., Ca-OH), and the reactivity of steel slag increases with its alkalinity. Hence, the alkalinity $A = CaO/(SiO_2+P_2O_5)$ can be used to evaluate the hydration activity of steel slag (Shi and Qian, 2000; Uibu *et al.*, 2009b; De Windt *et al.*, 2011). If alkalinity >
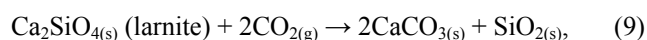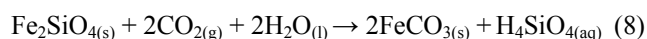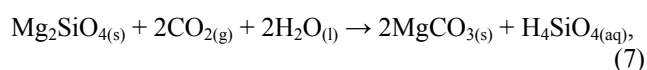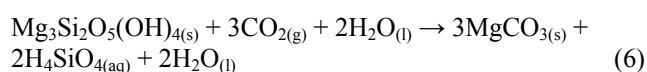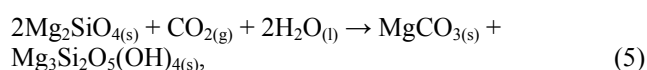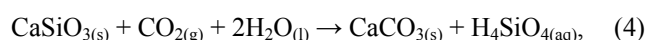
2.4, the steelmaking slag should be considered as highly reactive (Shi and Qian, 2000).

PRINCIPLES OF ACCELERATED CARBONATION REACTION

Process Chemistry

Mineral carbonation, a type of accelerated carbonation that utilizes natural ores such as wollastonite ($CaSiO_3$), olivine (Mg_2SiO_4), and serpentine ($Mg_3Si_2O_5(OH)_4$) to react with high-purity CO_2 as shown in Eqs. (4) to (9), has been extensively researched in the literature (e.g., O'Connor *et al.*, 2002; Costa *et al.*, 2007; Gerdemann *et al.*, 2007). The process is based on acid-base reactions in which carbonate acid is neutralized by a base (alkaline mineral). The major challenge hindering the large-scale use of silicate minerals for carbonation is their slow conversion rate. Therefore, most research in this field has focused on identifying reaction pathways by bench-scale experiments for determining reaction rates, as well as characterization of the mineralogy of the reactants and products.

$$CaSiO_{3(s)} + CO_{2(g)} + 2H_2O_{(l)} \rightarrow CaCO_{3(s)} + H_4SiO_{4(aq)}, \quad (4)$$

$$2Mg_2SiO_{4(s)} + CO_{2(g)} + 2H_2O_{(l)} \rightarrow MgCO_{3(s)} + Mg_3Si_2O_5(OH)_{4(s)}, \quad (5)$$

$$Mg_3Si_2O_5(OH)_{4(s)} + 3CO_{2(g)} + 2H_2O_{(l)} \rightarrow 3MgCO_{3(s)} + 2H_4SiO_{4(aq)} + 2H_2O_{(l)} \quad (6)$$

$$Mg_2SiO_{4(s)} + 2CO_{2(g)} + 2H_2O_{(l)} \rightarrow 2MgCO_{3(s)} + H_4SiO_{4(aq)}, \quad (7)$$

$$Fe_2SiO_{4(s)} + 2CO_{2(g)} + 2H_2O_{(l)} \rightarrow 2FeCO_{3(s)} + H_4SiO_{4(aq)} \quad (8)$$

$$Ca_2SiO_{4(s)} \text{ (larnite)} + 2CO_{2(g)} \rightarrow 2CaCO_{3(s)} + SiO_{2(s)}, \quad (9)$$

The overall carbonation reaction for magnesium and calcium silicates can be expressed as Eq. (10) (Teir, 2008):

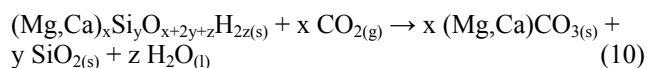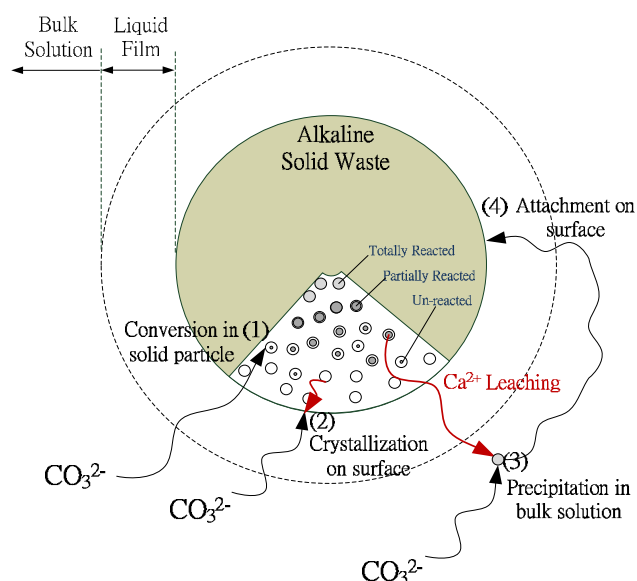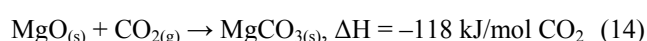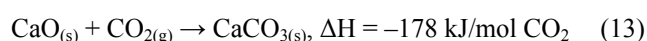$$(Mg,Ca)_xSi_yO_{x+2y+z}H_{2z(s)} + x\ CO_{2(g)} \rightarrow x\ (Mg,Ca)CO_{3(s)} + y\ SiO_{2(s)} + z\ H_2O_{(l)} \quad (10)$$
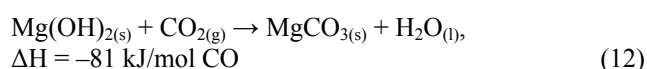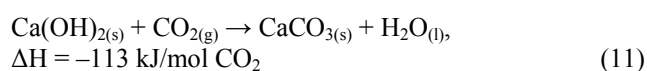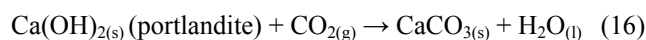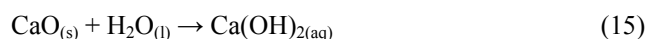
Fig. 5 illustrates the proposed mechanism of accelerated carbonation, which indicates that the carbonation reaction occurred in four routes. Similar results were also found in Huntzinger *et al.* (2009b) and Uibu and Kuusik (2009a), suggesting some mechanisms that can affect the rate and extent of carbonation: (a) transportation-controlled mechanisms such as CO_2 and Ca^{2+}-ions diffusion to/from reaction sites; (b) boundary layer effects (diffusion across precipitate coatings on particles); (c) dissolution of $Ca(OH)_2$ at the particle surface; (d) pore blockage; and (e) precipitate coating. Furthermore, their effects can change with time. The basic chemical processes of accelerated carbonation are shown in Eqs. (11) to (14):

$$Ca(OH)_{2(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)},$$
$$\Delta H = -113 \text{ kJ/mol } CO_2 \quad (11)$$

$$Mg(OH)_{2(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)} + H_2O_{(l)},$$
$$\Delta H = -81 \text{ kJ/mol } CO \quad (12)$$

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}, \Delta H = -178 \text{ kJ/mol } CO_2 \quad (13)$$

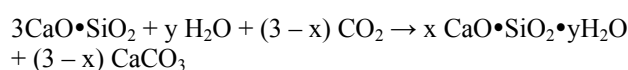$$MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}, \Delta H = -118 \text{ kJ/mol } CO_2 \quad (14)$$

Fig. 5. Proposed mechanism of accelerated carbonation reaction of alkaline solid wastes.

In addition, some investigations (Thiery *et al.*, 2007; Montes-Hernandez *et al.*, 2009) suggested a simple reaction mechanism for CO_2 sequestration by steelmaking slag in two successive steps: first, the irreversible hydration of calcium oxide or lime as shown in Eq. (15) and, second, the spontaneous carbonation of calcium hydroxide suspension as shown in below Eq. (16):

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} \quad (15)$$

$$Ca(OH)_{2(s)} \text{ (portlandite)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)} \quad (16)$$

Not only $Ca(OH)_2$ but also other hydrate compounds can react with CO_2. For instance, the calcium-silicate-hydrates (C-S-H) can react with CO_2, and produce $CaCO_3$ and a silica gel (Thiery *et al.*, 2007; Tsuyoshi *et al.*, 2010). Uibu *et al.* (2011) found that Ca_2SiO_4 and $Ca_3Mg(SiO_4)_2$ were the main CO_2 binding components in electric arc furnace (EAF) slag according to quantitative XRD analysis, and the main product was calcite. A similar conclusion was made by Fernández-Bertos *et al.* (2004a), which indicated that C-S-H becomes rapidly activated by CO_2 where carbonation is accomplished by hydration at first and is followed, after some delay, by secondary carbonation as shown in Eq. (17). However, Tsuyoshi *et al.* (2010) suggested that γ–C_2S does not react with water, and the leaching of Ca^{2+} and O^{2-} (or OH^-) is very low at normal temperature. Hence, $CaCO_3$ is directly generated in the carbonation of γ–C_2S without the formation of intermediate products such as $Ca(OH)_2$, due to the catalytic action of capillary water. On the other hand, the breakdown of C_2S and the formation of calcite can be observed by XRD (Fernández-Bertos *et al.*, 2004b).

$$3CaO \bullet SiO_2 + y\ H_2O + (3-x)\ CO_2 \rightarrow x\ CaO \bullet SiO_2 \bullet yH_2O + (3-x)\ CaCO_3$$

$$\text{↳} + z\ CO_2 \rightarrow (x - z)\ CaO \bullet SiO_2 \bullet yH_2O + z\ CaCO_3 \quad (17)$$
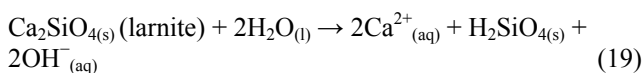
The actual process involving steelmaking slag should be more complicated, because most of the CaO is not present in pure form and combined with silicates or another complex oxide phase. For simplicity, we assumed that the aqueous carbonation by using steelmaking slags occurred mainly through three reaction routes: (a) the dissolution of CO_2-reactive species from a solid matrix; (b) the contemporary dissolution of CO_2 into a liquid phase and conversion of carbonic acid to carbonate/bicarbonate ions; and (c) the consequent nucleation and precipitation of carbonates. The balance between dissolution and precipitation is dependent on the kinetics and solubility of the present feedstock and possible products, where carbonates are probably the most important products.

The affinity of oxides for carbonate formation principally depends on the strength of the chemisorptions of CO_2 and number of basic sites at the surface and varies as follows: basic oxides (CaO, MgO) > amphoteric oxides (Al_2O_3, Cr_2O_3, TiO_2, MnO, iron oxides) > acidic oxides (SiO_2) (Bonenfant *et al.*, 2009). Hence, the capacity of sequestered CO_2 for these alkaline residues depends directly on the proportion of binary oxide (CaO and MgO) and/or hydroxide ($Ca(OH)_2$ and $Mg(OH)_2$) content in the matrix, which are primarily responsible for the CO_2 sequestration potential (Montes-Hernandez *et al.*, 2009; Bonenfant *et al.*, 2009). Moreover, CaO offers more potential for chemisorptions of CO_2 than MgO due to its basic character (Bonenfant *et al.*, 2009).

Ion Equilibrium in Solution

The first step of carbonation was believed to be the leaching of calcium in solid particles, and the properties of the solids may change considerably due to the leaching process. The rapid and strong increase in pH (10.88–11.88) is due to the dissolution of lime and larnite in the solid residues, as shown in Eqs. (18) and (19) (Uibu *et al.*, 2009b; De Windt *et al.*, 2011) However, CaO and MgO are rarely present in pure form in steelmaking slag. The alkaline-metal oxides are primary locked into the silicate, aluminate or ferrite phase (Lekakh *et al.*, 2008).

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \quad (18)$$

$$Ca_2SiO_{4(s)}\ (larnite) + 2H_2O_{(l)} \rightarrow 2Ca^{2+}_{(aq)} + H_2SiO_{4(s)} + 2OH^-_{(aq)} \quad (19)$$

The results reported by McCabe *et al.* (2005) suggest that coarse, hard, or granular feed solids should be disintegrated into pulp or mush when their soluble content is removed. Huijen and Comans (2006a) also suggested that calcium leaching and carbonation in steelmaking slag would occur simultaneously, and carbonation may reduce the leaching of alkaline earth metals (except Mg) by conversion of a Ca-phase such as portlandite, ettringite, and Ca-Fe-silicates into calcite, possibly containing traces of Ba and Sr.

The second step of carbonation was assumed to be the dissolution of CO_2 into the solution. CO_2 has a critical point at 31.06°C and 73.8 bars (1,070 lb/in^2) and a critical density of 0.469 g/cm^3. It could be dissolved from the atmosphere in available water, and carbonic acid can be created with a pH around 5.6 (Haug *et al.*, 2010). In addition, diffusion of CO_2 in water is approximately 10000 times lower than in air.

CO_2 can be physically absorbed in water (or a solvent) in accordance with Henry's law. Henry's law states that the relationship between the gas solubility in pore water and the partial pressure of the gas is strictly valid only for gases that can be infinitely diluted in solution. The binding of the solvent with CO_2 occurs at high pressure, and a reduction in pressure releases the gas (Klemeš *et al.*, 2007). The amount of CO_2 dissolution in water can be expressed by Henry's law as shown in Eq. (20):
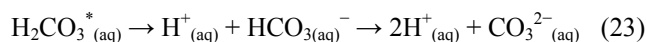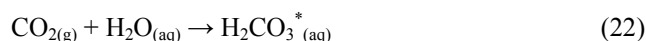
$$C'_{CO2} = H'_{CO2} \times P_{CO2} \quad (20)$$

where C' is the concentration of CO_2 dissolved in aqueous solution (M); H'_{CO2} is Henry's constant for CO_2 (= $10^{-1.46}$ M/atm at 25°C); and P_{CO2} is the partial pressure of CO_2 in the gas phase (atm). Hence, the higher partial pressure of CO_2 will result in a large amount of dissolved CO_2. In addition, Henry's constant is a function of temperature that can be modified by Eq. (21) (Morel and Hering, 1993):

$$K_{H,T} = K_{H,298K} \times exp\ [C \times (1/T - 1/298)] \quad (21)$$

where C is the constant for all gases (2400 K for CO_2) and T is the temperature (K).

Dissolution of CO_2 into water is pH-dependent because of the dissociation of carbonic acid ($H_2CO_3^*$) into carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions. The dissociation of the carbonic ions is shown in Eqs. (22) and (23):

$$CO_{2(g)} + H_2O_{(aq)} \rightarrow H_2CO_3^*{}_{(aq)} \quad (22)$$

$$H_2CO_3^*{}_{(aq)} \rightarrow H^+_{(aq)} + HCO_{3(aq)}^- \rightarrow 2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \quad (23)$$

The corresponding equilibrium constants could expressed as,

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad K_b = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (24)$$

where $K_a = 10^{-6.3}$ and $K_b = 10^{-10.3}$ at 25°C. Fig. 6 shows the mole balance and equilibrium conditions for carbonation of alkaline solid wasts. The mole balances of the carbonic acid system can be expressed as :

$$C_T = [H_2CO_3^*{}_{(aq)}] + [HCO_3^-{}_{(aq)}] + [CO_3^{2-}{}_{(aq)}] \quad (25)$$

where C_T is the total inorganic carbon (TIC) concentration (M). By substitution of Eq. (24) into Eq. (25), an explicit formula for $[H_2CO_3^*{}_{(aq)}]$, $[HCO_3^-{}_{(aq)}]$ and $[CO_3^{2-}{}_{(aq)}]$ is obtained as:

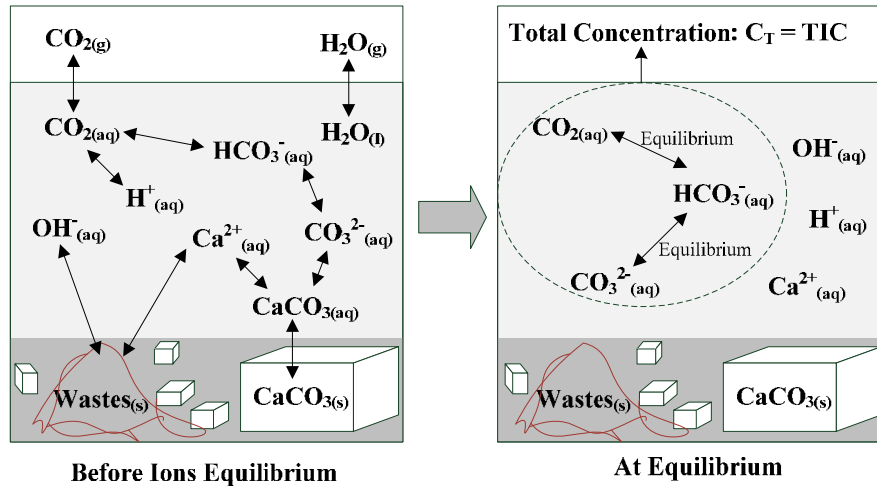$$[H_2CO_3^*{}_{(aq)}] = \alpha_0 \cdot C_T, \quad \alpha_0 = \frac{[H^+]^2}{[H^+]^2 + K_a[H^+] + K_aK_b} \quad (26)$$

Fig. 6. Mole balance and equilibrium conditions for carbonation of alkaline solid wastes.

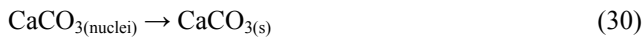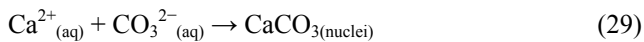$$[HCO_3^-{}_{(aq)}] = \alpha_1 \cdot C_T, \quad \alpha_1 = \frac{K_a[H^+]}{[H^+]^2 + K_a[H^+] + K_aK_b} \quad (27)$$

$$[CO_3^{2-}{}_{(aq)}] = \alpha_2 \cdot C_T, \quad \alpha_2 = \frac{K_aK_b}{[H^+]^2 + K_a[H^+] + K_aK_b} \quad (28)$$

The fraction (α_i) of each carbon species present is dependent on the solution pH. At a low pH (~4), the production of H_2CO_3 dominates, at a mid pH (~8) HCO_3^- dominates, and at a high pH (~12) CO_3^{2-} dominates (Morel and Hering, 1993). Therefore, accelerated carbonation is favoured at a basic pH due to the availability of carbonate ions.

Formulation of Carbonate Precipitation

The descending order for solubility of carbonates is as follows: $Mg^{2+} > Ca^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$ (Salminen and Prausnitz, 2007). The carbonation formulation can be simply described by Eqs. (29) and (30)

$$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3(nuclei)} \quad (29)$$

$$CaCO_{3(nuclei)} \rightarrow CaCO_{3(s)} \quad (30)$$

Contact between Ca^{2+}-ions and CO_2 leads to $CaCO_3$ precipitation, which is almost insoluble in water at pH levels above 9 (the solubility of $CaCO_3$ is 0.15 mmol/L at 25°C). The solubility-product constant (K_{sp}) of calcium carbonate as shown in Eq. (31) ranges from 3.7×10^{-9} to 8.7×10^{-9} at 25°C (Morel and Hering, 1993), and 4.47×10^{-9} has been widely used for calculation.

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \quad (31)$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the activities of calcium and carbonate ions (M) in the solution, respectively. In nature, calcium carbonate occurs most commonly in hexagonal form (as calcite) but also occurs in orthorhombic form (aragonite) (McCabe *et al.*, 2005). The super-saturation

ratio of $[Ca^{2+}]$ and $[CO_3^{2-}]$ in the interface can be expressed as shown in Eq. (32). A low super-saturation ratio is disadvantageous for the nucleation of $CaCO_3$ (Wang, 2004).

$$S_1 = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \quad (32)$$

Dissolution or crystallization of precipitations does not occur instantaneously. It was suggested that some characteristic time, often longer than the time constant for the overall process, is needed to achieve a new equilibrium (Salminen and Prausnitz, 2007). The carbonate precipitation using steelmaking slag as feedstock should be mainly calcite ($CaCO_3$) (Bonenfant *et al.*, 2008; Eloneva *et al.*, 2008a; Costa, 2009; Wang and Yan, 2010; Chang *et al.*, 2011a, b). The crystal volume of calcium carbonate is approximately 11.7 percent more than that of calcium hydroxide (Ishida and Maekawa, 2000). In general, the pore structures of solid wastes are thought to become finer with carbonation, thus leading to a solid of lower porosity, lower tortuosity, and lower pore area with calcite infilling the pore space after carbonation (Ishida and Maekawa, 2000; Fernández-Bertos *et al.*, 2004a).

Reaction Kinetics
Leaching of Metallic Ions from Solid Matrix

The rate and extent of calcium leaching in steelmaking slag was found to be inversely related to particle size and pH, and increased with increasing temperature, pressure, and surface area (Iizuka *et al.*, 2004; Tai *et al.*, 2006; Costa *et al.*, 2007; Gerdemann *et al.*, 2007; Lekakh *et al.*, 2008; Teir, 2008; De Windt *et al.*, 2011). Based on a report by Alexander *et al.* (2005), the effects of increased reaction temperature from 25°C to 50°C provided a 70% improvement on dissolution of the primary phase. Iizuka *et al.* (2004) proposed a new CO_2 sequestration process using carbonation of waste cement, which indicated that calcium extraction increased with pressure. They also found that the influence of S/L ratio was significant, with the calcium extraction

rate about 50% with an S/L ratio of 0.29 wt% and 22% with the ratio of 2.9 wt%.

In addition, research by Huijegn *et al.* (2005c) using steelmaking slag as feedstock for carbonation suggested that the leaching of Ca^{2+}-ions should result in a withdrawing Ca-silicate core surrounded by a Ca-depleted SiO_2 phase. This SiO_2 rim apparently hindered the diffusion of Ca^{2+}-ions from the particle interior, resulting in a declining reaction rate. Hence, Ca^{2+}-ions leaching rate, probably determined by diffusion through the Ca-depleted silicate rim, rather than by the boundary layer at the solid-liquid interface, seems to be the main rate-limiting step in aqueous carbonation (O'Connor *et al.*, 2002; Huijgen *et al.*, 2005c; Santos *et al.*, 2009).

Dissolution of Carbon Dioxide into Solution

The kinetics of dissolution of CO_2 and dehydration of H_2CO_3 has been studied intensively (Ishida and Maekawa, 2000). It was noted that these two reactions should occur simultaneously as shown in Eq. (33) (Morel and Hering, 1993).

$$
\begin{array}{c}
CO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2CO_3 \\[2mm]
\underset{k_{-2}}{\overset{k_2}{\searrow}} \qquad \overset{k_{\alpha 1}}{\nearrow} \\[2mm]
HCO_3^- + H^+
\end{array}
\qquad (33)
$$
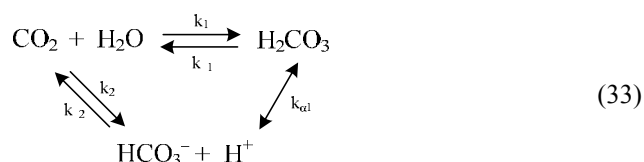
Therefore, the rate expression of the dissolution-dehydration reaction is:

$$
-\frac{d[CO_2]}{dt} = (k_1 + k_2)[CO_2] - k_{-1}[H_2CO_3] - k_{-2}[HCO_3^-][H^+]
$$
$$(34)$$

By substituting Eq. (24) into Eq. (34), we obtain:

$$
-\frac{d[CO_2]}{dt} = (k_1 + k_2)[CO_2] - (k_{-1} + k_{-2}K_{\alpha 1})[H_2CO_3]
$$
$$
= k_{CO_2}[CO_2] - k_{H_2CO_3}[H_2CO_3]
$$
$$(35)$$

where the overall rate constants in Eq. (35) were simplified to be k_{CO2} and k_{H2CO3}. The values of k_{CO2} and k_{H2CO3} at 25°C were 0.032 s^{-1} and 26.6 s^{-1}, respectively (Edsall and Wyman, 1958). However, at higher pH (e.g., pH > 9), an alternative reaction pathway would be expressed as (Morel and Hering, 1993):

$$
CO_2 + OH^- \overset{k_4}{\leftrightarrow} HCO_3^-
\qquad (36)
$$

where k_4 (i.e., 8500 1/M-s at 25°C) and k_{-4} (i.e., 0.0002 s^{-1} at 25°C) are the rate constants (Stumm and Morgan, 1981).

Rate of Carbonate Precipitation

The carbonation reaction is regulated by solution equilibrium, and the reaction of calcium ions combining with carbonate ions is very fast. It was widely assumed that the carbonation reaction as shown in Eq. (29) was of

the first order with respect to the concentrations of Ca^{2+} and CO_3^{2-} (Ishida and Maekawa, 2000); therefore, the rate of carbonation could be expressed by the following differential Eq. (37).

$$
Q_{CO_2} = \frac{d(C_{CaCO_3})}{dt} = -\frac{d(CO_3^{2-})}{dt} = k[Ca^{2+}][CO_3^{2-}]
\qquad (37)
$$

where C_{CaCO3} is the concentration of calcium carbonate (mole/L), and k is the reaction rate coefficient (1/mol-sec). The precipitation rate is related to the CO_3^{2-} concentration in the liquid phase, but not to the concentration of other species containing carbonate. In addition, the reaction rate coefficient (k) is dependent on the reaction temperature according to Arrhenius's law. On the other hand, the Boltzmann distribution law could be applied to determine the ratio of the molecular having a kinetic energy above the activation energy of the chemical reaction. The value of k reported by Ishida and Maekawa (2000) was 2.08 (L/mol/sec) at 25°C from several sensitivity analyses.

As the calcium ions are converted to metal carbonates and precipitated out, more calcium hydroxide dissolves to equalize the concentration of metal ions. Although the Ca^{2+}-ion dissolution kinetics improved with increasing temperature, carbonation precipitation was retarded at higher temperatures due to reduced CO_2 solubility (Park *et al.*, 2003; Costa *et al.*, 2007; Gerdemann *et al.*, 2007; Chang *et al.*, 2011a). In addition, limited $MgCO_3$ formation for carbonation of steelmaking slag under ambient conditions was expected due to the relatively low magnesium oxide content in the slag, low pressure of CO_2 and short reaction times. Typical process conditions for the formation of magnesium carbonation via aqueous carbonation are p_{CO2} > 100 bar and a reaction time of hours (Huijgen *et al.*, 2006c). However, $MgCO_3$ formation could be observed when natural ores (e.g., serpentine, olivine, etc) were selected as the feedstock for carbonation (Alexander *et al.*, 2007; Krevor and Lackner, 2011). Furthermore, the study reported by Haug *et al.* (2011) indicated that the mineral carbonation of olivine (generally rich in Mg contents) at 115 bar and 185°C is limited by $MgCO_3$ (magnesite) precipitation and not the olivine dissolution rate. O'Connor *et al.* (2002) also found that conversion of the silicate to carbonate does not occur in the solid state but appears to require mineral dissolution in the aqueous phase.

Summary of Theoretical Considerations

Minerals formed in pure calcium or magnesium oxide are rarely found in nature due to their high reactivity; thus, they instead present in a variation of these oxides in a silicate matrix. In addition, vast quantities of silicate minerals are required to sequester a significant fraction of emitted CO_2. On the other hand, it currently seems that aqueous carbonation of industrial solid wastes combined with alkaline wastewater is the most attractive route due to lower material and energy requirements.

From the view point of process chemistry, the challenge is that the dissolution of calcium species in alkaline solid waste is favoured at low pH; however, it is not favoured for

the precipitation of calcium carbonate. The balance between dissolution and precipitation is dependent on the kinetics and solubility of the present feedstock and possible products, where carbonates are probably the most important species. Therefore, finding a balanced operating condition between these two mechanisms is essential for optimizing the overall carbonation process.

From the view point of reaction kinetics, many researchers have attributed the rate-determined step of aqueous carbonation to reacted (product) layer diffusion. Therefore, this suggests that a well-designed reactor to enhance the mass transfer between the gas, liquid, and solid phases is needed to facilitate the carbonation reaction and increase the carbonation conversion.

APPLICATIONS OF ACCELERATED CARBONATION TECHNOLOGY (ACT)

Performance Evaluation

The carbonation of alkaline solid waste has been proved to be an effective way to capture CO_2 (Uibu *et al.*, 2009b; Wang and Yan, 2010; Chang *et al.*, 2011a; Nyambura *et al.*, 2011). Table 4 compares carbonation efficiency for different types of alkaline wastes operated under various conditions. In addition, summaries of factors required for effective accelerated carbonation are presented in Table 5. Multiple factors have been shown to affect the conversion of accelerated carbonation, as indicated by numerous investigations (e.g., Huijgen *et al.*, 2006c; Costa *et al.*, 2007; Li *et al.*, 2007; Chang *et al.*, 2011a). These factors must be further understood, since they determine the economic viability of the technology as well as help to identify the conditions that most favourable to reaction.

Particle size and specific surface area are the most important factors affecting the dissolution kinetics of any kind of material (Huijgen *et al.*, 2006c; Eloneva *et al.*, 2012). Since slag grinding is expected to be a fairly energy-intensive process, it is important to find out how large a particle size can be used. Average grain particle sizes of less than 100–150 μm are already in the optimum range for efficient carbonation (Costa, 2009). Eloneva *et al.* (2012) also suggested that a particle size preferably of ~100 μm, or no more than 500 μm, was found to be optimal based on the kinetics studies of calcium leaching. In addition, over 90% and less than 40% of calcium species dissolved in 24 hours were observed from 45–75 and 150–250 μm sized ladle slag, respectively (Lekakh *et al.*, 2008). The power consumption for grinding (crushing) can be calculated with Bond's equation as shown in Eq. (38) (Bond, 1961), which has been widely used in the literature (Huijgen *et al.*, 2006b; Kodama *et al.*, 2008; Eloneva *et al.*, 2012):

$$W = W_i \left(\frac{10}{\sqrt{W_{P80}}} - \frac{10}{\sqrt{W_{F80}}} \right) \qquad (38)$$

where W (kWh/ton) is the power consumption, W_{F80} (μm) and W_{P80} (μm) are the 80% passing size of the feed and the product, respectively, and W_i (kWh/ton) refers to the work

index of the slag. The work index for the slag obtained from the ball-mill test is approximately 30.4 kWh/ton (Kodama *et al.*, 2008).

The CO_2 content of the incoming gas did not seem to have a significant effect on the degree of $CaCO_3$ precipitation. As expected, the reaction time was inversely proportional to the CO_2 content of the ingoing gas flow: the lower the gas CO_2 content, the longer the duration of the carbonation (Eloneva *et al.*, 2008a).

Temperature also had a significant effect but only during the first 3 hours of the dissolution reaction according to the results by Lekakh *et al.* (2008). An investigation reported by Tai *et al.* (2006) also suggested that reaction temperature and solution composition should be the most important factors in the carbonation test. The carbonation reaction rate significantly increased with increasing reaction temperature; however, the amounts of CO_2 dissolution into the solution decreased at higher temperature. Chang *et al.* (2011a) suggested that the carbonation conversion of BOF slag in a slurry reactor is dependent on the reaction temperature and exhibits a maximum value at 60°C if the reaction temperature ranges between 30°C and 70°C. Kodama *et al.* (2008) also suggested that a reaction temperature higher than 80°C is unfavourable for the process design.

The pH value is another important factor related to the rate of calcium leaching, the rate of CO_2 dissolution, the rate of $CaCO_3$ nucleation, and the specific species that are precipitated (Druckenmiller and Maroto-Valer, 2005; Tai *et al.*, 2006). According to a report by Park and Fan (2004), the optimum pH for aqueous carbonation is around 10, while the dissolution of BOF slag occurs under low pH conditions. The pH decreases continuously as carbonation proceeds due to CO_2 dissolution into solution (Santos *et al.*, 2009). There is no change in pH after the carbonation is completed. On the other hand, it has been reported that sodium and potassium ions should cause pH fluctuations and also affect the carbonation rate (Ishida and Maekawa, 2000).

Li *et al.* (2007) studied the influence of L/S ratio on accelerated carbonation of municipal solid waste incineration fly ashes and found that the optimum L/S ratio was 0.3 by weight of ash at ambient temperature. Fernández-Bertos *et al.* (2004a) made similar observations, finding that the optimum L/S ratio was 0.2–0.3 for APC residues and 0.3–0.4 for BA residues. Moreover, Chang *et al.* (2011a, b) suggested that the optimum L/S ratio for carbonation of steelmaking slag is 10:1–20:1 (mL/g).

Another important factor is the surface activities of the feedstock. Various studies have addressed methods to speed up the kinetics of direct aqueous carbonation including physical and chemical pretreatment (Maroto-Valer *et al.*, 2005a, b), electrolysis and heat pretreatment (Li *et al.*, 2009), and mechanical activation methods (McKelvy *et al.*, 2004; Park and Fan, 2004; Li *et al.*, 2009; Haug *et al.*, 2010; Haug *et al.*, 2011). O'Connor *et al.* (2002) investigated approaches to reduce particle size, and increase surface area, and elevate process temperature and pressure by thermal treatment or steam activation. The chemical activations were found to be more effective than physical activation at

Table 4. Comparison of carbonation efficiency for different types of alkaline wastes operated under various conditions.

Material type	Method	Reactor	Carbonation conditions		Operating Conditions	Efficiency[1]	Reference
			Solid Comp.	Gas/Liquid Phases			
Steel slag Linz Donawitz	Aqueous carbonation	Autoclave (450 mL)	CaO: 31.7% MgO: 6.0% (d < 38μm)	100% vol. CO_2 (19 bar) DI Water (nanopure)	T = 100°C; t = 30 min	C.D. = 74% 250 g CO_2/kg slag	Huijgen et al., 2005c
LF slag (Ladle Furnace slag)	Direct carbonation	Flask (250 mL) (Suspensions)	CaO: 58.1% MgO: 6.2% (d: 38–106 μm) pH = 12.8 in water	15% vol. CO_2 (atmospheric) DI Water	T = ambient; t = 40 h; L/S = 10 (kg/kg); Q_L = 5 mL/min	247 g CO_2/kg slag	Bonenfant et al., 2008
Blast Furnace Slag (Ruukki Steel Plant)	pH-swing	Glass reactor (400 mL)	CaO: 40.6% MgO: 10.7% K_2O: 0.6%	100% vol. CO_2 (1 bar) NaOH (40g/L) and CH_3COOH Addition	T = 30°C; Stirring at 1000 rpm	C.D. = 90% 227 g CO_2/kg slag	Eloneva et al., 2008a
Converter slag	pH-swing	Flask (100 mL)	< 63 μm	13% vol. CO_2 (1.9 psig) Extraction solution (40 mL)	T = 40°C; t = 60 min	C.D. = 80%	Kodama et al., 2008
Stainless Steel Slag (EAF&AOD)	Aqueous carbonation	Batch absorber	Ca: 40–50 wt.% Mg: 2.2–4.5 wt.%	100% vol. CO_2 (3 bar) (100°C, 75% R.H.)	T = 50°C; t = 2 h; L/S = 0.4 (L/kg)	130 g CO_2/kg slag	Baciocchi et al., 2009b
BOF slag (China Steel Corporation)	Aqueous carbonation	Autoclave Reactor	CaO: 38–45% (63–90 μm) — CaO: 38–45% (< 45 μm)	100% vol. CO_2 (80 bar) DI Water — 100% vol. CO_2 (20 bar) DI Water	T = 150°C; t = 1 h; L/S = 15 (w/w) — T = 200°C; t = 1 h; L/S = 15 (w/w) (Preheat 900°C)	C.D. = 90% — C.D. = 92%	Chen, 2008
BHC (China Steel Corporation)	Aqueous carbonation	Autoclave	CaO: 52.82% MgO: 4.66% (d < 44 μm)	100% vol. CO_2 (700 psig) DI water — 100% vol. CO_2 (1300 psig) DI water	T = 160°C; t = 12 hr — T = 160°C; t = 60 min	C.D. = 69% 286 g CO_2/kg slag — C.D. = 59% 245 g CO_2/kg slag	Chang et al., 2011b
BHC (China Steel Corporation) — BOF slag (China Steel Corporation)	Aqueous carbonation	Slurry Reactor	CaO: 54.19% MgO: 3.97% (d < 44 μm) — CaO: 51.11% MgO: 4.17% (d < 44 μm)	100% vol. CO_2 (atmospheric) DI Water	T = 70°C; t = 2 h; L/S = 10 (mL/g); Q_L = 0.1 L/min	C.D. = 44% 187 g CO_2/kg slag — C.D. = 57% 229 g CO_2/kg slag	Chang et al., 2011a
BOF slag (China Steel Corporation)	Aqueous carbonation	Rotating Packed Bed (RPB)	CaO: 42.43% MgO: 9.15% (d~62 μm)	100% vol. CO_2 (1.5 kg/cm²) DI Water	T = 60°C; t = 30 min; L/S = 20 mL/g; Q_L = 1.2 L/min; Q_{CO_2} = 2.5 L/min	C.D. = 93.5% 289 g CO_2/kg slag	Chang et al., 2012

Steelmaking slag

Table 4. *(continued).*

Material type	Method	Reactor	Carbonation conditions Solid Comp.	Carbonation conditions Gas/Liquid Phases	Operating Conditions	Efficiency[*1]	Reference
Bottom ash — MSWI Bottom ash	Direct dry carbonation	Sanyo MCO-17AI chamber	CaO: Not specified; 25 g (d < 0.1 mm)	10% vol. CO_2 (1 bar) No liquid used	T = 50°C; t = 3 d; pH = 12.9; Moist. = 39.6% (w/w)	pH: 8.5 Moist. = 13.8%	Arickx *et al.*, 2006
MSWI Bottom ash	Direct dry carbonation	Metallic cylinder (150 mL)	CaO: 16.3% MgO: 2.6% (d~4 mm)	12% vol. CO_2 (17 bar) No liquid used	T = ambient; t = 180 min; Moistures = 20% (w/w)	24 L CO_2/kg dry BA	Rendek *et al.*, 2006
MSWI Fly Ash	Aqueous carbonation	Stainless steel chamber	CaO: 36.3%	100% vol. CO_2 (3 bar) DI Water	T = 8–42°C; t = 3 d	CO_2 Gain: 7–10% (solid phase)	Li *et al.*, 2007
MSWI Fly Ash	Aqueous carbonation	Glass cylinder (1000 mL)	CaO: 53.02% Na_2O: 5.71% K_2O: 5.46%	100% vol. CO_2 (1 bar) Water	T = ambient; t = 240 h; L/S = 0.25 (w/w)	Weight Gain: 12%	Wang *et al.*, 2010
Fly ash — Coal Combustion Fly-ash	Aqueous carbonation	Autoclave (600 mL)	CaO: 9.3% (d = 20–150 μm)	100% vol. CO_2 (4 MPa) Brine Solution	T = 30°C; t = 1 h; S/L = 0.5 (g/mL)	C.D. = 86.4% 71.8 g CO_2/kg FA	Nyambura *et al.*, 2011
Coal Combustion Fly-ash (Los Barrios power station)	Aqueous carbonation	Stirred reactor (2 L)	Lime: 4.1% Mullite: 20.8 wt.% (d~40 μm)	100% vol. CO_2 (atmospheric) High-purity Water (1 L)	T = 30°C; t = 18 h; L/S = 10(w/w); 450 rpm (Stirring)	C.D. = 82% 26 g CO_2/kg ash	Montes-Hernandez *et al.*, 2009
APC Residues — APC Residues	Aqueous carbonation	Stainless Reactor (150 mL)	Ca: 35% Mg: 0.0084%	100% vol. CO_2 (3 bar) DI Water	T = 30°C; t = 5 h; L/S = 0.2 (w/w)	C.D. = 67% 250 g CO_2/kg APC	Baciocchi *et al.*, 2009a
MSWI APC (Sardinia, Italy)	Aqueous carbonation	Open vessel	Ca^3: 308.1 ppm Mg^3: 0.029 ppm	100% vol. CO_2 (1 atm) DI Water	T = 20°C; t = 3 hr; L/S = 2.5 mL/g	200 g CO_2/kg APC	Cappai *et al.*, 2012
Paper Mill Waste — Calcium Mud	Aqueous carbonation	Autoclave (2 L)	CaO: 83.2% CO_2: 10.3%	100% vol. CO_2 (10 bar) DI Water (1 L)	T = 30°C; t = 2 h; L/S = 50	C.D. = 85% 218 g CO_2/kg waste	Pérez-López *et al.*, 2008
Cement Kiln Dust (Alpena, Michigan)	Direct carbonation	PVC end caps	CaO: 34.5% MgO: 2.1% Density: 0.74 IGWC[*2]: 68%	35,600 ppmv CO_2 (atmospheric) Q_G: 53 mL/min (< 1% R.H.) No liquid used	T = ambient; t = 12 d	C.D. = 70.6% 191 g CO_2/kg waste	Huntzinger *et al.*, 2009b
			CaO: 34.5% MgO: 2.1% Density: 0.60 IGWC[*2]: 75%	75,800 ppmv CO_2 (atmospheric) Q_G: 45 mL/min (> 98% R.H.) No liquid used	T = ambient; t = 3.4 d	C.D. = 75.0% 203 g CO_2/kg waste	
			CaO: 34.5% MgO: 2.1% Density: 0.61 IGWC[*2]: 45%	69,900 ppmv CO_2 (atmospheric) Q_G: 45 mL/min (> 98% R.H.) No liquid used	T = ambient; t = 4.9 d	C.D. = 94.3% 256 g CO_2/kg waste	

Table 4. (continued).

Material type	Method	Reactor	Carbonation conditions				Reference
			Solid Comp.	Gas/Liquid Phases	Operating Conditions	Efficiency [*1]	
			CaO: 34.5% MgO: 2.1% Density: 0.81 IGWC[*2]: 38%	84,900 ppmv CO_2 (atmospheric) Q_G: 61 mL/min (< 1% R.H.) No liquid used	T = ambient; t = 3.3 d	C.D. = 101.2% 274 g CO_2/kg waste	
Cement Kiln Dust *(Chamute)*	Direct carbonation	Glass absorber column (L = 6 cm, D = 5 cm)	CaO: 48.03% K2O: 7.04% MgO: 1.39%	100,000 ppmv CO_2 (atmospheric) Q_G: 40 mL/min (~100% R.H.) 40g Nanopure Water	T = ambient; t = 8 d; Dose =120 g (dry)	C.D. = 76.9% 290 g CO_2/kg waste	Huntzinger *et al.,* 2009a
Mining Processing Waste — Bauxite Residue (RM)	Aqueous carbonation	Plastic beaker (50 mL)	Ca: 4.8% Al: 11.3% Fe: 23.7%	100% vol. CO_2 (atmospheric) Water	T = 30 d; Dose = 5 g slurry	21 g CO_2/kg RM	Khaitan et al., 2009
Red Mud (RM) *(HINDALCO)*	Aqueous carbonation	Stainless steel reaction chamber	CaO: 2.99% Na$_2$O: 6.0% (d–30 μm)	100% vol. CO_2 (3.5 bar) NaOH	T = ambient; t = 3.5 h; L/S = 0.35(L/kg)	53 g CO_2/kg RM	Vadav *et al.,* 2010
Oil-shale Waste *(Estonia power production)*	Aqueous carbonation	Stirred reactor (D = 55mm, H = 550mm)	CaO: 50.75% MgO: 15.19% d–28 μm	10% vol. CO_2 (atmospheric)	T = ambient; L/S – 10	167.1 g CO_2/kg ash (PF/BA type)	Uibu *et al.,* 2009b
Oil Shale Ash — Oil Shale Ash	Aqueous carbonation	Stirred Absorber (D = 55 mm; H = 100 mm)	CaO: 50.16% CO_2: 1.49% (d–43 μm)	10% vol. CO_2 (atmospheric) DI water	T = ambient; L/S = 10 (w/w)	CO_2 Gain: 14.99% (solid phase)	Uibu and Kuusik, 2009a

*1: C.D. = Carbonation Degree
*2: IGWC = Initial gravimetric water content determined from forensic analysis after column dismantlement
*3: Measured by ICP-OES after hot plate acid digestion

Table 5. Summaries of factors required for effective carbonation.

	Solid Phase	Liquid Phase	Gas Phase
Physical Properties	· Particle size · Mineralogy · Specific surface area · Porosity · Permeability · Surface activities · Microstructure	· Temperature · L/S ratio	· Partial pressure · CO_2 flow rate · Relative humidity · Temperature
Chemical Properties	· Composition (e.g., Ca and f-CaO content, Ca/Si ratio, Ferrite/C_3A ratio) · Heavy Metals (e.g., Pb, Cd, Ni, Cr) · Free water content · Permeability	· Organics · Inorganic · Anions · Cations · pH · Permeability	· CO_2 Concentration · Organics · Inorganic · Particulate Matter

increasing the surface area (Maroto-Valer *et al.*, 2005a). In addition, O'Connor *et al.* (2002) evaluated the influence of heat-pretreated serpentine and a supercritical CO_2 on conversion, which indicated that the maximum conversion of 78% could be achieved in 30 minutes at 155°C, P_{CO2} = 185 atm and 15% solids. It is possible to enhance the reactivity of the minerals or alkaline solid wastes considerably, while these methods require additional chemicals and energy. With the present technology, there is always a net demand for high-grade energy to drive the mineral carbonation process that is needed for (i) preparation of the solid minerals, including mining, transport, grinding and activation when necessary; (ii) processing, including the energy associated with recycling and possible losses of additives or catalysts; (iii) disposal of carbonates and byproducts (IPCC, 2005; Gerdemann *et al.*, 2007).

From the view point of process modification, two-stage carbonation processes (indirect carbonation) have also been investigated in recent years to optimize the efficiency of the dissolution and carbonation processes, as well as to achieve a pure precipitate product for specific industrial applications (Eloneva *et al.*, 2008a, b; Kodama *et al.*, 2008; Teir *et al.*, 2009). Kodama *et al.* (2008) developed a process using the pH-swing of a weak base - strong acid solution, with the finest particle size (< 63 μm) at 80°C, in which the maximum calcium extraction yield and carbonation conversion achieved were 60% and 70%, respectively. Another research group investigated the performance of enhancing dissolution using acetic acid solutions and other chemicals (Eloneva *et al.*, 2008a, b; Teir *et al.*, 2009). The results indicate that a maximum conversion of 86% was achieved under a CO_2 concentration of 10% vol. at 30°C, with a precipitate ($CaCO_3$) purity of up to 99.8%.

On the other hand, the developed rotating packed bed (RPB) process possessed a relatively higher conversion of BOF slag with a short reaction time compared to the slurry and autoclave reactors (Chang *et al.*, 2011a, b; 2012). According to the previous study by Chang *et al.* (2012), the maximum conversion of BOF slag achieved in an RPB was 93.5% at 65°C and 30 min, corresponding to a capture capacity of 0.29 kg CO_2 per kg of slag. However, the

weakness of the developed RPB process was the large amount of energy requirements for the rotation of packed bed. Therefore, the operating modulus and conditions should be upgraded to minimize the energy consumption, and then maximize the overall capture capacity.

Utilization of Carbonated Residues

Table 6 summarizes the description of alkaline solid wastes for accelerated carbonation and utilization. The most common methods for disposal of MSW, for example, are: landfill (82%), recycling or composting (11%) and thermal treatment (7%) (Fernández-Bertos *et al.*, 2004a). On the other hand, the treatment approach for BOF residue is dumping and partial reuse as an aggregate for civil engineering due to its good technical properties (Geiseler, 1996; De Windt *et al.*, 2011). In the United States, steelmaking slag is currently sold and used for various applications, predominantly for asphalt and concrete aggregate and road base (Stolaroff *et al.*, 2005). In Taiwan, steelmaking slag research has been done in the following fields: (a) cement industry, (b) road construction, (c) glass making, (d) concrete or asphalt aggregate, (e) ceramic tiles, (f) agriculture, soil conditioner, (g) aquaculture, and (h) land amendments (CSC Group, 2003). Some research has already been done on the use of steelmaking slags in construction material, e.g., as alkaline fillers in the paper-making industry and asphalt concrete applications (Lim *et al.*, 2010), in bricks and tiles (El-Mahllawy, 2008), as aggregate for the production of bituminous paving mixtures (Sorlini *et al.*, 2012), and in cement-based materials as cement/sand replacements or binder known as "alkaline cements" (Fernández-Jimenez *et al.*, 2006; Lim *et al.*, 2010; Zhang *et al.*, 2011).

Nevertheless, reuse possibilities of carbonated slags are limited due to the small particle size of the feedstock needed for efficient carbonation reaction. In addition, there are both chemical and physical changes in the structure and surface characteristics of steelmaking slag properties after carbonation (Chang *et al.*, 2011a). Fernández-Bertos *et al.* (2004a) found that the carbonated product is a solid of lower porosity, lower tortuosity, and lower pore area

Table 6. Description of alkaline solid wastes for accelerated carbonation and utilization.

Waste group	Management issues	Major Compounds in Carbonation	Applications	
			Conventional Method	Utilization Potency after Carbonation
Steelmaking Slag	Risk of chromium and vanadium release (De Windt *et al.*, 2011).	Larnite (Ca_2SiO_4); Brownmillerite (Ca_2FeAlO_5); Lime (CaO); Ettringite ($Ca_6Al_2OH_{12}(SO_4)_3\cdot26H_2O$); Portlandite ($Ca(OH)_2$) (Huijgen *et al.*, 2006a; Eloneva *et al.*, 2009)	Disposed of in landfills, if not recovered	Reuse as an aggregate for civil engineering
MSWI fly ash	High levels of dioxin, soluble salts and heavy metals such as cadmium, lead, and zinc (hazardous) (Li *et al.*, 2007; Wang *et al.*, 2010)	Lime (CaO); Portlandite ($Ca(OH)_2$); $Ca(OH)Cl$; Gehlenite ($Ca_2Al_2SiO_7$) (Li *et al.*, 2007)	90% of fly ash produced in UK was sent to landfill (Li *et al.*, 2007)	Reuse as construction aggregates (Wang *et al.*, 2010)
MSWI bottom ash	Leaching of heavy metals such as Cu, Zn, Pb (Arickx *et al.*, 2006)	Gehlenite ($Ca_2Al(AlSiO_7)$); Portlandite ($Ca(OH)_2$); Ettringite ($Ca_6Al_2OH_{12}(SO_4)_3\cdot26H_2O$) (Rendek *et al.*, 2006)	More than 50% is used as a secondary building material, road bases, and civil engineering structures in Europe (Rendek *et al.*, 2006)	Replace the sand or gravel fraction in concrete bricks or Reuse as secondary raw construction material (Arickx *et al.*, 2006).
Cement kiln dust	Beneficial to agriculture application; however, increased concerns over the health and environmental hazards (Huntzinger *et al.*, 2009b)	Lime (CaO); Portlandite ($Ca(OH)_2$); Calcium silicates; Gehlenite ($Ca_2Al(AlSiO_7)$) (Huntzinger *et al.*, 2009b)	Recycling and reuse as a road base material is an established process (Iizuka *et al.*, 2004)	Reuse as road base or construction material. No free-CaO was observed in the reacted samples (Huntzinger *et al.*, 2009a)

with calcite infilling the pore space. However, both of those changes can be beneficial for subsequent uses. First, most applications for steelmaking slag require that it be crushed and sieved into relatively small particles, which need extremely fine grinding for a cement additive. Therefore, this can avoid additional energy consumption and the cost of grinding specifically for CO_2 sequestration. On the other hand, the hydration of CaO and MgO in the fresh slag may be undesired for usage as concrete and asphalt aggregate, road base, and fill materials due to the tendency of fresh slag to have high water absorption and expansion properties. This property would be eliminated in the course of carbonation. Carbonation is proven to be an effective method to improve the durability of concrete blended with the carbonated slag because relatively insoluble $CaCO_3$ is formed from the soluble $Ca(OH)_2$ in the slag (Tsuyoshi *et al.*, 2010). Furthermore, the carbonated particles became coarser due to agglomeration, which might be beneficial for use in aggregate manufacturing (Fernández-Bertos *et al.*, 2004b).

There are still some important issues for accelerated carbonation, such as the fate of the carbonated products, including calcium carbonates and magnesium carbonates. In recent years, some research has focused on the production of $CaCO_3$ from the carbonation of steelmaking slag because it could also be a profitable refining method for slag products if the purity requirements for commercial

PCC (precipitated calcium carbonate) can be achieved (Teir, 2008; Eloneva *et al.*, 2012). The potential for using the calcium carbonate produced from the carbonation process relies on the purity and variety of the crystal structures that can be achieved. Calcium carbonate could be used in the pulp, plastic, rubber, paint, and paper industries as a filler (instead of clay) and as coating pigments to provide opacity, high brightness, and improved printability due to its good ink receptivity (Eloneva *et al.*, 2008b; Teir, 2008). The most important crystalline forms of calcium carbonates are the rhombohedral calcite type, the orthorhombic acicular aragonite type, and scalenohedral calcite, which are the favoured form in most applications (Imppola, 2000).

Life Cycle Assessment (LCA)

Since CCS is an energy-intensive process, it would consume additional energy and lead to further emissions of CO_2. This is why a life cycle assessment (LCA) of the CCS process is particularly important (IPCC, 2007). The major purpose of LCA is to quantify the environmental impacts of energy consumption technologies over their lifetimes (e.g., GHG emissions, acidification, etc), using a "cradle to grave" approach (De Haes and Heijungs, 2007). LCA is also a systematic approach to estimate the performance as well as its associated environmental impacts of a product or a certain kind of service in the life cycle. The LCA process was structured by the International Standards

Organization (ISO) 14040–14044, which provided four-step guidelines for the practitioner: (1) definition of goal and scope; (2) life cycle inventory analysis (LCI); (3) life cycle impact assessment (LCIA); and (4) interpretation.

Park and Fan (2004) showed that the net CO_2 emission of the aqueous carbonation of serpentine by the pH-swing method was –0.02 kg CO_2/kg feedstock. However, prior investigations using the pH-swing method consumed a great amount of base and acid solvents, which would cause adverse effects on the environment. An investigation reported by Chang *et al.* (2011b) showed a capture capacity of 0.098 kg CO_2 per kg BHC in an autoclave reactor. Energy consumption including grinding, sieving, pressuring, and heating, was taken into account while carrying out the LCA. However, the process needed to be operated for at least 2 hr to achieve such a result. On the other hand, according to an investigation by Odeh and Cockerill (2008), the GHG emissions from UK fossil fuel plant stations with CCS can be reduced by 75–84% relative to a subcritical PC power plant. Therefore, CCS has the potential of decreasing GHG emissions proved by the results of LCA. On the other hand, CCS may increase other environmental impacts such as eutrophication or acidification due to the increase in the concentrations of other pollutants. Hence, the effects of CCS should be weighed and compared carefully due to changes in the environmental impacts (Odeh and Cockerill, 2008). In pulverized hard coal combustion, the energy penalty was found to range from 5–18% with application of the various CCS processes (Marx *et al.*, 2011).

Summary of Practical Considerations

In general, the dissolution of calcium species in alkaline solid waste was favored at the low pH and high temperature, which is not favored for the precipitation of calcium carbonate. It was noted that the accelerated carbonation include a large amount of energy requirements and the high costs (IPCC, 2007). It was thus concluded that the challenges encountered are to accelerate the reaction and utilize the heat of reaction to maximize the capture capacity and minimize energy demand, as well as to determine the optimal operating conditions. Therefore, alkaline solid wastes can be used to sequester great amount of CO_2, especially if the wastes are generated nearby the source of CO_2, for achieving both the environmental and economic benefits.

The rate of carbonation reaction can be enhanced by adding acids or caustic alkali-metal hydroxide (Beard *et al.*, 2004), utilizing a bicarbonate/salt ($NaHCO_3$/NaCl) mixture (Maroto-Valer *et al.*, 2005a; O'Connor *et al.*, 2005), employing various pretreatment techniques (i.e., including physical and chemical pretreatment (Maroto-Valer *et al.*, 2005a, b), electrolysis and heat pretreatment (Li *et al.*, 2009), mechanical activation methods (McKelvy *et al.*, 2004; Park and Fan, 2004; Li *et al.*, 2009; Haug *et al.*, 2010; Haug *et al.*, 2011)), and using wastewater/brine as liquid agents (Chou, 2011; Liu and Maroto-Valer, 2011; Nyambura *et al.*, 2011). However, pretreatments and addition of chemicals tend to consume additional energy and materials. As a result, the aqueous carbonation of alkaline solid wastes is suggested as a link to utilize wastewater for

large-scale application of this approach. It was concluded that significant technological breakthroughs, i.e., reactor design and waste-to-resource supply chain, and system optimization, i.e., response surface methodology (RSM) and LCA will be needed before deployment can be considered.

CONCLUSIONS AND RECOMMENDATIONS

This paper reviews the state-of-the-art of the accelerated carbonation of alkaline wastes for CO_2 capture. The carbonation of alkaline solid waste has been proved to be an effective way to capture CO_2. A combined approach was suggested for capturing CO_2, at the same time improving the environmental and mechanical properties of industrial solid wastes and wastewater/brine, for instance, carbonation of the steelmaking slags and metalworking wastewater in steelmaking industry. The process also enabled on-site recycle and reuse of wasted materials.

Since dissolution of reactive species (e.g., calcium ions) and the water solubility of CO_2 exhibit contradictory performances in the limiting step, the optimum operating conditions of accelerated carbonation should be proposed to compromise the above conflict phenomena. In addition, CCS process would consume additional energy and generate more CO_2 emissions. Furthermore, utilization of the reacted wastes for construction materials should be critically assessed from the view-point of 3E (Engineering, Environmental, and Economic) aspects. Consequently, RSM (Response Surface Methodology) and LCA (Life Cycle Assessment) techniques should be introduced and evaluated for system optimization.

REFERENCES

Alexander, G., Maroto-Valer, M.M., Aksoy, P. and Schobert, H. (2005). Development of a CO_2 Sequestration Module by Integrating Mineral Activation and Aqueous Carbonation, Annual Technical Progress Report, The Pennsylvania State University.

Alexander, G., Mercedesmarotovaler, M. and Gafarovaaksoy, P. (2007). Evaluation of reaction Variables in the Dissolution of Serpentine For mineral Carbonation. *Fuel* 86: 273–281.

Arickx, S., Van Gerven, T. and Vandecasteele, C. (2006). Accelerated Carbonation for Treatment of MSWI Bottom Ash. *J. Hazard. Mater.* 137: 235–43.

Baciocchi, R., Costa, G., Di Bartolomeo, E., Polettini, A. and Pomi, R. (2009a). The Effects of Accelerated Carbonation on CO_2 Uptake and Metal Release from Incineration APC Residues. *Waste Manag.* 29: 2994–3003.

Baciocchi, R., Costa, G., Polettini, A. and Pomi, R. (2009b). Influence of Particle Size on the Carbonation of Stainless Steel Slag for CO_2 Storage. *Energy*

Procedia 1: 4859–4866.

Baciocchi, R., Costa, G., Polettini, A., Pomi, R. and Prigiobbe, V. (2009c). Comparison of Different Reaction Routes for Carbonation of APC Residues. *Energy Procedia* 1: 4851–4858.

Beard, J.S., Blencoe, J.G., Anovitz, L.M. and Palmer, D.A. (2004). Carbonation of Metal Silicates for Long-Term CO_2 Sequestration, Canadian Patent Application, CA 2 523 135.

Birat, J.P. (2009). Steel and CO_2 - The ULCOS Program, CCS and Mineral Carbonation Using Steelmaking Slag, Proc. 1st International Slag Valorisation Symposium, Leuven, Belgium.

Bird, M. and Talberth, J. (2008). Waste Stream Reduction and Re-Use in the Pulp and Paper Sector, Washington State Department of Ecology Industrial Footprint Project, Center for Sustainable Economy, New Mexico.

Bobicki, E.R., Liu, Q., Xu, Z. and Zeng, H. (2012). Carbon Capture and Storage Using Alkaline Industrial Wastes. *Prog. Energy Combust. Sci.* 38: 302–320.

Bond, F.C. (1961). Crushing and Grinding Calculations. Part 1. *Br. Chem. Eng.* 6: 378–385.

Bonenfant, D., Kharoune, L., Sauve, S., Hausler, R., Niquette, P., Mimeault, M. and Kharoune, M. (2008). CO_2 Sequestration Potential of Steel Slags at Ambient Pressure and Temperature. *Ind. Eng. Chem. Res.* 47: 7610–7616.

Bonenfant, D., Kharoune, L., Sauve, S., Hausler, R., Niquette, P., Mimeault, M. and Kharoune, M. (2009). Molecular Analysis of Carbon Dioxide Adsorption Processes on Steel Slag Oxides. *Int. J. Greenhouse Gas Control* 3: 20–28.

Cappai, G., Cara, S., Muntoni, A. and Piredda, M. (2012). Application of Accelerated Carbonation on MSW Combustion APC Residues for Metal Immobilization and CO_2 Sequestration. *J. Hazard. Mater.* 207–208: 159–64.

Chang, E.E., Chen, C.H., Chen, Y.H., Pan, S.Y. and Chiang, P.C. (2011a). Performance Evaluation for Carbonation of Steel-Making Slags in a Slurry Reactor. *J. Hazard. Mater.* 186: 558–564.

Chang, E.E., Pan, S.Y., Chen, Y.H., Chu, H.W., Wang, C.F. and Chiang, P.C. (2011b). CO_2 Sequestration by Carbonation of Steelmaking Slags in an Autoclave Reactor. *J. Hazard. Mater.* 195: 107–114.

Chang, E.E., Pan, S.Y., Chen, Y.H., Tan, C.S. and Chiang, P.C., (2012). Accelerated Carbonation of Steelmaking Slags in a High-Gravity Rotating Packed Bed. J. Hazard. Mater. 227–228: 97–106.

Chen, Y.T. (2008). Effects of Process Variables on the Conversion of BOF Slag to Carbonate, Graduate Institute of Chemical Engineering, Master Degree, p. 122.

Chou, A.C. (2011). Carbonation of Basic Oxygen Furnace Slag with Metalworking Wastewater in a Slurry Reactor, Master Thesis, National Taiwan University, Taiwan.

Costa, G., Baciocchi, R., Polettini, A., Pomi, R., Hills, C.D. and Carey, P.J. (2007). Current Status and Perspectives of Accelerated Carbonation Processes on Municipal Waste Combustion Residues. *Environ. Monit. Assess.* 135: 55–

75.

Costa, G. (2009). Accelerated Carbonation of Minerals and Industrial Residues for Carbon Dioxide Storage, Università Degli Studi Di Roma.

CSC Group (2003). Slag Utilization.

CSLF (2011). inFocus: What is Carbon Utilization?

Daval, D., Martinez, I., Corvisier, J., Findling, N., Goffé, B. and Guyot, F. (2009). Carbonation of Ca-bearing Silicates, the Case of Wollastonite: Experimental Investigations and Kinetic Modeling. *Chem. Geol.* 265: 63–78.

De Haes, H.A.U. and Heijungs, R. (2007). Life-Cycle Assessment for Energy Analysis and Management. *Appl. Energy* 84: 817–827.

De Windt, L., Chaurand, P. and Rose, J. (2011). Kinetics of Steel Slag Leaching: Batch Tests and Modeling. *Waste Manag.* 31: 225–35.

Doucet, F.J. (2010). Effective CO_2-Specific Sequestration Capacity of Steel Slags and Variability in Their Leaching Behaviour in View of Industrial Mineral Carbonation. *Miner. Eng.* 23: 262–269.

Druckenmiller, M.L. and Maroto-Valer, M.M. (2005). Carbon Sequestration Using Brine of Adjusted pH to Form Mineral Carbonates. *Fuel Process. Technol.* 86: 1599–1614.

Edsall, J.T., and Wyman, J. (1958). *Biophysical Chemistry*, Vol. 1, Academic, New York, p.585.

El-Mahllawy, M.S. (2008). Characteristics of Acid Resisting Bricks Made from Quarry Residues and Waste Steel Slag. *Constr. Build. Mater.* 22: 1887–1896.

Eloneva, S., Teir, S., Salminen, J., Fogelholm, C.J. and Zevenhoven, R. (2008a). Fixation of CO_2 by Carbonating Calcium Derived from Blast Furnace Slag. *Energy* 33: 1461–1467.

Eloneva, S., Teir, S., Salminen, J., Fogelholm, C.J. and Zevenhoven, R. (2008b). Steel Converter Slag as a Raw Material for Precipitation of Pure Calcium Carbonate. *Ind. Eng. Chem. Res.* 47: 7104–7111.

Eloneva, S., Teir, S., Revitzer, H., Salminen, J., Said, A., Fogelholm, C.J. and Zevenhoven, R. (2009). Reduction of CO_2 Emissions from Steel Plants by Using Steelmaking Slags for Production of Marketable Calcium Carbonate. *Steel Res. Int.* 80: 415–421.

Eloneva, S., Said, A., Fogelholm, C.J. and Zevenhoven, R. (2012). Preliminary Assessment of a Method Utilizing Carbon Dioxide and Steelmaking Slags to Produce Precipitated Calcium Carbonate. *Appl. Energy* 90: 329–334.

Fernández Bertos, M., Li, X., Simons, S.J.R., Hills, C.D. and Carey, P.J. (2004a). Investigation of Accelerated Carbonation for the Stabilisation of MSW Incinerator Ashes and the Sequestration of CO_2. *Green Chem.* 6: 428–436.

Fernández Bertos, M., Simons, S.J., Hills, C.D. and Carey, P.J. (2004b). A Review of Accelerated Carbonation Technology in the Treatment of Cement-Based Materials and Sequestration of CO_2. *J. Hazard. Mater.* 112: 193–205.

Fernández-Jimenez, A., Delatorre, A., Palomo, A., Lopezolmo, G., Alonso, M. and Aranda, M. (2006).

Quantitative Determination of Phases in the Alkali Activation of Fly Ash. Part I. Potential Ash Reactivity. *Fuel* 85: 625–634.

Figueroa, J., Fout, T., Plasynski, S., McIlvried, H. and Srivastava, R. (2008). Advances in CO_2 Capture Technology—The U.S. Department of Energy's Carbon Sequestration Program☆. *Int. J. Greenhouse Gas Control* 2: 9–20.

Geiseler, J. (1996). Use of Steelworks Slag in Europe. *Waste Manag.* 16: 59–63.

Gerdemann, S.J., O'Connor, W.K., Dahlin, D.C., Penner, L.R. and Rush, H. (2007). Ex Situ Aqueous Mineral Carbonation. *Environ. Sci. Technol.* 41: 2587–2593.

Gunning, P.J., Hills, C.D. and Carey, P.J. (2010). Accelerated Carbonation Treatment of Industrial Wastes. *Waste Manag.* 30: 1081–90.

Haselbach, L. (2009). Potential for Carbon Dioxide Absorption in Concrete. *J. Environ. Eng.* 135: 465–472.

Haszeldine, R.S. (2009). Carbon Capture and Storage: How Green Can Black Be? *Science* 325: 1647−1651.

Haug, T.A., Kleiv, R.A. and Munz, I.A. (2010). Investigating Dissolution of Mechanically Activated Olivine for Carbonation Purposes. *Appl. Geochem.* 25: 1547–1563.

Haug, T.A., Munz, I.A. and Kleiv, R.A. (2011). Importance of Dissolution and Precipitation Kinetics for Mineral Carbonation. *Energy Procedia* 4: 5029–5036.

Huang, C.H., Chang, K.P., Yu, C.T., Chiang, P.C. and Wang, C.F. (2010). Development of High-Temperature CO_2 Sorbents Made of CaO-based Mesoporous Silica. *Chem. Eng. J.* 161: 129–135.

Huijgen, W.J.J. and Comans, R.N.J. (2003). Carbon Dioxide Sequestration by Mineral Carbonation: Literature Review, Energy Research Centre of the Netherlands (ECN), ECN-C--03-016.

Huijgen, W.J.J. and Comans, R.N.J. (2005a). Mineral CO_2 Sequestration by Carbonation of Industrial Residues: Literature Review and Selection of Residue, Energy Research Centre of the Netherlands (ECN), ECN-C--05-074 22.

Huijgen, W.J.J., Witkamp, G.J. and Comans, R.N.J. (2005b). Mineral CO_2 Sequestration in Alkaline Solid Residues. Proc. of the 7th International Conference on Greenhouse Gas Control Technologies, p. 2415–2418.

Huijgen, W.J.J., Witkamp, G.J. and Comans, R.N.J. (2005c). Mineral CO_2 Sequestration by Steel Slag Carbonation. *Environ. Sci. Technol.* 39: 9676–9682.

Huijgen, W.J.J. and Comans, R.N.J. (2006a). Carbonation of Steel Slag for CO_2 Sequestration: Leaching of Products and Reaction Mechanisms. *Environ. Sci. Technol.* 40: 2790–2796.

Huijgen, W.J.J., Ruijg, G.J., Comans, R.N.J. and Witkamp, G.J. (2006b). Energy Consumption and Net CO_2 Sequestration of Aqueous Mineral Carbonation. *Ind. Eng. Chem. Res.* 45: 9184–9194.

Huijgen, W.J.J, Witkamp, G.J. and Comans, R.N.J. (2006c). Mechanisms of Aqueous Wollastonite Carbonation as a Possible CO_2 Sequestration Process. *Chem. Eng. Sci.* 61: 4242–4251.

Huntzinger, D.N., Gierke, J.S., Kawatra, S.K., Eisele, T.C. and Sutter, L.L. (2009a). Carbon Dioxide Sequestration in Cement Kiln Dust through Mineral Carbonation. *Environ. Sci. Technol.* 43: 1986–1992.

Huntzinger, D.N., Gierke, J.S., Sutter, L.L., Kawatra, S.K. and Eisele, T.C. (2009b). Mineral Carbonation for Carbon Sequestration in Cement Kiln Dust from Waste Piles. *J. Hazard. Mater.* 168: 31–37.

Iizuka, A., Fujii, M., Yamasaki, A. and Yanagisawa, Y. (2004). Development of a New CO_2 Sequestration Process Utilizing the Carbonation of Waste Cement. *Ind. Eng. Chem. Res.* 43: 7880–7887.

Imppola, O. (2000). Precipitated Calcium Carbonate, In *Pigment Coating and Surface Sizing of Paper* Vol. 11, Paltakari, J. (Ed.), Paper Engineers' Association, Helsinki, Finland, p. 140–151

IPCC (2005). IPCC Special Report on Carbon Dioxide Capture and Storage.

IPCC (2007). Climate Change 2007: Mitigation of Climate Change.

Ishida, T. and Maekawa, K. (2000). Modeling of pH Profile in Pore Water Based on Mass Transport and Chemical Equilibrium Theory. *Proc. JSCE* 648: 203–215

Kakizawa, M., Yamasaki, A. and Yanagisawa, Y., (2001). A New CO_2 Disposal Process via Artificial Weathering of Calcium Silicate Accelerated by Acetic Acid. *Energy* 26: 341–354.

Khaitan, S., Dzombak, D.A. and Lowry, G.V. (2009). Mechanisms of Neutralization of Bauxite Residue by Carbon Dioxide. *J. Environ. Eng.* 135: 433–438.

Klemeš, J., Cockerill, T., I., B., Shackley, S. and Gough, C. (2007). Engineering Feasibility of Carbon Dioxide Capture and Storage, In *Carbon Capture and Its Storage: An Integrated Assessment,* Shackley, S. and Gough, C. (Eds.), Ashgate Publishing Limited, England, p. 43–86.

Kodama, S., Nishimoto, T., Yamamoto, N., Yogo, K. and Yamada, K. (2008). Development of a New pH-Swing CO_2 Mineralization Process with a Recyclable Reaction Solution. *Energy* 33: 776–784.

Krevor, S.C.M. and Lackner, K.S. (2011). Enhancing Serpentine Dissolution Kinetics for Mineral Carbon Dioxide Sequestration. *Int. J. Greenhouse Gas Control* 5: 1073–1080.

Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce, E.L. and Sharp, D.H. (1995). Carbon Dioxide Disposal in Carbonate Minerals. *Energy* 20: 1153–1170.

Lackner, K.S., Butt, D.P. and Wendt, C.H. (1997). Progress on Binding CO_2 in Mineral Substrates. *Energy Convers. Manage.* 38: S259–S264.

Lackner, K.S. (2002). Carbonate Chemistry for Sequestering Fossil Carbon. *Annu. Rev. Energy Environ.* 27: 193–232.

Lackner, K.S. (2003). A Guide to CO_2 Sequestration. *Science* 300: 1677–1678.

Lekakh, S.N., Rawlins, C.H., Robertson, D.G.C., Richards, V.L. and Peaslee, K.D. (2008). Kinetics of Aqueous Leaching and Carbonization of Steelmaking Slag. *Metall. Mater. Trans. B* 39: 125–134.

Li, W., Li, B. and Bai, Z. (2009). Electrolysis and Heat Pretreatment Methods to Promote CO_2 Sequestration by Mineral Carbonation. *Chem. Eng. Res. Des.* 87: 210–215.

Li, X., Bertos, M.F., Hills, C.D., Carey, P.J. and Simon, S. (2007). Accelerated Carbonation of Municipal Solid Waste Incineration Fly Ashes. *Waste Manag.* 27: 1200–1206.

Li, Z.S., Fang, F. and Cai, N.S. (2009). CO_2 Capture from Flue Gases Using Three Ca-Based Sorbents in a Fluidized Bed Reactor. *J. Environ. Eng.* 135: 418–425.

Lim, M., Han, G.C., Ahn, J.W. and You, K.S. (2010). Environmental Remediation and Conversion of Carbon Dioxide (CO_2) into Useful Green Products by Accelerated Carbonation Technology. *Int. J. Environ. Res. Public Health.* 7: 203–228.

Liu, Q. and Mercedes Maroto-Valer, M. (2011). Investigation of the Effect of Brine Composition and pH Buffer on CO_2-Brine Sequestration. *Energy Procedia* 4: 4503–4507.

Maroto-Valer, M.M., Fauth, D.J., Kuchta, M.E., Zhang, Y. and Andrésen, J.M. (2005a). Activation of Magnesium Rich Minerals as Carbonation Feedstock Materials for CO_2 Sequestration. *Fuel Process. Technol.* 86: 1627–1645.

Maroto-Valer, M.M., Tang, Z. and Zhang, Y. (2005b). CO_2 Capture by Activated and Impregnated Anthracites. *Fuel Process. Technol.* 86: 1487–1502.

Marx, J, Schreiber, A, Zapp, P, Haines, M, Hake, J. Fr. and Gale, J. (2011). Environmental Evaluation of CCS Using Life Cycle Assessment - A Synthesis Report. *Energy Procedia* 4: 2448–2456

McCabe, W., Smith, J. and Harriott, P. (2005). Leaching and Extraction, In *Unit Operations of Chemical Engineering,* McGraw Hill, New Delhi p. 764.

Mckelvy, M.J., Chizmeshya, A.V.G., Diefenbacher, J., Bearat, H. and Wolf, G. (2004). Exploration of the Role of Heat Activation in Enhancing Serpentine Carbon Sequestration Reactions. *Environ. Sci. Technol.* 38: 6897–6903.

Mikkelsen, M., Jørgensen, M. and Krebs, F.C. (2010). The Teraton Challenge. A Review of Fixation and Transformation of Carbon Dioxide. *Energy Environ. Sci.* 3: 43–81.

Montes-Hernandez, G., Pérez-López, R., Renard, F., Nieto, J.M. and Charlet, L. (2009). Mineral Sequestration of CO_2 by Aqueous Carbonation of Coal Combustion Fly-Ash. *J. Hazard. Mater.* 161: 1347–1354.

Morel, F.M.M. and Hering, J.G. (1993). *Principles and Applications of Aquatic Chemistry*, John Wiley & Sons, New York.

Nyambura, M.G., Mugera, G.W., Felicia, P.L. and Gathura, N.P. (2011). Carbonation of Brine Impacted Fractionated Coal Fly Ash: Implications for CO_2 Sequestration. *J. Environ. Manage.* 92: 655–664.

O'Connor, W.K., Dahlin, D.C., Rush, G.E., Dahlin, C.L. and Collins, W.K. (2002). Carbon Dioxide Sequestration by Direct Mineral Carbonation: Process Mineralogy of Feed and Products. *Miner. Metall. Process* 19: 95–101.

O'Connor W.K., Dahlin, D.C., Rush, G.E., Gerdemann, S.J., Penner, L.R. and Nilsen, D.N. (2005). Aqueous Mineral Carbonation: Mineral Availability, Pretreatment, Reaction Parameters, and Process Studies. DOE/ARC-TR-04-002, Albany Research Center (ARC), US.

Odeh, N.A. and Cockerill, T.T. (2008). Life Cycle GHG Assessment of Fossil Fuel Power Plants with Carbon Capture and Storage. *Energy Policy* 36: 367–380.

Olajire, A.A. (2010). CO_2 Capture and Separation Technologies for End-of-pipe Applications – A Review. *Energy* 35: 2610–2628.

Pacala, S. and Socolow, R. (2004). Stabilization Wedges: Solving the Climate Problem for the next 50 Years with Current Technologies. *Science* 305: 968–972.

Park, A.H.A., Jadhav, R. and Fan, L.S. (2003). CO_2 Mineral Sequestration: Chemically Enhanced Aqueous Carbonation of Serpentine. *Can. J. Chem. Eng.* 81: 885–890.

Park, A.H.A. and Fan, L.S. (2004). CO_2 Mineral Sequestration: Physically Activated Dissolution of Serpentine and pH Swing Process. *Chem. Eng. Sci.* 59: 5241–5247.

Pérez-López, R., Montes-Hernandez, G., Nieto, J.M., Renard, F. and Charlet, L. (2008). Carbonation of Alkaline Paper Mill Waste to Reduce CO_2 Greenhouse Gas Emissions into the Atmosphere. *Appl. Geochem.* 23: 2292–2300.

Rendek, E., Ducom, G. and Germain, P. (2006). Carbon Dioxide Sequestration in Municipal Solid Waste Incinerator (MSWI) Bottom Ash. *J. Hazard. Mater.* 128: 73–79.

Salminen, J. and Prausnitz, J. (2007). Carbon Dioxide in Chemical Processes, In *Development and Applications in Solubility*, Letcher, T.M. (Ed.), Royal Society of Chemistry, UK, p. 337–349.

Santos, A., Ajbary, M., Morales-Florez, V., Kherbeche, A., Pinero, M. and Esquivias, L. (2009). Larnite Powders and Larnite/Silica Aerogel Composites as Effective Agents for CO_2 Sequestration by Carbonation. *J. Hazard. Mater.* 168: 1397–1403.

Seifritz, W. (1990). CO_2 Disposal by Means of Silicates. *Nature* 345: 486–486.

Shi, C.J. and Qian, J.S. (2000). High Performance Cementing Materials from Industrial Slags - A Review. *Resour. Conserv. Recycl.* 29: 195–207.

Sorlini, S., Sanzeni, A. and Rondi, L. (2012). Reuse of Steel Slag in Bituminous Paving Mixtures. *J. Hazard. Mater.* 209–210: 84–91.

Stolaroff, J., Lowry, G. and Keith, D. (2005). Using CaO- and MgO-Rich Industrial Waste Streams for Carbon Sequestration. *Energy Convers. Manage.* 46: 687–699.

Stumm, W. and Morgan, J.J. (1981). *Aquatic Chemistry*, 2nd ed., Willer-Interscience, New York, p. 210–212.

Styring, P., Jansen, D., Coninck, H.d., Reith, H. and Armstrong, K., (2011). Carbon Capture and Utilisation in the Green Economy: Using CO_2 to Manufacture Fuel, Chemical and Materials, The Centre for Low Carbon Futures.

Symonds, R.T., Lu, D.Y., Macchi, A., Hughes, R.W. and Anthony, E.J. (2009). CO_2 Capture from Syngas via Cyclic Carbonation/Calcination for a Naturally Occurring Limestone: Modelling and Bench-Scale Testing. *Chem. Eng. Sci.* 64: 3536–3543.

Tai, C.Y., Chen, W.R. and Shih, S.M. (2006). Factors Affecting Wollastonite Carbonation under CO_2

Supercritical Conditions. *AlChE J.* 52: 292–299.

Tan, C. and Chen, J. (2006). Absorption of Carbon Dioxide with Piperazine and Its Mixtures in a rotating Packed Bed. *Sep. Purif. Technol.* 49: 174–180.

Teir, S. (2008). Fixation of Carbon Dioxide by Producing Carbonates from Minerals and Steelmaking Slags, Doctoral Dissertation, Department of Energy Technology, Helsinki University of Technology.

Teir, S., Eloneva, S., Fogelholm, C. and Zevenhoven, R., (2009). Fixation of Carbon Dioxide by Producing Hydromagnesite from Serpentinite. *Appl. Energy* 86: 214–218.

Thiery, M., Villain, G., Dangla, P. and Platret, G. (2007). Investigation of the Carbonation front Shape on Cementitious Materials: Effects of the Chemical Kinetics. *Cem. Concr. Res.* 37: 1047–1058.

Tsuyoshi, S., Etsuo, S., Minoru, M. and Nobuaki, O. (2010). Carbonation of γ-Ca_2SiO_4 and the Mechanism of Vaterite Formation. *J. Adv. Concr. Technol.* 8: 273–280.

Uibu, M. and Kuusik, R. (2009a). Mineral Trapping of CO_2 via Oil Shale Ash Aqueous Carbonation: Controlling Mechanism of Process Rate and Development of Continuous-Flow Reactor System. *Oil Shale* 26: 40–58.

Uibu, M., Uus, M. and Kuusik, R. (2009b). CO_2 Mineral Sequestration in Oil-Shale Wastes from Estonian Power Production. *J. Environ. Manage.* 90: 1253–1260.

Uibu, M., Kuusik, R., Andreas, L. and Kirsimäe, K. (2011). The CO_2 -Binding by Ca-Mg-Silicates in Direct Aqueous Carbonation of Oil Shale Ash and Steel Slag. *Energy Procedia* 4: 925–932.

Wang, L., Jin, Y. and Nie, Y. (2010). Investigation of Accelerated and Natural Carbonation of MSWI Fly Ash with a High Content of Ca. *J. Hazard. Mater.* 174: 334–343.

Wang, M. (2004). Controlling Factors and Mechanism of Preparing Needlelike $CaCO_3$ under High-Gravity Environment. *Powder Technol.* 142: 166–174.

Wang, Q. and Yan, P. (2010). Hydration Properties of Basic Oxygen Furnace Steel Slag. *Constr. Build. Mater.* 24: 1134–1140.

Wang, X. and Maroto-Valer, M. (2011). Integration of CO_2 Capture and Storage Based on pH-Swing Mineral Carbonation Using Recyclable Ammonium Salts. *Energy Procedia* 4: 4930–4936.

Yadav, V.S., Prasad, M., Khan, J., Amritphale, S.S., Singh, M. and Raju, C.B. (2010). Sequestration of Carbon Dioxide (CO_2) using Red Mud. *J. Hazard. Mater.* 176: 1044–1050.

Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R.B., Bland, A.E. and Wright, I. (2008). Progress in carbon Dioxide Separation and Capture: A Review. *J. Environ. Sci.* 20: 14–27.

Yu, C.H., Cheng, H.H. and Tan, C.S. (2012). CO_2 Capture by Alkanolamine Solutions Containing Diethylenetriamine and Piperazine in a Rotating Packed Bed. *Int. J. Greenhouse Gas Control* 9: 136–147.

Zevenhoven, R., Teir, S. and Eloneva, S. (2008). Heat Optimisation of a Staged Gas-Solid Mineral Carbonation Process for Long-Term CO_2 Storage. *Energy* 33: 362–370.

Zhang, T., Yu, Q., Wei, J., Li, J. and Zhang, P. (2011). Preparation of High Performance Blended Cements and Reclamation of Iron Concentrate from Basic Oxygen Furnace Steel Slag. *Resour. Conserv. Recycl.* 56: 48–55.