

# CO<sub>2</sub> Sequestration by Solid Residues Carbonation for Building Materials Preparation

Jun Chang, Yanfeng Fang and Jingru Wang

**Abstract**—Mineral carbonation combining with material preparation was studied in this work. Four kinds of solid residues (carbide slag, residues lime, steel slag, waste concrete) were respectively used as raw materials to sequester CO<sub>2</sub> and prepare artificial aggregate after accelerated carbonation. The experimental results showed that the optimum conditions of accelerated carbonation were carbonation time t=125 min, CO<sub>2</sub> concentration c=100%, CO<sub>2</sub> pressure p=0.6032 MPa, temperature T=55 °C, particle size of solid waste 74 μm~150 μm and liquid-solid ratio L/S=6 kg/kg. Under these carbonated conditions, the degree of carbonation were carbide slag 64%, waste lime 72%, steel slag 52% and waste concrete 32% and each kilogram of carbide slag, waste lime, steel slag and waste concrete could sequester CO<sub>2</sub> gas 0.4428 kg, 0.5855 kg, 0.2023 kg and 0.0752 kg respectively. Furthermore, after accelerated carbonation, the four solid residues were much more suitable to manufacture artificial aggregate which had higher strength.

**Keywords**—accelerated carbonation; carbon dioxide; industrial solid residues; artificial aggregate.

## I. INTRODUCTION

THE likelihood of significant environmental and social damage will increase significantly if concentrations of CO<sub>2</sub> in the atmosphere exceed about 550 ppm[1-2]. A variety of removal methods have been considered such as deep-sea disposal, recycling to methanol, or conversion to solid carbonate[3-4]. Problems appear to remain with all these strategies, and more work is needed to develop a more feasible and efficient method. The idea of converting the gas to solid carbonate is particularly appealing, and it is a permanent disposal on a human time scale. Lackner and Wu[5-6] pointed out that a large number of calcium and magnesium silicate minerals exist in nature, such as wollastonite, forsterite, serpentine and talcum, could sequester carbon dioxide to form stable carbonates. Huijgen and Comans measured the carbonation of steel slag in an autoclave reactor[7-8]. In comparison with naturally occurring wollastonite (CaSiO<sub>3</sub>), steel slag was able to sequester 11 times more CO<sub>2</sub> at ambient temperature.

In China, industrial solid residues generated amounted to

1,757,670,000 tons, of which 11,970,000 tons were stacked in 2007[9]. A lot of solid residues occupy land and pollute soil, air, water and contaminate our environment[10-11]. Some of industrial solid residues (such as carbide slag, residues lime, steel slag and waste concrete) are also calcareous materials. Therefore they were used as alternative feedstock for mineral CO<sub>2</sub> sequestration in this study. These different industrial solid waste (including steelmaking slag[12]) were accelerated carbonated to sequester CO<sub>2</sub>, meanwhile the aggregate was manufactured by carbonation. Through Mercury Porosimeter (MP) analysis, the change of the distribution of pore of steel slag before and after carbonation were observed, and through mechanics performance testing, artificial aggregate made by carbonated solid residues could be used as one type of replacing natural limestone in some projects.

## II. EXPERIMENT

### A. Experimental procedure

Table 1 shows the chemical analysis results of these materials.

TABLE I

CHEMICAL ANALYSIS OF MATERIALS USED

Materials	Composition (weight %)								
	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	FeO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	LOSS
Carbide slag	69.19	7.36	12.14	—	1.10	—	1.21	3.52	5.46
Waste lime	81.32	8.06	6.53	—	—	0.34	—	—	3.64
Steel slag	38.91	13.32	1.57	23.11	7.61	21.62	1.47	—	2.80
Waste concrete	23.51	48.24	15.47	1.12	1.64	0.72	1.80	1.94	3.56

Large granules (up to 450 μm) of raw materials were released during grinding and removed, and the rest particles were classified by Tyler standard screen. Distilled water (H<sub>2</sub>O), raw materials and carbonation additives (Na<sub>2</sub>SiO<sub>3</sub>, m=1.67 wt% and NH<sub>4</sub>Cl, m=0.84 wt%) were added at specific liquid-solid ratios into an autoclave (Fig.1). Carbon dioxide pressure was p=0.6032 MPa, however, carbon dioxide concentration varied, and the changes of temperature (T), pressure (P) and weight of the specimen (m) in the autoclave were monitored by sensors. The mass gain of solid residues, due to carbonation, was tested by thermal gravimetric analysis (TGA, NETZSCH STA 409EP). In addition, the major

Jun Chang, Yanfeng Fang and Jingru Wang, are with School of Civil Engineering, Dalian University of Technology, Dalian 116024, P. R. China

changes of minerals, reaction progress and pore structure changes before and after carbonation were investigated by X-ray Diffraction (XRD, BRUKER D8 ADVANCE), Scanning Electron Microscopy (SEM, Hitachi S-2500) and Mercury Intrusion Porosimeter (MIP, Quicmtachrome Poremastier-60). Carbonated and non-carbonated materials were turned into about 5 mm artificial aggregates (sphericity) by a pelletizer. Strengths of samples were tested by Universal testing machine.

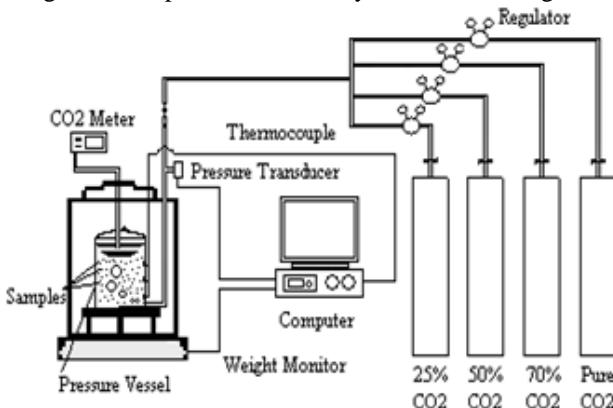


Fig. 1: Schematic diagram of the device to accelerate carbonation

#### B. Evaluation of accelerated carbonation

Significant formation of other carbonates (mainly  $MgCO_3$ ) are improbable<sup>[13]</sup>, due to the relatively low Mg content of these raw materials (see Table 1) and the very limited Mg conversion expected at the relatively low  $CO_2$  pressure and short reaction time applied in this study. Thus the degree of carbonation ( $\Psi_{Ca}$ ) can be determined from the total CaO content in specimen (MCaO total), the molar weights of Ca (MW<sub>Ca</sub>), CaO (MW<sub>CaO</sub>) and  $CO_2$  (MW<sub>CO2</sub>), and the  $\Delta M_{782-1076K}$  measured by TGA. And Eq.1 was derived assuming that only Ca was carbonated during the carbonation process.

$$\Psi_{Ca} = \frac{\Delta M_{782-1076K}(\text{kg/kg}) \times \frac{\text{MW}_{Ca}(\text{kg/mol})}{\text{MW}_{CO_2}(\text{kg/mol})}}{MCaO_{\text{total}}(\text{kg/kg}) \times \frac{\text{MW}_{Ca}(\text{kg/mol})}{\text{MW}_{CaO}(\text{kg/mol})}} \times 100\% \quad (1)$$

$$MCO_2(\text{kg/kg}) = \Psi_{Ca} \times M_{CaO \text{ total}}(\text{kg/kg}) \quad (2)$$

$MCO_2$  was the mass (kg) of  $CO_2$  gas which could be sequestered by 1 kg industrial solid waste through accelerated carbonation (Eq.2), and  $MCO_2$  increases with the increase of  $\Psi_{Ca}$ .

### III. RESULTS AND DISCUSSION

#### A. Optimization of Process

Several factors were taken into consideration in order to carbonate these materials effectively. Process conditions in the autoclave reactor were varied systematically to determine their influences on the Ca conversion and to identify the optimum carbonation conditions.

#### a. Particle size

Specific surface area can be calculated directly from the diameter (D) value [14] obtained from particle size analysis if materials were assumed sphere particles. The particle size of the raw materials shows an exponential relation. Thus, reducing the mean particle size will increase carbonation degree remarkably (Fig.2(a)). Taking into account energy consumption of grinding, particle sizes of 74  $\mu\text{m}$ ~150  $\mu\text{m}$  were selected for raw materials.

#### b. Reaction temperature

The carbonation reaction is a neutralization reaction<sup>[15]</sup>, so significant heat evolved in this reaction. For the optimum temperature of reaction, some data were acquired (Fig.2(b)). It showed that degree of carbonation increased with temperature ranging from 20 °C to 60 °C. As temperature went beyond the optimum of around 55 °C, conversion decreased with further temperature increase. It was demonstrated that the optimum temperature zone were 55° C~65 °C.

#### c. Reaction Time

As shown in Fig.2(c), the rate of carbonation reaction was initially rapid and then declined gradually. In the first  $t=42$  min period, most  $Ca^{2+}$  was converted to calcium carbonate crystals by combining with  $CO_3^{2-}/HCO_3^-$ ; and in the first  $t=27$  min, the conversion was faster and higher in carbide slag and waste lime, because Ca exists in the form of oxide or hydroxide, which is easier to be leached.

#### d. Carbon dioxide concentration

As shown in Fig.2(d), with carbon dioxide concentration increase, there was significant increase in the degree of carbonation.

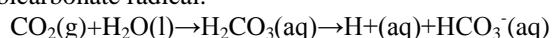
#### e. Water Content

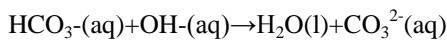
It is well known that water, either in the solid, liquid or gaseous state plays a prominent role in the behavior of porous materials like cementitious composites. Carbonation is not an exception<sup>[16]</sup>. Water is a medium for the carbonation reactions to take place. Too little water prevents the reactions from taking place while too much water can block the pores in the materials, acting as a barrier to the carbon dioxide diffusion. Variation of specimen weight gain with respect to the water content is shown in Fig.2(e).

Under these carbonated conditions, the degree of carbonation were carbide slag 64%, waste lime 72%, steel slag 52% and waste concrete 32% and each kilogram of carbide slag, waste lime, steel slag and waste concrete could sequester  $CO_2$  gas 0.4428 kg, 0.5855 kg, 0.2023 kg and 0.0752 kg respectively.

#### B. Carbonation process and mechanism

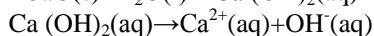
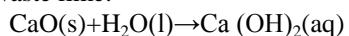
In moist condition, accelerated carbonation reaction could be divided into three steps<sup>[17]</sup>. In each step, the reaction Gibbs free energy ( $\Delta G$ ) is negative<sup>[15]</sup>, which means that carbonation reaction carried out is spontaneous. As a first step, carbon dioxide gas reacted with water to form carbonic acid/bicarbonate radical.



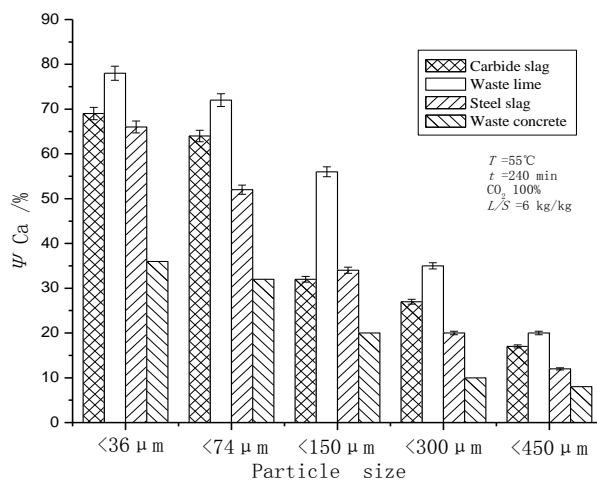


The second step,  $\text{Ca}^{2+}$  leached from raw materials.

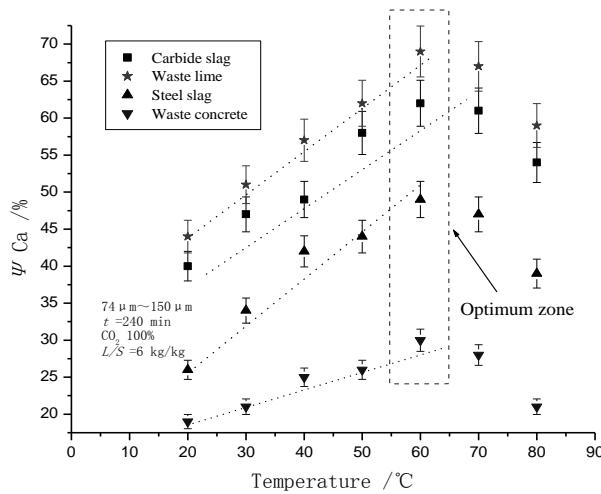
In carbide slag/waste lime:



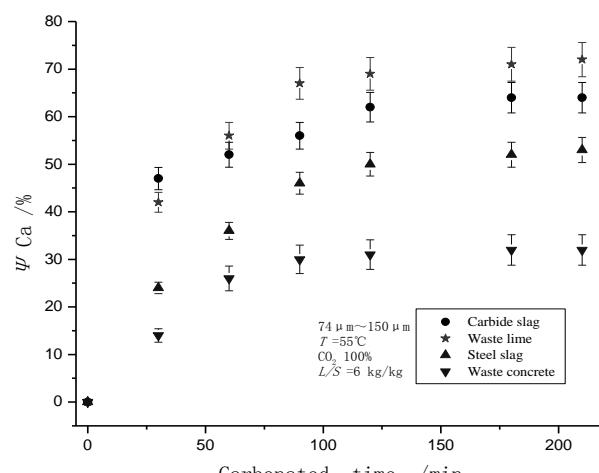
In steel slag/waste concrete:



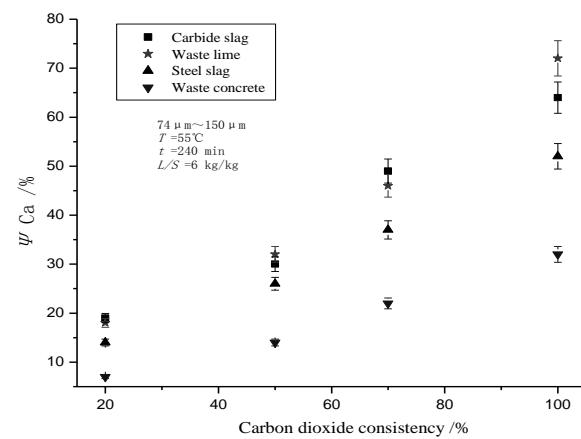
(a) Particle size



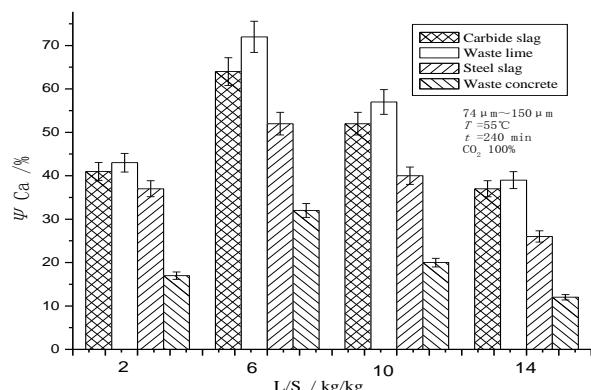
(b) Temperature



(c) Carbonation time

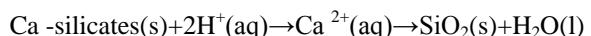


(d) Carbon dioxide concentration



(e) Liquid/Solid

Fig.2: Process variation in accelerating carbonation



$\text{Ca}^{2+}$  combined with carbonic acid/bicarbonate radical to generate calcium/magnesium carbonate in the last step.

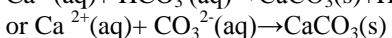
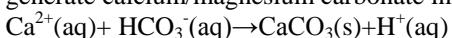


Fig.3 was the pH variation with the progress of accelerated carbonation, and it was tested by fine pH paper. Calcium hydroxide found in carbide slag/waste lime was carbonated quickly, so that the pH value of the samples declined rapidly at the first 27 min and then tended to gently decrease with the Ca consumption.

The calcium existing in steel slag/waste concrete diffused through the solid matrix towards the surface<sup>[16]</sup>. However, the Ca diffusion was found to be hindered by the formation of a  $\text{CaCO}_3$ -layer/coating and a Ca-depleted silicate zone during the carbonation process (as shown in Fig. 4). For this reason, carbonation rate would be decreased subsequently.

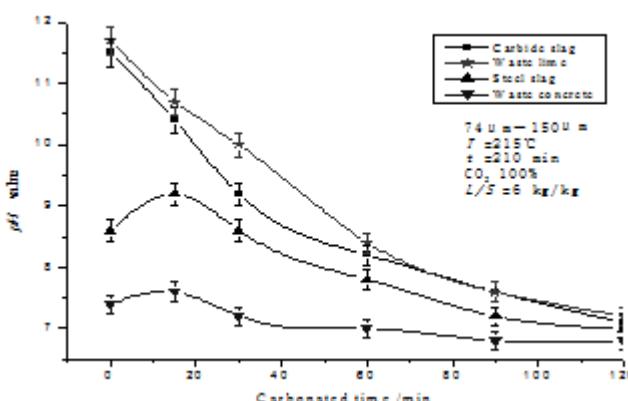


Fig.3: pH variation with the progress of accelerated carbonation

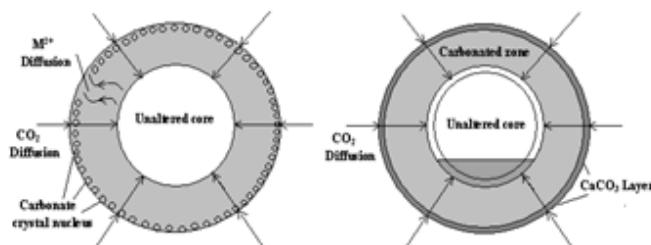


Fig.4: Model of accelerated carbonation of industrial solid waste

Fig.5 was the SEM photos of steel slag. Under typical carbonation reaction conditions ( $t=125$  min,  $\text{CO}_2$  concentration  $c=100\%$ ,  $\text{CO}_2$  pressure  $p=0.6032$  MPa,  $T=55^\circ\text{C}$ , particle size  $74\sim150\ \mu\text{m}$  and liquid-solid ratio  $L/S=6\text{kg/kg}$ ), some calcium carbonate crystals were formed on the sample surfaces (the kind of mineral was identified by XRD, as shown in Fig.7). Solid waste accelerated carbonation reaction was carried out from exterior towards interior, with carbonate crystal nucleus generated on the surface of samples and growing continuously until  $\text{CaCO}_3$ -layer/coating was formed which hindered Ca diffusion and carbon dioxide diffusion.

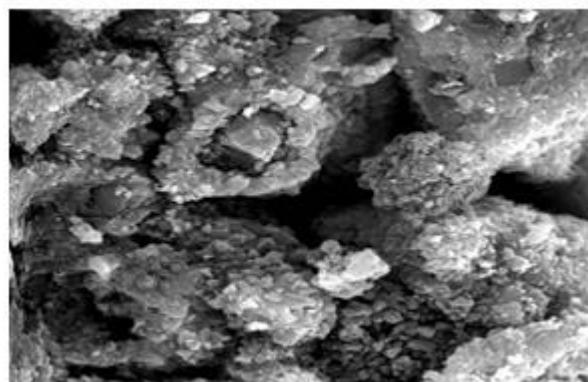


Fig.5: SEM photos of steel slag

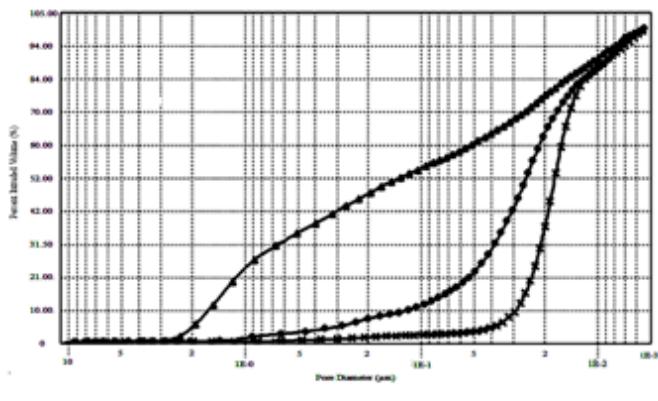


Fig.6: MIP curves of steel slag before and after carbonation

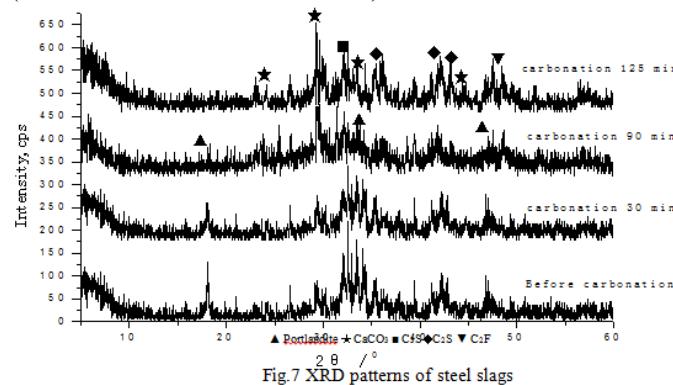
#### C.Preparation of construction aggregate

Fig.6 was the MIP curves of aggregate samples before and after carbonation. As shown in Fig.6, the pore in the raw steel slag had a wider size distribution, which mainly fell between  $0.3\ \mu\text{m}\sim2.0\ \mu\text{m}$ ; the pore size were reduced to  $0.03\ \mu\text{m}\sim0.3\ \mu\text{m}$  after 90 min accelerated carbonation due to the formation of calcite crystal nucleus which filled up the pores. The pores in samples carbonated for  $t=125$  min mainly had sizes between  $0.01\ \mu\text{m}\sim0.03\ \mu\text{m}$ . Most of the  $\text{CaCO}_3$  crystals grew up between  $t=90$  min and 125 min, making pore sizes further reduced.

Under the optimum accelerated carbonation conditions (carbonation time  $t=125$  min,  $\text{CO}_2$  concentration  $c=100\%$ ,  $\text{CO}_2$  pressure  $p=0.6032$  MPa,  $T=55^\circ\text{C}$ , particle size of solid waste= $74\ \mu\text{m}\sim150\ \mu\text{m}$  and  $L/S=6\text{kg/kg}$ ), samples had more compact structure and lower porosity. The compressive strength of natural limestone (5 mm) is about  $300\ \text{N}\sim400\ \text{N}$ <sup>[18]</sup>, and it is an nonrenewable mineral resource. Compression test showed that the strength of artificial aggregate manufactured by the non-carbonated solid residues (carbide slag, residues lime, steel slag, waste concrete) were 86 N, 47 N, 62 N and 39 N, then strength of artificial aggregate manufactured by carbonated one were higher than 224 N, 277 N, 198 N and 104 N respectively, which could be used as one kind of construction aggregate for replacing natural limestone in some projects.

Fig.7 shows the XRD patterns of samples carbonated with

100% CO<sub>2</sub> gas and carbonation time t=0, t=30 min, t=90 min and t=125 min respectively. The intensity of 2θ = 18.1 (Ca(OH)<sub>2</sub>) decreased and that of 2θ=29.4(calcite) increased with longer carbonation time. Some amount of C<sub>3</sub>S was also found reacted. During the first t=90 min of accelerated carbonation, there is a drastic increase in the percentage of calcite. The XRD analysis of carbonated steel slag confirms that the carbonation process converts the gaseous carbon dioxide to solid calcium carbonates in the preferred form of geologically stable calcite. Chemically unstable calcium hydroxide disappears totally after 125-minutes carbonation. It is, therefore, conclusive that the carbonation curing of steel slag can produce a chemically and geologically stable product [19]. So it could solve the problem that a lot of solid residues occupy land and pollute environment, what's more, these solid residues were recycled and non-renewable natural resources (such as limestone and silver sand) were saved.



#### IV. CONCLUSION

As an advanced technology, accelerated carbonation could be used to combine the field of CO<sub>2</sub> sequestration with industrial solid waste disposal. In this process, greenhouse effect was alleviated and solid residues were carbonated to manufacture construction aggregate. The optimum reaction conditions of accelerated carbonation were carbonation time t=125 min, CO<sub>2</sub> concentration c=100%, CO<sub>2</sub> pressure p=0.6032 MPa, T=55 °C, particle size of solid waste=74 μm~150 μm and L/S=6kg/kg. Under these carbonated conditions, the degree of carbonation were carbide slag 64%, waste lime 72%, steel slag 52% and waste concrete 32% and each kilogram of carbide slag, waste lime, steel slag and waste concrete could sequestrate CO<sub>2</sub> gas 0.4428 kg, 0.5855 kg, 0.2023 kg and 0.0752 kg respectively. Accelerated carbonation was initially rapid and carried out from exterior towards interior, calcium carbonate crystals were formed on the surface of samples which hindered calcium leaching and carbon dioxide diffusion. Accelerated carbonation could result in more compact structure and lower porosity of solid residues, and the strength of artificial aggregate (5 mm) made by these carbonated residues were much higher than these non-carbonated ones, so carbonated solid residues could be used as materials to manufacture one type of artificial aggregate replacing natural limestone in some projects.

#### ACKNOWLEDGMENT

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