

# Chapter 15

## Supplementary Cementitious Materials (SCMs) in Cement Mortar

**Abstract** In this chapter, the performance of the blended cement mortar with carbonated solid wastes, including physico-chemical properties, morphology, mineralogy, compressive strength, and autoclave soundness, is illustrated. The specification of performance testing for constricted materials with carbonated solid waste is also provided. In general, a high carbonation conversion of solid waste exhibits a higher mechanical strength in the early stage than pure Portland cement mortar. Moreover, the mortar with carbonated solid waste generally possesses superior soundness to the mortar using fresh solid waste. Since the chemistry of the cement hydrations is complicated and has not been completely clear, the principles and mechanisms of performance enhancement due to the use of carbonated waste in blended cement system are reviewed and discussed.

### 15.1 Introduction

Cement is a binder substance used in construction that sets and hardens to bind other materials together. The most widely used cement is for producing mortar in masonry and concrete (a combination of cements and aggregates to form a strong building material). Fresh alkaline solid wastes, such as iron and steel slags [1], fly ash [2], and bottom ash [3], have been extensively evaluated for potential use as supplementary cementitious materials (SCMs) in a blended cement and/or concrete block.

According to a report from the Portland Cement Association [4], the use of SCMs in blended cement could increase the later-age strength of the concrete, as compared with the use of only Portland cement. SCMs can be divided into two categories: (1) self-cementing or (2) pozzolanic. Self-cementing materials react in a similar manner to Portland cement. In contrast, the pozzolanic materials (primarily siliceous in composition) does not exhibit cementitious properties in the presence of water [5]. In those alkaline solid wastes, several components are known to contribute the hydration of cement, thereby enhancing the strength development of cement. For example,  $\beta$ -C<sub>2</sub>S and C<sub>3</sub>S are known as the primary strength-contributing hydraulic phases in Portland cement (see details in Sect. 15.3: Cement Chemistry). However, in some case, it also may reduce the early-age strength of the

concrete and cement. As a result, in this section, the challenges in the utilization of fresh solid wastes as SCMs are addressed. To overcome the barriers, an alternative is proposed and illustrated by utilizing the carbonated solid wastes (from accelerated carbonation) as SCMs.

### ***15.1.1 Utilization of Fresh Solid Wastes as SCMs***

Table 15.1 presents the uses of fresh alkaline solid wastes as SCMs in cement and/or concrete. For instance, basic oxygen furnace slag (BOFS) and fly ash (FA) are accepted as a pozzolanic material and have been utilized in civil engineering projects for construction. Fresh BOFS or FA is often mandatory material in the production of high-strength concrete as SCMs [6]. The high strength is frequently achieved through an increase in the cementitious material content [4]. For BOFS, however, the following challenges in the utilization as a concrete product or a road base material exist [7–10]:

- It is hard, so grinding to a certain fineness as SCMs is energy-intensive and costly.
- Free-CaO and free-MgO may lead to fatal expansion of hardened cement-BOFS paste.
- The strength of the cement mortar is low, especially for early stage due to their large crystal size in BOFS, although it contains large amounts of  $\beta$ -C<sub>2</sub>S and C<sub>3</sub>S.
- The predominant minerals in BOFS, e.g.,  $\gamma$ -C<sub>2</sub>S, generally have no cementitious characteristics.
- Potential environmental impacts of heavy metal leaching and high alkalinity.

Therefore, the utilization of fresh BOFS as a concrete product or a road base material is still restricted.

### ***15.1.2 Utilization of Carbonated Solid Wastes as SCMs***

To overcome the above challenges, a viable treatment for alkaline solid wastes is through accelerated carbonation process with flue gas CO<sub>2</sub> prior to utilization as SCMs. The use of carbonated solid wastes as SCMs provides several benefits [8, 11]:

- keep globally available industrial alkaline solid wastes out of landfills,
- provide an economic approach to sequester CO<sub>2</sub> at the same time producing SCMs for construction use,
- create an alternative source, thereby reducing the need to transport suitable natural sands or the energy required to produce manufactured aggregates,
- reduce the amount of leachable metals such as chromium after carbonation, and
- reduce the amount of free-CaO and its associated hydration expansion in service.

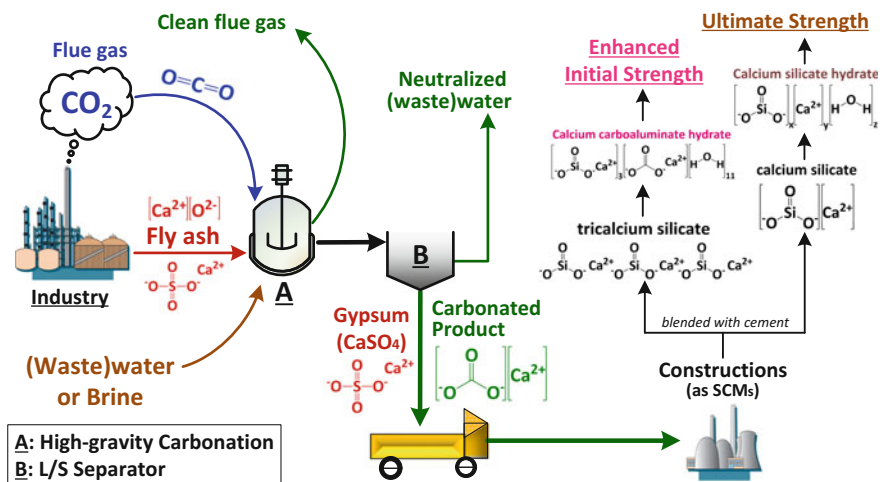
**Table 15.1** Use of fresh alkaline solid wastes as SCMs

Types	Clinker substitutes	Positive characteristics	Limiting characteristics
Self-cementing	Ground blast furnace slag (GBFS)	Higher long-term strength Improved chemical resistance	Low early strength High electric power demand for grinding
	Class C fly ash	Lower water demand Improved workability Higher long-term strength Better durability (depending on application)	Lower early strength Availability changed with fuel sources by the power sector Heavy metal leaching potential
pozzolan	Natural pozzolan (e.g., volcanic ash), rice husk ash, silica fume	Contributes to strength development Better workability Higher long-term strength Improved chemical resistance	Most natural pozzolan leads to reduced early strength Cement properties may vary significantly
	Limestone	Improved workability Improved mechanical properties	Maintaining strength may require additional power for grinding clinker
	Artificial pozzolan (e.g., calcined clay)	Similar to natural pozzolan	Calcination requires extra thermal energy and Reduces positive CO <sub>2</sub> abatement effect
	Basic oxygen furnace slag (BOFS)	Improved workability Improved chemical resistance	Difficulty in grinding potential heavy metal leaching High alkalinity low early-stage strength (<3 days) Low soundness
	Class F coal fly ash	Lower water demand Improved workability Higher long-term strength Mitigated alkali-silica reaction (lower inclusion rates) Raised sulfate resistance	Availability changed with production from bituminous coal Heavy metal leaching potential

Although reuse potentials of carbonated solid wastes are sometimes limited due to the small particle size of the feedstock needed for efficient carbonation reaction, it could be beneficial for subsequent uses. Most applications for iron and steel slags 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<sub>2</sub> sequestration.

Figure 15.1 shows an integrated approach to capturing CO<sub>2</sub> in flue gas and stabilizing solid wastes for utilization as supplementary cementitious materials via a carbonation process. Several researches have investigated the use of carbonated steel slag as SCMs in blended cement [12] and a fine aggregate in concrete [8]. After carbonation, there are both chemical and physical changes in the structure and surface characteristics of alkaline solid waste properties, thereby affecting the performance of blended cement. It is noted that the carbonated product is a solid of lower porosity, lower tortuosity, and lower pore area with calcite infilling the pore space.

Steel slag (such as BOFS) was shown to exhibit less cementitious activity due to the nature of  $\beta$ -C<sub>2</sub>S and C<sub>3</sub>S formed in BOFS compared to those in cement clinker, thereby resulting in a relatively lower early strength. In comparison, iron slag (such as BFS) possesses great cementitious properties, which have been successfully utilized as SCMs in the cement industry. Accelerated carbonation can offer an overall solution to most of the encountered barriers of steel slag utilization, including low cementitious activity, volume instability, and heavy metal leaching. The hydrations of CaO and MgO in the fresh slag may be undesirable for usage as concrete and asphalt aggregate, road base, and fill materials due to the tendency of



**Fig. 15.1** An integrated approach to capturing CO<sub>2</sub> in flue gas and stabilizing solid wastes for utilization as supplementary cementitious materials via a carbonation process. Reprinted with the permission from Ref. [13]. Copyright 2016 American Chemical Society

fresh slag to have high water absorption and expansion properties. This property would be eliminated in the course of carbonation.

## 15.2 Specification of Performance Testing for Constriction Materials

### 15.2.1 Workability, Durability, and Mechanical Properties

Table 15.2 presents the most important properties, including bulk density, shape, resistance to fragmentation (i.e., resistance to impact and crushing), strength, water absorption, resistance to freezing and thawing, volume stability, and resistance to abrasion and polishing. After carbonation, the changes in physico-chemical properties of alkaline solid wastes are observed. The details of changes in physico-chemical properties of solid wastes can be referred to Sect. 5.4 in Chap. 5.

Table 15.3 summarizes the important tests and the associated specifications of cement paste, mortar, and concrete, including workability, mechanical properties, and durability. The use of alkaline solid wastes is closely related to their chemical and physical characteristics. They must be able to withstand static and dynamic forces and environmental strains (such as heat, freeze, rain, and thaw) over the long term. Consequently, the technical properties of processed construction materials are of fundamental importance. In this section, technical requirements in both the American Society for Testing and Materials (ASTM) and Chinese National Standards (CNS) are discussed and compared.

**Table 15.2** Key physico-chemical properties for the application of alkaline solid waste in civil engineering

Properties	Major effect on material performance	Testing methods
Bulk density	Resistance to fragmentation (i.e., resistance to impact and crushing)	ASTM C29/C29 M-16
Shape		Microscope
Hardness	Resistance to abrasion and polishing	Rockwell harness test
C <sub>3</sub> S, C <sub>3</sub> A	Early strength	Chemical analysis
C <sub>2</sub> S	Late strength	Chemical analysis
Sulfate (gypsum)	Set (hardening) of cement	Chemical analysis
Free-CaO, free-MgO	Volume stability	Immersion expansion ratio (USA and Japan) steel slag stability test method (China)
	Water absorption	
Active components (Ca(OH) <sub>2</sub> , free-CaO)	Resistance to freezing and thawing	Chemical analysis
Heavy metals	Leaching behavior	Tank leaching test (Germany) TCLP (Taiwan, ROC)

**Table 15.3** Important testing items and the associated specifications of cement paste, mortar, and concrete

Categories	Testing items	Specimen	Applicable test method	Descriptions
Workability	Normal consistency	Paste	ASTM C187	Amount of water required
	Setting time	Paste	ASTM C150, C191	Vicat time of setting
	Flow test	Mortar	ASTM C1437	Flow and water content
	Bleeding test	Paste/Mortar	ASTM C243	Bleeding rate/capacity
Mechanical property	Compressive strength	Mortar	ASTM C109	Compressive strength
	Flexural strength	Mortar	ASTM C348	Flexural strength
	Tensile strength	Mortar	ASTM C496	Tensile strength
Durability	Autoclave expansion (soundness)	Paste	ASTM C151	Potential delayed expansion caused by hydration of CaO and MgO
	Drying shrinkage	Mortar	ASTM C596	Change in length on drying of mortar bars
	Sulfate resistance	Mortar	ASTM C452	Potential expansion of mortars exposed to sulfate
		Mortar	ASTM C1012	Length change of mortars exposed to sulfate
		Mortar	ASTM C150	
	Permeability	Concrete	DIN 1048	Related to pore structure
Frost resistance	Concrete	DIN 1045	Maximum w/c ratio = 0.60	
Stability	Marshall stability	Asphalt	ASTM D6927	Monitor the plant process
	Resilient modulus	Bituminous	ASTM D7369	Pavement design, evaluation and analysis

Note *MSRC* moderate sulfate-resisting cement; *HSRC* high sulfate-resisting cement

### 15.2.1.1 Workability

Workability is one of the physical parameters of cement mortar or concrete, which indicates the amount of useful internal work to fully compact the mortar or concrete without bleeding or segregation in the finished product. In other words, a cement-based material is said to be “workable” when it is easily placed and

compacted homogeneously without bleeding or segregation. The workability can be determined by several indicators, including

- normal consistency,
- setting time, and
- flowability.

Numerous factors are largely related to the workability and the cement paste hydration, such as

- water-to-cement (w/c) ratio,
- nature of aggregates or supplementary cementitious materials,
- curing age,
- curing temperature,
- mode of compaction,
- placement and transmission methods, and
- humidity of the environment.

It is noted that the rule of thumb for improving the workability of cement/concrete is to increase the mixing time and temperature. Other approaches to improving workability for concrete are to (1) use well-rounded and smooth aggregate instead of irregular shape and (2) use non-porous and saturated aggregate. Regarding the w/c ratio, a significant increase of hydration was observed with the increase of the w/c ratio from 0.23 to 0.47, while the change of hydration becomes insignificant when the w/c ratio increases beyond 0.47 [14].

To maintain consistent workability in cement pastes, a standard flowability of  $110 \pm 5\%$ , as specified by the ASTM C 230 [15], should be maintained by adjusting the quantity of mixing water. Similarly, in CNS, the workability of blended cement, including normal consistency (followed CNS 3590 [16]), flow test (followed CNS 786 [17]), and setting time (followed CNS 786 [17]), should be evaluated. For instance, the setting time of the blended cement via the Vicat test should meet the following standards:

- ASTM C595 [15]: no less than 45 min and no more than 7 h.

### 15.2.1.2 Mechanical Properties

The important mechanical properties for a cement-based material are as follows:

- compressive strength,
- flexural strength, and
- tensile strength.

Concrete can offer relatively high compressive strength but significantly low tensile strength. Therefore, it is usually reinforced with materials that are strong in tension such as steel and rebar, so-called reinforced concrete (RC). The major

composition of concrete includes cement, water, aggregates, supplementary cementitious materials, and chemical admixture. There are several types of blended cement regulated in the ASTM, such as IS (Portland blast furnace slag cement), IP (Portland-pozzolan cement), IL (Portland-limestone cement), and IT (ternary blended cement). The requirements for minimal compressive strength of cement mortar (comparable to Portland cement type I) are provided as follows:

- ASTM C595 [15] and C109 requirements for IL, IP, IS (<70), and IT (S < 70):
  - 3-days strength >1890 psi (13.0 MPa),
  - 7-days strength > 2900 psi (20.0 MPa), and
  - 28-days strength >3620 psi (25.0 MPa).
- CNS 61-R2001 requirement [18]:
  - 3-days strength >1800 psi (12.4 MPa),
  - 7-days strength >2800 psi (19.3 MPa), and
  - 28-days strength >4000 psi (27.6 MPa).

### 15.2.1.3 Durability

The volume stability of mortar with alkaline solid wastes may be a key criterion for using them as a construction material [19]. All applications of alkaline solid wastes and carbonated products would be practicable only if there was sufficient volume stability as the decisive criterion. Since the contact of alkaline solid wastes with water (or moisture in air) might cause these mineral phases to react to hydroxides, a volume increase of the solid waste would be observed, thereby resulting in a disintegration of the pieces and a loss of strength.

#### 1. Contents of free-CaO and free-MgO

The contents of free-CaO (lime) and free-MgO in materials are the most important indicator of volume stability. Typically, the MgO content in the cement is limited to less than 6% [20]. In Germany, good engineering practice (GEP) shows that steel slags with a free-lime content up to 7% may be used in unbound layers, and up to 4% in asphaltic layers [19].

#### 2. Autoclave expansion

In Germany, the steam test is commonly conducted to measure that of iron and steel slags for road construction, while the boiling test is used for hydraulic construction [19]. The standards for a maximum autoclave expansion of blended cement mortar can be found as follows:

- ASTM C596 requirement [15]: <0.80%
- CNS 1258 specification [18]: <0.80%



### 3. Immersion expansion

For iron and steel slags, the test of immersion expansion ratio is commonly used in the USA and Japan to evaluate the volume stability [21]. According to the CNS for “steel slag stability test method” in 2009, the immersion expansion ratio should be limited to

- CNS [22]: <2% for road construction

### 4. Drying shrinkage

The standards for a maximum drying shrinkage of blended cement mortar are shown below:

- ASTM C157/C596 [15]: <0.15% for blended cement with low heat of hydration.

### 5. Sulfate resistance

The sulfate resistance is evaluated by measuring sulfate expansion which represents the formation of expansive ettringite and gypsum. The important factors in determining sulfate resistance of blended cement include [23]

- alumina content of SCMs,
- substitution ratio of SCMs in blended cement, and
- C<sub>3</sub>A content of clinker.

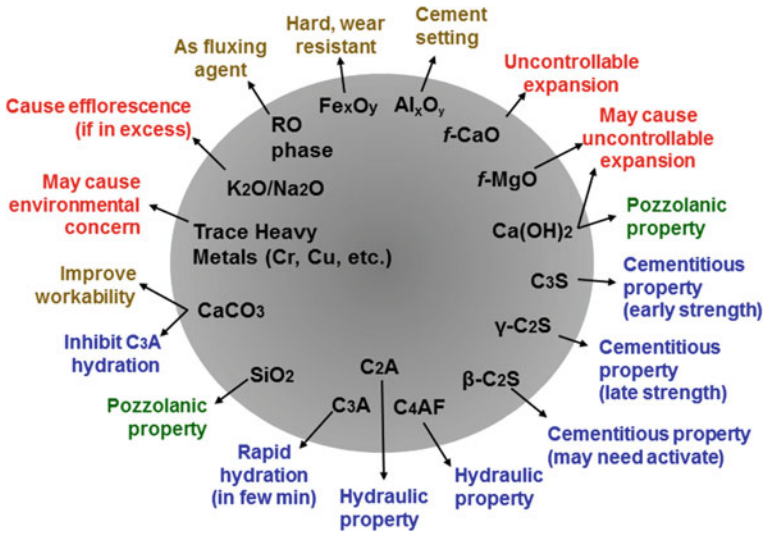
The standards for sulfate resistance of blended cement mortar are shown below:

- ASTM C-1012 requirement:
  - <0.10% (6-month) for moderate sulfate resistance cements,
  - <0.05% (6-month) for high sulfate resistance cements, and
  - <0.10% (12-month) for high sulfate resistance cements.

Several approaches to increasing the sulfate resistance of blended cement have been reported, such as the addition of extra materials (e.g., calcium sulfate and limestone powder) to control the hydration process of blended cement. Extra additions of limestone filler and calcium sulfate reduce the transformation of monosulfate to ettringite by reaction with external sulfate ions by Hoshino et al. [24].

## ***15.2.2 Effect of Chemical Properties on Material Functions***

Figure 15.2 shows the important chemical properties in alkaline solid waste associated with its related properties for the utilization in civil engineering. For example, the physico-chemical properties of steel slags mainly depend on the cooling technique applied [10]. The major mineral compositions contained in steel



**Fig. 15.2** Major chemical compositions in solid wastes (or natural ores) associated with its related properties for utilization in civil engineering

slags include tricalcium silicate ( $C_3S$ ), dicalcium silicate ( $C_2S$ ), RO phase ( $CaO$ – $FeO$ – $MnO$ – $MgO$  solid solution), tetra-calcium aluminoferrite ( $C_4AF$ ), dicalcium-ferrite ( $C_2F$ ), olivine ( $Mg_2SiO_4$ ), merwinite, wustite ( $Fe_xO_y$ ), and lime ( $f$ - $CaO$ ) [19, 25]. As mentioned before, the contents of free- $CaO$  (lime) and free- $MgO$  in materials may cause uncontrollable expansion.

Table 15.4 presents the function of various compounds in cement clinker and their associated ratio in cement. According to their compositions and application, there are five types of Portland cement that exist, as regulated in the ASTM C150. Type 1 Portland cement is known as common (or general-purpose) cement.  $Ca_3SiO_5$  ( $C_3S$ ) and  $Ca_2SiO_4$  ( $C_2S$ ) contents are considered to be the main constituents for strength development in cement. The sum of their component percentage varies from 70 to 80%. For type 1 Portland cement, the compound compositions are 55%  $C_3S$ , 19%  $C_2S$ , 10%  $C_3A$ , 7%  $C_4AF$ , 2.8%  $MgO$ , and 1.0% free- $CaO$ . A limitation on the composition of  $C_3A$  is that it should not exceed 15% [26].

### 15.2.3 Key Evaluation Parameters

Following are the major physico-chemical requirements of ordinary cement and/or supplementary cementitious materials:

**Table 15.4** Function of various compounds in cement clinker and their associated ratio in cement. Information was collected from [27–29]

Categories	Items	Features	Specification
Ingredients of cement	CaO	<ul style="list-style-type: none"> <li>• In excess: (1) cement unsound and (2) to expand and disintegrate</li> <li>• In deficiency: (1) the strength of cement decreases and (2) cement sets quickly</li> </ul>	
	SiO <sub>2</sub>	<ul style="list-style-type: none"> <li>• Imparts strength to cement due to the formation of C<sub>2</sub>S, C<sub>3</sub>S</li> <li>• In excess: (1) greater strength, (2) but prolongs its setting time</li> </ul>	
	Al <sub>3</sub> O <sub>2</sub>	<ul style="list-style-type: none"> <li>• Imparts quick setting quality to cement</li> <li>• Acts as a flux to lower clinkering temperature</li> <li>• In excess: strength of cement decreases</li> </ul>	<7%
	CaSO <sub>4</sub>	<ul style="list-style-type: none"> <li>• Increasing initial setting time of cement</li> <li>• Also added during grinding process for controlling initial setting time</li> </ul>	Added by 3–4% (during clinker grinding)
	Fe <sub>2</sub> O <sub>3</sub>	<ul style="list-style-type: none"> <li>• Provides color, hardness, and strength to cement</li> <li>• Helps fusion of raw materials during manufacture</li> </ul>	<3%
	MgO	<ul style="list-style-type: none"> <li>• Imparts hardness and color to the cement (if in small amount)</li> <li>• In excess: makes cement unsound and leads cracks after mortar or concrete hardness</li> </ul>	< 5%
	SO <sub>3</sub>	<ul style="list-style-type: none"> <li>• Makes cement sound (if present in very small quantity)</li> <li>• In excess: makes cement unsound</li> </ul>	2.1–2.8%
	Alkalies (K <sub>2</sub> O and Na <sub>2</sub> O)	<ul style="list-style-type: none"> <li>• Should be present in small quantities</li> <li>• In excess: cause efflorescence and lead to the failure of concrete from that cement</li> </ul>	<1%
Impurity	Chloride	<ul style="list-style-type: none"> <li>• May restrict the use of some marine deposits</li> </ul>	<0.01%
Composition of cement clinker	C <sub>3</sub> S	<ul style="list-style-type: none"> <li>• Generates more heat and hydrates rapidly than C<sub>2</sub>S</li> <li>• Possesses less resistance to chemical attack than C<sub>2</sub>S</li> <li>• Develops initial strength for the first 28 days</li> </ul>	
	C <sub>2</sub> S	<ul style="list-style-type: none"> <li>• Hydrates and hardens more slowly</li> <li>• Offers resistance to chemical attack (e.g., sulfate)</li> </ul>	

(continued)

**Table 15.4** (continued)

Categories	Items	Features	Specification
		<ul style="list-style-type: none"> <li>• Imparts ultimate strength to the cement (beyond 7 days)</li> <li>• Takes 2 to 3 years for complete hydration</li> </ul>	
	C <sub>3</sub> A	<ul style="list-style-type: none"> <li>• Weak against sulfate attack</li> <li>• Reacts fastly, generating a large amount of heat</li> <li>• Does not contribute to development strength</li> <li>• Causes initial setting of cement</li> </ul>	<15%
	C <sub>4</sub> AF	<ul style="list-style-type: none"> <li>• Poor cementing value</li> <li>• Reacts slowly, generating small amount of heat</li> <li>• Comparatively inactive</li> <li>• Acts as a flux during manufacturing</li> <li>• Contributes to the color effects that makes cement “Gray”</li> </ul>	

### 1. Blaine fineness

The Blaine fineness of a cement powder, usually expressed in units of m<sup>2</sup>/kg, is a single parameter for the characterization of the specific surface area. It is based on the Blaine air permeability test, which is described by ASTM C204. The Blaine fineness of a cement is assumed to be linked to physical and mechanical properties, such as strength, setting time, and flow properties (or rheology) [30]. Table 15.5 presents the Blaine fineness for different materials. For example, the Blaine fineness of OPC is typically in the ranges between 300 and 500 m<sup>2</sup>/kg (i.e., from 3000 to 5000 cm<sup>2</sup>/g).

### 2. Loss of ignition (LOI)

The percentage of loss on ignition (LOI, %) can be calculated as follows:

$$\text{LOI}(\%) = (W/W') \times 100 \quad (15.1)$$

where W is the loss in mass between 105 and 750 °C (221 and 1382 °F), and W' is the mass of moisture-free sample used. It is noted that a high LOI value may result

**Table 15.5** Blaine fineness for different materials

Material	Blaine (m <sup>2</sup> /kg)
Ordinary Portland cement (OPC)	300–500
Limestone filler	200–1100
Raw meal	200–800
Fly ash	200–600
Ground clay	100–200

in discoloration, poor air entrainment, segregation, and low compressive strength of the mixed components. Therefore, the LOI of pozzolanic materials containing fly ashes is typically limited by regulations and standards, for example, to less than 6% in accordance with the ASTM C 618 [2].

### 3. Lime saturation factor (LSF)

The LSF is actually the ratio between the lime (CaO) in the raw material and the maximum amount of lime that can be combined with silica, alumina, and ferrite in the raw meal during burning and cooling. The LSF ranges from 0.90 to 1.04 for ordinary Portland cement (OPC) clinkers, with an average of 0.97 [27].

$$\text{LSF} = (\text{CaO} - 0.7 \text{SO}_3) / (2.8 \text{SiO}_2 + 1.18 \text{Al}_2\text{O}_3 + 0.65 \text{Fe}_2\text{O}_3) \quad (15.2)$$

### 4. Silica ratio (SR)

The SR indicates the solid-to-liquid ratio in the sintering zone of the cement kiln, typically ranging between 1.5 to 4.0, with favorable values between 2.3 and 2.8 [27].

$$\text{SR} = \text{SiO}_2 / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \quad (15.3)$$

### 5. Alumina ratio (AR)

For clinker of normal composition, the AR lays between 1.5 and 4, with favorable values between 1.4 and 1.6 [27].

$$\text{AQ} = \text{Al}_2\text{O}_3 / \text{Fe}_2\text{O}_3 \quad (15.4)$$

### 6. Alkalinity

Alkalinity (A) can be used to evaluate the hydration activities of alkaline solid wastes. If alkalinity is greater than 2.4, the solid wastes should be considered as highly reactive [31].

$$\text{A} = \text{CaO} / (\text{SiO}_2 + \text{P}_2\text{O}_5) \quad (15.5)$$

It is noted that the hydrolysis of BOFS can induce a rapid increase of alkalinity (e.g., the presence of Ca-OH and free-CaO), and the reactivity of steel slag increases with its alkalinity. The contents of free-CaO (as much as 6% in total) in steelmaking slag come from two sources: (1) residual free-lime from the raw material and (2) precipitated lime from the molten slag [32].

### 7. Pozzolanic activity

According to the ASTM: C311-11b [33], the strength activity index (SAI) is usually used to evaluate the pozzolanic activity of the materials:

$$\text{SAI (\%)} = (A/B) \times 100 \quad (15.6)$$

where A is average compressive strength of test mixture cubes (MPa), and B is average compressive strength of control mix cubes (MPa). Normally, the compressive strength of mixture samples at ages of 7 d and 28 d is determined for the pozzolanic activity.

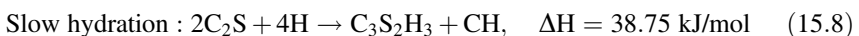
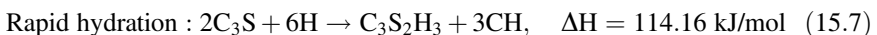
In the ASTM C595, the properties of pozzolanic materials for use in the blended cements are regulated. For example, the SAI index with Portland cement at 28 d should be higher than 75% [15], in accordance with the ASTM C311 test method. Moreover, the LOI of natural pozzolan, fly ash, and silica fume should be lower than 10, 6, and 6%, respectively. Table 15.6 compares the standards of physical properties for ordinary cement (OC) in various regions and/or regulations, such as ASTM, IS, and EN.

### 15.3 Cement Chemistry: Principles

Cements used in construction can be characterized as either hydraulic or non-hydraulic, depending on the ability of the cement to set in the presence of water. In principle, hydraulic cement hardens by hydration in the presence of water, while non-hydraulic cement (such as slaked lime) hardens by carbonation in the presence of CO<sub>2</sub>. Table 15.7 presents the chemical constituents of major oxides in a raw meal for ordinary Portland cement clinker. In the case of hydraulic cement, the components of silicates are responsible for the mechanical properties of the cement. The chemistry of the cement hydration reactions is quite complicated and has not been completely clear.

#### 15.3.1 C<sub>3</sub>S and C<sub>2</sub>S Hydrations

Ca<sub>3</sub>SiO<sub>5</sub>(C<sub>3</sub>S) and Ca<sub>2</sub>SiO<sub>4</sub>(C<sub>2</sub>S) contents are considered to be the main constituents for strength development in cement, where the sum of their component percentage varies from 70 to 80%. As shown in Eq. (15.7), the C<sub>3</sub>S hydrates more rapidly with a higher hydration heat than that of C<sub>2</sub>S and would enhance the initial strength development for the first 28 days. Conversely, the C<sub>2</sub>S hydrates slowly (long-term hydration), as shown in Eq. (15.8), which is responsible for the ultimate strength development (usually takes 2–3 years for its completion hydration).



**Table 15.6** Properties of ordinary cement (OC) regulated in various standards

Standards	LSF	Percentage of alumina to that of iron oxide	Insoluble residue	Weight of magnesia (MgO)	Sulfur trioxide, SO <sub>3</sub>	Loss on ignition, LOI	SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	Standard flow
ASTM C 618 [34], for fly ash	–	–	–	–	<4.0%	<10.0%	>70.0%	110 ± 5%
IS 269-1967/1975 (Indian standard) [28], for OC	0.66– 1.02	>0.66	>2%	<5%	<2.75%	<4%	–	–
EN 196-1	–	–	–	<5%	–	–	–	–

**Table 15.7** Chemical constituents of major oxides in a raw meal for ordinary Portland cement clinker

Types	Constituents	Units	Values		
			[28]	[27]	[7]
XRF	CaO	%	63.0	63–70	–
	SiO <sub>2</sub>	%	22.0	19–24	–
	Al <sub>2</sub> O <sub>3</sub>	%	6.0	3–7	–
	Fe <sub>2</sub> O <sub>3</sub>	%	3.0	1–5	–
	MgO	%	2.50	0.7–4.5	–
	SO <sub>3</sub>	%	1.75	–	–
Mineralogy	C <sub>3</sub> S	%	40	52–85	62.9 ± 1.1
	β-C <sub>2</sub> S + γ-C <sub>2</sub> S	%	32	0.2–27	15.9 ± 0.4 <sup>a</sup>
	C <sub>3</sub> A	%	10.5	7–16	–
	C <sub>4</sub> AF	%	9	4–16	–
	Free-lime (CaO)	%	–	0.1–5.6	–
Thermal analyses	Loss on ignition	%	1.50	–	1.39
	Insoluble residue	%	0.25	–	0.26

<sup>a</sup>for only β-C<sub>2</sub>S

where C, S, and H represent CaO, SiO<sub>2</sub>, and H<sub>2</sub>O, respectively. C<sub>3</sub>S<sub>2</sub>H<sub>3</sub> represents calcium silicate hydrate (C–S–H colloid), which is in a non-crystalline amorphous solid–liquid phase. CH represents Ca(OH)<sub>2</sub>. The C<sub>3</sub>S hydration is considered to contribute to the initial strength development; however, the hydration reaction will release two molar calcium hydroxide, which is unfavorable for the long-term durability of concrete.

### 15.3.2 C<sub>3</sub>A Hydration

In cement, 3CaO·Al<sub>2</sub>O<sub>3</sub>(C<sub>3</sub>A) is the first component to react with water and causes the initial set, as shown in Eq. (15.9). Therefore, the setting speed is mainly related to the reaction of C<sub>3</sub>A with water, where the reaction immediately hardens the paste (i.e., ~ mins) [20].

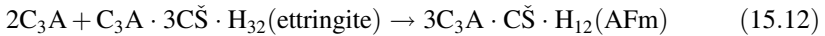
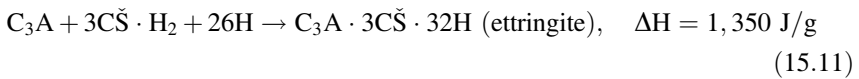
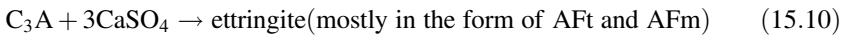


where A represents Al<sub>2</sub>O<sub>3</sub>. The hydration of C<sub>3</sub>A phase displays several features for cement development:

- little contribution to the strength of concrete,
- easily affected by sulfates, and
- great heat of hardening (self-heating), leading to a negative effect on the strength after 28 days.



The negative effect on the ultimate strength development is caused by weakening of cement matrix bond with microcrack formation due to high thermal expansion of air and water in the mortar [35]. Therefore, it is rendered ineffective by adding gypsum ( $\text{CaSO}_4$ ) during the grinding of clinkers [28]. By doing so, the  $\text{C}_3\text{A}$  component is not available in substantial quantity for hydration reaction when water is added to the cement. In Portland cement, when the ratio of  $\text{CaSO}_4$  to  $\text{C}_3\text{A}$  is low, ettringite forms during the early hydration (Eqs. (15.10) and (15.11)) and then converts to the calcium aluminate monosulfate (AFm). When the ratio is intermediate, only a portion of the ettringite converts to AFm and both can coexist, as shown in Eq. (15.12). However, at higher ratios, ettringite is unlikely to convert to AFm.

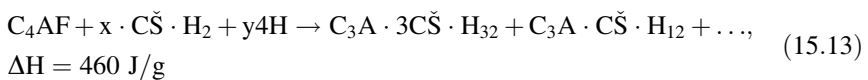


where  $\overset{\check{S}}{\text{C}} \cdot \text{H}_2$  represents  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{C}_3\text{A} \cdot 3\overset{\check{S}}{\text{C}}$  represents ettringite, and  $3\text{C}_3\text{A} \cdot \overset{\check{S}}{\text{C}}$  represents monosulfidic-type calcium aluminate. Magistri et al. [29] suggested that an optimum  $\text{SO}_3$  content in cement mortar should be ranged between 2.1 and 2.8% for early development of compressive strength.

Similarly, using carbonated alkaline solid wastes (with the presence of  $\text{CaCO}_3$  product) in cement mortar as SCMs would affect the  $\text{C}_3\text{A}$  hydration. It is noted that the hydration of  $\text{C}_3\text{A}$  could be suppressed by  $\text{CaCO}_3$  due to the formation of the calcium carboaluminate ( $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ ) on the surface of the  $\text{C}_3\text{A}$  grains [36]. In the absence of  $\text{CaSO}_4$ , the  $\text{C}_3\text{A}$  would react with  $\text{CaCO}_3$  to form both “hexagonal prism” phase (tricarboaluminate,  $\text{C}_3\text{A} \cdot 3\text{CaCO}_3 \cdot 30\text{H}_2\text{O}$ ) and “hexagonal plate” phase (monocarboaluminate,  $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$ ). The formation of the hexagonal  $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$  phase could offer high mechanical strength to the cement samples on the first day of curing [37]. More details are discussed in Sect. 15.4.3.1.

### 15.3.3 $\text{C}_4\text{AF}$ Hydration

$\text{C}_4\text{AF}$ , the main component of ferrite, reacts slowly and generates small amount of reaction heat. It is comparatively inactive and acts as a flux during manufacturing. It contributes to the color effects that makes cement “gray”.



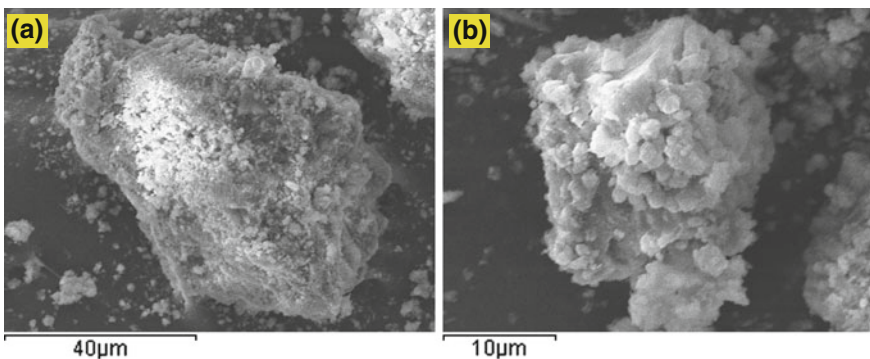
## 15.4 Blended Cement with Carbonated Wastes: Performance and Mechanisms

As aforementioned, various types of carbonated alkaline solid wastes could be considered as a suitable resource in substituting cement as a mortar or concrete block. In this section, the physico-chemical properties of the carbonated solid waste are illustrated, in terms of physical property and morphology, chemical property, and toxicity characteristic leaching procedure (TCLP). Moreover, the performance of workability, mechanical strength development, and durability of blended cement with carbonated solid wastes is reviewed.

### 15.4.1 Physico-chemical Properties

#### 15.4.1.1 Physical Property and Morphology

After accelerated carbonation, both the density and particle size distribution of alkaline solid waste may decrease because the reactive calcium species in the fresh solid waste are gradually leached out during carbonation. This might result in a less dense and shrinking matrix of solid waste [12]. On the other hand, the formation of fine  $\text{CaCO}_3$  precipitates after carbonation would lead to an increase in both fineness and specific surface area. Figure 15.3a, b shows the SEM images of fresh and carbonated steel slag, respectively. Before carbonation, the entire fresh solid waste is smooth without crystallized precipitates on the surface of the particle. After carbonation, the carbonated solid waste exhibited rhombohedral crystals (i.e.,  $\text{CaCO}_3$ ), with a size of 1–3  $\mu\text{m}$ , formed uniformly on the surface of the carbonated solid waste. In addition, the carbonation conversion of alkaline solid waste should affect the changes in physical properties of alkaline solid waste, such as particle size and specific surface area.



**Fig. 15.3** SEM images of (a) fresh and (b) carbonated solid wastes, exemplified by basic oxygen furnace slag

### 15.4.1.2 Chemical Property

The content of free-CaO was observed to be eliminated after carbonation, which can be beneficial to mitigate the expansion potential of mortar containing solid waste. For example, the crystallography of steel slag was examined by XRD analysis [12], indicating that the formed product was  $\text{CaCO}_3$  (i.e., calcite). This evidence reveals that the gaseous  $\text{CO}_2$  is successfully mineralized as calcium carbonate precipitates.  $\text{CO}_2$  was attached onto the surface of the steel slag in the course of carbonation.

### 15.4.1.3 Toxicity Characteristic Leaching Procedure (TCLP)

One of the purposes of toxicity characteristic leaching procedure (TCLP) tests is to evaluate the heavy metal leachability, in accordance with NIEA R201.14C [38]. The TCLP was originally developed by the United States Environmental Protection Agency (USEPA) to simulate the pollutant leaching for solid waste disposal in a landfill [39]. Depending on the pH of the sample, the TCLP procedure uses acetic acid solution ( $\text{pH} = 2.88 \pm 0.05$ ) or acetate buffer solution ( $\text{pH} = 4.92 \pm 0.05$ ) to simulate the presence of metals and organic compounds leached by acid rain. The concentrations of different heavy metals in the solution can be analyzed with inductively coupled plasma-optical emission spectroscopy (ICP-OES), or atomic absorption spectroscopy (AAS).

For example, Table 15.8 presents the TCLP results of basic oxygen furnace slag (BOFS) before and after carbonation. The results indicated the fresh BOFS (F-BOFS) might be classified as hazardous materials because of its high leaching concentration of heavy metals, such as total chromium (Cr) metal greater than 5 mg/L. After the HiGCarb process, however, the carbonated BOFS (C-BOFS) can potentially be used as green building materials since both the C-BOFS-1 and C-BOFS-2 were above the related standards. The leaching concentrations of total Cr metal were significantly reduced, by 99.3%, after carbonation [12]. With the increase of carbonation conversion to 48%, the leaching concentrations of Hg, Cr, and Cr(VI) from BOFS were not detected by ICP-OES. It thus suggests that the accelerated carbonation can effectively improve the physico-chemical properties of BOFS and minimize the leaching of heavy metals (such as Hg, Cr, Ag, and Ba) from solid matrix to become environmentally friendly products.

## 15.4.2 Workability

Extensive studies have been conducted to evaluate the effect of fresh alkaline solid waste on the performance of workability. The water demand of cement paste largely depends on the physical properties of the SCMs and its portion in the blending. It is noted that blended cement with SCMs having a higher surface area would demand a

**Table 15.8** Toxicity characteristic leaching procedure (TCLP) results of fresh and carbonated BOFS comparable to limits by regulations in Taiwan. Reprinted with the permission from Ref. [12]. Copyright 2015 American Chemical Society

Items	Units	Values			Limits by regulations in Taiwan		
		F-BOFS	C-BOFS-1	C-BOFS-2	Utilization Product	Green Building Materials <sup>b</sup>	Hazardous Materials <sup>c</sup>
δ	%	8.8	17.0	47.9	–	–	–
Hg	mg/L	0.0009	0.0005	ND (<0.0003)	0.016	0.005	0.2
Pb	mg/L	ND (<0.029)	ND (<0.029)	ND (<0.029)	4.0	0.3	5.0
Cd	mg/L	ND (<0.0035)	ND (<0.0035)	ND (<0.0035)	0.8	0.3	1.0
Cr	mg/L	6.77	0.065	ND (<0.047)	4.0	–	5.0
Cr <sup>6+</sup>	mg/L	ND (<0.0035)	0.030	ND (<0.0035)	0.2	1.5	2.5
As	mg/L	ND (<0.0007)	0.001	0.002	0.4	0.3	5.0
Se	mg/L	ND (<0.0010)	ND (<0.0010)	ND (<0.0010)	0.8	–	1.0
Cu	mg/L	ND (<0.012)	ND (<0.012)	ND (<0.012)	12.0	0.15	15.0 <sup>d</sup>
Ag	mg/L	0.014	0.007	0.006	–	0.05	5.0 <sup>e</sup>
Ba	mg/L	0.249	0.124	0.088	10.0	–	–

<sup>a</sup>δ = carbonation conversion; <sup>b</sup>leaching limit regulated by Taiwan Architecture & Building Center; <sup>c</sup>leaching limit regulated by NIEA R201.14C, EPA, Taiwan; <sup>d</sup>only for bottom and fly ash from incinerator, sludge, dust, catalyst, filter, etc; <sup>e</sup>only for waste solution from photograph and heliograph production

large amount of water. For instance, compared to a pure Portland cement, the blended cements with fresh alkaline solid waste (e.g., steel slag [7]) present higher water requirement for normal consistency and longer setting time. Moreover, compared to that with fresh solid wastes, the blended cements with carbonated solid wastes exhibit higher water demand due to larger surface areas of the carbonated particles.

On the other hand, the setting time increases with the increase of substitution ratios of SCMs in blended cement pastes. The setting speed is mainly related to the reaction of C<sub>3</sub>A with water, as shown in Eq. (15.14), where the reaction would immediately harden the paste in few minutes [20].

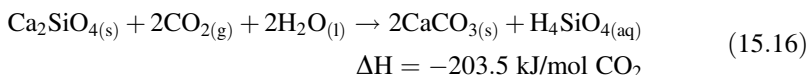
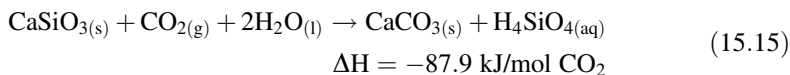


In the case of fly ash (FA) [13], the water demands for both fresh and carbonated FA are typically in the range between 0.26 and 0.29 mL-water/g-cement.

Meanwhile, the setting times for the fresh and carbonated FA at a substitution ratio of 20% were 225 and 320 min, respectively. For comparison, the initial and final setting times of pure cement are approximately 150 and 250 min, respectively. As the FA substitution ratios increase, the total content of  $C_3A$  in cement pastes decreases since the main compositions of FA are  $CaSO_4$  and  $CaCO_3$ , thereby leading to a delay of exothermic peak. According to the experiences [13], the setting times of blended cement pastes with up to 20% substitution ratio of the fresh or carbonated FA met the ASTM and CNS requirements. Furthermore, several studies indicated that incorporation of fine pure  $CaCO_3$  in blended cement could reduce set retardation in ternary blended cement [40–43]. This might be attributed to the fact that the  $CaCO_3$  can provide additional nucleation sites for hydration reaction, thereby reducing the setting time.

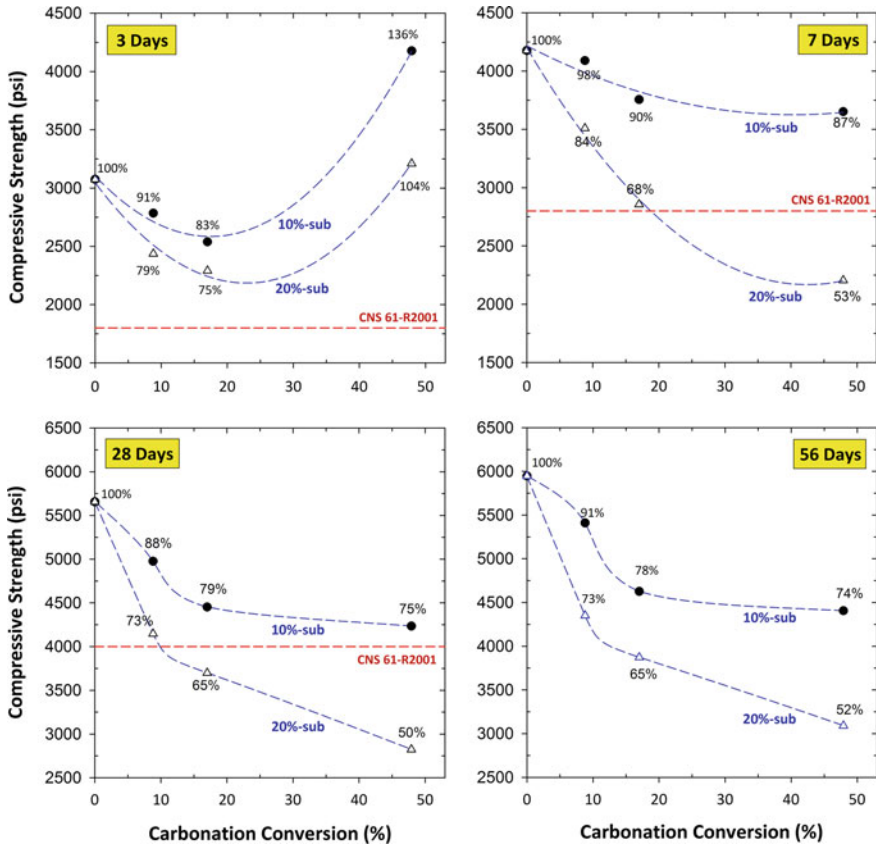
### 15.4.3 Compressive Strength

As the substitution ratio of either fresh or carbonated solid waste increases, the compression strength of blended cement generally decreases due to less OPC amount in mortars, thereby reducing the available  $Ca_3SiO_5(C_3S)$  and  $Ca_2SiO_4(C_2S)$  contents. In addition, after aqueous carbonation, the available calcium silicate contents (e.g., CS,  $C_2S$ , and  $C_3S$ ) may be reduced due to the reaction with  $CO_2$  to form carbonates as shown in the following reaction formulas:



For carbonated BOFS as example, Fig. 15.4 shows the effect of carbonation conversion and substitution ratio on the compressive strength of cement mortar. The percentage numbers (%) presented on each dot represent the relative compressive strength to Portland cement type I mortar. It was found that the cement mortar using carbonated BOFS with a carbonation conversion of 48% exhibited superior 3-day compressive strength to that using pure Portland cement or fresh BOFS. It might be attributed to the fact that the hydration of  $C_3A$  could be enhanced by  $CaCO_3$  to form calcium carboaluminate, which helps to develop a higher mechanical strength in the early stage.

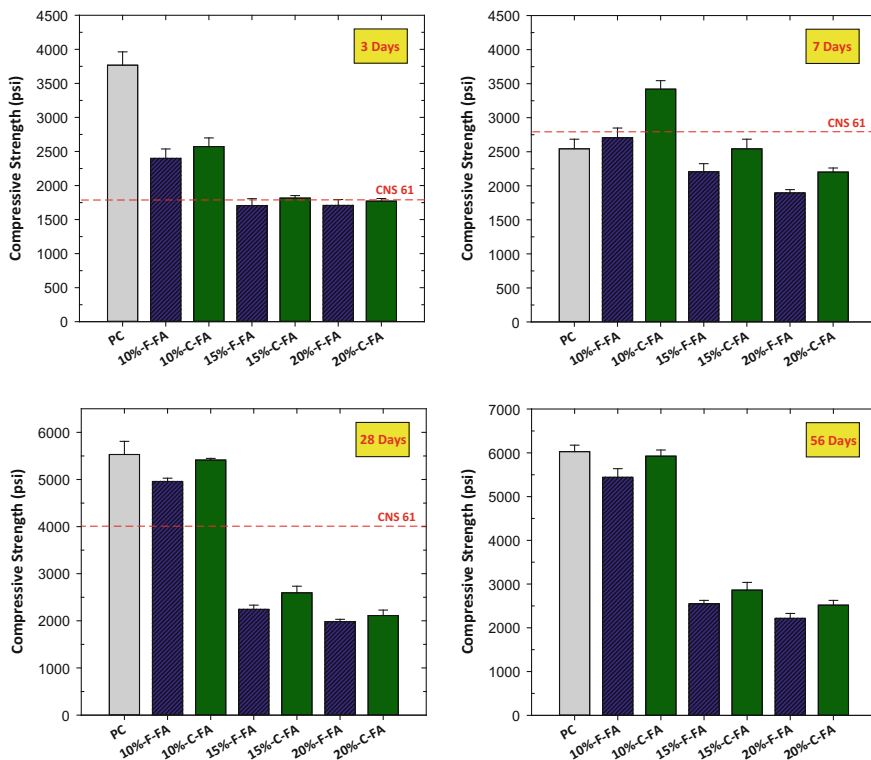
Figure 15.5 shows the compressive strength of blended cement with different substitution ratios of fresh (F-) or carbonated (C-) FA on 3, 7, 28, and 56 days, comparable to CNS-61 requirement in Taiwan. It was noted that similar observation was found in the case of carbonated FA.



**Fig. 15.4** Effect of carbonation conversion and substitution ratio on compressive strength at 3, 7, 28, and 56 days. Carbonation conversion of F-BOFS = 8.8%, carbonation conversion of C-BOFS-1 = 17.0%, and carbonation conversion of C-BOFS-2 = 47.9%. Reprinted with the permission from Ref. [12]. Copyright 2015 American Chemical Society

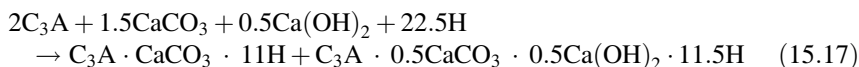
### 15.4.3.1 Early Strength Development

The use of carbonated solid wastes as SCMs can be beneficial to the strength development of blended cement, especially the early-age strength. In some case of carbonated steel slag [12] and fly ash [13], at 7 days, mortar with 10% substitution ratio of carbonated solid waste even exhibited higher initial compressive strength than the OPC mortar. Moreover, Pang et al. [44] found that replacing non-carbonated slags with carbonated slags can result in a 20% increase in compressive strength in 28 days, as well as reduce environmental problems such as the leaching of heavy metals. Compared to non-carbonated slag, the hydration activity indexes of carbonated slag on 3 d and 28 d increase by 97 and 16% at the initial water content of 19% [45]. Similar observations were made in several reports [12]. This might be attributed to the enhanced hydration of  $C_3A$  by  $CaCO_3$  to form stable

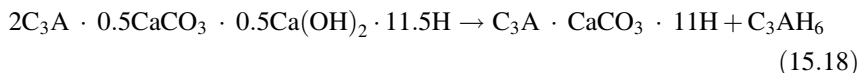


**Fig. 15.5** Compressive strength of blended cement with different substitution ratios of fresh (F-) or carbonated (C-) FA on 3, 7, 28, and 56 days, comparable to CNS-61 requirement in Taiwan. Reprinted with the permission from Ref. [13]. Copyright 2016 American Chemical Society

calcium carboaluminate hydrate ( $C_3A \cdot CaCO_3 \cdot 11H$ ), as described in Eq. (15.17). This helps to develop a higher mechanical strength in the early stage [36].



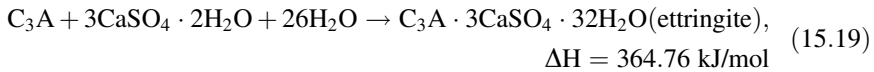
The formed unstable compound ( $C_3A \cdot 0.5CaCO_3 \cdot 0.5Ca(OH)_2 \cdot 11.5H$ ) will continuously convert to calcium carboaluminate after 1 d, as shown in Eq. (15.18).



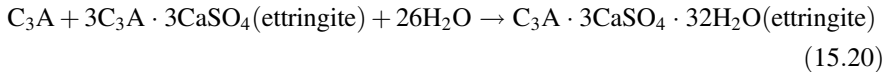
Although the contents of free-CaO and  $Ca(OH)_2$  were reduced in the carbonated solid wastes, the exothermic reaction by the carbonation product ( $CaCO_3$ ) would be faster than  $C_3S$ , which would enhance hydration heat and form carboaluminate hydrate for initial strength development [46]. It suggests that the carbonated BOFS

should be suitable for use as high early strength (HES) cement, specified by the ASTM C39, [47] where rapid strength development is desired.

In some cases, the original matrix of solid wastes comprises a great amount of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), e.g., fly ash (due to the wet desulfurization of flue gas using  $\text{CaO}$ ). The  $\text{C}_3\text{A}$  easily reacts with sulfates (e.g., gypsum) and water to form ettringite, as shown in Eq. (15.19). The formed ettringite can cover the  $\text{C}_3\text{A}$  crystal to prevent  $\text{C}_3\text{A}$  from further hydration. This could also improve the strength development and prolong the setting time of blended cement (as discussed in Sect. 15.2). In general, gypsum is added to reduce the rate of  $\text{C}_3\text{A}$  hydration because  $\text{C}_3\text{A}$  hydration can be hindered by the ettringite layer covering the aluminate crystals and forming an impermeable barrier.

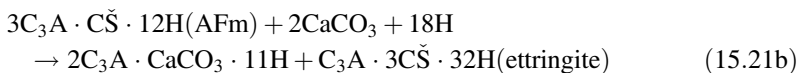
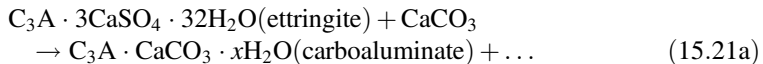


The direct reaction of  $\text{C}_3\text{A}$  with ettringite is also possible, as shown in Eq. (15.20).



The formed ettringite could further react with the uncovered  $\text{C}_3\text{A}$  to form monosulfate (AFm). This means that the amount of ettringite formed at the early stage of hardening will be reduced with the increase of gypsum content. As a result, disturbing the hydration process at early age will also affect the strength development at later age and may even reduce the strength. This suggests that the optimum gypsum content in blended cement is of crucial importance to achieve maximum strength and minimum drying shrinkage. Therefore, the optimal  $\text{SO}_3$  content in blended cement should be in a range between 3.1 and 3.3% [13].

Meanwhile, in the presence of  $\text{CaCO}_3$  (i.e., carbonated solid wastes), the above reaction can be delayed and reduced, due to the formation of monocarboaluminate, as shown in Eqs. (15.21a) and (15.21b). The carboaluminates are more voluminous and potentially stiffer than sulfoaluminates. Similar observation was also found in the literature [48], which indicated that the formation of ettringite was accelerated by  $\text{CaCO}_3$  at the very beginning of hydration (e.g., 30 min).



Tricarbonate is less stable than ettringite at ambient temperature. Sulfate ions are more effective in controlling setting than carbonate ions because sulfate ions enter more readily than carbonate ions into solid solution due to the differences in the



stereochemistry [36]. The contribution of  $\text{CaCO}_3$  in the hydration reactions is only observed primarily on the surface of  $\text{CaCO}_3$  particle. In other words, the  $\text{CaCO}_3$  should be considered an inert material.

Aside from the aforementioned chemical enhancement, physical improvement of blended cement mortar with carbonated solid wastes, which is in highly fine particle size, could result in

- High surface area: This provides activate and favorable sites for nucleation and growth of hydration products, such as C–S–H, thereby accelerating hydration reactions [49, 50].
- Microfiller effect: The  $\text{CaCO}_3$  product can serve as microfiller occupying free spaces between clinker grains, thereby leading to a more compact structure in the early stage. Moreover, liquid cannot intrude into the structure to induce corrosion and further damage to the structure [51].
- Reduced porosity of mortar system: The mechanical properties of cement blended with carbonated solid wastes are also superior to those with uncarbonated solid wastes, especially for early strength [9, 45, 52].

With continuous curing, this effect does not produce additional increases in strength at early stages, unless the blended particle (e.g., cement) is ground finer to compensate. For instance, in the presence of sulfate, the monocarboaluminate can be formed by the hydration of  $\text{C}_3\text{A}$  or  $\text{C}_4\text{AF}$ , if the fineness of  $\text{CaCO}_3$  particles was greater than  $680 \text{ m}^2/\text{kg}$  [53], revealing an increase in reactivity with finer  $\text{CaCO}_3$  or particles.

It suggests that the carbonation product, i.e.,  $\text{CaCO}_3$ , should be superior to the original  $\text{CaO}$  or  $\text{Ca}(\text{OH})_2$  in solid wastes, in terms of physical properties. The volume of  $\text{CaCO}_3$  product is 11.8% greater than that of  $\text{Ca}(\text{OH})_2$  [54]. Pang et al. [44] reported that the number of pores smaller than  $1 \mu\text{m}$  in steel slag decreased by 24.4% after carbonation, resulting in a decrease in water absorption and an increase in impermeability. Moreover,  $\text{CaCO}_3$  is a kind of highly elasticity-resistant material, which can improve early strength when used as SCMs in blended cement [55]. During the carbonation process, the product of micron-sized  $\text{CaCO}_3$  formed gradually in the C–S–H matrix, building up a denser and more compacted structure, which is beneficial to the strength development of blended cement [56–58].

Similar observations were found in the literature for cement pastes containing  $\text{CaCO}_3$ , either as a chemical reagent or as a limestone constituent [12, 35, 49]. At a low addition level of less than 5%, some modification on the heat of hydration at early ages may occur depending on the fineness of  $\text{CaCO}_3$  particles. Also the long-term heat flow would be a bit lower than without limestone because of the smaller fraction of hydrating clinker [49].

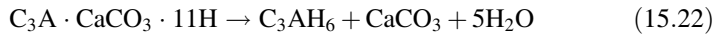
#### 15.4.3.2 Late Strength Development

Most of the strength-developing properties of cement are controlled by  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  (see discussion in Sect. 15.2); however, these components are partially

consumed during carbonation. With the increase of substitution ratio from 10 to 15%, a significant difference in compressive strength after 28 days was observed in the case of carbonated steel slag [12] and fly ash [13]. Therefore, the low pozzolanic (cementitious) activity of carbonate solid waste (such as steel slag) with a relatively higher carbonation conversion caused by the consumption of  $\text{Ca}(\text{OH})_2$  during carbonation can lead to a low strength development at the late stage.

Although the  $\text{C}_3\text{A}$  content in cement (typically  $\sim 10\%$  in clinker) contributes little to the strength of concrete, the  $\text{C}_3\text{A}$  hydration will result in a great amount of hardening heat. The hydration of  $\text{C}_3\text{A}$  provides a decisive effect on the rheological properties of cement paste. A high rate of hydration would result in the saturation of the solution with aluminate and calcium ions and as a consequence to the crystallization of  $\text{C}_4\text{AH}_x$ , leading to the quick stiffening of paste [59]. This might lead to a negative effect on the strength after 28 days by weakening of cement matrix bond with microcrack formation due to its high thermal expansion of air and water in the mortar [35].

In addition, the decomposition of monocarbonate could still occur depending on time, temperature, and humidity of the environment [37]. Partial decomposition of the  $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}$  phase might occur to form  $\text{C}_3\text{AH}_6$  and  $\text{CaCO}_3$  on 7 days, as shown in Eq. (15.22).

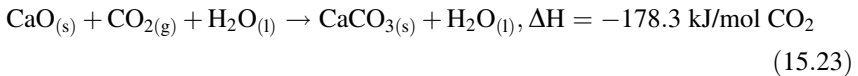


This seems to be one of the key factors that lead to a decrease in the compressive strength after 3 days.

## 15.4.4 Durability

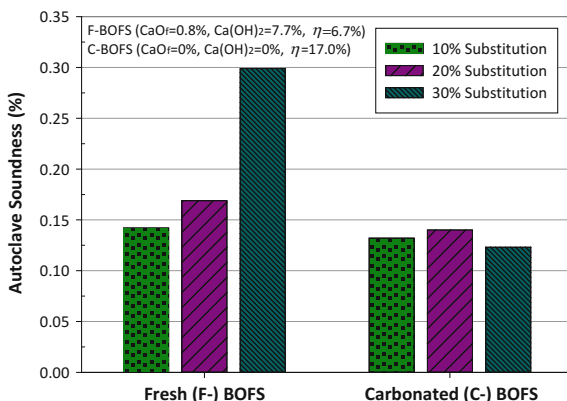
### 15.4.4.1 Autoclave Expansion

Accelerated carbonation is an effective method to improve the durability of blended cement or concrete block because relatively insoluble  $\text{CaCO}_3$  is formed from the soluble and active components, e.g., free- $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$ , in alkaline solid wastes [60, 61]. After carbonation, free- $\text{CaO}$  content in alkaline solid waste could be depleted, even entirely eradicated, as presented in Eq. (15.23), which reduces the risk of fatal fracture from volume expansion [51].



In the case of basic oxygen furnace slag (BOFS), Fig. 15.6 shows the soundness of blended cement mortars with different substitution ratios of F-BOFS (as fresh) or C-BOFS (as carbonated). The expansion capacity of mortar increases with the increases of the substitution ratio of F-BOFS due to higher free- $\text{CaO}$  contents in

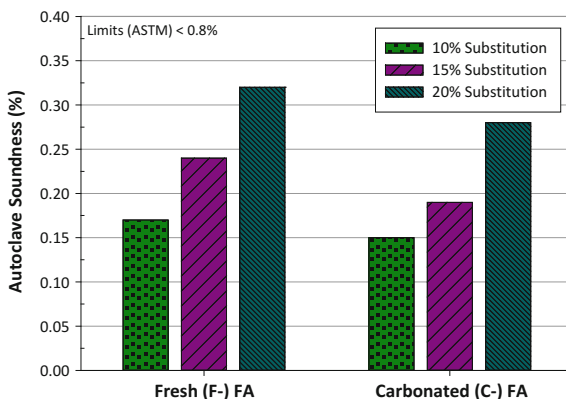
**Fig. 15.6** Autoclave soundness expansion of cement mortar with different substitution ratios using fresh BOFS (F-BOFS) or carbonated BOFS (C-BOFS) with a carbonation conversion of 17%



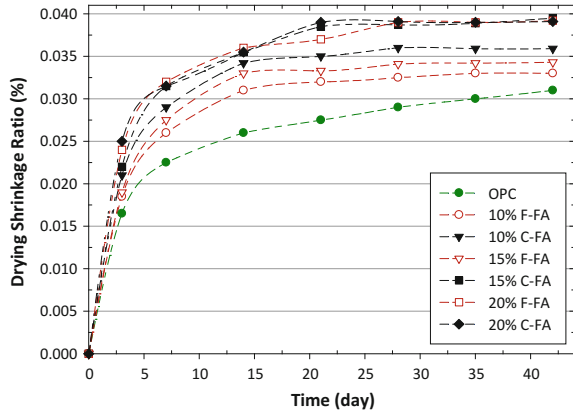
mortar. Using the F-BOFS at a substitution ratio of 20%, the maximal autoclave expansion of mortar was approximately 0.3%. Instead, using C-BOFS in blended cement, the expansion increment could be successfully stabilized at a value of less than 0.15%. This was attributed to the elimination of free-CaO content in C-BOFS with relatively stable compounds (e.g.,  $\text{CaCO}_3$ ).

In the case of fly ash (FA), Fig. 15.7 shows the autoclave expansion of blended cement mortars with F-FA (as fresh) and C-FA (as carbonated). The results indicated that the autoclave expansion of the blended cement mortars increased with the increase of substitution ratio of the FA because of higher free-CaO contents in mortar. In the case of 20% substitution ratio, the maximal expansions for the F-FA and C-FA were about 0.34 and 0.28%, respectively. In all cases of using the C-FA, the expansion increment could be successfully stabilized. This was attributed to the elimination of reactive free-CaO content in the C-FA with relatively stable compounds ( $\text{CaCO}_3$ ).

**Fig. 15.7** Autoclave expansion ratio (soundness) of cement mortars blended with different substitution ratios of F-FA (as fresh fly ash) and C-FA (as carbonated fly ash)



**Fig. 15.8** Drying shrinkage of blended cement with different substitution ratios of F-FA (as fresh fly ash) and C-FA (as carbonated fly ash). All samples were cured in air and exposed a dry environment at 23 °C



Similar observations were also found that the durability of cement mixtures could be greatly enhanced by employing either pure limestone powder [62, 63] or carbonated materials [64, 65] in blended cement. As mentioned before, this can improve not only the dimensional stability but also the tensile strength, stiffness, and durability of cement and/or concrete.

#### 15.4.4.2 Dry Shrinkage

Figure 15.8 displays the drying shrinkage of blended cement mortars, which is comparable to the OPC mortar. This is likely caused by the volume change due to water loss by evaporation in a specimen when the blended cement is exposed to a dry environment. The results revealed that the drying shrinkages of all specimens increased rapidly within the first 7 d and gradually reached to a steady state up to 42 days. The drying shrinkages of all the blended cement mortars containing BOFS were higher than those of OPC control within 42 days. However, no significance damage was observed in the blended cement with up to 20% substitution ratio of the fresh or carbonated FA. All specimens met the ASTM requirement for blended cement with low heat of hydration, i.e., a maximal shrinkage of 0.15% [15].

#### 15.4.4.3 Sulfate Resistance Capacity

Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) in cement paste can react with external sulfates, forming gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) in the hardened cement paste. It is generally believed that the formation of gypsum participates results in the expansion and cracking due to the external sulfate attack [66]. The replacement of Portland cement with SCMs can reduce the amount of calcium hydroxide in cement paste [67]. This

is likely caused by (1) dilution of the Portland cement and (2) consumption of  $\text{Ca}(\text{OH})_2$  by pozzolanic reaction of the SCMs. Therefore, the replacement of Portland cement with SCMs decreases the availability of  $\text{Ca}(\text{OH})_2$  to participate in the formation of gypsum with external sulfates.

## 15.5 Multiple Blended Systems

As described in Sect. 15.4, the encountered barriers of fresh alkaline solid wastes (e.g., F-BOFS) utilization as SCMs in the blended cement, such as instable expansion property and low early-age compressive strength, can be overcome by the carbonation process. However, partial Portland cement replacement by carbonated solid wastes should be limited to a certain ratio (e.g., C-BOFS should be up to 20%), as higher contents would result in a negative impact on the compressive strength of the cement compositions. This is largely due to the reduced amount of the main hydration products which are able to induce bonding properties. Furthermore, the particle size distribution of solid waste as SCMs plays an important role in compressive strength development of blended cement. In the case of both fresh and carbonated steel slag, mortar prepared with either the coarsest (<1.6 mm) or finest fractions (<0.08 mm) of steel slag exhibited significantly lower compressive strengths than the reference OPC mortar [68]. To overcome this challenge, using a mixture formula with different particle sizes of alkaline solid wastes might be a synergetic solution.

The new approach is to introduce the ternary (or multiple) blended system, which might be able to produce high-performance blended cement, with a larger amount of SCMs. A ternary system is a cement mixture that includes two cementitious alternatives into a cement mix, and quaternary mixes utilize three amendments [5]. Due to the variety in characteristics and availabilities of SCMs, it is achievable to blend several types of SCM together in a cement mixture system to meet desired functions. Based on the close packing theory, Zhang et al. [69, 70] proposed a gap-graded blended cement using discontinuous particle size distribution of solid residuals, for example, combined fine and coarse SCMs. This novel method can effectively increase the initial packing density of blended cement paste, thereby enhancing early and late strength development of cement [70]. Moreover, the gap-graded blended cements exhibit a shorter setting time, higher early strength, and superior durability [71].

The use of ternary system and quaternary system can be designed to incorporate less commonly used waste materials and improve the performance of the cement products by combining with different pozzolan [5]. According to the calorimetric and thermogravimetric analyses, a favorable slag–limestone synergy exists that enables high-volume replacement of OPC cement without significant loss in early- and later-age properties [72]. The early-age compressive strengths are beneficially

impacted by the presence of limestone, whereas the clinker factor does not play a significant role in later-age strengths in the blended systems. Compared to direct mixture of limestone OPC, the method of interground limestone with OPC had limited the improvement on the mechanical properties and sulfate resistance [67, 72].

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