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Assessment of long-term reactivity of initially lowly-reactive solid wastes as supplementary cementitious materials (SCMs)

Hafiz Asad Ali[1], Dongxing Xuan[2] and Chi Sun Poon[3*]

1. Ph.D. Candidate, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, Email: asad.ali@connect.polyu.hk
2. Laboratory Manager, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, Email: d.x.xuan@polyu.edu.hk
3. *Chair Professor (Corresponding author), Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, Email: chi-sun.poon@polyu.edu.hk

Abstract

Recently, due to various reasons, the amount of commercial supplementary cementitious materials (SCMs) available for the concrete industry has depleted and hence a wide range of moderately to lowly active solid wastes are being considered as SCMs. However, using such wastes as SCMs needs an efficient and practical procedure to estimate their long-term reactivity. For this purpose, different mechanical and chemical testing schemes have been specified (e.g. Chapelle test, relative strengths, activity index, modified lime reactivity test, R^3 method) to assess their reactivities. In this study, a wide range of solid wastes including incinerated bottom ash (IBA), different colored soda-lime glass powders, fluorescent lamp glass powder (FLGP) and pulverized fly ash (PFA) were tested to evaluate their reactivities. It was found that there were moderate correlations between 180-day relative strengths (RS_{180day}) of standard mortars and the bound water content or portlandite consumption of the R^3 method. Moreover, the mortar strength values of the modified lime reactivity test were adequately correlated with RS_{180day} of the standard mortars. In comparison, the portlandite consumption values of the Chapelle test had a poor correlation with RS_{180day}. In addition, the studied materials can be classified as lowly-reactive (IBA), moderately-reactive (MGP, BGP, WGP, GGP, BGP, FLGP) and highly-reactive (PFA) SCMs.

Keywords: supplementary cementitious materials; reactivity; R^3 test method; Chapelle test; bound water;

1. Introduction

A supplementary cementitious material (SCM) is defined as “an inorganic material that contributes to the properties of a cementitious mixture through hydraulic or pozzolanic activity, or both” (ASTM C125, 2018, p.3). According to this definition, SCMs can be divided into two types: hydraulic material and pozzolanic material (ASTM C125, 2018, p3 and p.6). Natural minerals and industrial by-products can be the sources of SCMs. Traditionally, SCMs commercially used include ground granulated blast furnace slags (GGBS), coal fly ashes (Ca rich and Si rich as FA Class C and Class F), metakaolin (MK) and silica fume (SF) (Carsana et al, 2014; Chen & Poon, 2017; Ferraz et al, 2015; Pal et al, 2003; Poon et al, 2001; Cyr et al, 2007; Donatello et al, 2010; Snellings, 2016; Dyer & Dhir, 2001; Xuan et al, 2018; Chen et al, 2018; Juenger et al, 2019). The use of such SCMs in cement and concrete has many beneficial effects including reducing carbon footprints, lowering costs and improving the physical and durability properties of concrete products.

However, the availability of some of these conventional SCMs has decreased. For instance, in some regions, due to environmental pressure to reduce the burning of coal for energy production, the production of fly ash cannot meet the demand of its usage in concrete (Hossain et al, 2018). Consequently, researchers are looking for alternative SCMs and thus, a wide range of moderately to lowly reactive solid wastes such as incinerated ashes and soda-lime waste glasses are being explored to be used as SCMs.

Different end uses of soda-lime glass wastes (consisting of SiO_2 (65-75%), CaO (6-12%), Na_2O (12-15%), Al_2O_3 (0.5-5%) and Fe_2O_3 (0.1-3%) in its chemical composition) have been explored (Jiang et al, 2019). Dyer and Dhir (2001) studied the pozzolanic activities and alkali silica reactions of finely ground white, green and amber glass powders in blended cements. Their results revealed that high strength and good control of ASR could be achieved in PC blended with finely ground glass cullet (GGC) at low PC replacement levels. Shi et al, (2005) highlighted the influences of morphology and fineness of glass powders (GP-fine, GP-dust, GP-4000 and GP-6000) as well as curing temperature on their pozzolanic activity. Kou and Poon (2009) produced SCC prepared with recycled glass cullet as a replacement of river sand. Bignozzi et al, (2015) investigated sustainable cements blended with different types of waste glass such as crystal glass, cathode ray tubes funnel glass, fluorescent lamps glass and soda lime glass to study their effects on cement hydration and concluded that the use of glasses with a higher amount of glass modifiers with less number of formers and stabilizers were responsible for ASR, while an increased quantity of glass formers and stabilizers with a low quantity of modifiers favored the pozzolanic reaction. Kamali and Ghahremaninezhad (2016) investigated the hydration and microstructure of cement pastes blended with two types of finely ground glass powders and found that glass powders with micro-size distribution as pozzolans could perform better than fly ash-cement pastes. Lu et al. (2017) improved the durability of architectural mortar incorporating waste glass as a pozzolan and aggregates and highlighted that the replacement of 20% cement by GP reduced the drying shrinkage and improved the high temperature and ASR resistance. Liu et al, (2019) produced high strength mortars containing 60% recycled waste glass as a SCM and found a denser microstructure compared with the control.

Another urban waste, namely solid waste incineration ashes, also has the potential to be used as SCM. Bertolini et al, (2004) studied Municipal solid waste incinerator (MSWI) ashes as mineral additions in concrete to investigate the fresh and hardened properties of the resulting products. Their results revealed that wet ground MSWI bottom ash had a good pozzolanicity and enhanced the performance of concrete. Qiao et al, (2008) used thermally treated incinerator bottom ash (IBA) as a cementitious material to produce novel materials. In another study (Qiao et al, 2009) investigated the influences of chemical activators on milled and thermally treated IBA as pozzolans and found that the reactivity of thermally treated IBA was higher than milled IBA. Figueiredo & Pavia (2017) indicated that incinerator bottom ashes also exhibited pozzolanic activity in lime mortars. Another study (Chen and Yang, 2017) investigated the effects of using different size fractions of municipal solid waste IBA on blended cement hydration at the early age and found that smaller particle fraction of IBA had calcareous substances and leachable heavy metals that showed retarding effect on early age hydration. Liu et al (2018) studied the use of alkali treated incineration bottom ash (IBA) in blended cement mortars and indicated that the activity enhancement of IBA was comparable to coal fly ash because of the removal of metallic aluminum which reduced the formation of hydrogen gas during concrete production. However, it normally takes a long time (i.e. usually 90 days) to address the long-term reactivity of such SCMs. Therefore, it can be found that there is no efficient procedure to estimate the long-term reactivity in practice in assessing the lowly-reactive solid wastes as SCMs.

Some researchers proposed using basicity indices to assess the hydraulic activity, and one being the simplest was the measuring the ratio between CaO and SiO_2. The higher ratio means a higher basicity, which would lead to a better hydraulic activity (Pal et al, 2003). Since when the content of CaO is above a certain value, granulation of the ash would be difficult and the glass content would be less likely to contribute to the strength developing of the final products. Similarly, at the constant CaO/SiO_2 ratio, Al_2O_3 plays an important role. A higher content of Al_2O_3, lead to a better strength. It has been observed that increasing the amount of CaO, Al_2O_3 and MgO results in a better activity, while increasing SiO_2 reduces the hydraulic activity. However, these cannot be used to assess the mechanical performance of slags adequately because the hydration mechanism of slag is far more complex.

Traditionally, there are different methods, either mechanical or chemical for the evaluation of the activity of SCMs. For chemical methods, the activity of SCMs is measured by monitoring the consumption of $Ca(OH)_2$ by SCMs and these methods include Chapelle test (NF P18-513), Frattini test (EN 196-5) and saturated lime test (Bahurudeen et al, 2016). On the other hand, mechanical test methods assess and indicate the level of hydraulicity/pozzolanicity of SCMs by the measurement of physical properties such as compressive strength. For instance, the strength activity index (SAI) test method (ASTM C618) classifies a material as a pozzolan if it has a SAI value higher than 75% at 7 or 28 days. Table 1 gives an overview of different test methods currently implemented for the evaluation of the activity of SCMs.

Table 1 Overview of some test methods currently available for evaluating the activity of SCMs

Method	Principle	Limitation
• ASTM C311 "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete"; • ASTM C618 "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete"; • ASTM C989 "Standard Specification for Slag Cement for Use in Concrete and Mortars";	Mechanical performance of SCMs at different curing ages (assessing and indicating the level of hydraulicity or pozzolanicity of SCMs by the measurement of compressive strength)	a) Requires longer time to complete. b) Higher amount of lime in SCMs (e.g. GGBS) may interfere with $Ca(OH)_2$ produced by cement hydration and not assessing the reactivity of SCMs alone. c) The effect of water content on different types of SCMs is unknown d) Fineness of the SCMs may influence the result due to the filler effect.

• ASTM C1240 “Standard Specification for Silica Fume Used in Cementitious Mixtures”; and • IS 1727 “Methods of test for pozzolanic materials, Bureau of Indian Standards, New Delhi, India”		
• Saturated lime test (Modified Frattini test) • Frattini test (BS EN 196-5) • Chapelle or Modified Chapelle test (NF P18-513) • Electrical conductivity test • Selective dissolution techniques	Chemical approaches for evaluation of SCMs activity (Activity of SCMs is measured by monitoring the chemical reaction between SCMs and $Ca(OH)_2$, produced by cement hydration in terms of consumption of $Ca(OH)_2$ by SCMs or treatment with acids/bases or a combination of both to determine the active components in SCMs)	a) Specifically, Frattini test does not give quantitative results b) In Chapelle test, some problems related to carbonation may affect the results; c) Liberation of calcium from other sources d) Leaching of alkalis e) No correlation with mechanical performance f) Aggressive environment for testing g) Reproducibility is low
• R^3 test method	Simplified approach that separates the reactivity of SCMs and easily quantifies from the heat release measurement or bound water content determination during the reaction between SCM and portlandite with the aid of necessary alkali sulfates/carbonates	a) Moisture content (organic residues) in solid wastes such as untreated red mud may interfere with bound water content. b) R^3 pastes preserved under a low vacuum for a long time may introduce the variations (such as carbonation)

However, these test methods might not be appropriate for assessing moderately and lowly active SCMs because of 1) their activities are slow at early ages 2) their strength development increases at later ages 3) variability in properties and heterogeneity in quality of SCMs from different sources. In the light of the aforementioned issues, this study aims to find an efficient procedure to estimate the long-term reactivity of selected lowly active solid wastes when used as supplementary cementitious materials (SCMs) and to classify these materials based on their reactivity in the tests.

2. Materials and Experimental Program

2.1 Materials

Different types of SCMs including incinerated bottom ash (IBA), mixed glass powder (MGP), different colors of soda-lime glass powders (i.e. green glass powder (GGP), brown glass powder (BGP), white glass powder (WGP), blue glass powder (BLGP)), fluorescent lamp glass powder (FLGP) and pulverized fly ash (PFA) were investigated for their activities.

- Quartz sand powder (QSP) was used as a reference due to its inert nature and it was obtained after grinding standard quartz sand (supplier in China) in a ball mill for 4 hours in the laboratory.
- PFA was supplied by a local power plant in Hong Kong, which is a commercial SCM used in concrete.
- Mixed soda-lime glass cullet, glass beverage bottles of different colors and fluorescent lamp glass cullet, were obtained from a local recycler in Hong Kong and ground by a ball mill.
- IBA was sourced from an MSW incinerator and further ground by a ball mill.
- Ordinary Portland cement OPC CEM, ASTM Type I (Green Island Cement in Hong Kong), $Ca(OH)_2$ and all other chemicals (laboratory grade) were also used in this study.
- Standard sand, particle diameter ranging from 0.5mm to 1mm was used, as fine aggregate.

2.2 Properties of materials

2.2.1 Particle size distribution

The raw materials were ground in a ball mill for 4 h by keeping all other factors constant to try to achieve the same particle size distribution. The PSD of all SCMs and their Dv_{mean} sizes (Table. 2) are shown in Fig. 1, measured by using a Laser diffraction particle size analyzer (LS13 320). Most of SCMs exhibited a mean grain dimension of about 20 – 30 μm. In addition, the activity of SCM is highly influenced by the fineness. It’s influence on the reactivity will be evaluated in Section 3.4.3.

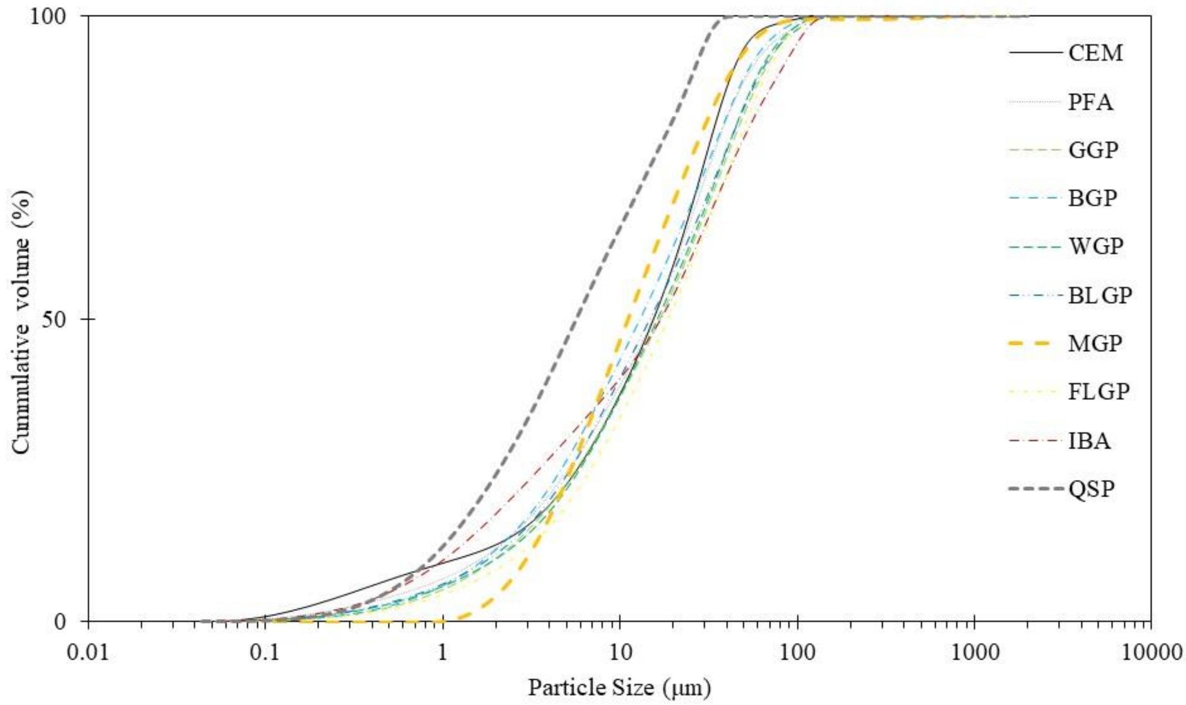

Fig. 1 Particle size distributions of different types of SCMs

2.2.2 Chemical composition

The chemical compositions of SCMs were measured by x-ray fluorescent (XRF) spectrometry and the sum of SiO_2, Al_2O_3 and Fe_2O_3 are shown in Table 2. A good pozzolanic material should contain the sum of SiO_2, Al_2O_3 and Fe_2O_3 higher than 70% in accordance with ASTM C618. In terms of this definition, QSP has 99.2% of SiO_2+Al_2O_3+Fe_2O_3. but this does not mean that it is a good pozzolan because the SiO_2 present in QSP is crystalline. Therefore, a good active SCM cannot be determined by the chemical composition alone, and the mineralogical phases are also important.

Table 1 Chemical compositions of SCMs

Chemical Composition (% by mass)	Type of SCM									
	MGP	WGP	GGP	BGP	BLGP	FLGP	CEM	PFA	IBA	QSP
Na_2O	13.17	13.2	13.2	14	14	15.5			2.52	
MgO	1.64	1.3	1.7	1.2	0.7	2.9	1.47	1.5	1.75	0.1
Al_2O_3	2.10	1.7	2.5	2.2	1.4	2.3	3.77	32.6	8.46	0.5
SiO_2	67.89	71.8	69.9	70	70.9	69.6	19.37	48.5	37.72	97.5
P_2O_5	0.1							0.5	4.02	0.1
SO_3	0.14	0.2	0.1	0.1	0.1	0.2	5.38	1	2.33	
Cl	0.02		0.1			0.1			0.95	
K_2O	0.72	0.1	1	0.7	0.4	1.4	0.69	1.1	1.61	0.2

CaO	10.80	11.4	10.4	11	12.1	6.3	63.85	6.6	21.60	0.2
TiO_2	0.1		0.1		0.1		0.26	1.5	1.1	
Cr_2O_3	0.2		0.2	0.1		0.1			0.2	0.1
MnO							0.06	0.1	0.2	
Fe_2O_3	0.5	0.2	0.7	0.5	0.4	0.3	3.08	6.6	3.95	1.2
others	0.24					0.35			0.9	
SiO_2+Al_2O_3+Fe_2O_3	70.49	73.7	73.1	72.7	72.7	72.2	26.2	87.7	50.13	99.2
Specific gravity	2.75	2.66	2.7	2.64	2.72	2.62	3.21	2.41	2.94	2.73
LOI	2.38	0.1	0.1	0.2		0.95	2.07		12.69	0.1
$D_{V_{mean}}$	17.33	27.21	27.98	22.88	27.05	30.57	21.61	24.57	30.99	10.49

2.3 Mix proportioning of mortars

The mix design of the mortars used as the control and all SCM mixes are given in Table 3. A constant water-to-binder ratio of 0.484 was used. The aggregate-to-binder ratio of 2.75 was chosen (Li et al, 2018; Snellings & Scrivener, 2016; ASTM C311, 2017; ASTM C618, 2012). 20% of cement was replaced by the alternative SCMs in accordance with ASTM C-618 which stipulates this substitution level to evaluate the reactivity of fly ash and natural pozzolans.

Table 3 Mix proportioning of cement mortars used as the control and different types of SCMs

Specimen	Cement (g)	SCM (g)	Aggregate (g)	Water (g)	w/b	a/b
Control	100	-	275	48.4	0.484	2.75
X*	80	20	275	48.4	0.484	2.75

X* represents each SCM mortar

2.4 Preparation of samples for compressive strength test

The compressive strength tests were chosen as a reference test method. The proportioned raw materials were mixed using a laboratory mixer. The dry materials were first mixed for 1 minute. Afterwards, the required water was added into the mixer and mixed for another 3 minutes. At the end, the fresh mixture was cast into 40 mm cubic plastic molds. After casting, the surface of mortar molds was covered with a polyethylene sheet to avoid the loss of moisture. Demolding was carried out after 24 hours. Three control specimens and SCM blended cement mortar specimens were immediately tested for 1-day compressive strength using a compression testing machine with a maximum capacity of 300 kN at a loading rate of 0.6 kN/s. The remaining specimens were placed in a water curing tank at 23^{o}C until the age of 7-day, 28-day, 90-day and 180-day for testing the compressive strength. The relative compressive strength values of the SCM mortars to that of the control were used to serve as benchmarks to compare with other reactivity test methods (i.e.

Chapelle test, R^3 method, modified lime reactivity test) described in the later sections, and is defined as:

$$RS_{time} = \frac{x}{y} \times 100 \quad (1)$$

Where, RS = relative compressive strength at time t, x = compressive strength of mortar blended with 20% SCM/QSP at time t and y = compressive strength of control mortar (100% CEM) at same time t.

2.5 Determination of activity index (AI)

Another way to represent the activity of different types of SCM is the index approach (Hooton and Emery 1983; Pal et al 2003). Keil introduced the hydraulic index of slags using 70% by weight of slag to predict their reactivity alone, i.e. independent of the strengths due to 1) Portland cement in slag-Portland cements and 2) filler effect when finely ground inert material was used. This index also exhibited good relationship with the glass content, fineness and composition of slags. It was opined that this index could give a better range than the ASTM SAI test when applied to other SCMs at lower replacement levels since it reflects the reactivity of SCM alone. So, based on Keil's concept, the activity index (AI) was defined as:

$$AI_{age} = \frac{(a-c)}{(b-c)} \times 100 \quad (2)$$

Where, a = compressive strength of mortar blended with 20% SCM at a specified age, b = compressive strength of control mortar with 100% cement at the same age; and c = compressive strength of mortar blended with 20% QSP at the same age. AI assesses the activity of different types of SCMs and thus indicates their hydraulic or pozzolanic natures.

2.6 Chapelle test (NF P18-513)

The Chapelle test (NF P18-513; Snellings & Scrivener, 2016) is a quick chemical approach to assess the activity of SCM based on the lime consumption by SCM and provides quantitative results. In this approach, 1 g of SCM and 1 g of $Ca(OH)_2$ are first mixed with 200 mL of distilled water. The solution is heated up and kept at the boiling temperature for 16 hours. To prevent water loss, a reflex condenser is used. After 16 hours of boiling, the solution is allowed to cool and then 20 g of sucrose is added and the mixture is stirred for 20 minutes to allow the complex of the Ca^{2+} ions and to dissolve the remaining $Ca(OH)_2$. Afterwards, the solution is filtered through a Buchner filter with a filter paper of 2 μm and titrated with 0.1N HCl using methyl orange as an indicator.
In this study, two blank solutions are made 1) a solution of distilled water and $Ca(OH)_2$ for correction of carbonation and 2) a solution of distilled water and SCM for correction of alkali release from the SCM using the similar setup. The amount of $Ca(OH)_2$ consumed in mg/g of SCM is calculated as:

$$A_{SCM} = \left(\frac{a-b+c}{d} \times 74000\right) \quad (3)$$

Where,
A_{SCM} = activity of SCM in mg of $Ca(OH)_2$ per g of SCM;

a = moles of $Ca(OH)_2$ for reaction products and carbonation;
b = moles of $Ca(OH)_2$ for carbonation;
c = moles of $Ca(OH)_2$ from SCM itself; and
d = weight of SCM

2.7 R^3 method

The aim of the R^3 system is to predict the reactivity of SCM alone and not to interfere with cement hydration in a blended cement system. This simplified approach not only separates the reactivity of SCMs from cement hydration but also easily quantifies from the heat release measurement or bound water content determination during the reaction between SCM and portlandite with the aid of necessary alkali sulfates/carbonates. The use of alkali sulfates/carbonates in R^3 method aims to simulate the cement hydration environment in real situations. The mix proportion (Table 4) and preparation of this system is adopted according to previous studies (Avet et al, 2016; Li et al, 2018). The required materials were weighed, mixed manually for 2 min and placed in an oven at 40°C overnight. Then, these dry materials were mixed with water in a propeller mixer at the speed of 1600 rpm for 2 min and the prepared pastes were used to measure the bound water content and portlandite consumption using thermogravimetry.

Table 4 Mix proportion of R^3 test method

Mix components	**Mass (%)**
SCM	11.11
$Ca(OH)_2$	33.33
KOH	0.24
K_2SO_4	1.20
$CaCO_3$	5.56
H_2O	60.00

2.7.1 R^3 bound water content

The prepared fresh R^3 pastes were placed in plastic containers and sealed to cure at 40°C for 7days. After curing, the hardened samples were crushed into small pieces and placed in an oven to dry at 105°C till constant weight was attained. Then, the dried samples were transferred to cleaned crucibles and placed in a furnace for heating at 350°C for 2h and the bound water was measured according to the Li et al's (2018) approach.

2.7.2 R^3 portlandite consumption

The stopping of hydration of the R^3 pastes (small crushed pieces) after 7 days curing at 40°C were carried out in accordance with Santhanam et al, (2018). Then, the analysis of the dried samples was conducted using thermogravimetry and the portlandite consumption was measured in accordance with previous studies (Li et al, 2018; Scrivener et al, 2016).

2.8 Modified lime reactivity test (modified IS 1727)

The mortar cubes for the modified lime reactivity test were prepared with portlandite: pozzolan: standard sand in the ratio 1:2M:9 (where $M = \frac{specific\ gravity\ of\ pozzolan}{specific\ gravity\ of\ portlandite}$) by weight to maintain the ratio of binder-paste constant in the test mortars. A constant water-to-binder ratio of 0.5 was adopted to assess and compare the reactivity of the pozzolana in terms of compressive strength (modification to IS 1727). After casting, the specimens were placed at 27°C and 90 – 100% RH for 48h. Then the specimens were demolded (except the CH-IBA and CH-QSP samples which were directly transferred to an environmental chamber without demolding due to their low reactive/inert nature), kept at 60°C and 90 – 100% RH for further curing. The compressive strength of the specimen was measured using a compression testing machine with a maximum capacity of 300 kN at a loading rate of 0.6 kN/s after 10 days of curing.

3. Results and discussion

3.1 Relative Compressive strengths

Fig. 2 shows the relative compressive strengths of the mortar specimens at 1, 7, 28, 90 and 180 days for different types of SCMs. All the tested SCMs mortars had lower strengths compared to the control at the early ages (i.e. 1 day and 7 days). Also, a clear difference in strength development could be observed between the control and the tested SCMs at 28th day of curing except for the PFA samples which exhibited higher strengths than the control. The strength of the PFA sample further gradually increased up-to 90 and 180 days indicating that continuous reaction of PFA with portlandite. After a longer curing time, the reaction between the other tested SCMs and $Ca(OH)_2$ generated from cement hydration also increased the strength. Among the glass powders, MGP mortars showed the highest strength. FLGP mortars had lower strengths at early ages and attained comparable strength to that of the other glass powders at the later ages. These results were consistent with previous studies by Bignozzi et al, (2015). They indicated better pozzolanic activities for soda lime glass than fluorescent lamp glass (LMP) because of the higher amounts of glass modifiers in LMP affected its pozzolanicity negatively. It is worth noting that there were no significant strength differences observed among the soda lime waste glasses with different colors. Lastly, IBA mortars showed the lowest compressive strengths at all ages. QSP being the inert material could cause 20% strength reduction due to cement dilution (Donatello et al, 2010).

Based on the above findings, it could be suggested that IBA samples showed low pozzolanic activity; different colors of soda lime glasses and fluorescent lamp glass had moderate pozzolanic nature and PFA exhibited excellent pozzolanic activity.

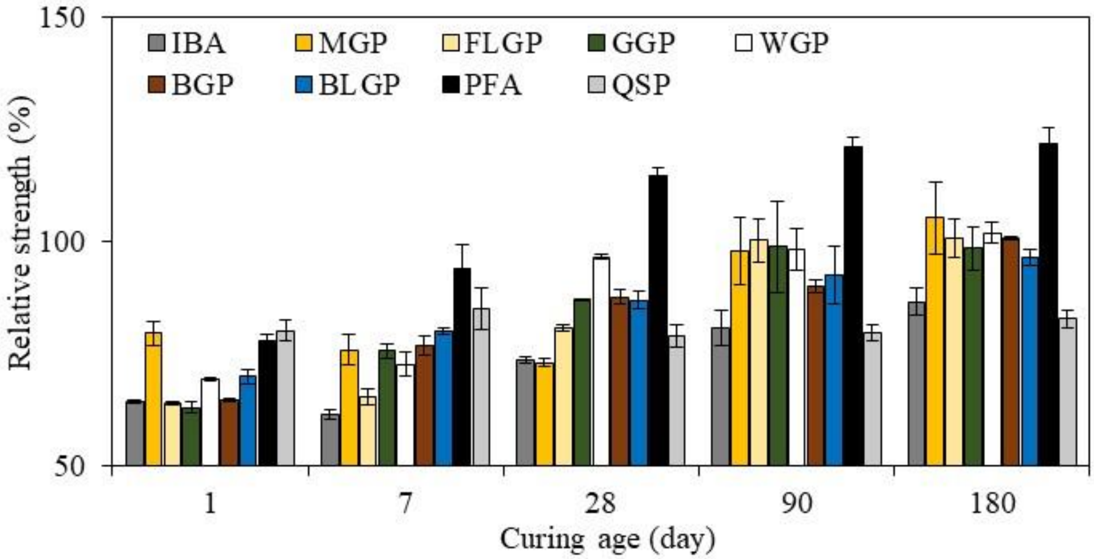

Fig.2 Relative strength of mortars prepared with different SCMs

3.1.1 Activity index (AI) values

Based on Keil's formula, a modified parameter, named activity index (AI) by considering lower replacement levels of tested SCMs in blended cement systems, was used in this study to assess the activity of SCMs since this parameter relates to the activity of SCMs alone (Hooton & Emery, 1983; Pal et al 2003; Gutteridge and Dalziel 1990a; 1990b). Fig. 3 shows the activity indices of cement mortars containing the tested SCMs at different curing ages. This parameter gave the value of 100 for the control and the value of 0 for inert (QSP) mortar specimen. It can be observed that most of the SCMs at early ages gave negative values of AI indicating that these were not active at these ages. A more negative value of AI means a less active SCM. With the increase of the curing time, the reactivity of cement mortars containing the tested SCMs increased. The 1-day AI value of the cement mortars blended with 20% fly ash was negative. However, it gradually increased after a longer curing time due to the formation of additional calcium silicate and calcium aluminum hydrates and reached the highest (AI=225%) among all the SCMs mortars after 180 days. MGP mortars gave slightly negative 1-day AI value (more reactive) compared with other different colored waste glass (BLGP, WGP, BGP, GGP) and FLGP mortars and showed higher AI values at 180 days (higher than control, such as AI=130% for MGP) indicating their higher reactivity at the later ages. SCMs could be classified more precisely based on AI results at the later ages. PFA was the most active material, followed by MGP and WGP which constituted as good active materials. FLGP, BGP, GGP and BLGP represented the class of moderate active materials and IBA was only a slight active material.

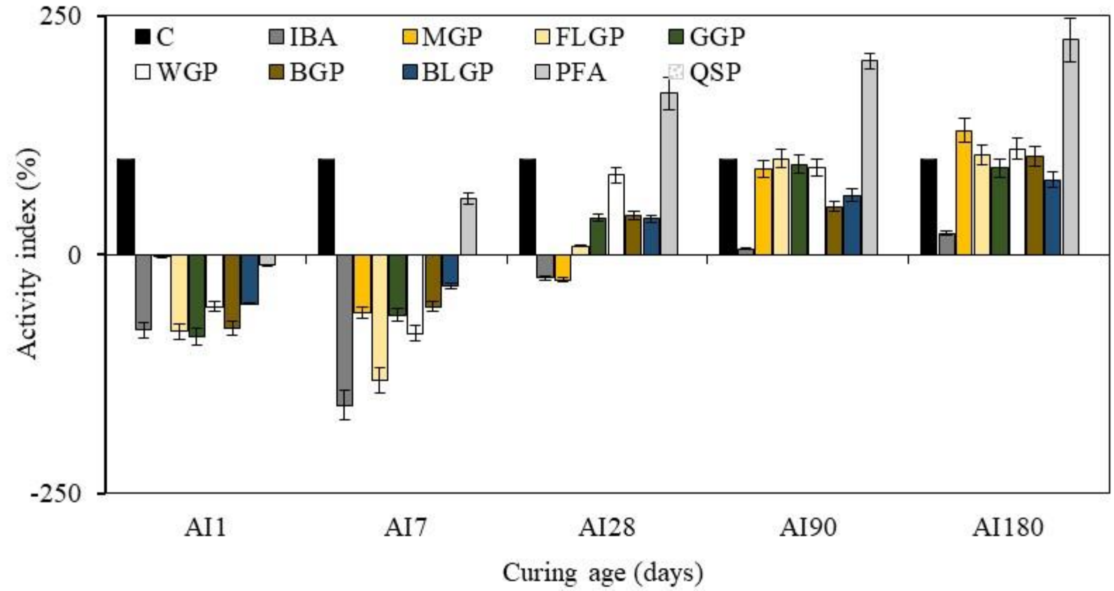

Fig. 3 Activity indices of SCM cement mortars at different curing ages

3.2 Portlandite consumption based on Chapelle test

Fig. 4 shows the portlandite consumption abilities of different SCMs based on the Chapelle test. In this system, a blank solution with portlandite and no SCM was taken as the reference to correct for carbonation. In addition, the same setup without the addition of $Ca(OH)_2$ was used to test each solid waste to phase out the amount of portlandite released from each SCM (Fig. 4). The reactivity order of the chosen SCMs in the Chapelle test was MGP>PFA>GGP>WGP>FLGP>BGP>BLGP>IBA>QSP. MGP consumed more portlandite and it was even higher than PFA because of its smaller particle size as reactivity fundamentally relates to reaction surface area. On the other hand, QSP due to its inert nature was the least reactive in this test method.

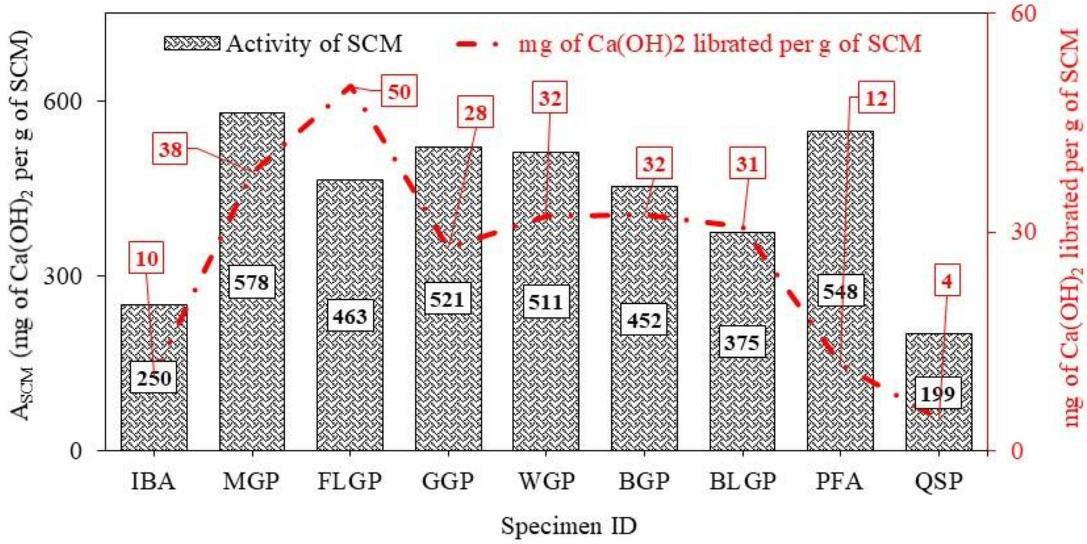

Fig. 4 Activity of SCM (mg of $Ca(OH)_2$ consumed per g of SCM) (portlandite consumption by different SCM based on Chapelle test NF P18-513) and mg of $Ca(OH)_2$ liberated per g of SCM

Even after applying the corrections for carbonation and portlandite released from the material itself, there might be reaction products, unreacted and carbonated portlandite formed and difficult to control during the vigorous hydrothermal treatment at the boiling temperature which would limit the usefulness of this method.

3.3 Portlandite – SCM mortar strength test results based on modified lime reactivity test (modified IS 1727)

Fig. 5 shows the compressive strengths of Portlandite – SCM mortar samples. Higher reactivity of PFA was found due to its reaction with $Ca(OH)_2$ to form more C-S-H, while no reactivity of QSP was found due to its inert nature. On the other hand, incineration ash such as IBA showed less portlandite SCM strength due to their less reactive nature. High curing temperature (60°C) and 10 days of curing were not enough to thoroughly predict their reactivity. Unlike IBA, high temperature curing resulted in reactivity increase of different types of waste glasses.

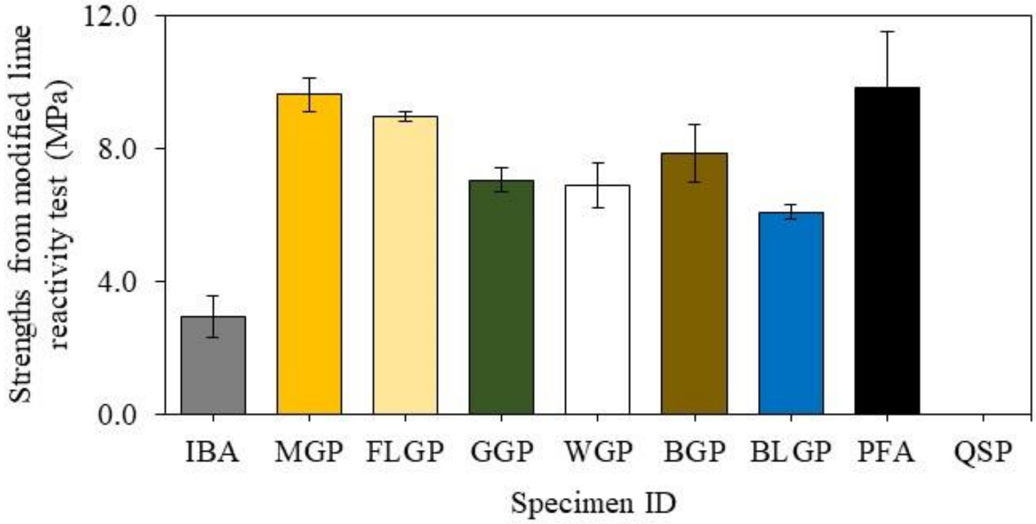

Fig.5 Portlandite-SCM mortar strength results (modified lime reactivity test)

3.4 Results from R^3 test method

3.4.1 Chemical bound water content (BWC) determination

Fig. 6 shows the bound water content of different R^3 SCM systems. It was found that the bound water content (≈ 2.143 g/100g dry paste) was higher for the PFA system. This might demonstrate the higher reaction rates of PFA with portlandite compared with other systems. From the literature (Li et al., 2018), the BWC of a typical PFA is approximately ranged between 2.1 – 2.5 g/100g dry paste and that was consistent with this study. The other solid wastes showed slower reactivities in terms of BWC. Comparing to PFA (Fig. 6), the BWC values for different types and colors of glass powder were ranged between 1.900 – 1.264 g/100g dry paste. Among the studied SCMs, IBA showed the lowest east BWC value (≈ 0.775 g/100g dry paste). This difference in BWC indicates the low reactive nature of the studied SCMs compared to PFA.

3.4.2 Residual portlandite from R^3 test method

Fig. 6 also shows the residual portlandite of different solid wastes in the R^3 SCM pastes. It was noticed that the PFA sample had the lowest amount of residual portlandite (≈ 4.88 wt. %) compared with other SCMs tested. In different kinds of waste glasses, the residual portlandite content was ranged between 6.77 – 8.62 wt. %. The IBA sample consumed the lowest amount of portlandite (≈ 8.77 wt. %). This result also indicates the lowly reactive nature of the studied SCMs.

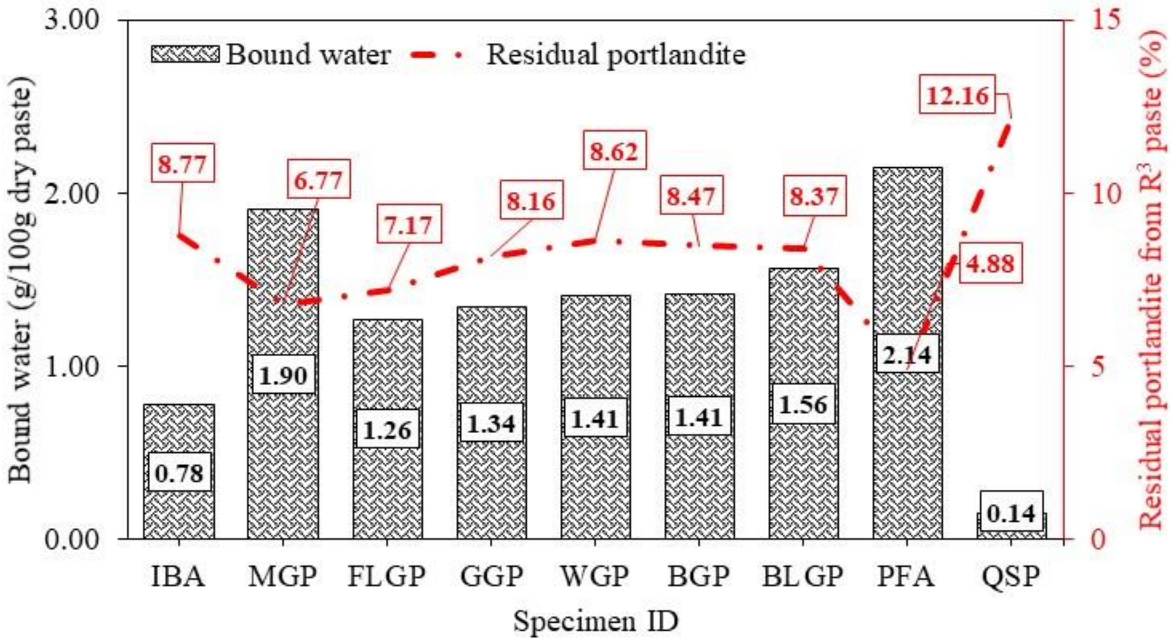

Fig.6 R^3 bound water and residual portlandite contents of different samples

3.4.3 Influence of particle size

In Fig. 7, it can be observed that the bound water content was higher for the MGP (≈ 1.900 g/100g dry paste) compared to other glass powders. This is because of the smaller particle size of MGP as reactivity is fundamentally dependent on the surface area. The other colored glass powders with a similar mean grain dimension between ~23 – 27 µm, had nearly the same reactivity in terms of BWC.

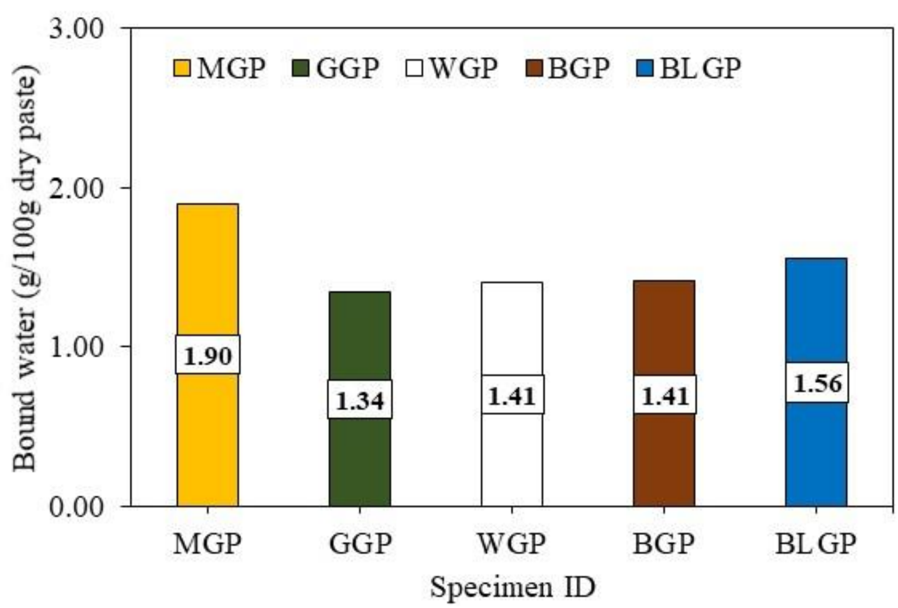

Fig.7 R^3 bound water content of different types of waste glass

3.5 Correlations between reactivity test results

Table 5 shows the linear correlation coefficient (R^2) values between the test results of different reactivity tests and the relative strengths (RS) of the tested SCMs at different curing ages. It can be observed that there were poor correlations between the results of all the reactivity test and RS at ages up to 90 days. That might be due to i) slow reaction between $Ca(OH)_2$ and the tested SCMs in the blended cement system and ii) different SCMs had different strength development rates at different curing time. An increase R^2 values with time can be observed and this could be due to the formation of additional calcium silicate and/or aluminum hydrates after the longer curing time in the systems. Adequate to moderate correlations ($R^2 > 0.75$) can be found between the reactivity test results and RS at the age of 180 days. However, the middle part of the correlation plots was constituted by values obtained from different colored glass wastes that nearly had the same composition and PSDs. Data from a variety of SCMs were therefore required (PFA and QSP in this case) that not only gave some meaningful correlations but also could classify the SCMs as inert (QSP), lowly-reactive (IBA), moderately-reactive (BGP, WGP, GGP, BGP, FLGP) and highly-reactive (PFA).

In addition, at the early ages, the R^3 test method did not work well for the studied SCMs. That might be due to their lowly-reactive nature and slow dissolution rates. In previous literature (Avet et al., 2016; Li et al., 2018), the R^3 test method was mainly used for assessing calcined clays and other highly reactive SCMs which have much better activation potential at early ages compared to the materials used in this study. Also, in a previous study (Suraneni et al, 2019), the authors performed extensive work on assessing the reactivity of a variety of SCMs. Their work mainly focused development of test methods based on portlandite consumption and heat released. But they did not provide relationships between strength development and the results obtained by the different test protocols on lowly reactive SCMs and did not consider the role of sulfates and carbonates in the mix design to simulate real cement environments.

Table 5 Correlation coefficient (R^2) values between reactivity test results and relative strengths at different ages

RS test	Reactivity test results and relative strengths	R^2
1 days	R^3 bound H_2O~RS	0.0138
	Modified lime reactivity~RS	0.1005
	R^3 portlandite consumption~RS	0.0302
	Chapelle test~RS	0.0623
7 days	R^3 bound H_2O~RS	0.1016
	Modified lime reactivity~RS	0.0115
	R^3 portlandite consumption~RS	0.0218
	Chapelle test~RS	0.0378
28 days	R^3 bound H_2O~RS	0.6349
	Modified lime reactivity~RS	0.4107

	R^3 portlandite consumption~RS	0.4702
	Chapelle test~RS	0.5193
90 days	R^3 bound H_2O~RS	0.7435
	Modified lime reactivity~RS	0.6937
	R^3 portlandite consumption~RS	0.7686
	Chapelle test~RS	0.7130
180 days	R^3 bound H_2O~RS	**0.8469**
	Modified lime reactivity~RS	**0.7724**
	R^3 portlandite consumption~RS	**0.8015**
	Chapelle test~RS	0.7320

3.5.1 Correlations between RS_{180day} and R^3 bound water content

Fig. 8 shows a moderate linear correlation (R^2 = 0.85) between R^3 bound water content and $RS_{180days}$, which suggests that the bound water test could be used to assess the strength development of these materials. Using the R^3 bound water might be a good alternative approach to assess the reactivity of such lowly-active SCMs.

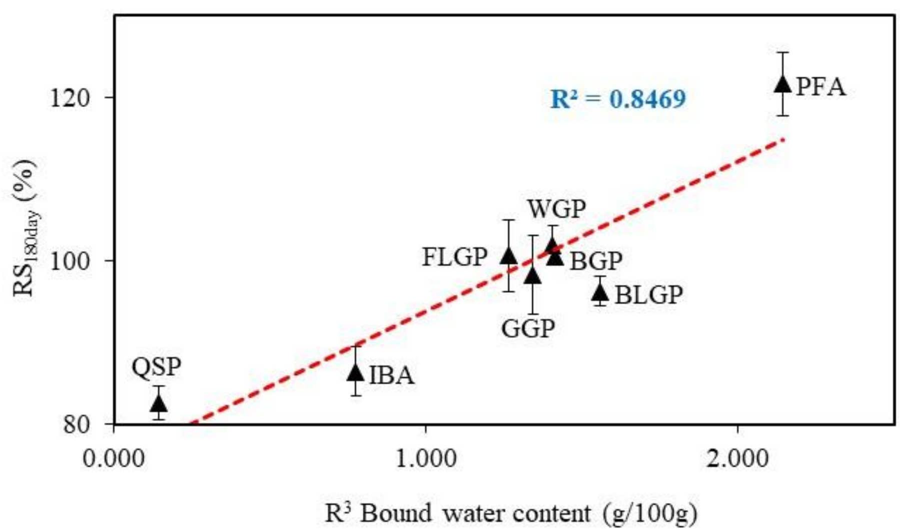

Fig.8 Correlation between R^3 bound water content and relative strength at the age of 180 days

3.5.2 Correlation between RS_{180day} and R^3 residual portlandite

Fig. 9 shows the linear correlation (R^2 = 0.80) between the residual portlandite and $RS_{180days}$. Because this test method involves the stoppage of hydration by an organic solvent, and the specimens are preserved under a low vacuum over silica gel for a longer period. This may introduce errors to some extent (such as by carbonation). This can be overcome by conducting the thermogravimetry as soon as the dried specimens are obtained.

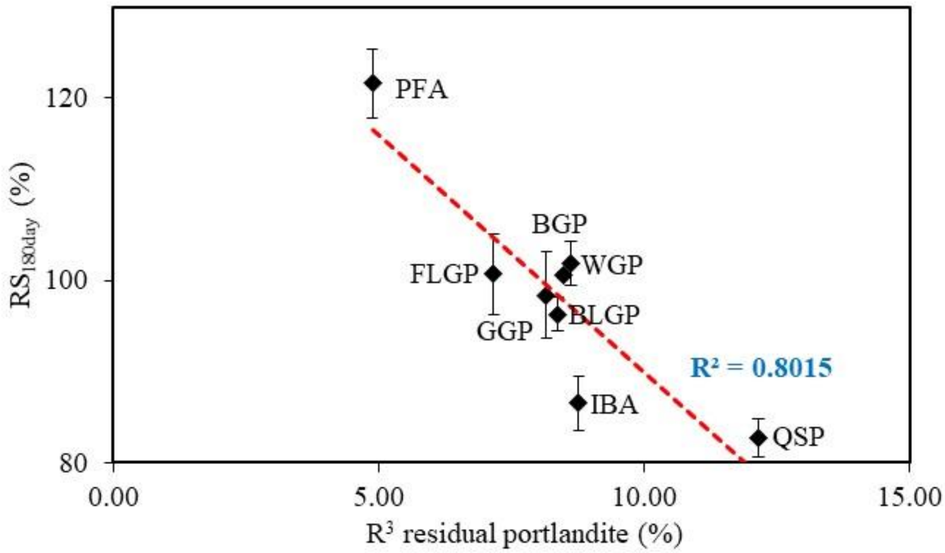

Fig.9 Correlation between residual portlandite (R^3 pastes) and relative strength at the age of 180 days

3.5.3 Correlation between RS_{180day} and portlandite-SCM mortar strengths from modified lime reactivity test

Fig. 10 shows an acceptable linear correlation (R^2 = 0.77) between portlandite-SCM mortar strengths based on the modified IS 1727 test and $RS_{180days}$. To assess the lowly reactive SCMs and to improve the correlation, an increase in the curing temperature, normally to above 60°C, and curing for a longer period (such as >10 days of curing) are suggested. Because it was observed in this study that the 10 days curing at 60°C in the modified IS1727 test gave acceptable although lower correlation coefficients than the R^3 method (might be due to presence of sulfate and carbonates in the R^3 test).

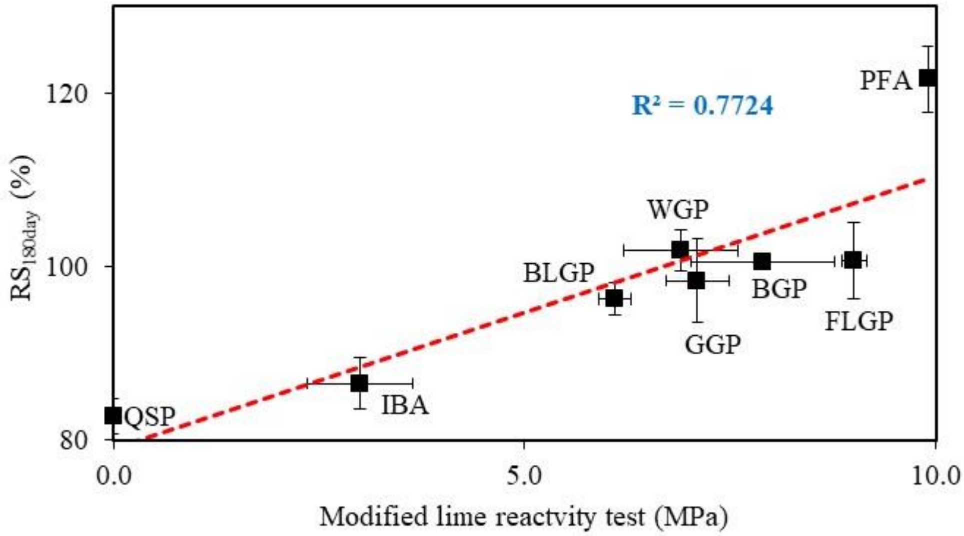

Fig.10 Correlation between portlandite-SCM mortar strengths from modified lime reactivity test and relative strength at the age of 180 days

3.5.4 Correlation between RS_{180day} and Ca $(OH)_2$ consumption based on Chapelle test results

Poor linear correlation (R^2 = 0.73) can be observed between Ca $(OH)_2$ consumption based on the Chapelle test results and $RS_{180days}$ in Fig.11. Even after considering the corrections for carbonation and alkali ($Ca(OH)_2$) released from the SCM itself, correlation ($R^2 < 0.75$) was still not satisfactory. This could be because of the reaction products (such as NASH), unreacted and carbonated portlandite formed during the hydrothermal treatment that could not be controlled.

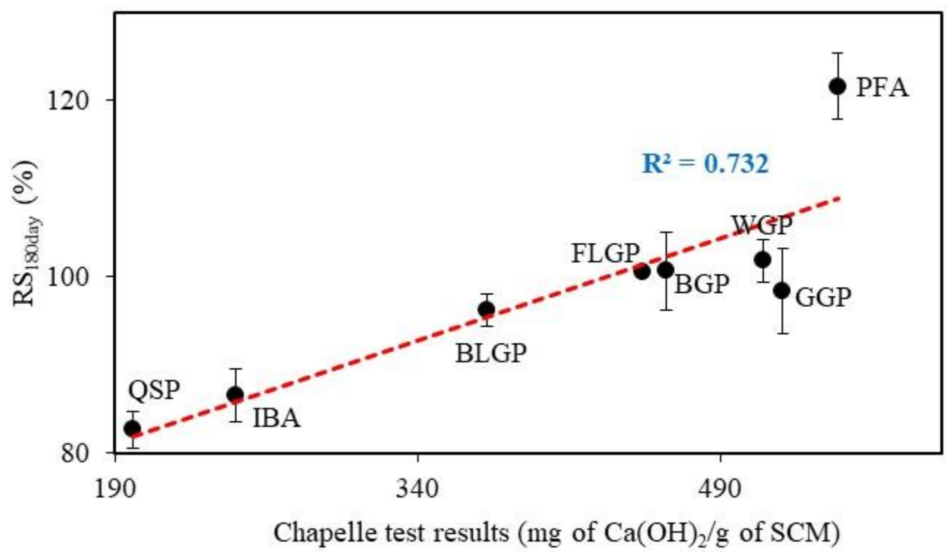

Fig.11 Correlation between Chapelle test results and relative strength at the age of 180 days

4. Conclusions

Due to the limited amount of high-quality SCMs (i.e. fly ash, GGBS), the use of a wide range of moderately to lowly-reactive solid wastes such as soda-lime waste glass and incineration ashes as cement replacement have drawn increasing attention. To apply such SCMs in construction, there is a pressing need to find an efficient and practical procedure for estimating the long-term reactivity of the solid wastes as supplementary cementitious materials (SCMs). In this study, soda-lime waste glass and incineration ashes were evaluated by various available mechanical and chemical testing schemes (i.e. Compressive strengths test, Chapelle test, activity index, modified lime reactivity test, R^3 method). The main findings can be given below:

- There are moderate to good linear correlations (R^2 = 0.85 and R^2 = 0.80) between $RS_{180days}$ and the bound water content based on the R^3 method or the residual portlandite based on the R^3 method, suggesting that the bound water content and the residual portlandite values based on the R^3 method could be used to assess the long term strength development of SCMs.
- An adequate linear correlation (R^2 = 0.77) between $RS_{180days}$ and portlandite – SCM mortar strengths based on the IS 1727 method was found. An increase in the curing temperature and a longer curing period (such as >10 days of curing) may be used to modify IS 1727 in order to improve the correlation for such lowly-active SCMs.
- A poor linear correlation (R^2 = 0.73, less than 0.75) was observed between $RS_{180days}$ and the lime consumption based on the Chapelle test. This could be due to the uncertainties related to the formation of various reaction products (such as NASH) during the vigorous hydrothermal treatment of this approach.

Based on the above findings, the studied materials can be classified as inert (QSP), lowly-reactive (IBA), moderately-reactive (MGP, BGP, WGP, GGP, BGP, FLGP) and highly-reactive (PFA) SCMs. Also, it is suggested that R^3 bound water or R^3 portlandite consumption or the modified lime reactivity test (modified IS 1727) could be used as the alternative rapid approaches instead of SAI test (normally 90 or 180 days of curing are required to assess such SCMs) to predict the long term reactivity of a wide range of moderately to lowly-reactive solid wastes.

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