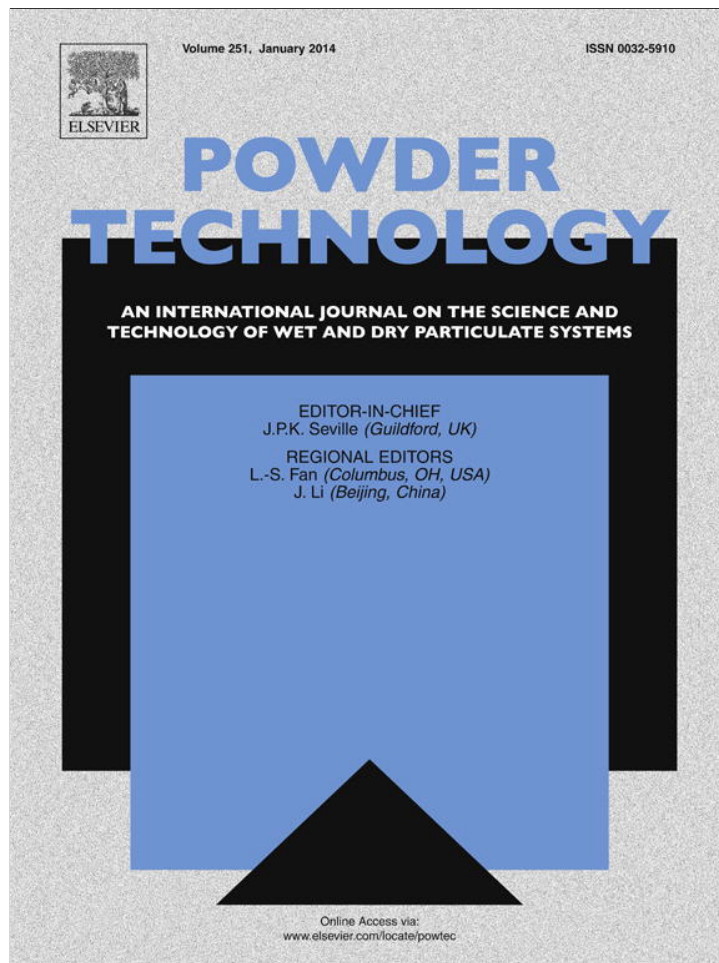


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/authorsrights>



Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Mechanical activation of silicomanganese slag and its influence on the properties of Portland slag cement



Ali Allahverdi*, Salim Ahmadnezhad

Cement Research Center, School of Chemical Engineering, Iran University of Science and Technology, Narmak 1684613114, Tehran, Iran

ARTICLE INFO

Article history:

Received 3 July 2013

Received in revised form 26 August 2013

Accepted 7 October 2013

Available online 24 October 2013

Keywords:

Silicomanganese slag

Setting time

Compressive strength

ABSTRACT

Granulated air-cooled silicomanganese slag from ferro-alloy manufacturing plants is mainly disposed as a landfill waste. On the other hand, it is highly advisable and beneficial to partially replace Portland cement with suitable industrial wastes. The present work investigates the viability of using air-cooled silicomanganese slag as a supplementary cementing material. The silicomanganese slag possesses an acid composition with SiO_2 , CaO , and Al_2O_3 , as main oxides and a MnO -content of nearly 10% by weight. The lime combinability test by thermogravimetry and the results obtained by FT-IR confirm weak to moderate pozzolanic properties compared to silica fume and natural pozzolans. Experimental results prove the effectiveness of mechanical activation for replacement levels up to 35% with no significant variation in setting times. The blended cements fulfill all the chemical requirements of the standard specification and do not exhibit any volume instability. The compressive strength reduction for replacement levels up to 15% and for 3, 7 and 28 days of curing is limited to only about 10%.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Various supplementary cementing materials either natural or artificial (natural pozzolanic materials, fly ash, slags, silica fume, etc.) are currently being utilized as additive in cement production process [1–4]. This is a worldwide experience on sustainable development for conserving non-reproducible raw materials and fuels. Using useless industrial byproducts as a cement replacement, however, provides more benefits including considerable increase in cement production and significant reduction in greenhouse gas emission. Some industrial byproducts (fly ash and slags) are produced in very large quantities worldwide. Traditionally these materials have been used for enhancing concrete properties, but studies have shown that relatively high-volume fly ash or slag concretes can be designed to meet strength requirements for structural as well as high strength applications [5–7]. This has resulted in serious replacement of plain cements with blended or composite cements and considered as an effective and low cost method for increasing cement production capacities in many countries. For example, total US slag shipment including both slag cement as a separate product and slag powder as a component in blended cements has increased from 1.1 million metric tons in 1988 to almost 3.4 million metric tons in 2007 showing more than 200% growth [8]. Therefore it is highly advisable and beneficial to look for suitable supplementary cementing materials to make use of all these benefits.

Slags, which are the secondary products of pyro-processing industries, are considered as an important group in supplementary cementing materials. They are usually produced by water quenching of molten slags.

The resulting glassy materials exhibit some latent hydraulic activities in addition to some pozzolanic character. Some of the industrial slags are now being disposed due to the lack of awareness of their properties. Silicomanganese slag is an example of these slags. This metallurgical slag is different in chemical composition and properties compared to blast-furnace slag produced in steel plants that is widely used in slag cement production. Few research studies are devoted to metallurgical slags other than blast-furnace slag (slags produced in the smelting of non-ferrous metals such as lead, zinc and copper and in the manufacturing of ferro-manganese, ferro-chrome and ferro-silicon alloys) [9–19] and most of these slags are currently useless and simply accumulated or disposed in landfills. Shi et al. [9,11] has reviewed the recent achievements in the development of high performance cementing materials based on activated slags such as blast-furnace slag, steel slag, copper slag and phosphorus slag. Penpolcharoen [10] reported the use of lead slag as an admixture and/or aggregate in the production of concrete blocks. He claimed that the partial replacement of Portland cement with lead slag increased compressive strength and water absorption. Moukwa [12] showed that cements of sufficient quality for general use can be obtained from cobalt furnace slag. Pera et al. [13] characterized the properties of blast-furnace slag containing up to 21% MgO and claimed that high strength mortar and concretes can be produced upon mechanical activation. Rai et al. [16] investigated the possibility of utilizing high MnO and low MnO metallurgical slags from ferro-manganese and ferro-manganese-silicon alloy manufacturing plants. He reported that the composition of a 50:50 blend based on low MnO granulated slag, ground to $300 \text{ m}^2/\text{kg}$ (Blaine), was found to conform to Indian standard for Portland slag cements. Frias et al. [17–19] characterized silicomanganese slag by determining its pozzolanic activity and claimed a denser matrix for hardened cement pastes of

* Corresponding author. Tel.: +98 21 7724 0475; fax: +98 21 7724 0397.
E-mail address: ali.allahverdi@iust.ac.ir (A. Allahverdi).

Table 1
Mix proportions (wt.%, by total weight of the mix).

Silicomanganese slag	0	3	10	15	20	25	30	35
Clinker + Gypsum ^a	100	97	90	85	80	75	70	65

^a All mixes contain 2 wt.% gypsum (by total weight of the mix).

silicomanganese slag blended cements. He also studied the influence of silicomanganese slag on the resistance of cement paste in different aggressive solutions. The results showed good resistance in some aggressive solutions for blended cement pastes incorporating silicomanganese slag (5% and 15% addition) after 56 days of curing. Unfortunately, there is no easy access to reliable statistics on the amount of useless metallurgical slags, but according to Rai et al. [16] India, for example, produces such slags in nearly 30 major alloy-steel plants besides those from foundries and mini-steel plants, and all that simply accumulate.

Silicomanganese slag that is produced in ferro-alloy manufacturing plants is characterized by its relatively high content of manganese oxide (MnO). The few experimental results published on silicomanganese slag offer contradictory conclusions. Some research works concluded a loss of hydraulic properties in slag due to relatively high amount of MnO [13,14], while other works, for example, Taneja et al. [15], did not find any relationship between hydraulic properties and MnO content. These contradictory results show the need for more detailed investigations on possibility of utilizing silicomanganese slag as a suitable supplementary cementing material.

This work is devoted to mechanical activation of granulated air-cooled silicomanganese slag as the byproduct of silicomanganese ferro-alloy industry. A number of cement mixes with different replacement levels and different Blaine finenesses were prepared and investigated for their soundness, main engineering properties and microstructures.

2. Experimental

2.1. Materials

The silicomanganese slag was provided from Faryab ferro-alloy plant located in Hormozgan province in Iran. This industrial unit has two semi-closed electric arc furnaces and annually produces 15,000 tons of slag. A huge pile of almost 200,000 tons of slag has also been accumulated adjacent to the plant site. Since air-cooling is more economical than water-cooling and there is no need for water treatment plant, the unit benefits from air-cooling operation. The silicomanganese slag is, therefore, supposed to exhibit weak

Table 2
Chemical composition of the starting materials.

%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	MnO	LOI
Clinker	21.54	5.29	3.77	64.96	1.88	2.08	0.39	0.69	–	0.10
Gypsum	1.66	0.60	0.30	30.93	1.48	44.18	0.02	0.06	–	19.88
Slag	38.17	14.78	1.79	29.30	2.77	0.12	0.42	0.76	10.29	1.12

Table 3
Fixed lime content of silicomanganese slag, silica fume and some natural pozzolans upon hydration in the presence of lime.

Material	Fixed lime (wt.% by weight of material)				
	1 day	3 days	7 days	14 days	28 days
Silica fume	84.46	97.57	100	–	–
Taftan natural pozzolan	22.50	42.26	58.75	60.36	64.87
Bojnord natural pozzolan	–	28.18	37.98	40.03	53.14
Sirjan natural pozzolan	–	33.39	38.45	42.58	48.72
Silicomanganese slag	–	27.34	35.84	40.08	46.28

pozzolanic activity. The following tests were performed to characterize the properties of the silicomanganese slag:

- Wet chemical analysis in accordance with ASTM C114
- X-ray diffractometry (Siemens D5000 diffractometer with the following conditions: 35 kV, 20 mA, Cu-K α radiation)
- FTIR spectroscopy (Shimadzu 8400S spectroscope)
- Thermogravimetry (Netsch, STA 449C, thermogravimeter)

The hydraulic and/or pozzolanic properties of the slag were evaluated based on lime combinability tests carried out by thermogravimetry and FTIR spectroscopy. A thoroughly homogenized binary mixture of

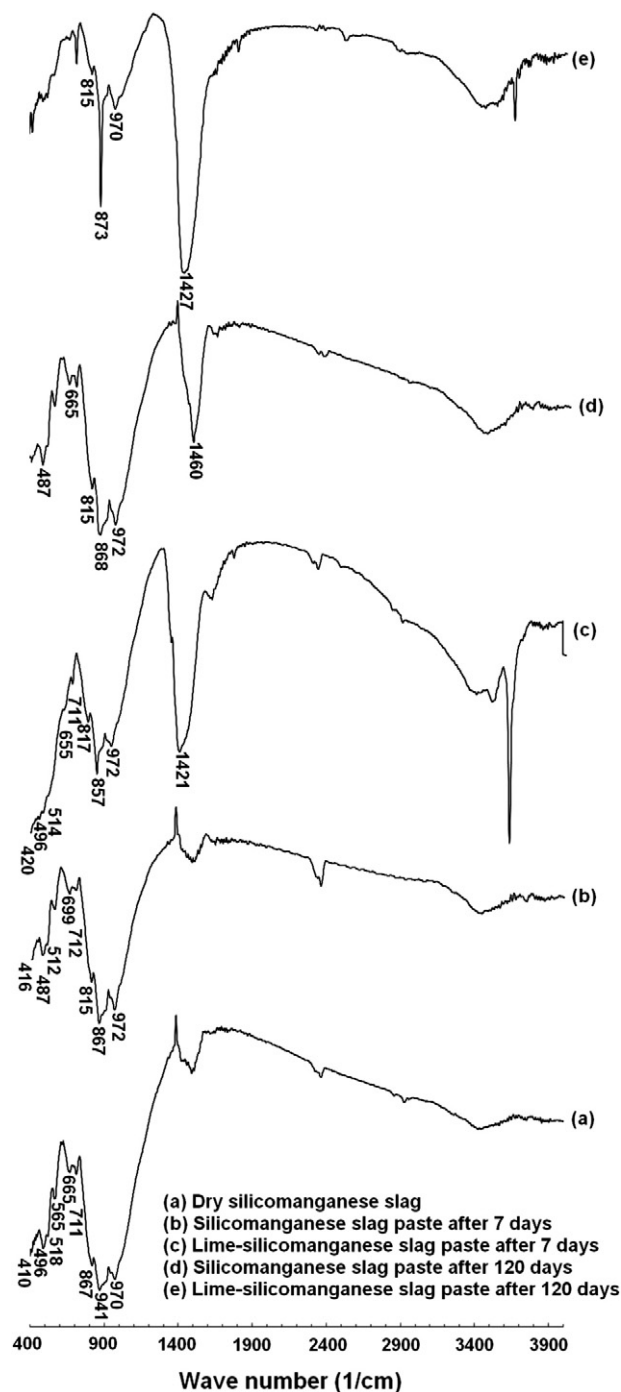


Fig. 1. FTIR spectra of dry silicomanganese slag (a), slag paste after 7 days of curing (b), lime/slag paste after 7 days of curing (c), slag paste after 120 days of curing (d) and lime/slag paste after 120 days of curing (e).

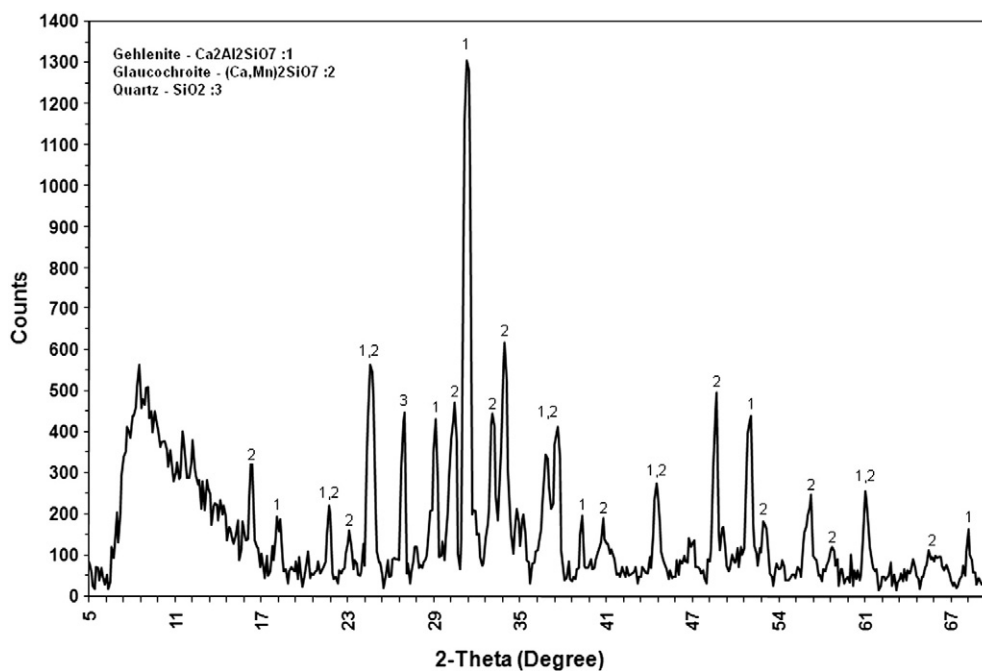


Fig. 2. X-ray diffractogram of silicomanganese slag.

calcium hydroxide and ground slag at equal proportions was utilized for preparing a paste of normal consistency. The paste was then stored at an ambient of N_2 atmosphere at $60^\circ C$ for being cured. After the given time periods, the paste was firstly dried with acetone and N_2 gas and then utilized for measuring the amount of reacted calcium hydroxide by thermogravimetry analysis.

For FTIR studies, plain slag powder and four different samples including pastes of plain slag and binary mixture of calcium hydroxide and ground slag (1:1) were prepared at normal consistency (water-to-binder ratios of 0.25 and 0.42, respectively) and cured for 7 and 120 days at an atmosphere of more than 95% relative humidity at $25^\circ C$.

Type II Portland cement clinker in accordance to ASTM standard was used both as reference and for preparing the binary cement mixes. The prepared clinker was characterized for its chemical composition (wet analysis, ASTM C114), phase composition (Bogue's potential composition). Natural gypsum was also used for preparing the binary cement mixes. The used gypsum was characterized for its chemical composition (wet analysis, ASTM C471M).

2.2. Methods

The prepared slag and clinker were weighed and mixed together at different proportions shown in Table 1. The binary mixes were then inter-ground in a laboratory ball mill to four different Blaine specific surface areas of almost 2900, 3300, 3700, and $4100\text{ cm}^2/\text{g}$, so that ultimately 32 cement mixes were obtained for further testing.

The following tests were then carried out on the prepared mixes:

Dry cement mixes:

- Residue on 90 and $212\ \mu\text{m}$ sieves (wt.%) using Hosokawa Alpine apparatus model 200LS-N and standard sieves model Haver & Boecker.

Table 4

Bogue's potential phase composition of type II Portland cement clinker.

Phase	C_3S	C_2S	C_3A	C_4AF
wt.%	53.89	21.12	7.64	11.47

- Density (g/cm^3) using Le Chatelier apparatus in accordance with ASTM C188.
- Blaine specific surface area (cm^2/g) test using Toni Perm Electronic Air Permeability Tester apparatus model 6565 and in accordance with ASTM C204.

Fresh and hardened cement pastes:

- Water consistency test (wt.%) using Toni Technik Vicat apparatus model 1801 and in accordance with ASTM C187.
- Setting time (min) using automatic Vicat device model ToniSET compact 7322 and in accordance with ASTM C191.
- Volume stability (expansion in %) using Autoclave equipment model E70 and in accordance with ASTM C151 and ASTM C490.
- X-ray diffractometry (Siemens D5000 with the following conditions: 35 kV, 20 mA, $\text{Cu-K}\alpha$ radiation).
- Scanning electron microscopy (in both SE and BSE modes using TESCAN VEGA II with accelerating voltage of 20 kV).
- Electron Dispersive X-ray Analysis (EDAX) using an Oxford inca250 model instrument with standardless ZAF quantification method. The calibration energy scale of the spectra was performed by using Al/Mn samples at their respective $\text{K}\alpha$ peaks with 5000 counts.

Hardened cement mortars:

- Density (g/cm^3), Total open pore volume (%), and water absorption using cylindrical mortar specimens with approximate volume of 400 cm^3 (prepared and cured for 28 days according to ASTM C348) and in accordance with ASTM C642.
- Mechanical strengths after 3, 7, and 28 days of curing using $4 \times 4 \times 16\text{ cm}^3$ prisms and in accordance with ASTM C348 and ASTM C349. After casting, the molds were firstly stored at an atmosphere of more than 95% relative humidity at $20^\circ C$ in constant climate chamber model KBF-240 for 24 h, and then the prisms were submerged in lime-saturated water for further curing. Flexural strength was measured by Toni NORM model 20.20 test machine. Broken portions of prisms were then

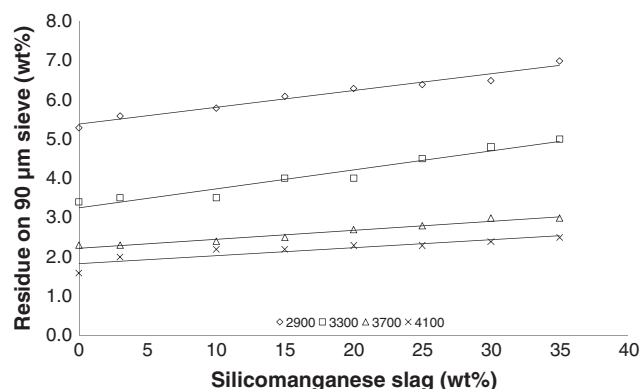


Fig. 3. Residue on 90 µm sieve versus silicomanganese slag at different Blaine finenesses.

used for determination of compressive strength using Toni NORM model 2060.10.20 test machine.

3. Results and discussion

3.1. Materials

3.1.1. Chemical composition

Table 2 shows the chemical composition of the materials. As seen, the main oxides of the silicomanganese slag include SiO_2 , followed by CaO , Al_2O_3 , and MnO . The sum of these three oxides amounts to almost 82% by the weight of the material. The other oxides including Fe_2O_3 , MgO , and alkalis are present in relatively small amounts. The CaO/SiO_2 ratio is less than 1 ($C/S = 0.77$) providing acidic character for the slag [16].

3.1.2. Pozzolanic and latent hydraulic properties

3.1.2.1. Thermogravimetry. As the chemical composition shows (see Table 2), the silicomanganese slag possesses acidic character due to its relatively high content of silica. This implies that silicomanganese slag may exhibit some pozzolanic activity. This can be simply investigated by determining the amount of fixed lime upon hydration in the presence of lime. The results obtained for the amount of fixed lime in hydrated lime/slag paste are shown in Table 3. This table also represents the results obtained for silica fume and some typical natural pozzolans that are currently being used in cement industry as relatively good (Taftan), moderate (Bojnord) and poor (Sirjan) quality natural pozzolans for commercial blended cements manufacture. As seen, the amounts of fixed lime for silicomanganese slag are comparable with values obtained for natural pozzolans, especially those of relatively poor quality (Sirjan natural pozzolan).

Similar results are also reported by Frias et al. [17,18] for pozzolanic activity of silicomanganese slag. It must, however, be noted that the determination of the amount of fixed lime as a measure for evaluating the pozzolanic activity of silicomanganese slag is not an accurate method, because industrial slags may contain some amorphous hydraulic phases that result in the formation of binding compounds, e.g. calcium silicate and/or aluminosilicate hydrates, upon hydration. Formation of these compounds upon hydration and their decomposition at high temperatures during thermogravimetry measurements interferes in the measurement of pozzolanic activity. In fact, the values of fixed lime reported for silicomanganese slag, include both the lime fixed through pozzolanic reactions plus the fixed lime present in the hydration products of amorphous hydraulic phases originally present in the slag. The scientific significance of the results obtained by thermogravimetry is, therefore, that silicomanganese slag can exhibit considerable cementing properties through pozzolanic hydration reactions and probably

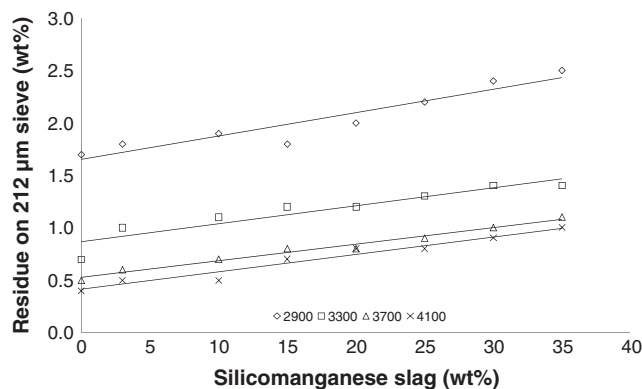


Fig. 4. Residue on 212 µm sieve versus silicomanganese slag at different Blaine finenesses.

hydration reactions of amorphous hydraulic phases. For this reason, in this study we also considered studies by FTIR spectroscopy (see the next section).

3.1.2.2. FTIR spectroscopy. To confirm the cementing properties of the silicomanganese slag and to clarify the presence of any latent hydraulic property, FTIR spectroscopy studies on dry slag powder and cured plain slag paste, in addition to cured lime/slag paste, have also been considered. Fig. 1 represents the FTIR spectra obtained from plain slag and lime/slag (1:1) pastes after 7 and 120 days of curing, in addition to dry slag powder as reference.

The major peaks include:

1. The absorption peak at 3653 cm^{-1} in lime/slag paste after 7 days (spectrum c) is due to the bending vibration of OH group in calcium hydroxide [20] and indicates the presence of lime in the paste. The intensity of this peak has been considerably reduced after 120 days of curing (spectrum e) confirming the consumption of lime in pozzolanic reactions.
2. The strong peaks at 1421 , 1460 and 1427 cm^{-1} in lime/slag paste after 7 days (spectrum c), slag paste after 120 days (spectrum d) and lime/slag paste after 120 days (spectrum e), respectively, are assigned to asymmetric stretching vibration of C–O bonds of calcite [21–24]. Formation of secondary calcium carbonate is due to the carbonation of some of the non-reacted calcium hydroxide in the pastes with atmospheric carbon dioxide. The intensity increase of this peak in lime/slag paste with curing time is due to the progress of lime carbonation reaction. The absence of this peak in the two spectra “a” and “b” is an indication of the absence of calcite in dry slag powder and slag paste after 7 days of curing. Appearance of this peak in slag paste after 120 days of curing (spectrum d) is due to the carbonation

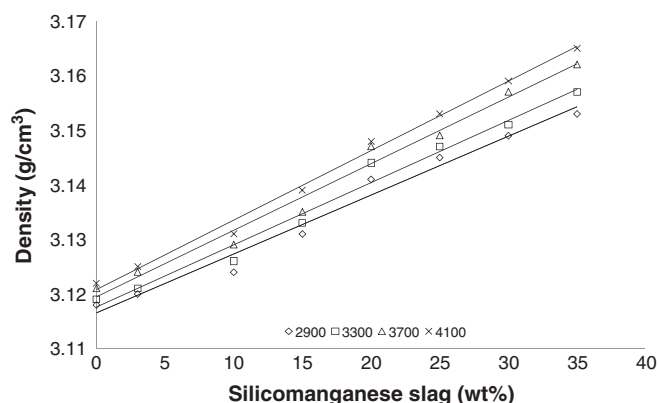


Fig. 5. Density versus silicomanganese slag at different Blaine finenesses.

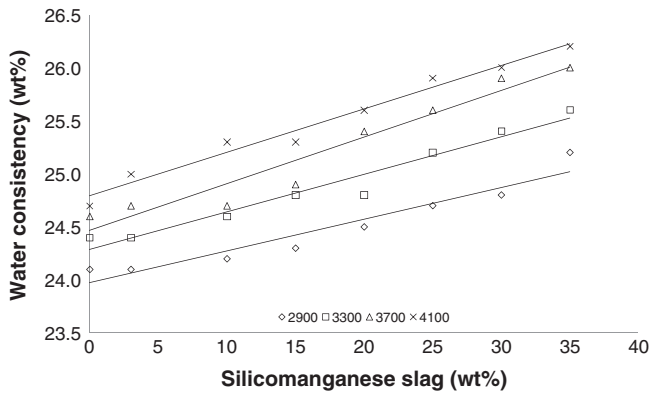


Fig. 6. Variations in water-to-cement ratio for normal consistency versus silicomanganese slag at different Blaine finenesses.

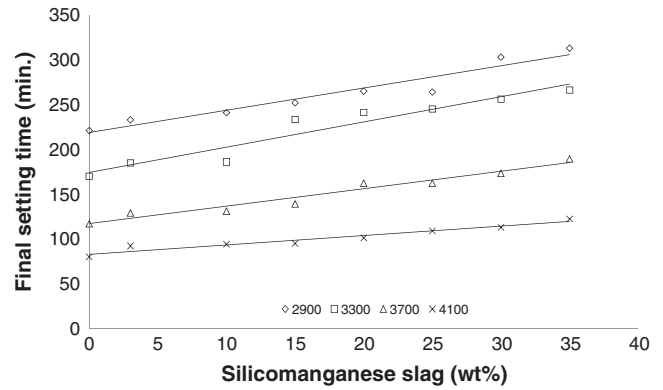


Fig. 8. Final setting times versus silicomanganese slag at different Blaine finenesses.

of calcium hydroxide formed in the hydration reactions of amorphous hydraulic phases present in slag. The silicomanganese slag, therefore, exhibits some latent hydraulic properties, in addition to some pozzolanic properties. Available peaks at 873 and 868 cm^{-1} in lime/slag paste after 120 days (spectrum e) and slag paste after 120 days of curing (spectrum d), respectively, can also be attributed to the bending vibration of C–O bonds in CO_3^{2-} [25].

- The available peaks at around 670 cm^{-1} in only slag and lime/slag pastes after 120 days of curing are related to symmetric bending of Si–O–Si bonds in the chemical structure of C-A-S-H [26,27].
- Appearance of many peaks at different positions around 440 and 480 cm^{-1} is due to absorption bands for Si–O and Al–O bonds in aluminum silicates in the slag and non-reacted slag particles in the pastes [26–28].

3.1.3. Silicomanganese slag and clinker mineralogical phase compositions

Fig. 2 shows the X-ray diffractogram of silicomanganese slag. The identified crystalline phases include: gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) as the main phase, glaucobroite ($(\text{Ca},\text{Mn})_2\text{SiO}_4$), and quartz (SiO_2). Gehlenite is a crystalline phase that is typical for burning temperatures less than 1200 °C. The presence of this phase in silicomanganese slag is an indication of relatively low processing temperatures and low cooling rates. Glaucobroite is a hydraulic crystalline phase usually found in silico- and ferromanganese slags. It has the same structure as the cement mineral, belite (Ca_2SiO_4), and presence of which in industrial slags enhances latent hydraulic properties. Other minor phases can also be present, but their identification is doubtful due to the overlapping of characteristic peaks.

Table 4 represents the Bogue's potential phase composition of the used type II Portland cement clinker.

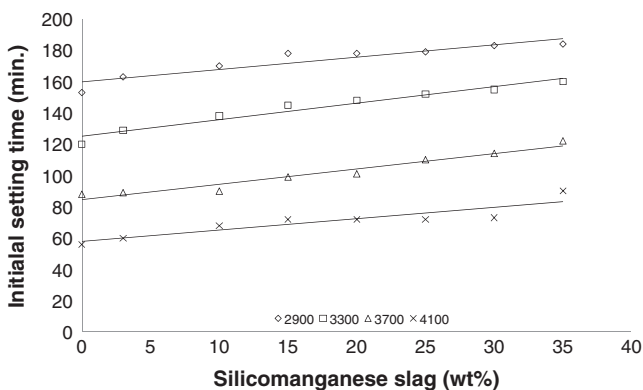


Fig. 7. Initial setting times versus silicomanganese slag at different Blaine finenesses.

3.2. Dry cement mixes

3.2.1. Fineness

Fineness is an important quality parameter for cements that significantly influences the rate of hydration and hence the rate of gain of strength, especially at early ages, and also the rate of evolution of heat. Cement manufacturers control this quality parameter by measuring both Blaine specific surface area and residue on 90 and/or 212 μm sieves. In cement industry, the values of 90- and 212- μm sieve residues are usually controlled below 10 and 3 wt.%, respectively, for ordinary Portland cement.

Figs. 3 and 4 show residues on 90 and 212 μm sieves versus silicomanganese slag (wt.%) at different Blaine finenesses.

As seen, residues on both 90 and 212 μm sieves slowly increase with increasing slag percent and Blaine fineness. The increase in residue with silicomanganese slag (wt.%) is relatively less, especially at higher Blaine finenesses. All the values of residue on both 90 and 212 μm sieves are lower than the conventional limits of the cement industry and this confirms a suitable grindability for silicomanganese slag under inter-grinding technique with Portland cement clinker.

3.2.2. Density

Particle density is another important physical property of Portland cements. It ranges from 3.10 to 3.25 g/cm^3 with an average value of 3.15 g/cm^3 . The practical significance of this property is its use in calculations of concrete mixture proportioning. The influence of silicomanganese slag on density of cement is shown in Fig. 5. It is clear that particle density of the cement mix increases with increasing slag percent and increasing Blaine fineness.

3.3. Fresh cement pastes

3.3.1. Water consistency

Water consistency refers to the relative mobility of a freshly mixed cement paste or mortar or its ability to flow. No limit has been defined

Table 5
Autoclave expansion versus silicomanganese slag at different Blaine finenesses.

% Slag	Autoclave expansion (%)			
	2900	3300	3700	4100
0	0.06	−0.03	−0.03	−0.06
3	0.01	−0.02	−0.04	−0.01
10	0.02	0.03	−0.04	−0.04
15	0.00	0.05	0.02	0.03
20	0.02	−0.03	−0.02	−0.01
25	0.05	−0.04	0.01	−0.02
30	0.03	−0.04	−0.01	−0.02
35	0.04	0.06	−0.07	0.03

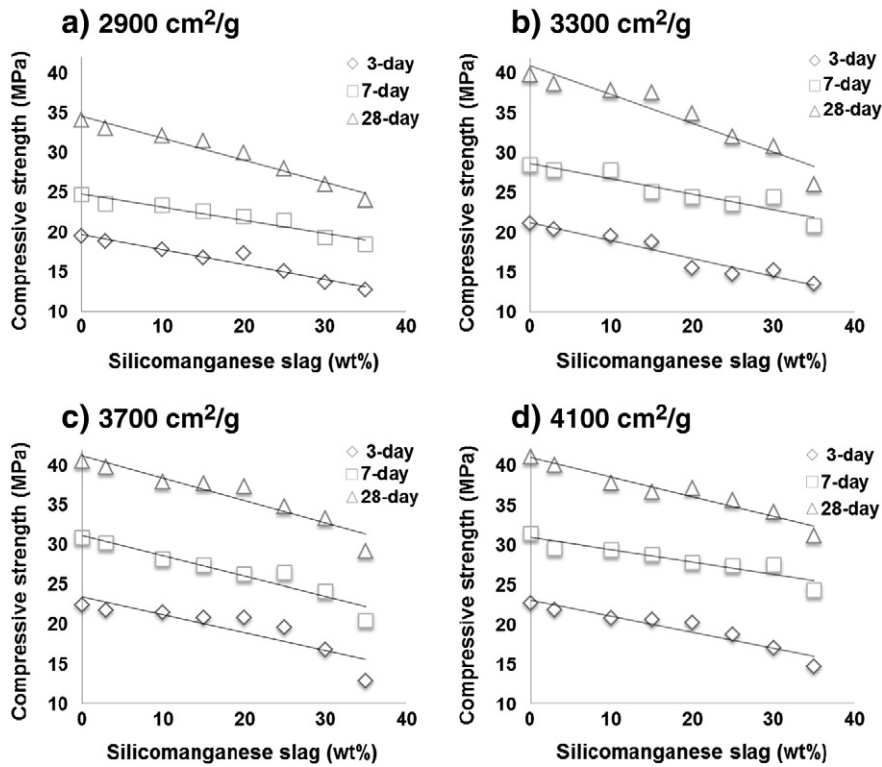


Fig. 9. Compressive strength versus silicomanganese slag at different Blaine finenesses: a) 2900 cm²/g; b) 3300 cm²/g; c) 3700 cm²/g; d) 4100 cm²/g.

in standards for the amount of water needed to achieve normal consistency in freshly prepared Portland cement pastes. The values of water-to-cement ratio for normal consistency usually range from 0.22 to 0.28 for Portland cements. Fig. 6 represents the variations in water-to-cement ratio for normal consistency versus silicomanganese slag at

different Blaine finenesses. When cement is partially replaced by silicomanganese slag, the test results show that the amount of water required for normal consistency increases. The required water also increases with increasing Blaine fineness. In general, the effects brought about by silicomanganese slag and Blaine fineness are not very

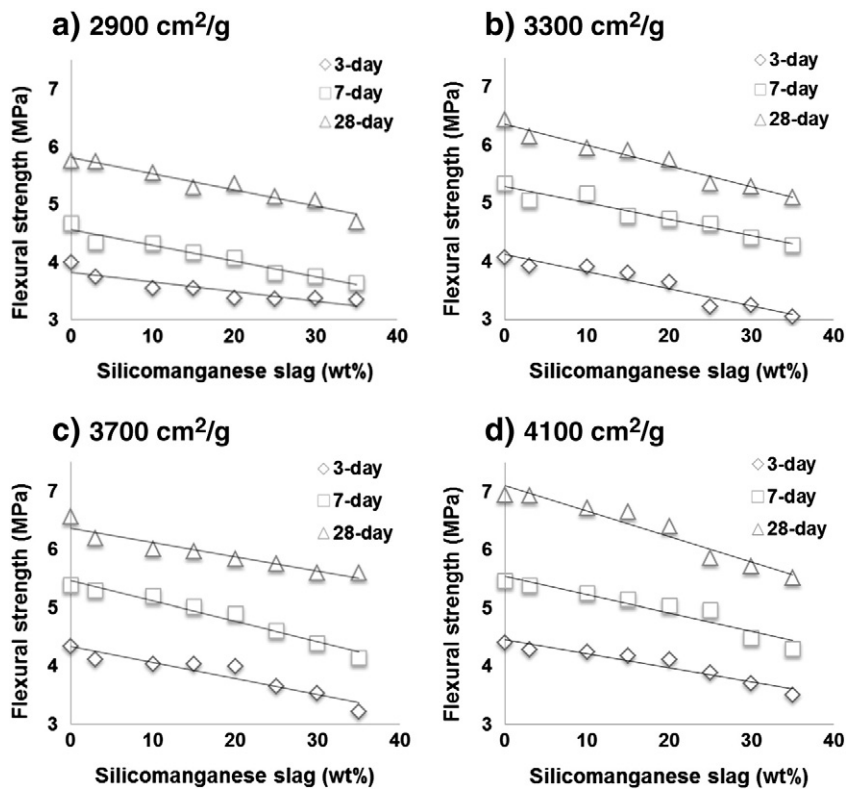


Fig. 10. Flexural strength versus silicomanganese slag at different Blaine finenesses: a) 2900 cm²/g; b) 3300 cm²/g; c) 3700 cm²/g; d) 4100 cm²/g.

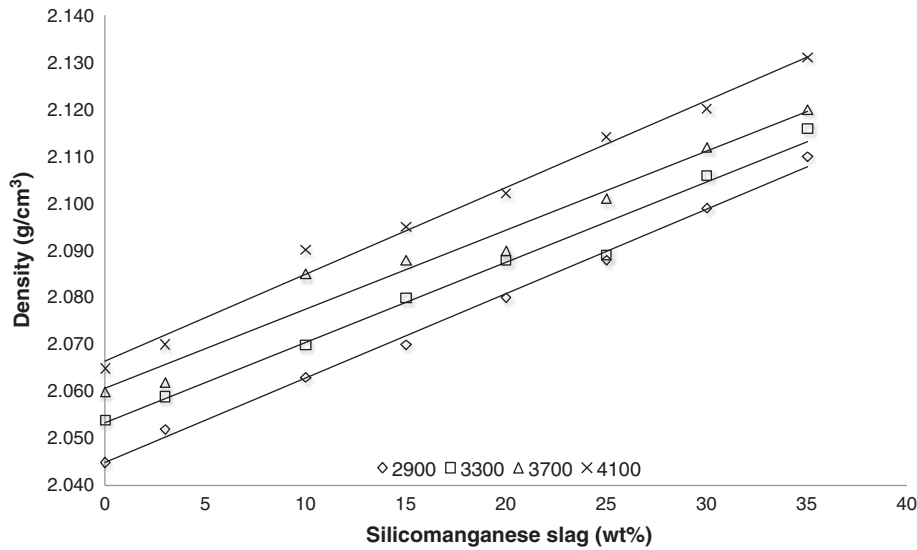


Fig. 11. Density versus silicomanganese slag at different Blaine finenesses.

significant, so that the highest replacement level (i.e. 35%) results in about 1 and 1.5% increase in water at Blaine finenesses of 2900 and 4100 cm²/g, respectively.

3.3.2. Setting times

Setting times describe the stiffening behavior of the cement paste. The results obtained for initial and final setting times of the cement mixes are shown in Figs. 7 and 8, respectively. It is clear that both initial and final setting times gradually increase with replacement level. It is also seen that at a constant replacement level, both initial and final setting times decrease with increasing Blaine fineness. Knowing that Portland cement must have a minimum initial setting time of 45 min and a maximum final setting time of 375 min in accordance with ASTM C150, all the obtained values are within the standard range.

3.4. Hardened cement pastes

3.4.1. Volume stability

Soundness is defined as the ability of a hardened cement paste to retain its volume after setting. Unsoundness of cements can be determined by autoclave expansion test in accordance with ASTM C151. Table 5 represents the results of autoclave expansion tests for all the 32 cement mixes. As seen, all the obtained values are very small and within the standard limit (less than 0.80%). Therefore silicomanganese slag does not affect the volume stability of the cement pastes. It is also

clear that the measured values do not show any meaningful relation with replacement level and Blaine fineness. This is due to the infinitesimalness of the measured values and the possible experimental errors.

3.5. Hardened cement mortars

3.5.1. Mechanical strengths

The results obtained from both compressive and flexural strength measurements are represented in Figs. 9 and 10. As seen, incorporation of silicomanganese slag causes reductions in both compressive and flexural strengths. The higher the replacement level, the higher the strength loss. The loss of strength with slag, however, is limited and can be significantly reduced by increasing the Blaine fineness. All 3- and 7-day compressive strengths are acceptable in accordance with ASTM C150 standard.

Slag substitution up to 20 wt.% causes the 28-day compressive strength of the lowest Blaine fineness (2900 cm²/g) approaching the optional standard limit of 28 MPa. Raising Blaine to higher values, however, effectively increases the strengths and makes it possible to cover the optional standard limit with higher replacement levels so that at the Blaine fineness of 4100 cm²/g the substitution level of 35% can also provide 28-day compressive strength above the optional limit. Similar trends can also be seen for changes in flexural strength with replacement level and Blaine fineness.

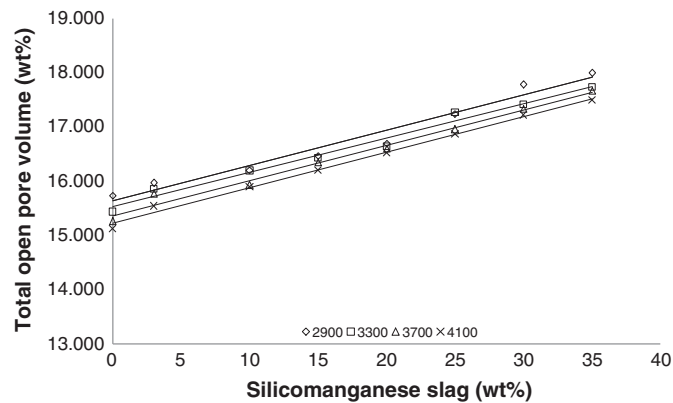


Fig. 12. Total open pore volume versus silicomanganese slag at different Blaine finenesses.

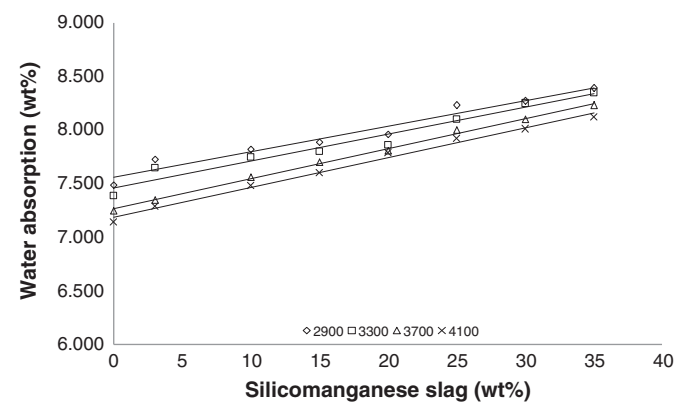


Fig. 13. Water absorption versus silicomanganese slag at different Blaine finenesses.

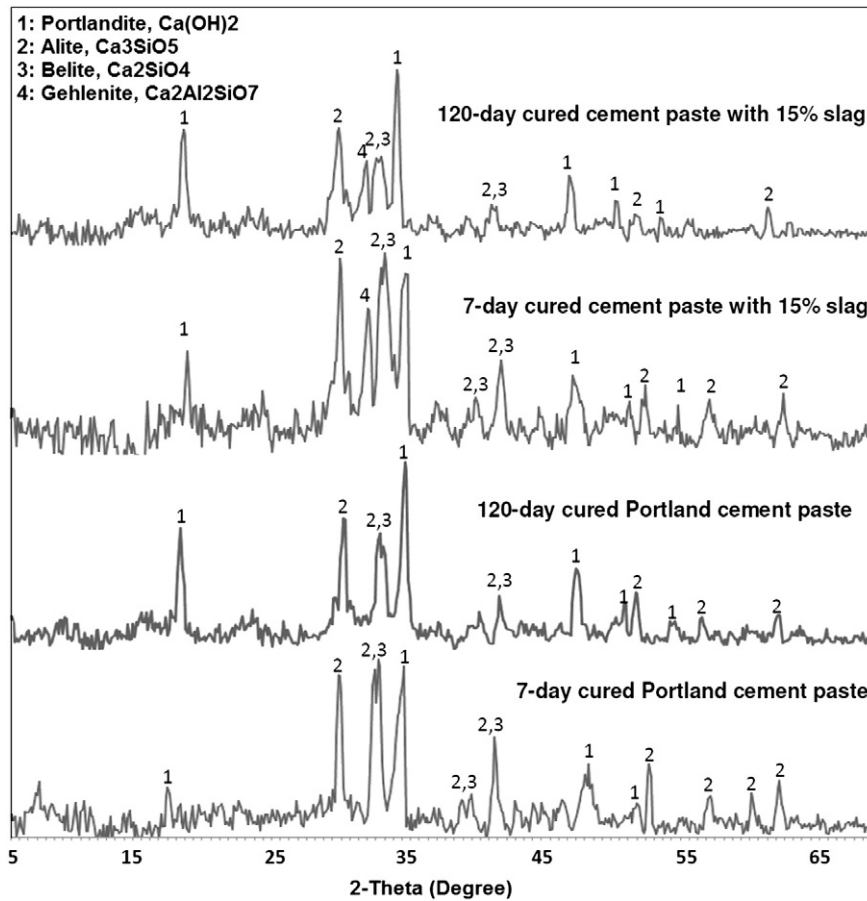


Fig. 14. X-ray diffractograms of hardened plain cement paste and hardened cement paste of the mix containing 15% silicomanganese slag ground to the Blaine fineness of 3200 cm²/g after 7 and 120 days of curing.

These results are in agreement with those reported by Frias et al. [17,18]. They claimed that addition of 5% and 15% silicomanganese slag leads to slight decrease in both compressive and flexural strengths

at early ages. Between 7 and 90 days of curing, there is a clear gain of strength and after 90 days the strength values are equal or very close to those of control mortars.

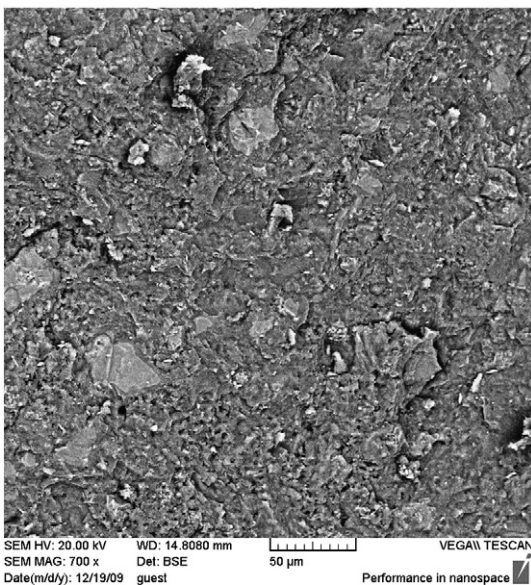


Fig. 15. SEM image of non-reacted slag particles present in the microstructure of 120-day cured paste specimens incorporating 15 wt.% silicomanganese slag ground to the Blaine fineness of 3200 cm²/g.

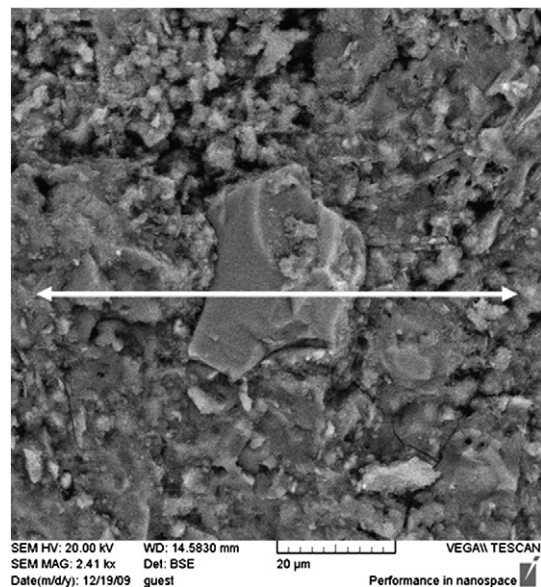


Fig. 16. SEM image of a non-reacted slag particle present in the microstructure of 120-day cured paste specimen and the line considered for EDAX elemental analysis.

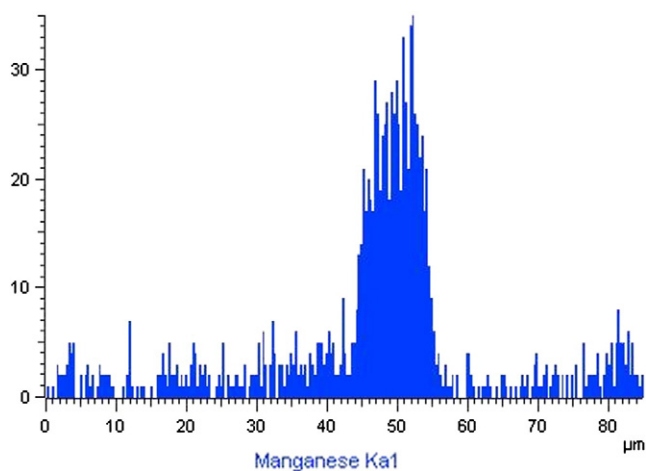


Fig. 17. Manganese concentration profile along the line shown in Fig. 16.

3.5.2. Density, total open pore volume, and water absorption

The results obtained for changes in density, total open pore volume, and water absorption of 28-day cured mortar specimens versus silicomanganese slag at different Blaine finenesses are represented in Figs. 11 to 13, respectively. As seen, changes in Blaine fineness and, especially replacement level can result in considerable changes in these properties.

Density increases with increasing replacement level and Blaine fineness. This is due to both the higher density of the slag and the better packing of the particles at higher Blaine finenesses. In fact, with increasing Blaine fineness, a more compact structure is formed that is accompanied by decreasing of the amounts of pores. Continued grinding, therefore, makes the coarse particles finer with a lower porosity. This is the main reason why the density increases with prolonged grinding time [29].

Figs. 12 and 13 indicate that total open pore volume and water absorption also increase with increasing replacement level confirming that progress in hydration reactions (due to both pozzolanic and latent hydraulic properties) during 28 days of curing could not effectively result in any microstructural densification. The increases in water-to-cement ratio at higher replacement levels (see Fig. 6) are, therefore, responsible for increases in both total open pore volume and water absorption.

As expected, any increase in Blaine fineness can positively affect total open pore volume and water absorption through the influence of

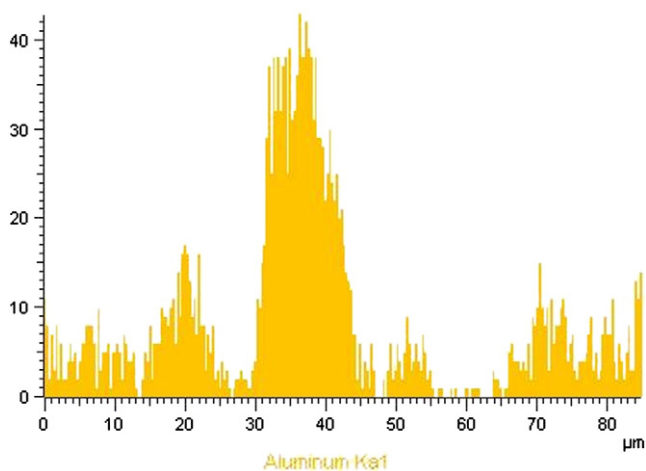


Fig. 18. Aluminum concentration profile along the line shown in Fig. 16.

continued grinding on both microstructural densification and accelerating hydration reactions.

These results are in agreement with trends obtained for variations of compressive and flexural strengths with replacement level and Blaine fineness. The results also agree with those reported by Frias et al. [18].

3.6. Complementary studies

As observed in the previous sections, despite the relatively low pozzolanic and latent hydraulic properties of the silicomanganese slag, all physical and chemical characteristics of the cement mixtures, except their 28-day compressive strengths, comply with the main standard specifications. It is also observed that the loss of compressive strength at relatively high replacement levels can be effectively reduced by increasing the Blaine fineness. Increasing Blaine fineness, however, results in significantly higher production costs through increased rate of energy consumption in the mill and, therefore, relatively high replacement levels may not be practically suitable. For this reason a cement mix of relatively moderate replacement level (i.e. 15 wt.%) has been considered for complementary studies.

3.6.1. X-ray diffractometry

Fig. 14 represents the X-ray diffractograms obtained from hardened cement paste of the mix containing 15% silicomanganese slag ground to the Blaine fineness of 3200 cm²/g after 7 and 120 days of curing. The X-ray diffractograms of hardened plain Portland cement paste after 7 and 120 days of curing are also given for a better comparison. The X-ray diffractograms of the slag-containing pastes are very similar to the corresponding diffractograms of plain Portland cement pastes, except the characteristic peak appearing at around 2θ angle of 32°. This peak is due to the presence of gehlenite as the main crystalline phase of silicomanganese slag. Gehlenite is a non- or very low hydraulic crystalline phase [30–32] usually found in industrial slags. A comparison of the diffractograms shows that with curing time, the intensity of the characteristic peaks of Portlandite increases with a decrease in the intensity of characteristic peaks of anhydrous hydraulic phases (alite and belite) confirming the progress of the hydration reactions in slag-containing paste as well as in plain Portland cement paste.

3.6.2. Scanning electron microscope studies

Studies by SEM confirmed different microstructural morphologies between 120-day cured paste specimens incorporating 15 wt.% silicomanganese slag ground to the Blaine fineness of 3200 cm²/g and 120-day cured plain cement paste. The microstructure of the slag-containing paste involves small non-reacted slag particles, which can be simply recognized by their light gray color under the mode of backscattered secondary electrons of the microscope. Fig. 15 represents a SEM image of non-reacted slag particles embedded in the hydration products. These non-reacted slag particles, which are responsible for microstructural defects and loss of strengths are due to the presence of non- or very low reactive phase, gehlenite, in the silicomanganese slag. The results obtained from EDAX elemental analysis are helpful to characterize these non-reacted slag particles. Fig. 16 represents a SEM image from a non-reacted slag particle present in the microstructure of 120-day cured paste specimen and the line considered for EDAX elemental analysis across the slag particle and the adjacent paste. The elemental profiles obtained for manganese and aluminum are shown in Figs. 17 and 18, respectively. As seen, the elemental composition of the slag particle is highly rich in both manganese and aluminum compared to the adjacent paste. These two elements originate from slag and its non-hydraulic phase, gehlenite, respectively.

Neglecting the non-reacted slag particles, slag containing pastes cured for 7 and 120 days showed similar microstructural morphologies compared to control pastes. Figs. 19 and 20 show SEM images from microstructures of both slag-containing and plain cement pastes after 7 and 120 days of curing, respectively. As seen, after 7 days of curing the

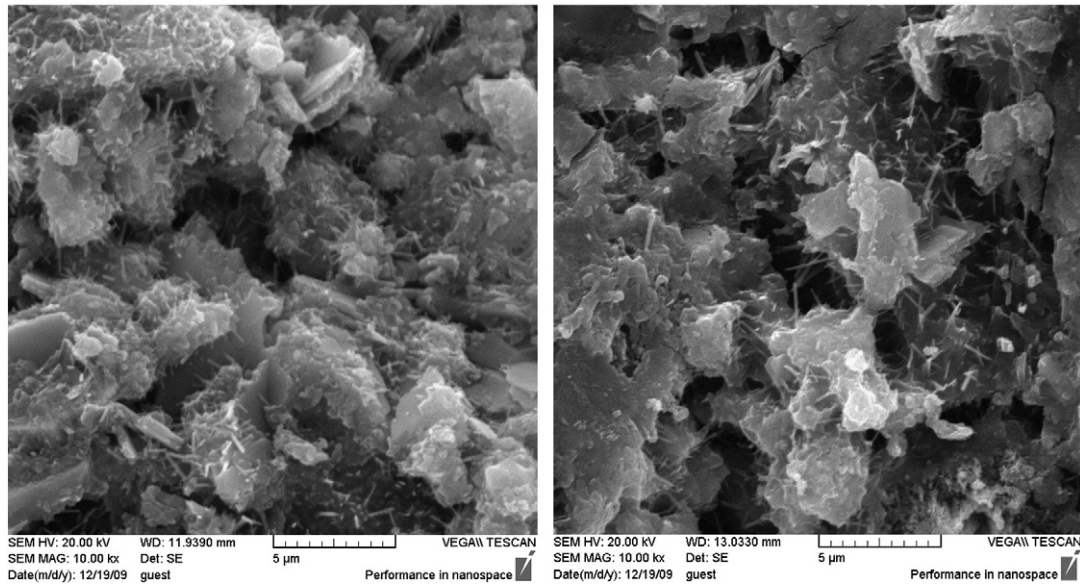


Fig. 19. SEM images from microstructures of plain cement (left) and slag-containing (right) pastes after 7 days of curing at a magnification of 10,000 \times .

microstructures are composed of early age hydration products around cement and slag particles along with hexagonal Portlandite crystal and finely distributed very small needle-like ettringite crystals. After 120 days of curing, ettringite crystals disappeared and more compact microstructures are developed.

4. Conclusions

The air-cooled silicomanganese slag with a silico-alumino-calcium composition ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} > 82$) and acidic character exhibits relatively low to moderate pozzolanic and latent hydraulic properties. The main crystalline phase of the material is gehlenite with very poor or non-hydraulic properties. The results obtained show that replacement levels up to 35% do not significantly modify the setting times. The blended cements fulfill all the chemical requirements of the standard specification and do not exhibit any volume instability. The loss of mechanical strengths for replacement levels up to 15% is limited to about 10% for 3, 7 and 28 days of curing. Mechanical activation or raising Blaine fineness

to higher values effectively increases the strengths and makes it possible to cover the ASTM optional standard limit for 28-day compressive strength with replacement levels up to 35%.

References

- [1] V.G. Papadakis, S. Tsimas, Supplementary cementing materials in concrete: Part I: efficiency and design, *Cem. Concr. Res.* 32 (2002) 1525–1532.
- [2] V.G. Papadakis, S. Antiohos, S. Tsimas, Supplementary cementing materials in concrete: Part II: a fundamental estimation of the efficiency factor, *Cem. Concr. Res.* 32 (2002) 1533–1538.
- [3] V.S. Ramachandran, R.M. Paroli, J.J. Beaudoin, H. Delgado, Supplementary cementing materials and other additions, *Handbook of Thermal Analysis of Construction Materials*, First ed., William Andrew Publishing, Norwich, New York, 2002. 293–353.
- [4] S. Chandra, L. Berntsson, Supplementary Cementing Materials, *Lightweight Aggregate Concrete*, First ed. William Andrew Publishing, Norwich, New York, 2002. 67–90.
- [5] M.J. McCarthy, R.K. Dhir, Development of high volume fly ash cements for use in concrete construction, *Fuel* 84 (2005) 1423–1432.
- [6] K. Sobolev, Mechano-chemical modification of cement with high volumes of blast furnace slag, *Cem. Concr. Compos.* 27 (2005) 848–853.

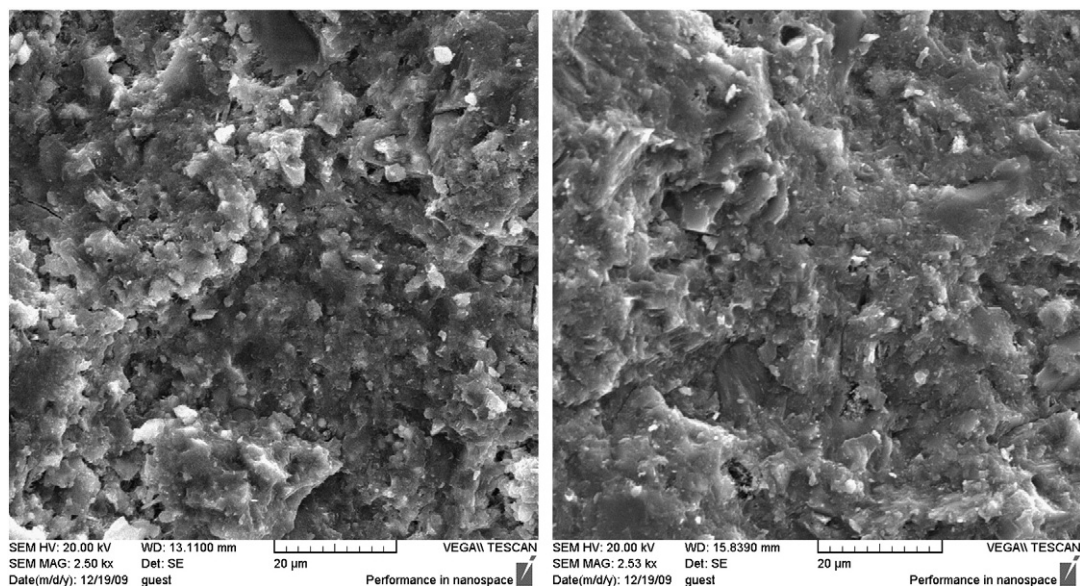


Fig. 20. SEM images from microstructures of plain cement (left) and slag-containing (right) pastes after 120 days of curing at a magnification of 2500 \times .

- [7] K. Kuder, D. Lehman, J. Berman, G. Hannesson, R. Shogren, Mechanical properties of self consolidating concrete blended with high volumes of fly ash and slag, *Cons. Build. Mater.* 34 (2012) 285–295.
- [8] US Slag Cement Association, <http://slagcement.org>.
- [9] C. Shi, J. Qian, High performance cementing materials from industrial slags – a review, *Resour. Conserv. Recycl.* 29 (2000) 195–207.
- [10] M. Penpolcharoen, Utilization of secondary lead slag as construction material, *Cem. Concr. Res.* 35 (2005) 1050–1055.
- [11] C. Shi, Ch. Meyer, A. Behnood, Utilization of copper slag in cement and concrete, *Resour. Conserv. Recycl.* 52 (2008) 1115–1120.
- [12] M. Moukwa, Cobalt furnace slag: a latent hydraulic binder, *Cem. Concr. Res.* 20 (1990) 253–258.
- [13] J. Pera, J. Ambroise, M. Chabannet, Properties of blast-furnace slags containing high amount of manganese, *Cem. Concr. Res.* 29 (1999) 171–177.
- [14] K. Chopra, C.C. Taneja, Coordination state of aluminium, magnesium and manganese ions in synthesis slag glasses, *Proceeding of the 5th International Symposium on the Chemistry of Cement*, Tokyo, Japan, vol. 4, 1968, pp. 228–236.
- [15] C.A. Taneja, S.P. Tehri, M. Singh, High manganese and alumina slag for cement manufacture, *Proceedings of the 7th International Congress on Chemistry of Cement*, Paris, France, vol. II, 1980, pp. 48–51.
- [16] A. Rai, J. Prabakar, C.B. Raju, R.K. Morchalle, Metallurgical slag as a component in blended cement, *Cons. Build. Mater.* 16 (2002) 489–494.
- [17] M. Frias, M. Isabel Sanchez de Rojas, J. Santamaria, C. Rodriguez, Recycling of silicomanganese slag as pozzolanic material in Portland cements: basic and engineering properties, *Cem. Concr. Res.* 36 (2006) 487–491.
- [18] M. Frias, C. Rodriguez, Effect of incorporating ferroalloy industry wastes as complementary cementing material on the properties of blended cements matrices, *Cem. Concr. Compos.* 30 (2008) 212–219.
- [19] M. Frias, M. Isabel Sanchez de Rojas, C. Rodriguez, The influence of SiMn slag on chemical resistance of blended cement pastes, *Constr. Build. Mater.* 23 (2009) 1472–1475.
- [20] J. Li, Q. Yu, J. Wei, Structural characteristics and hydration kinetics of modified steel slag, *Cem. Concr. Res.* 41 (2011) 324–329.
- [21] T.C. Lee, W.J. Wang, P.Y. Shin, Slag cement mortar made with cement and slag vitrified from MSWI fly ash/scrubber-ash and glass frit, *Constr. Build. Mater.* 22 (2008) 1914–1921.
- [22] T.C. Lee, Z.S. Li, Conditioned MSWI ash-slag-mix as a replacement for cement in cement mortar, *Constr. Build. Mater.* 24 (2010) 970–979.
- [23] K. Thirupathi, N. Anandhan, G. Sivakumar, Effect of fly ash and water in hydrated Srpc-A FTIR study, *Appl. Phys. Res.* 1 (2009) 59–67.
- [24] F. Puertas, M. Palacios, H. Manzano, J.S. Dolado, A. Rico, J. Rodriguez, A model for the C-A-S-H gel formed in alkali-activated slag cements, *J. Eur. Ceram. Soc.* 31 (2011) 2043–2056.
- [25] F.B. Reig, J.V.G. Adelantado, M.C.M.M. Moreno, FTIR quantitative analysis of calcium carbonate (calcite) and silica (quartz) mixtures using the constant ratio method application to geological samples, *Talanta* 58 (2002) 811–821.
- [26] D.E. Macphee, I.G. Lodeiro, Activation of aluminosilicates—some chemical considerations, *Proceedings of the 2nd International Slag Valorization Symposium on the Transition to Sustainable Materials Management*, Leuven, Belgium, 2011.
- [27] G. Renaudin, J. Russias, F. Leroux, C.C. dit Coumes, F. Frizon, Structural characterization of C-S-H and C-A-S-H samples – Part II: local environment investigated by spectroscopic analyses, *J. Solid State Chem.* 182 (2009) 3320–3329.
- [28] A.R. Sakulich, E. Anderson, C. Schauer, M.W. Barsoum, Mechanical and microstructural characterization of an alkali-activated slag/limestone fine aggregate concrete, *Constr. Build. Mater.* 23 (2009) 2951–2957.
- [29] X. Fu, Q. Li, J. Zhai, G. Sheng, F. Li, The physical–chemical characterization of mechanically-treated CFBC fly ash, *Cem. Concr. Compos.* 30 (2008) 220–226.
- [30] N.Y. Mostafa, S.A.S. El-Hemaly, E.I. Al-Wakeel, S.A. El-Korashy, P.W. Brown, Characterization and evaluation of the hydraulic activity of water-cooled slag and air-cooled slag, *Cem. Concr. Res.* 31 (2001) 899–904.
- [31] S. Goto, T. Yoshii, M. Daimon, Effects of the thermal history on the hydraulic properties of slags, *Cem. Concr. Res.* 15 (1985) 964–968.
- [32] M. Palou, J. Majling, M. Doval, J. Kozankova, S.Ch. Mojumdar, Formation and stability of crystallohydrates in the non-equilibrium system during hydration of SAB cements, *Ceram. Silik.* 49 (2005) 230–236.



Ali Allahverdi is an associate Professor of Chemical Engineering working in Iran University of Science and Technology since 2002. He received his Ph.D. in special and new cements in 2001 from the Institute of Chemical Technology, Prague. His research interests include material and process technology of special and new cements and concretes and he has published 80 international journal and conference papers.



Salim Ahmadnezhad has been working in Hormozgan Cement Company, located in Hormozgan province, Iran, since 1994. Now, he is the manager of the quality control department of the company. He received his master's degree in chemical engineering from Iran University of Science and Technology.