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

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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%.

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 m^2/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

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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 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–Kα 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

Table 2
Chemical composition of the starting materials.

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	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

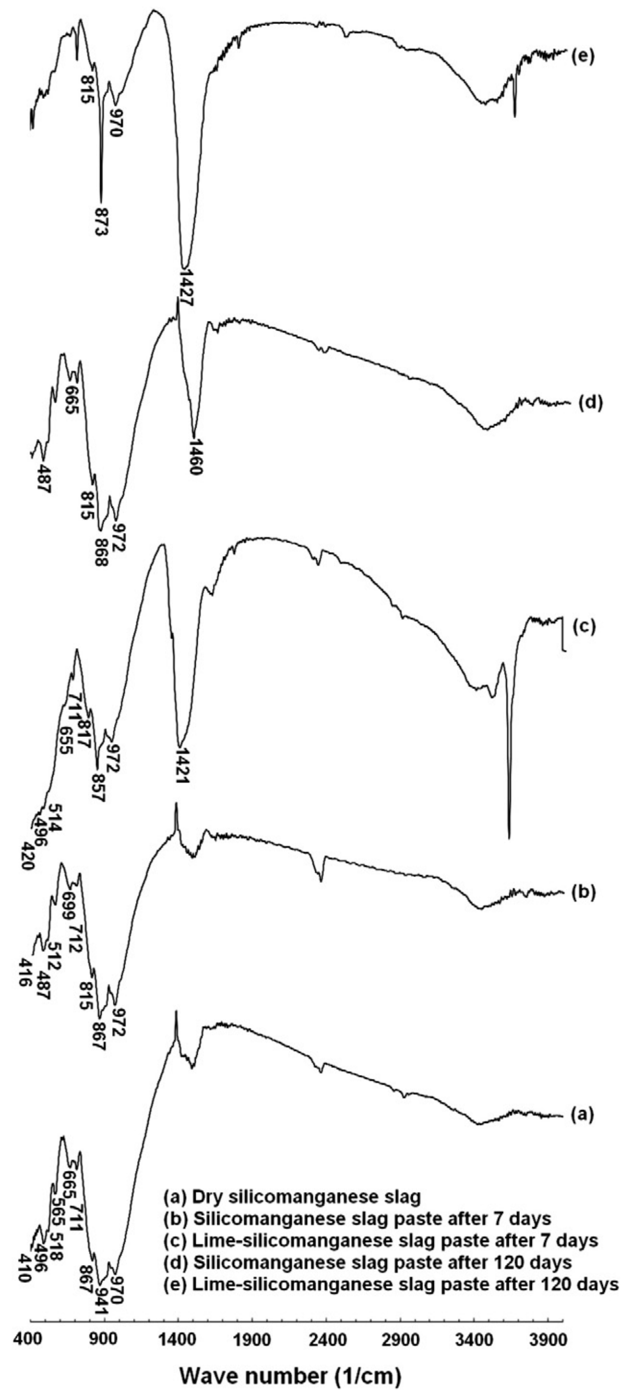

Fig. 1. FTIR spectra of dry silicomanganese slag (a), slag paste after 7 days of curing (b), lime/slag paste after 7 days of curing (c), slag paste after 120 days of curing (d) and lime/slag paste after 120 days of curing (e).