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Producing Portland cement from iron and steel slags and limestone

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Abstract

The slags from blast furnace (iron making) and converter (steel making) after magnetic separation are mixed with limestone of six different compositions. The ground materials are fired in a pilot plant scale rotary kiln to 1350°C for 1 h. The clinker is cooled, crushed, mixed with 3% gypsum, and ground to fineness of more than 3300 cm^2/g. Initial and final setting times, consistency of standard paste, soundness, free CaO, and compressive and fractural strengths after 3, 7, and 28 days are measured. Samples with higher lime saturation factor developed higher C_3S content and better mechanical properties. Blending 10% extra iron slag to a cement composed of 49% iron slag, 43% calcined lime, and 8% steel slag kept the compressive strength of concrete above standard values for type I ordinary Portand cement.

Keywords: Clinker; Portland cement; Granulated blast-furnace slag; Compressive strength

1. Introduction

Portland cement is manufactured by grinding a mixture of calcareous materials (limestone), argillaceous materials (caly), and silica and iron oxide-bearing materials, burning them at a clinkering temperature, and fine grinding the resulting clinker. According to the definition of the American Standard (ASTM C150-84) and British Standard (BS12: 1978), no material other than gypsum, water, and grinding aids may be added after burning [1].

The different general groups of Portland cement are ordinary (type I), modified (type II), rapid hardening (type III), low heat (type IV), and sulfate resisting (type V). There are also some other special types. Portland blast-furnace cement (type IS) is made by intergrinding or blending Portland cement clinker with granulated blast-furnace slag, which is a waste product in the manufacture of pig iron. The hydration of slag is initiated when lime liberated in the hydration of Portland cement provides the correct alkalinity. Subsequent hydration does not depend on lime. The slag cement is comparable to type I with regard to fineness, setting times, and soundness, but its early strengths are lower. It typically is used in mass concrete because of the lower heat of hydration and in sea-water construction because of better sulfate resistance due to lower C_3A content.

In the iron and steel industry, when pig iron from blast furnace is changed to steel in the converters, basic converter slag is produced in large quantities. This has not been useful in Portland cement and has only found limited applications in construction or stabilisation of dams, dikes, embankments, road building, and agriculture (to lower the natural acidity of soils or other fertilisers). The main problem with using converter slag in civil engineering is the possible presence of free lime, especially large-sized components of heated undissolved limestone, because when it hydrates, its volume increases and this swelling can lift the top layers [2].

In this paper, use of both iron and steel slags as the raw materials for Portland cement production before firing is discussed. Additional mixing of blast-furnace slag with the clinker after firing is considered.

2. Raw materials

The quality of Portland cement clinker depends on its chemical and mineralogical composition. Clay contains basically three oxides: SiO_2, AI_2O_3, and Fe_2O_3. Limestone decomposes to CaO and CO_2 during firing. CO_2 is removed and CaO reacts to form alite ($3CaO{\cdot}SiO_2$), belite ($2CaO{\cdot}SiO_2$), celite ($3CaO{\cdot}Al_2O_3$), and tetracalcium aluminoferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$), abreviated as C_3S, C_2S, C_3A, and C_4AF, respectively. Silica and iron oxide are added to balance the composition, so that the content of oxides in cement is approximately 62–68% CaO, 21–24% SiO_2, 4–8% Al_2O_3, and 2–5% Fe_2O_3. This composition leads to 45–65% C_3S, 15–35% C_2S, 4–14% C_3A, and 10–18% C_4AF [3].

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Table 1
Analysis of several samples of blast-furnace slag

	First blast furnace		Second blast furnace		Open-air store (old stock)
	Min.	Max.	Min.	Max.	
CaO	32.60	35.08	32.49	35.91	39.50
SiO_2	32.83	36.80	32.16	34.59	36.40
Al_2O_3	9.08	9.84	9.15	9.90	4.55
Fe_2O_3	0.77	1.50	0.77	1.49	0.41
MgO	10.46	11.93	10.58	12.05	6.99
MnO	0.58	1.88	0.49	1.57	0.82
S	1.05	1.19	1.08	1.23	1.81
TiO_2	4.05	4.81	3.94	5.10	4.77
V_2O_5	0.10	0.17	0.09	0.25	—
$Na_2O + K_2O$	—	0.15	—	0.16	0.91

Table 2
Analysis of a random batch of pig-iron slag selected from three different sources and used for all the experimental work

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	S	TiO_2	V_2O_5	$Na_2O + K_2O$
37.2	36.2	8.0	0.7	10.3	0.9	1.5	4.7	0.1	0.4

Other impurity oxides can affect adversely the quality of cement. MgO slakes very slowly when mixed with water and causes cracks after concrete hardens; therefore, it should not exceed 5%. Presence of more than 1% of alkali oxides K_2O and Na_2O may cause failure of the concrete. Free CaO acts like MgO and causes cracking of concrete as it hardens. This paper is based on industrial research to establish a cement factory near the Isfahan Iron and Steel Mill in Iran, which is near the limestone rock deposits. Three raw materials are considered individually.

Table 3
Analysis of converter slag after magnetic separation

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	S	TiO_2	V_2O_5	$Na_2O + K_2O$
56.4	10.4	2.0	21.0	1.7	2.5	0.2	3.1	2.4	0.3

2.1. Blast-furnace slag

From two blast furnaces of Iron and Steel Mill in Isfahan, about 600,000 tons of slag per year are produced and more than 10 million are stored. Table 1 lists the results of analysis of several samples by energy-dispersive X-ray fluorescence (EDX).

A random batch of about 100 kg was taken from different sources and mixed completely. This batch was used for the experiments and analysis listed in Table 2.

X-ray diffraction study of this slag indicated a large amount of glassy material and minor amounts of gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$).

2.2. Converter slag of steel

Almost the same amount of converter slag (production of about 600,000 tons per year and more than 10 million tons in stock) exists in the mill and is increased daily. Being high in iron oxide (Fe_2O_3, Fe_3O_4) and metallic Fe particles, this slag has not been used in the cement industry, although

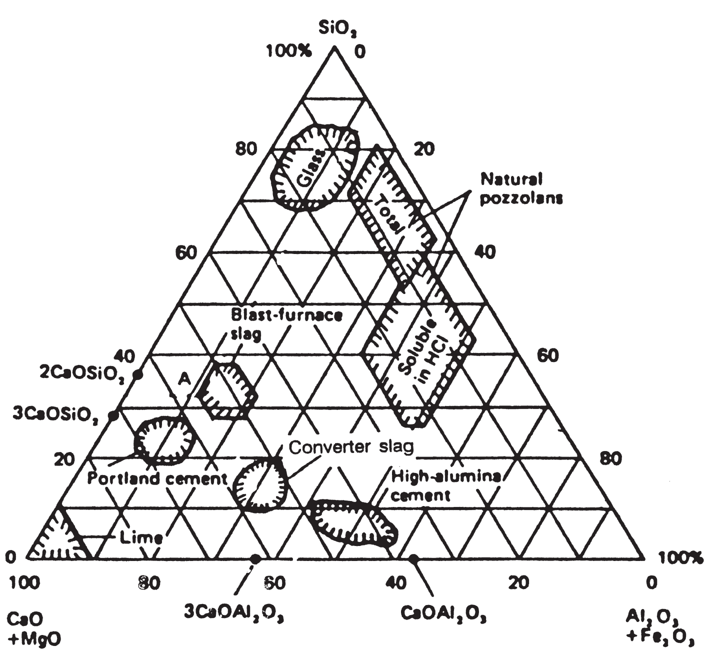

Fig. 1. Composition of blast-furnace and converter slags with respect to Portland cement.

Table 4
Analysis of limestone rock deposits near the plant

Sample no.	CaO (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	Na_2O (%) +K_2O (%)	Loss of ignition (%)
1	51.42	4.24	0.55	0.39	1.63	0.33	41.12
2	52.10	3.13	0.30	0.31	1.75	0.23	42.12
3	51.90	3.67	0.36	0.26	1.01	0.26	42.24
4	51.94	4.12	0.47	0.39	1.12	0.37	41.57
5	51.35	3.95	0.57	0.35	1.37	0.37	41.65
6	52.12	4.01	0.46	0.36	1.07	0.37	41.69
7	49.22	8.07	1.13	0.80	1.27	0.29	39.11
8	52.14	3.33	0.36	0.24	0.98	0.26	42.34
9	51.46	4.26	0.46	0.34	1.06	0.26	41.86
10	50.45	3.68	0.55	0.33	0.97	0.38	41.85
11	50.26	3.98	0.45	0.31	1.00	0.26	41.82
12	50.25	5.23	0.38	0.51	1.10	0.27	41.51
13	50.75	4.45	0.49	0.32	0.99	0.27	41.68
14	50.70	4.40	0.50	0.40	1.00	0.30	41.60

it is rich in CaO and SiO_2. Fig. 1 shows the composition of both slags with respect to Portland cement.

To separate the unwanted iron, magnetic separation was used and about 15% by mass of iron-rich particles were collected, which are being worked out for metal recovery. The remaining 85% portion of slag was analysed by EDX, wavelength dispersive X-ray fluorescence (WDX), and wet analytical chemistry. The average of results from different samples is given in Table 3.

X-ray diffraction analysis of this slag indicated portlandite (calcium hydroxide), phase CaO-FeO, and free CaO, and possiby CaO_2, CaO_4, C_2S, hematite, and magnetite.

2.3. Limestone rock deposits

Different areas in the limestone deposits near the Isfahan Iron and Steel Mill were identified by the mineralogists and analysed by WDX in the Isfahan Refractory Research Center (Azar Company), as listed in Table 4.

A uniform batch of suitable rocks that was obtainable on an industrial large scale was prepared, crushed, and blended. The analysis before and after calcination is shown in Table 5.

3. Experimental

A computer program was developed for calculation of the proper amounts of each of the three components. This was performed on the basis of selection of lime saturation factor (LSF), silica ratio (SR), and alumina ratio (AR).The related equations are given in Eqs. (1), (2), and (3):

$$LSF = 100\ (CaO + 1.5) / (2.85\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3) \quad (1)$$

$$SR = SiO_2 / (Al_2O_3 + Fe_2O_3) \quad (2)$$

$$AR = Al_2O_3 / Fe_2O_3. \quad (3)$$

Six different mixtures, M_1 to M_6, were selected. The compositions and calculated values at LSF, SR, and AR is listed in Table 6.

Table 5
Analysis of uniform batch of limestone before and after calcination

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O + K_2O	Loss of ignition (%)
Before	51.2	4.3	0.5	0.4	1.2	0.6	41.8
After	87.7	7.3	0.9	0.6	2.0	1.0	—

Table 6
Composition and analysis of the six different mixes

Sample no.	M_1	M_2	M_3	M_4	M_5	M_6
Calcined lime (%)	28.0	36.0	43.0	28.0	31.0	51.0
Iron slag (%)	48.0	51.0	49.0	54.0	42.0	49.0
Steel slag (%)	24.0	13.0	8.0	18.0	27.0	0.0
Limestone (%)	40.0	49.0	57.0	40.0	44.0	64.0
Iron slag (%)	40.0	41.0	37.0	45.0	34.0	36.0
Steel slag (%)	20.0	10.0	6.0	15.0	22.0	0.0
Calculated chemical analysis						
CaO (%)	56.0	57.9	60.5	54.8	58.0	63.0
SiO_2 (%)	21.9	22.4	21.7	23.5	20.3	21.5
Al_2O_3 (%)	4.6	4.7	4.5	4.9	4.2	4.4
Fe_2O_3 (%)	5.5	3.3	2.3	4.3	6.2	0.7
MgO (%)	5.9	6.2	6.0	6.4	5.4	6.1
Others (%)	6.1	5.5	5.0	6.1	5.9	4.3
LSF	80.5	83.0	90.3	74.8	89.0	96
SR	2.3	2.8	3.2	2.5	2.0	4.2
AR	0.8	1.4	2.0	1.1	0.7	6.3
Measured chemical analysis						
CaO (%)	54.2	58.2	58.7	57.7	58.4	61.8
SiO_2 (%)	19.9	19.9	19.0	20.9	17.9	18.3
Fe_2O_3 (%)	5.4	3.0	2.6	3.8	6.6	1.5
MgO (%)	5.9	4.8	5.1	6.0	6.6	5.8

Table 7
Physical properties of the cements produced and semiquantitative phase analysis by X-ray diffraction

Sample no.	M_1	M_2	M_3	M_4	M_5	M_6
Fineness (cm^2/g), Blaine method, ASTM C204-84	3662	3397	3801	3619	4053	5453
Consistency of standard paste (water %), Vicat apparatus	23.6	26.4	25.4	24.3	24.4	28.0
Setting time (min), ASTM C191-82						
Initial set	136	165	113	15	25	51
Final set	249	265	196	33	65	65
Soundness expansion (mm), ASTM C151-84	0	0	2	1	1	41.5
Free CaO (%)	0.6	0.4	1.4	0.3	0.4	7.3
Compressive strength (kg/cm^2), ASTM C150-86						
3 days	12.5	16.7	156.3	18.8	100.0	139.6
7 days	16.5	22.9	204.2	25.0	116.7	166.7
28 days	20.8	91.7	362.5	33.3	256.3	312.5
Fractural strength (kg/cm^2), ASTM C348-80						
3 days	—	—	37.0	—	22.0	39.0
7 days	—	—	50.0	—	29.0	42.0
28 days	—	24.0	62.0	—	51.0	58.0
Phase amounts compared to industrial product (ratio of slopes method [4])						
C_3S	—	0.45	0.91	0.45	1.00	1.09
C_2S	—	0.70	0.55	0.55	0.52	0.52
C_3A	—	1.09	0.66	0.42	0.54	0.45
C_4AF	—	0.60	1.00	1.00	0.80	0.60

About 15 kg of each mixture was prepared using industrial instruments in the Isfahan Cement Factory and fired in a pilot plant rotary furnace of 60-cm external and 40-cm internal diameters and 220-cm length with 1 r.p.m. at about 1350°C for 1 h.

4. Results

After firing, the clinkers were cooled, crushed, mixed with 3% gypsum, and ground. Physical properties of the cements produced were measured according to the standards

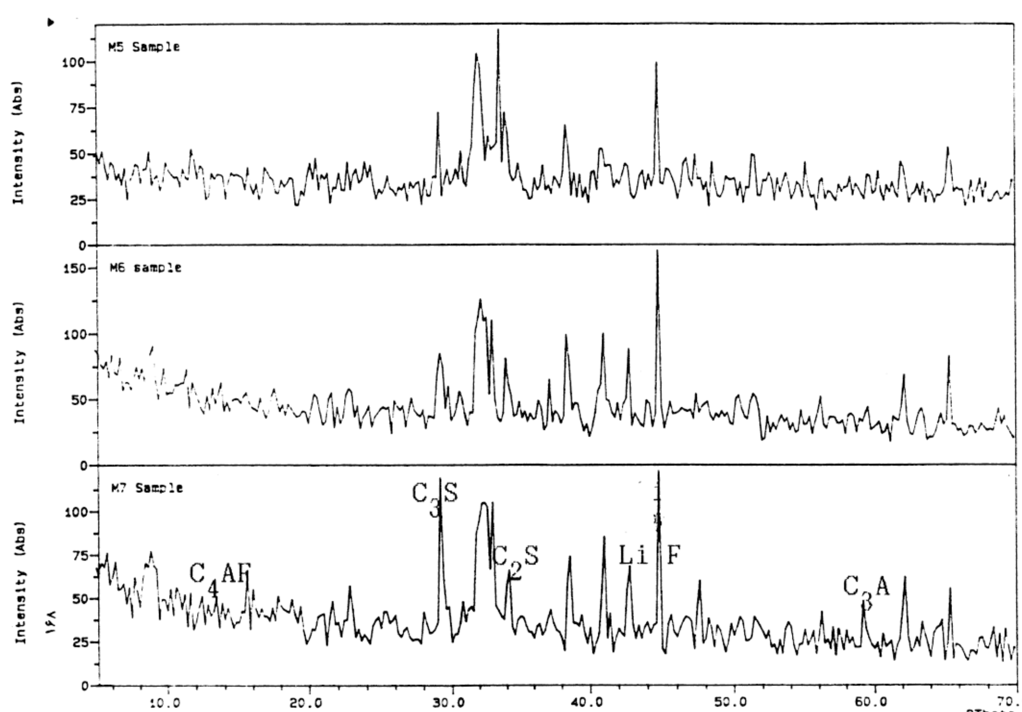

Fig. 2. X-ray diffraction pattern of cements M_5, M_6, and the industrial type I Portland cement (M_7) together with internal standard LiF.

available in the laboratory of Isfahan Cement Factory. The ratio of slopes method [4] for X-ray diffraction studies was used to compare the phases formed semiquantitatively. LiF was added as internal standard. The results are listed in Table 7. Fig. 2 shows some of the X-ray diffraction patterns.

5. Conclusions

From the six different mixtures of limestone, blast-furnace slag, and converter slag, samples M_3, M_5, and M_6 showed relatively good mechanical properties. It was concluded that, in these compositions, the LSF was higher and the alite phase, C_3S, developed better. Sample M_6 needs more attention because there is no converter slag, the iron content is low, and SR and AR are high; therefore, a higher firing temperature is required to decrease free CaO. Cement M_3 was blended with 10% iron slag as in the Portland blast-furnace cement, and compressive strengths of 140.3, 193.8, 333.3 kg/cm^2 were obtained after 3, 7, and 28 days, respectively. The minimum compressive strength of concrete for type I Portland cement according to ASTM C150-86 for 3, 7, and 28 days are 12, 19, and 28 MPa, respectively (about 120, 190, and 280 kg/cm^2). Successful production of Portland cement from iron slag, steel slag, and limestone is confirmed in this work, and the establishment of a cement factory near the Iron and Steel Mill in Isfahan is being studied.

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