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PREPARATION OF CEMENT RAW MIX CONTAINING METALLIC PARTICLES

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ABSTRACT

This paper investigates the difficulties encountered in the optimisation of cement raw mix during utilization of by-products containing metallic particles. Laboratory investigations revealed that the mechanical strength of clinkers from raw mixes containing unburnt slurry, greatly differ from those containing burnt abrasive slurry.

Commonly used formulae based only on the expected chemical transformation, for determining the lime saturation factor, alumina and silicate modules can not be utilized for raw mixes containing metallic particles. Therefore, modification of existing characteristic formulae must take into account also the nature and technology of the by-product production, ageing process—especially the influence of atmospheric conditions during storage and prevailing conditions in the furnace during clinker production. © *1997 Elsevier Science Ltd*

Introduction

Portland cement clinker (PCC) is a semi-finished product, obtained by sintering of calcium oxide and acidic oxides to produce C_3S, C_2S, C_3A and a ferrite phase approximating C_4AF (1). The chemical composition of PCC is, mass %: 62–67 CaO; 20–24 SiO_2; 4–7 Al_2O_3; 2–5 Fe_2O_3; 1.5–4 MgO, SO_3, etc.

The sweetability of portland cement raw mix is characterised using the content of the individual oxide and parameters such as lime combination factor (LCF), silica (SR) and alumina (AR) modules (2,3).

$$LCF = \frac{(CaO - CaO_{free})}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3} \quad (1)$$

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

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

In PCC, the preferable LCF, SR and AR values are in the range of 0.92–0.96, 2.3–2.7 and 1.3–2.7 respectively.

Chemical composition of raw mix always differ from that of the clinker. This is as a result of losses due to the removal of fine particles in form of dust and the dissociation of alkali metal salts to produce K_2O, Na_2O, SO_3, that can easily be removed in form of vapour or gas.

The use of industrial by-products in the production of PCC is widely practiced (4,5).

Unlike raw materials of natural origin, some industrial by-products such as metallurgical slag and abrasive slurry—a by-product of machine building industry, contain metallic particles. Optimisation of raw mix containing such by-product can not be performed using known method based on the Kind or Okorokov formulae.

The major objective of this research is to highlight the difficulty encountered during the preparation of raw mix containing metallic particles and to propose a base for the formulation of a theory to be used during optimisation of cement raw mix containing metallic particles.

Theory

During heating in air, the weight of metallic particles is expected to increase by 1.8–2.1 times, depending on the extent of oxidation (6). From the chemical reaction stoichiometry, the increase in weight of $Fe \rightarrow FeO$, $Fe \rightarrow Fe_2O_3$ and $FeO \rightarrow Fe_2O_3$ are 1.286, 1.430 and 1.111 times respectively. Earlier results by the author have shown that the weight of abrasive slurry during burning can increase by about 8%, depending on its age (7). It is therefore clear that the raw mix composition and consequently the mineral and chemical composition of PCC obtained from natural raw materials and industrial by-products with metallic particles can not be calculated using existing formulae without introduction of corrective coefficients accounting for increases in weight due to oxidation of Fe and FeO.

In this research the optimisation of cement raw mix components was conducted experimentally using the composition—properties diagram (8). The raw mixes were chemically analyzed and the LSF, SR and AR values calculated using equations 1 to 3. The obtained values were then compared with theoretically calculated values assuming that all the metallic particles were converted to Fe_2O_3.

Experiment

The raw materials used for the experiments were limestone, sand, abrasive slurry and open hearth slag. The compositions of the raw materials are presented in Table 1. The granulometric composition of abrasive slurry is, mass %: 0–0.12 mm 48–80, 0.2–1 mm 20–29 and above 1 mm the remainder. Part of the abrasive slurry was burnt at 500°C and the chemical composition was also determined. The observed disproportion in chemical composition of the unburnt abrasive slurry and the calculated completely oxidized composition is as a result of the introduction of oxygen molecules. This is clearly observed in X-ray diagrams presented in (9).

Using the simplex–lattice diagram Composition–Properties (8), the compositions of the raw mixes were determined (Table 2 and 5). The dried raw materials mixed in the required proportion were ground in a ceramic lined ball mill to a fineness of 6–8 mass % residue on a 80 μm size mesh. They were then watered and manually granulated. Their granules were dried and burnt in an electric furnace using silicon heating elements. The burning temperature was gradually raised to 1400°C, with a retention time of 30 min. at the maximum temperature. The entire mass of the produced clinkers were ground to a surface area of 3200 cm^3/kg. The mechanical strength of the clinkers, determined in accordance with British standard

TABLE 1
Chemical Composition of Raw Materials

Material	Oxides contents, mass %								
	SiO_2	Al_2O_3	Fe_2O_3	FeO	Fe	CaO	Cr_2O_3	MnO	LOI*
Limestone	7.66	1.19	0.62			49.50			39.95
Sand	76.71	6.60	22.81			6.64			5.61
Open hearth slag	37.17	11.05	14.56			20.72	3.57	9.32	
Abrasive slurry	3.02	27.00	4.34	6.72	54	0.84	1.82	0.66	
*1400°C	1.10	22.54	74.24				1.10		
Abrasive slurry burnt at 500°C	1.32	16.42	60.52	9.5	10.3		1.31		

* Expected chemical composition of abrasive slurry. LOI*—Loss on ignition.

(vibrated mortar) are presented in Table 2 and 5. The optimisation parameters were 7, 28 and 180 days compressive strength.

All the samples were chemically analyzed and the results are presented in Table 3 and 6.

Results and Discussion

Analyses of the simplex–lattice diagram, taking maximum compressive strength as the optimisation criteria, showed that the optimum composition of the raw mix lay in the region of limestone 79.20–79.35, open hearth slag 7.36–7.58, abrasive slurry 3.40–3.70 and sand 9.37–10.04 mass % (Table 2, Fig. 1).

The chemical compositions of clinkers (Table 2) are presented in Table 3. Chemical analysis of extent of oxidation of Fe is presented in (9). Results showed that the total content of Fe_2O_3 in clinker introduced via abrasive slurry and open hearth slag was between 9.5–13.0

TABLE 2
Composition of Raw Mix and Compressive Strength of Cement

N	Composition of raw mix, mass %				Compressive strength Mpa, after, days		
	Limestone	Open hearth slag	Abrasive slurry	Sand	7	28	180
1	82.00	5.00	4.00	9.00	37.0	40.1	52.5
2	79.00	7.00	5.00	9.00	25.0	37.7	46.7
3	80.00	8.00	3.00	9.00	28.5	34.5	52.5
4	80.33	6.34	4.33	9.00	26.5	36.4	46.0
5	79.67	6.66	4.67	9.00	34.0	43.5	52.5
6	79.25	7.30	4.40	9.00	19.0	35.0	49.1
7	79.53	7.80	3.67	9.00	34.0	48.2	61.9
8	81.03	6.67	3.30	9.00	40.0	34.4	59.9
9	79.73	7.60	3.67	9.00	32.0	42.6	53.7
10	80.03	6.67	4.30	9.00	23.0	37.7	49.1

TABLE 3
Chemical Composition of Clinker

	Oxides content, mass %							Clinker module		
N	CaO	Fe_2O_3	Al_2O_3	C_f*	SiO_2	MnO	Cr_2O_3	LCF	SR	AR
1	65.00	9.80	3.40	1.4	20.20	0.60	0.30	0.99	1.53	0.35
2	62.30	13.00	3.40	0.2	20.10	0.68	0.34	0.92	1.22	0.26
3	64.50	9.50	3.70	1.0	20.90	0.76	0.34	0.94	1.58	0.39
4	64.50	10.40	3.00	0.8	21.30	0.62	0.30	0.94	1.54	0.29
5	62.70	11.30	3.90	0.6	20.40	0.60	0.32	0.91	1.32	0.36
6	62.70	11.20	3.60	0.6	21.10	0.70	0.34	0.89	1.42	0.32
7	63.30	10.70	3.20	0.4	20.80	0.75	0.34	0.93	1.50	0.30
8	64.50	9.60	3.60	1.1	21.30	0.64	0.30	0.92	1.61	0.37
9	63.00	11.00	3.60	0.4	21.00	0.73	0.34	0.90	1.44	0.33
10	64.30	10.40	3.10	0.7	20.40	0.65	0.31	0.97	1.57	0.30

C_f*—CaO_{free}

mass %. Therefore the total Fe_2O_3 is more than the 2.0–5.0 mass % content allowed for in ordinary PCC (2).

These results showed the difficulties encountered during utilization of materials containing metallic particles and abrasive.

Predominant among the factors hindering prognosis of chemical composition of the raw mixes is the granulometric composition of the abrasive slurry. The relatively large disparity between their particles makes it very difficult to ensure proper homogenisation of raw mix components containing metallic particles and abrasive. Therefore, it is not easy to forecast with high degree of certainty the expected chemical composition of the clinker. An increase in the abrasive slurry content of 0.37 mass % (sample 7 and 8) can increase the relative Fe_2O_3 content by almost 11.4%.

To reduce the Fe content in the raw mix and enhance the prognosis accuracy, the abrasive slurry was burnt at 500°C. The produced clinkers (Table 5) were analyzed using the same techniques as earlier adopted.

Analyses based on the Composition–Properties diagram showed that the optimum composition region, with the highest compressive strength lay in: limestone 80.4–81.0; open hearth slag 5.4–6.5; burnt abrasive slurry 2.0–3.0; and sand 9.5–11.9 mass % (Fig. 2).

The chemical composition of the clinkers (Table 5) is presented in Table 6. Analyses of

TABLE 4
Calculated Chemical Composition of Clinker using unburnt abrasive slurry

	Oxides content, mass %				Clinker modules		
N	CaO	Fe_2O_3	Al_2O_3	SiO_2	LCF	SR	AR
1	65.79	6.13	4.45	23.63	0.87	2.23	0.73
2	64.27	6.35	4.77	24.98	0.81	2.25	0.75
3	64.29	6.36	4.78	24.57	0.82	2.20	0.75

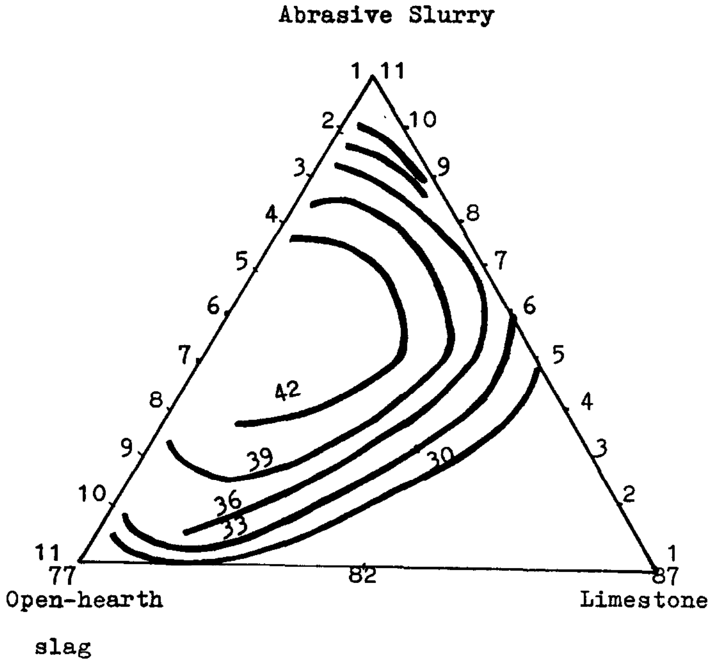

FIG. 1.
Composition–mechanical strength diagram for 28 days cement concrete.

TABLE 5
Composition of Cement Raw Mix and Compressive Strength

N	Composition of raw mix, mass %				Compressive strength MPa, after, days	
	Limestone	Open hearth slag	Abrasive slurry burnt at 500°C	Sand	7	28
1	82.00	7.00	2.00	9.00	33.6	52.5
2	80.00	8.00	3.00	9.00	32.5	57.5
3	81.00	5.00	4.00	9.00	34.0	50.2
4	81.66	5.68	2.66	9.00	38.0	56.2
5	81.34	6.33	3.33	9.00	37.5	53.7
6	80.68	6.66	3.66	9.00	39.1	54.8
7	80.33	7.33	3.33	9.00	41.2	56.3
8	80.66	7.68	2.66	9.00	35.0	55.3
9	81.33	7.33	2.33	9.00	36.0	52.5
10	81.00	7.00	3.00	9.00	41.7	63.5

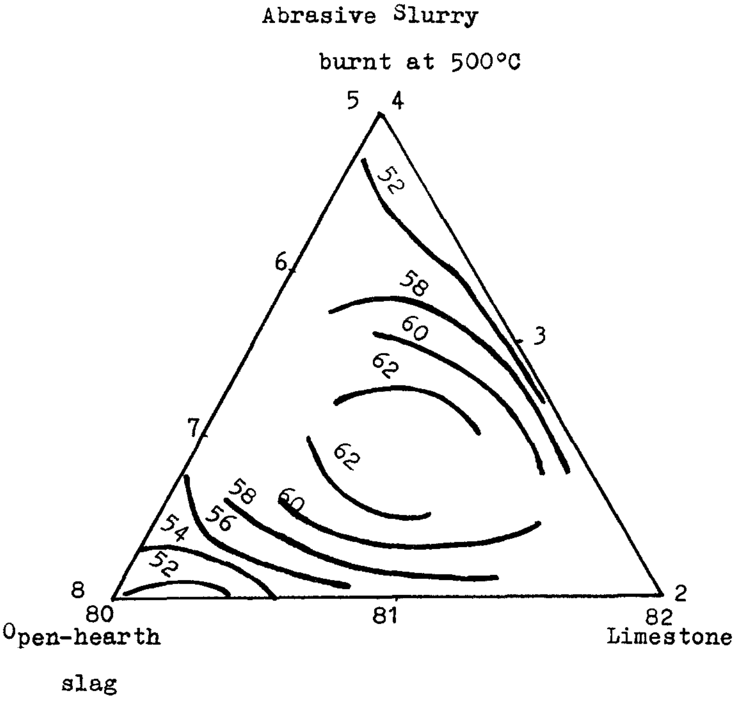

FIG. 2.
Composition–Mechanical strength diagram for 28 days cement concrete.

the Table 3 and 6 showed that except for sample 1, no other clinker produced satisfied the accepted minimum alumina module value required for PCC.

The calculated values fell below those obtained experimentally (Tables 6 and 7). Calculated clinker Fe_2O_3 content based on the stoichiometry of the chemical reaction and those

TABLE 6
Chemical Composition of Clinker

	Oxides content, mass %				Clinker modules		
N	CaO	Fe_2O_3	Al_2O_3	SiO_2	LCF	SR	AR
1	66.1	4.4	4.4	23.1	0.91	2.62	1.00
2	64.9	5.6	4.7	23.4	0.87	2.27	0.84
3	64.7	5.9	4.6	21.8	0.92	2.07	0.78
4	65.6	4.8	4.4	22.2	0.93	2.44	0.89
5	65.6	5.6	4.6	22.6	0.91	2.21	0.82
6	65.2	5.9	4.8	22.7	0.89	2.12	0.81
7	65.1	5.8	4.8	23.0	0.88	2.17	0.82
8	65.5	5.3	4.7	22.3	0.92	2.33	0.88
9	65.9	4.9	4.5	23.2	0.90	2.46	0.92
10	65.4	5.4	4.8	23.0	0.89	2.25	0.89

Note: No free CaO present.

TABLE 7
Calculated Chemical Composition of Clinker using unburnt abrasive slurry

	Oxides content, mass %				Clinker modules		
N	CaO	Fe_2O_3	Al_2O_3	SiO_2	LCF	SR	AR
1	64.95	5.28	4.34	24.42	0.85	2.54	0.82
2	64.26	6.69	4.52	24.60	0.83	2.19	0.68
3	65.00	7.39	4.25	23.35	0.86	2.00	0.58
10	65.57	5.63	4.34	24.46	0.85	2.73	0.77

obtained experimentally showed a discrepancies of more than 20%. However, the extent of disparity between the calculated and the experimentally obtained values, for clinkers produced using burnt abrasive slurry were relatively reduced (Tables 6, 7).

Apart from the possible errors due to the presence of impurities, the observed disparity can be attributed to the fact that complete oxidation of Fe might be hindered as a result of the diffusion controlled reaction condition in the furnace. There is no evidence to show that the reactions were influenced by the reducing atmospheric condition in the furnace as no FeO was found in the clinkers produced. Therefore, the quantity of FeO, Fe_2O_3 and metallic particles in the industrial by-products, (a product of the production technology, the age of the by-products and prevailing atmospheric condition during storage) can be considered as a function of its granulometric composition.

Comparative analysis of chemical composition of raw mixes prepared using unburnt and burnt abrasive slurry, samples 1, 3 and 3, 2 of Table 2 to 7 respectively, showed that despite the equal mass percentages in all components used, expect that of limestone, there were discrepancies in the LCF, silica and alumina modules. Calculated values presented in Tables 5 and 7 showed that the nature of the raw materials used greatly influenced the expected clinker composition. It is quite difficult to ascertain the physio-chemical condition of the raw materials containing oxidizable metallic particles. Burning of abrasive slurry does not completely eliminate the effect of granulometric composition on homogenisation of the raw mixes, and consequently on the chemical composition and morphology of the clinker produced (10).

The nature of the raw materials, most especially their granulometric composition, and ageing conditions negatively affects prognosis of the chemical state of metallic particles there present. Consequently the overall composition of industrial by-products and optimisation of raw mixes containing metallic particles should be based on a theory allowing for the dynamic changes in chemical composition that might occur during storage and production of portland cement clinker.

Conclusion

Currently used characteristic formulae for optimisation of PCC raw mix can not be applied for cement raw mix component containing metallic particles.

Modification of existing formulae should be based on a theory that takes cognisance of the technology of production of the by-products, physical state of the raw materials, ageing process, including the prevailing atmospheric condition during storage and oxidation condition in the furnace.

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