Pergamon

Cement and Concrete Research 29 (1999) 303–307

CEMENT AND CONCRETE RESEARCH

Grindability of cement clinker from raw mix containing metallic particles

Joseph O. Odigure *

Chemical Engineering Department, Federal University of Technology, P.M.B. 65, Minna, Niger State, Nigeria

Manuscript received 7 October 1997; accepted manuscript 21 September 1998

Abstract

The grindability of cement clinker is influenced greatly by the quantity of liquid phase produced. The use of by-products can increase significantly the liquid phase content and consequently influence not only the clinker formation processes but also the grindability of the clinker produced. Using microscopic methods, this research investigated the influence of Fe_2O_3 on the potential grindability of cement clinker produced from raw mix containing metallic particles. It showed that controlled introduction of such industrial by-product could encourage increased formation and growth of microcracks on the mineral crystal surfaces and consequently enhance the grindability of clinker produced.

Keywords: Metallic particles; Raw mix, Clinker; Grindability; Microscopy

The present scarcity of iron pyrite has prompted numerous investigations into the use of machine building iron containing by-product—abrasive slurry and open hearth slag—as cement raw mix components and their effect on the clinker formation process [1,2].

Grindability of cement clinker to a great extent determines the economy of cement production. It is influenced not only by changing conditions, such as temperature, presence of surface active substances (SAS), etc., in the mill, but also by the formation and growth of microcracks in the minerals crystal surfaces during clinker formation. Although the influence of SAS is not a subject of this present research, an attempt will be made to investigate the contribution of the presence of metallic particles and consequently the production of Fe_2O_3, and of temperature on the development and propagation of microcracks on mineral crystal surfaces during clinker formation.

The grindability of cement clinker is influenced by the relative proportions of the minerals present. The grindability of clinker containing a high belite and aluminoferrite content is quite poor due to the high mechanical strength of these minerals. Investigation by Butt et al. [3] showed that for cement minerals possessing higher mechanical strength, the higher the quantity of liquid phase produced during sintering.

Investigation into the influence of technical grade iron oxides on clinker mineral formation processes showed that, depending on the burning conditions, iron can have valencies of 0 to 3 in reducing and 3 in oxidising environments [4]. Intensive oxidation of finely dispersed metallic particles in abrasive slurry and cement raw mix begins at 450 and 500°C and ends at 905 and 760°C, respectively [2].

The influence of iron oxides on the mechanism of clinker formation depends on their quantity and valency in the solid solutions of calcium aluminoferrite, belite, and alite [5–7]. The stability of these compounds depends on the homogeneity of the raw mix, ratio of the reacting phases, burning temperature [8], velocity of cooling, etc. Increasing the quantity of Fe_2O_3 in the raw mix could cause destabilization and disintegration of alite and polymorphic inversion of $\beta \rightarrow \gamma C_2S$, with consequent loss in clinker mineral mechanical strength and hydration activeness [2,9,10].

The use of microimpurities, such as Cr_2O_3 and MnO_2, in the stabilization of clinker minerals and enhancement of its grindability have been reported [11–13]. There is evidence to suggest that the presence of FeO, Fe_2O_3, and other microimpurities in optimum quantity could significantly influence the stability and fixation of microcracks on clinker mineral crystal surfaces.

This research is aimed at investigating the influence of iron oxides, produced from raw mix containing metallic particles and open hearth slag, on the microstructure and grindability of cement clinker.

1. Experiment

Abrasive slurry is a by-product of the machine building industry. It consist of 50% to 60% metallic particles, 22% to

---

* Tel.: 234-66-222397/222887; Fax: 234-66-224482.

PII: S0008-8846(98)00175-6

Table 1
Chemical composition of raw materials

Material	Loss on ignition	SiO_2	Al_2O_3	Fe	Fe_2O_3	FeO	CaO	MgO	Cr_2O_3	MnO
Chalk	39.9	7.7			0.6		49.6	0.4		
Open hearth slag		37.2	11.1		14.6		26.7	2.3	3.6	9.3
Abrasive slurry		3.1	27.0	54	4.3	6.7	0.8	0.1	1.8	0.7
Sand	5.6	76.7	6.6		2.8		6.6	1.2		
Abrasive slurry burnt 500°C		1.32	16.4	10.3	60.5	9.5			1.3	

Table 2
Composition of raw mix and physiomechanical strength of clinker (mass %)

Sample no.	Limestone	Abrasive slurry	Abrasive burnt at 500°C	Open hearth slag	Sand	Physiomechanical strength (MPa)	
						7 days	28 days
1	81.00	3.30		6.7	9.0	40.0	43.4
2	79.63	7.56		6.8	9.0	29.3	37.0
3	82.00		2.0	7.0	9.0	33.6	52.5
4	80.30		3.3	7.4	9.0	41.2	56.2
5	82.00	2.00		7.0	9.0	18.3	21.2
6	85.00	5.00			13.0		

25% liquid coolant, and 18% to 22% abrasive (electrocorundum and ceramic binder). The chemical compositions of the dry raw materials are presented in Table 1.

To determine the influence of Fe and Fe_2O_3 from industrial by-products on cement mineral crystal morphology, raw mixes were prepared from the dried raw materials as listed in Table 2. The raw mixes were ground and prepared as indicated previously [14]. Part of each mix was converted to pellets 12 mm in diameter and 5 mm long, weighing about 2.5 g, using a hydraulic press for microscopic analysis. The other part was rolled into a ball shape for other analyses. All samples were burnt at 1380 and 1420°C for 30 min in an electric furnace using silicon heating elements and quenched in air to ambient temperature. The entire mass of the produced clinkers were ground to a surface area of 3200 cm^2/g. No gypsum was added. All samples were analyzed chemically and examined using optical and electron microscopes. The physiomechanical strength was determined for all cement clinker samples produced at 1380°C, except for sample 5, burnt at 1420°C, according to the British standard (vibrated mortar). The lime saturation factor (LSF), the silica ratio (SR), and the alumina ratio (AR) were calculated using their respective formulae. The mineralogi-

Table 3
Chemical analysis and modules values of clinker

Sample no.	Chemical composition (mass%)					Clinker characteristics		
	CaO	Fe_2O_3	Al_2O_3	SiO_2	Total	LSF	SR	AR
1	64.5	9.6	3.6	21.3	99.0	0.92	1.51	0.37
2	58.6	17.4	3.8	20.2	100	0.81	0.95	0.22
3	66.1	4.4	4.4	23.1	98.0	0.91	2.63	1.00
4	65.1	5.8	4.8	23.0	98.7	0.88	2.17	0.83
5	69.8	5.7	2.7	20.8	99.0	1.07	2.48	0.47
6	62.9	12.1	1.8	23.2	100	0.84	1.67	0.15

Table 4
Mineral composition of clinker

Sample no.	Mineral composition (mass %)					CaO_{free} at	
	C_3S	C_2S	C_3A	C_4AF	Total	1380°C	1420°C
1	48.6	25.6	6.7	17.1	98	3.5	1.0
2	33.0	33.0	19.4	18.1	101.5	0	0
3	56.2	23.8	4.2	13.4	97.5	0.4	0.1
4	50.7	27.7	2.9	17.6	98.9	0	0
5	>82.7			17.3	>100	4.2	2.4

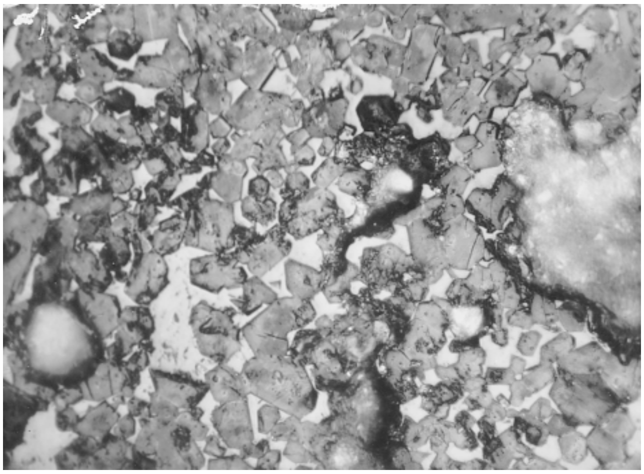

Fig. 1. Optical microscopic photograph of sample 5 burnt at 1380°C.

cal composition of the clinker was calculated using the Kind V.A. formula as follows [15]:

$$\begin{aligned} \text{At AR} > 0.64,\ C_4AF &= 3.04Fe_2O_3 \\ C_3A &= 2.65(Al_2O_3 - 0.64Fe_2O_3) \\ \text{At AR} < 0.64,\ C_4AF &= 4.77Al_2O_3 \\ C_3A &= 1.7(Fe_2O_3 - 1.57Al_2O_3) \end{aligned}$$

Results are as presented in Tables 3 and 4.

2. Results and discussion

Chemical analysis and calculated characteristic values of samples 1 to 4 are presented in Tables 3 and 4. Table 3 shows that there is a clear distinction in chemical composition between samples containing abrasive slurry and burnt abrasive slurry. The presence of metallic particles greatly increased the amount of Fe_2O_3 in the produced clinker. Table 4 shows that the sum of C_3A and C_4AF for samples 1

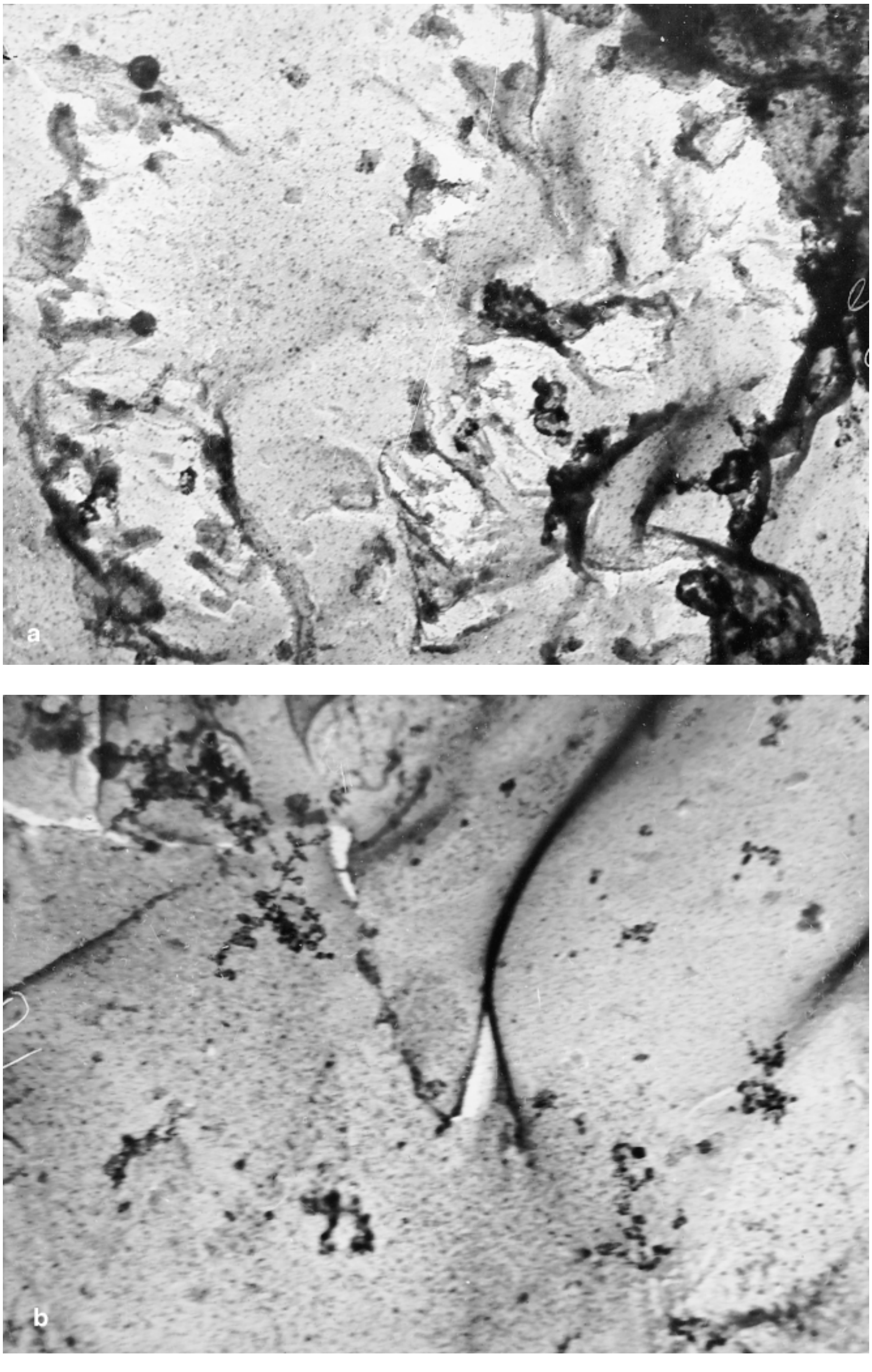

Fig. 2. (a, b) Electron microscopic photograph of sample 1 burnt at 1380°C.

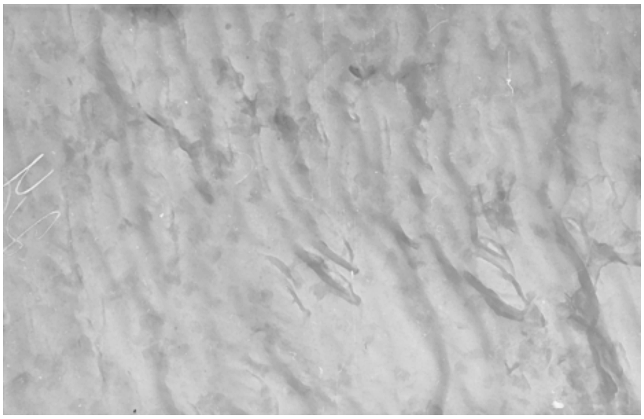

Fig. 3. Electron microscopic photograph of sample 6 burnt at 1420°C.

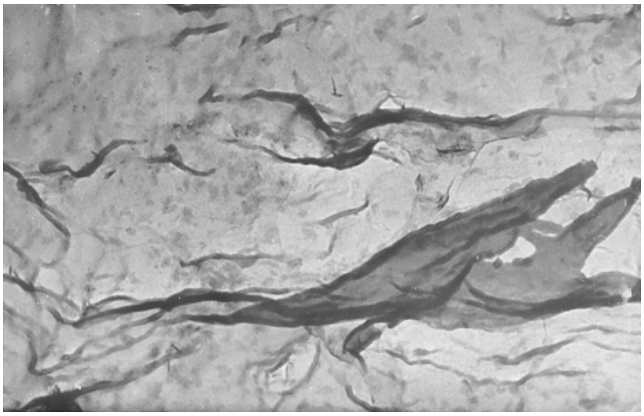

Fig. 5. Electron microscopic photograph of sample 3 (18000×).

and 2 far exceeded the recommended 18 to 22 mass % value [3], an indication of the presence of high liquid phase content during sintering. Investigations using X-ray diffraction showed the absence of C_3A and the predominance of calcium aluminoferrite solid solution lying between C_6AF_2 and C_2F [16]. Therefore, calculation of C_3A based on Kind's formula could be misleading. However, it shows the presence of high liquid phase, chemically different from the traditional Portland cement clinker content during sintering.

Earlier investigation of the morphology of cement clinker produced using abrasive slurry revealed the following: the effect of high liquid phase content was clearly evident in the optical photograph of sample 1 burnt at 1380°C. The alite crystals were large, predominantly 50 to 80 μm in length and readily disintegrated with an increase in temperature. The optical photograph of sample 3 burnt at 1380°C showed the formation of uniformly sized alite of predominantly 20 to 30 μm in size. However, an increase in temperature to 1420°C led to recrystallization and formation of larger alite crystal. No evidence of mineral disintegration was observed at 1420°C [2,17].

Clinkers with high aluminoferrite and glass phase content are known to possess poor grindability [18]. The use of 2 mass % abrasive slurry and 7 mass % slag (sample 5) resulted in the production of alite crystals of predominantly 10 to 30 μm in size (Fig. 1). The 18.3- and 21.2-MPa mechanical strength after 7 and 28 days of hardening is an indication of the slow hardening properties of sample 5. The cement is theoretically expected to possess good grindability when compared to samples 1 and 2. However, it might not be economical to sinter, considering the high LSF and low AR and SR values and considerably high quantity of free CaO content, even at the optimum 1420°C. Calculation of mineral content showed the possible absence of C_3A and C_2S. This probably accounted for the low strength gain with time.

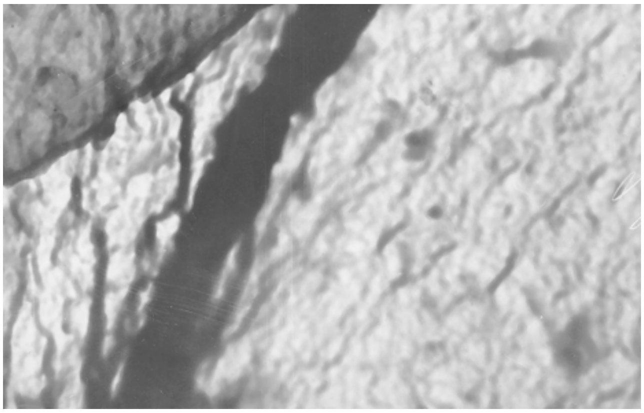

Fig. 4. Electron microscopic photograph of sample 4 (18000×).

Analysis of mineralogical composition of the clinker showed that the C_3S value decreased with increase in Fe_2O_3 content, resulting in the formation of more C_2S, which is known to possess poor grindability and produce low physiomechanical strength concrete, especially at the early stage of hardening (Table 4).

Comparative analyses of electron microscopic photographs of sample 1, 3, and 6 produced at 1380°C showed that sample 1 possessed large quantity of pores and many channels (Fig. 2). The large volume of capillary pore space is an indication of uneven distribution of the liquid phase. The dendritic nature of the pores and capillaries shows that the clinker minerals crystals could easily be dissolved by the corrosive liquid phase or disintegrated into smaller grains. The presence of high Fe_2O_3 or FeO content, due to the use of industrial by-products, in the crystalline lattice of the clinker minerals and the high percentage of iron oxides in the liquid phase greatly affected the stability of belite mineral and led to disintegration of C_3S.

This is supported by earlier results from the optical photographs and mineral composition of the clinker [17] and electron microscopic photograph of sample 6 (Fig. 3). The high liquid phase content of sample 6, consisting predominantly of $Fe_2O_{3,}$ tends to corrode and "level out" would-be obstacles during liquefication and subsequent flow. The observed phenomena might be applicable to samples burnt in the electric furnace, due to the reducing atmosphere at the peak of the reaction. In a rotary kiln, the possible oxidation and reduction kinetics of an already reduced Fe component in raw mix need to be investigated.

The presence of pores and microcracks are very minimal in samples 3 and 4 (Figs. 4 and 5). No defined pattern of microcrack formation or growth was observed.

Analysis of the theoretical and experimental results shows that the quantity of localized Fe_2O_3, due to the presence of metallic particles, could seriously affect the development and growth of capillary pores and microcracks, and consequently enhance the diffusion of cations into the clinker mineral lattices. This seriously affects the morphology and could be responsible for the observed smooth river bank-like surface of the clinker minerals.

However, the use of optimum and evenly distributed Fe_2O_3 content, introduced via pretreatment of some industrial by-product, could enhance the production of clinker minerals with optimum microcracks and consequently improved grindability.

3. Conclusion

Controlled introduction of industrial by-products containing metallic particles could encourage increased formation and growth of microcracks on the mineral crystals surfaces and consequently enhance the grindability of clinker produced.

References

[1] J.O. Odigure, M.I. Kuzmenkov, O.P. Usova, Russian Pat. A.C. 1608155, bul. 43. 1990.

[2] J.O. Odigure, Cem and Concr Res 26 (1996) 1435–1442.

[3] Y.M. Butt, M.M. Cichev, V.V. Timashev, Chemical Technology of Binding Material, Vishaya Shola, Moscow, 1990.

[4] Russian Pat A.C. 334800, bul. 47, 1973.

[5] E. Voerman, VIth International. Congress on Cement Chemistry, Moscow, 1964, pp. 108–117.

[6] H.A. Toropov, B.V. Volkonski, J Cement, Moscow 6 (1960), 17–20 (1960).

[7] M.M. Sichev, J Cem Moscow 7 (1985) 14–16.

[8] V. Johansen, J Cem and Concr Res 2 (1) (1972) 33.

[9] J.O. Odigure, J Cem and Concr Res 24 (8) (1994) 1549–1557.

[10] A.I. Boikova, Solid Solutions of Cement Minerals, Nauka Publishing, Leningrad, 1974.

[11] K.N. Zilbermag, J Cem Moscow 4 (1953) .

[12] M.M. Sichev, V.I. Korneev, V.I. Fedorov, Alite and Belite in Portland Cement Clinker and Doping Process, Stroiidat, Petersburg, 1965.

[13] V.I. Korneev, M.M. Cichev, J Giprocement Moscow, bul. 86, 1971, pp. 108–111.

[14] J.O.Odigure, Cem and Concr Res 27 (1997) 1641–1648.

[15] A.V.Voljencki, Mineral Binding Materials, fourth edition, Stroiizdat, Moscow, 1986.

[16] J.O. Odigure, M.I.Kuzmenkov, J Beloruss Acad Sci Chem Sci Ser 5 (1991) 101–106.

[17] J.O. Odigure, J Cem. and Concr Res 26 (8) (1996) 1171–1178.

[18] V.M. Kolbacov, I.I. Leonov, L.M. Sulimenko, Technology of Binding Materials, Stroiizdat, Moscow (1987)