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INFLUENCE OF ZnO ON CLINKERIZATION AND PROPERTIES OF VSK CEMENT

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ABSTRACT

The mineralizing ability of zinc oxide in the clinkerization of black meal used in the shaft kiln process is compared with that of white meal for the rotary kiln, and the properties of the cement produced are discussed. Zinc oxide exhibits superior activity in clinkerization of black meal. Zinc oxide doping lowers the water requirement and prolongs the setting time of the cement. The cement exhibits high early strength but the strength improvement beyond 7 days is poor. *© 1998 Elsevier Science Ltd*

Introduction

The mineralizing ability of zinc oxide in the clinkerization of raw meal and the properties of the resulting cements have been investigated by many workers (1–8). The raw meal used was mostly confined to synthetic mixtures of pure substances or commercial raw materials used for manufacturing cement in the rotary kiln. ZnO was found to act as a flux and a mineralizer. It increases the clinker whiteness and delays the setting time of the cement. Knofel (1) observed improvement in strength while Odler and Schmidt (2) observed reduction in strength of the cement due to ZnO doping. ZnO-doped clinkers produced by the rapid heating and burning process exhibit high early strength and superior late strength (6).

The vertical shaft kiln (VSK) technology for cement manufacture is gaining popularity in many countries (9–12). The technology is based on the black meal process. In this process, the fuel, conventionally breeze coke, is incorporated in the raw meal and the mixture in the form of nodules is burnt in a vertical kiln under a regulated supply of air. The reaction sequence leading to clinkerization in VSK is naturally influenced by the coke, a reductant, and carbon monoxide gas, also a reductant likely to be formed during burning of the raw meal. As such, substances that are established as mineralizers in the rotary kiln may exhibit a different behaviour in the shaft kiln. The present communication reports on the behaviour of ZnO in the clinkerization of black meal in a conventional shaft kiln and the properties of the cement produced.

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TABLE 1
Chemical analysis of raw materials.

	Constituents (wt.%)					
Materials	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	LOI
Lime stone	50.04	3.40	1.60	0.36	2.30	40.00
Clay	3.29	56.58	22.18	6.58	0.74	9.30
Coke* Ash	3.77	53.40	25.43	14.25	1.75	—

* Calorific value, 5463 kcal/kg and ash = 30.98%.

Experimental

Materials

Cement grade limestone from Orissa, coke breeze from M/S Rourkela Steel Plant, Orissa, India, and a local clay were used as the raw materials. The zinc oxide used was of analytical grade. The chemical composition of the raw materials are presented in Table 1.

Sample Preparation

The raw materials were dried and pulverized to around 90 microns in a Raymond Pulverizer. Three raw meals, one white (Raw Meal 1) and two black (Raw Meals 2 & 3, to which respectively 9.3 and 11.9% coke breeze, equivalent to heat input of 850 and 1100 kcal/kg of clinker, were added) were prepared and homogenized. The compositions of the mixes along with the modulii values are presented in Table 2. Weighed amounts of Raw Meals 1 and 2 were mixed separately with 0.31, 0.63, 1.26, and 3.10% by weight of zinc oxide, homogenized, and pressed in a mould to obtain cylindrical pellets. The pellets were heated in a furnace having provision for fast heating and cooling rates and kept for 30 min at 1250 and 1300°C and then allowed to cool rapidly to room temperature.

Separately, about 30 kg of each of the black meals (Raw Meal 2 was previously mixed with 0.32% ZnO) was homogenized and nodulized in a disc-type rotating nodulizer using a spray

TABLE 2
Chemical composition and moduli values of the raw meals.

Constituents (wt.%)	Raw Meal 1	Raw Meal 2	Raw Meal 3
CaO	64.03	63.88	64.18
SiO_2	21.26	21.11	21.14
Al_2O_3	8.66	8.86	8.79
Fe_2O_3	2.42	2.86	2.72
MgO	3.11	3.17	3.15
SM	1.91	1.80	1.83
AM	3.57	3.09	3.23
LSF	0.89	0.89	0.89

TABLE 3
Physical characteristics of cement.*

Sample No.	A**	B
Fineness Blain (cm^2/gm)	3352	3080
Water requirement	26.85	31.42
Setting times (min.)		
Initial	187	80
Final	214	110
Compressive strength (kg/cm^2)		
3 day	196	180
7 day	282	258
28 day	284	431

* Free lime contents in clinkers for Cement A and B are 3.0 and 4.9%, respectively.
** using raw meal containing 0.32% ZnO.

of water. The green nodules were placed in a conical shaped sintering furnace provided with an air blowing facility at the bottom (prototype of shaft kiln) as described elsewhere (12) and fired. The temperatures of burning and cooling were controlled through regulation of air supply. The clinkers produced were ground in a laboratory ball mill with 4% by weight of mineral gypsum to obtain cements (Samples A and B in Table 3) having Blaine's surface area of over 3000 cm^2/g.

Product Characterization

Small quantities of the burnt pellets and nodules were powdered in an agate mortar, and the free lime contents were determined by the ethylene glycol method.

The chemical composition of the raw materials and products were determined by following standard wet chemical analysis methods. The mineralogy of the clinkers was determined by a JDX-11 P3A JEOL X-ray diffractometer using Cu K-alpha X-radiation.

The physical properties of the cements were determined as per Indian Standard (IS 4031–1968). The setting times were determined by the Vicat needle penetration method. The compressive strengths were determined on 70.71 mm × 70.71 mm × 70.71 mm cubes prepared using a mix of standard sand and cement in the proportion of 3:1. The mortars were stored for 24 h at 90% relative humidity prior to curing under water for 3, 7, and 28 days.

Results and Discussions

The free lime content of the samples obtained from black and white raw meals doped with varying amounts of ZnO and burnt at different temperatures are presented in Figure 1.

Figure 1 reveals that the amount of free lime, which is an indication of the progress of clinkerization of the raw meal, decreases with the amount of ZnO for all the samples except the black meal samples burnt at 1300°C. The mineralizing ability of the oxide is both temperature- and quantity-dependent. The free lime content in the samples burnt at 1250°C using the white raw meal without ZnO (blank) is 10.9%. It decreases sharply to 3.2% with

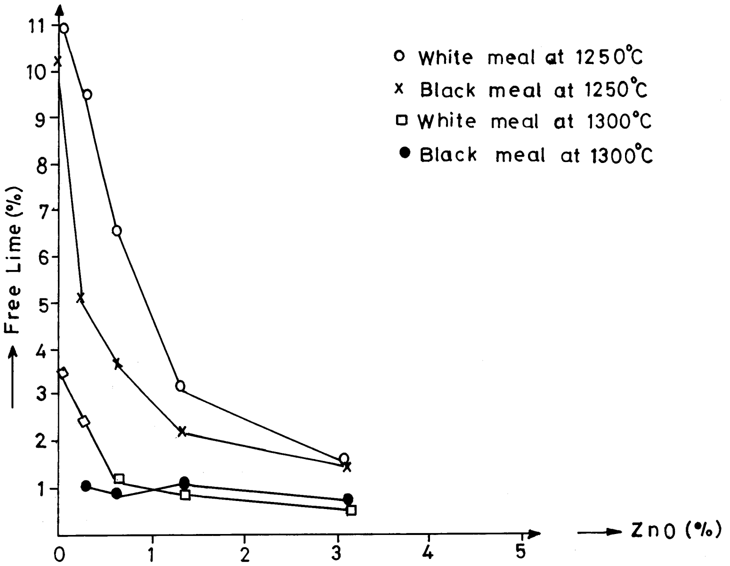

FIG. 1.
Free lime in ZnO-doped samples burnt at different temperatures using black and white raw meal.

the addition of ZnO up to 1.26% and thereafter reduction is gradual. At 1300°C, it drops from 3.4% in the blank to 1.32% at a dose of 0.63% ZnO only. It therefore appears that the same effect of burning the white raw meal at 1300°C can be achieved at 1250°C by the presence of 1.26% ZnO in the raw meal. Earlier investigators also reported lowering of burning temperature by 50–100°C by the presence of 1–2% ZnO in the raw meal (1–8).

The mineralizing action of ZnO on lime assimilation is intensified by the presence of coke. At 1300°C, the effect of 0.31% ZnO in the black meal is equivalant to 1.26% ZnO in the white meal. The practical significance of this is obvious; the addition of ZnO alone or in conjunction with carbonaceous material makes it possible to lower the clinkerization temperature and save fuel. In the black meal process, a relatively small amount of ZnO is sufficient to achieve the effect.

The mineralizing action of ZnO is due to various reasons (1–8,13). It lowers the liquid phase appearance temperature and increases the liquid phase content. It also modifies the physical properties of the liquids, lowers the activation energy, and accelerates the clinker-forming reactions. In the presence of carbon, ZnO also behaves as an oxidant and undergoes redox reactions forming nascent oxygen and elementary zinc. Further investigation, however, is necessary to establish whether this reaction has some bearing on the enhanced activity of the oxide in clinkerization of black meal.

The XRD pattern of the samples burnt at 1250°C from both white and black raw meal containing ZnO exhibit peaks in the 29–35 and 40–42°C 2T ranges attributable to both C_2S and C_3S phases. The samples prepared using the black meals, in addition, exhibit prominent peaks at 51–52°C characteristic of C_3S only (14).

The physical characteristics of the cements produced using black meals of different heat input and with or without ZnO are presented in Table 3. The water requirement for obtaining paste of workable consistency is less in the ZnO-doped cement. Initial and final setting times of the ZnO-doped cement are long. The 3- and 7-day compressive strengths of the ZnO-doped cement are high, but beyond 7 days, no enhancement in strength is observed. This may be due to formation of insoluble zinc hydroxide as reported earlier (15), which coats the silicate grains and prevents further hydration.

Conclusions

1. Zinc oxide exhibits improved mineralizing ability in the clinkerization of black meal.
2. The water requirement of ZnO-doped cement is low and setting times are long.
3. The cement exhibits superior 3- and 7-day strength.

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References

1. D. Knofel, Zem-Kalk-Gips 31, 157 (1978).
2. I. Odler, and O. Schemidt, J. Am. Ceram. Soc. 63, 13 (1980).
3. T. Tulin, Cimento Bull. 22, 222 (1985).
4. K.C. Mishra and P. C. Borthakur, Transaction of the Indian Chemical Society 44, 101 (1985).
5. K.C. Mishra and P.C. Borthakur, Proc. 1st NCB International Seminar (Pragmatic Strategies for Productivity and Modernization) National Council for Cement and Building Materials, New Delhi, 1987.
6. G. Xu, W. Huang, Z. Lu, and G. Qian, Proc. 9th Int. Congr. Chem. Cem., New Delhi, 2, 372 (1992).
7. I. Masood, S.P. Mehrotra, and S.P. Tehri, Indian J. Tech. 31, 535 (1973).
8. G. Kakali and G. Parissakis, Cem. Concr. Res. 25 79 (1995).
9. S.N. Dutta, A.K. Agarwalla, and M.S. Iyengar, POWIET, 10, 3 (1967).
10. S.N. Dutta and J.N. Baruah, Cem. Ind. 81 (1982).
11. C.D. Rajbhandari, World Cement 26, 65 (1995).
12. P. Barkakati, D. Bordoloi, and P.C. Borthakur, Cem. Concr. Res. 24, 613 (1994).
13. K.C. Misra and P.C. Borthakur, Proc. 9th Int. Congr. Chem. Cem., New Delhi, 2, 301 (1992).
14. H F.W. Taylor, Cement Chemistry, p. 4–109, Academic Press, London, 1990.
15. G. Arliguie and J. Grandet, Cem. Concr. Res. 20, 517 (1990).