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COMMUNICATIONS

USE OF MINERALIZER IN BLACK MEAL PROCESS FOR IMPROVED CLINKERIZATION AND CONSERVATION OF ENERGY

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ABSTRACT

The high cost of energy and the consumption of almost three times the net theoretical heat required in clinkering process continue to be a nagging problem faced by VSK plants. There is, therefore, a need for energy conservation which could be rapidly and economically accomplished by promoting the clinker formation at lower temperature. The use of fluxes for lowering the melting point of the raw mix is an important measure to save energy, giving economic benefits. Fluxes and mineralizers improve burnability and quality of clinker, solving particularly the free lime problem faced by cement plants.

The purpose of the present paper is to highlight the role of CaF_2 and $CaSO_4$ as mineralizers with industrial raw mix in VSK technology in conserving energy and improving the quality of clinker. The use of CaF_2, $CaSO_4$, or a mixture of CaF_2 and $CaSO_4$ promotes the clinker formation at lower temperature, giving direct implication on commercial production with economic benefits without affecting the quality. *© 1998 Elsevier Science Ltd*

Introduction

Vertical shaft kiln (VSK) technology is based on a black meal process where low volatile fuel is interground during the raw meal preparation. Due to the stationary nature of kiln, the black meal is pelletized and fed to the VSK for burning (1). Since the VSK process requires a pelletized meal for proper burning the emphasis goes to the nature of fuel (2) which has to have low volatile matter. The low volatile fuel normally used in VSK plant is a reject from steel plants known as coke breeze.

The prices of coke breeze are continuously going up due to demand. Though alternative fuels have been identified (3) and are becoming popular among some VSK cement plants, but the prices of these fuels are not significantly low as compared to coke breeze. The quality of such fuels is not constant, and availability is scarce.

The high cost of thermal energy and the consumption of almost three times the net theoretical heat that is required in clinkering process continues to be a nagging problem faced

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TABLE 1
Chemical composition of raw materials (%).

Material	LOI	Si_2O	Fe_2O_3	Al_2O_3	CaO	MgO	F^-	SO_3
Limestone	43.09	0.97	0.03	0.31	53.06	0.98	-	-
Clay	4.72	76.53	4.21	9.42	1.64	1.21	-	-
Laterite	11.47	16.28	54.96	14.16	0.74	0.37	-	-
Coke Breeze	75.74	11.16	2.29	5.11	2.55	1.68	-	-
Fluorspar	3.30	18.33	0.78	2.06	45.13	0.30	29.85	-
Gypsum	14.22	18.55	0.83	1.40	23.83	0.97	-	34.99

by VSK cement plants. It is well known that the most energy-demanding phases of cement manufacturing is the clinkering process, which consumes 80% of the total energy for pyroprocessing. There is therefore a potential for energy conservation, which could be rapidly and economically accomplished by promoting the clinker formation at lower temperature in the kiln by using mineralizers that promote certain reactions and fluxes that lower the melting point of clinker liquid phase.

The addition of minor components to the raw meal provides many economic benefits, which include an increase in clinker output, a decrease fuel input, and utilization of marginal-grade limestone. Some additions act as either fluxes or mineralizers; others act both as mineralizers and fluxes. For the sake of convenience, these products will be termed as mineralizers in this paper. The reduction of temperature by 100°C is expected to result in a saving of fuel by about 80–100 KCal/Kg of clinker. Use of mineralizers as a possible means of energy conservation has been reported (4,5), but is still not popular in India. The aim of the present paper is to establish relative suitability of gypsum and calcium fluoride as mineralizers individually as well as in combination. Their effect on clinkering process is studied.

Experimental

As shown in Table 1, raw materials were used for preparing raw mixes which were obtained from a running VSK cement plant.Natural gypsum ($CaSO_4$) and fluorspar (CaF_2) were used

TABLE 2
Chemical composition of cement raw mixes (%).

Raw Mix	LOI	Si_2O	Al_2O_3	Fe_2O_3	CaO	MgO	$CaF_2/CaSO_4$	SM	AM	LSF
RM-1 (cont.)	40.80	12.58	2.81	3.87	37.19	1.07	-	1.88	0.73	0.90
RM-2	39.67	13.01	2.84	3.85	37.39	1.21	0.50	1.94	0.73	0.88
RM-3	39.17	12.97	2.81	3.85	37.47	1.21	1.00	1.95	0.73	0.88
RM-4	39.75	12.77	2.77	3.84	36.99	1.23	1.00*	1.93	0.72	0.89
RM-5	39.29	12.82	2.78	3.84	37.13	1.21	0.5 + 1.0*	1.93	0.73	0.89
RM-6	38.76	12.68	2.75	3.83	37.18	1.21	1.0 + 1.0*	1.92	0.72	0.90

* as SO_3

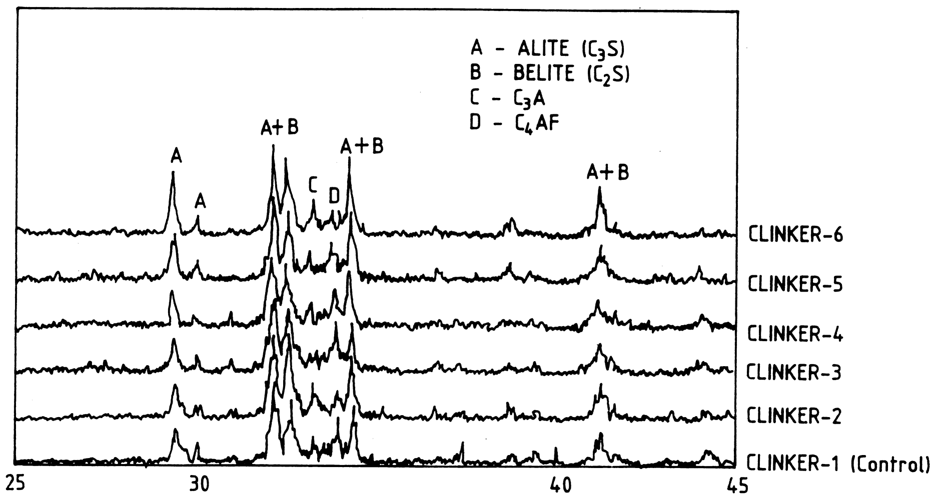

FIG. 1.
XRD patterns of clinker with and without mineralizers.

as mineralizers alone or together. The raw mixes prepared were ground to a fineness of 10% retained on 170 mesh. The chemical composition of the raw mixes is shown in Table 2.

After proper blending, the raw mixes were nodulised and fired on a platinum dish in a laboratory high temperature furnace under conditions of steady increase in temperature similar to those in a vertical shaft kiln. The clinker obtained was analysed to determine burnability and potential composition. X-ray diffraction (XRD) studies were conducted on powdered samples using a D MAX X-ray diffractometer (Rigaku, Japan) for the study of mineral phases formed in presence of mineralizers as shown in Figure 1. Studies of the mineralogical composition of clinker in presence of mineralizer were carried out on polished sections using a Carl-Zeiss Amplivol polarizing microscope with a magnification range of 260×. Table 3 summarizes mineral composition of the clinker and compares it with the potential composition obtained using Bogue's equation. Morphological studies were conducted on fractured clinker samples using a Philips CM 301 scanning electron microscope (SEM), using gold for coating the sample. SEM micrographs are shown in Figure 2.

TABLE 3
Mineral composition of clinker

	Mineral Composition (%)										
Clinker	Bogue's Equation				Optical Microscopy			Granulometry (um)			
Sample	C_3S	C_2S	C_3A	C_4AF	C_3S	C_2S	I. MAT.	C_3S	avg.	C_2S	avg.
CL-1 (cont.)	52.9	21.3	1.5	19.9	48	25	27	5-36	25	5-28	20
CL-2	47.27	26.04	3.21	19.32	46	30	24	5-25	22	5-20	21
CL-3	48.58	24.50	1.51	19.20	48	31	21	5-28	20	5-25	23
CL-4	48.91	24.02	1.41	19.38	47	30	23	5-27	18	5-22	21
CL-5	48.84	23.96	1.42	19.26	49	29	22	5-25	20	5-21	21
CL-6	50.60	21.25	1.31	18.98	50	30	20	5-20	20	5-21	20

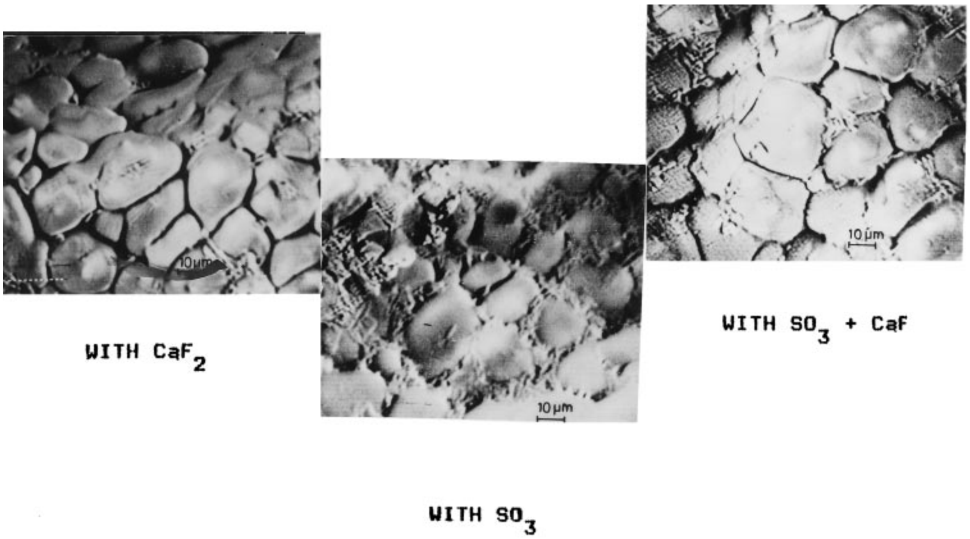

FIG. 2.
SEM of clinker using mineralizers.

The clinker was ground by adding gypsum to the fineness of about 3000 cm^2/g. Cement thus obtained was subjected to physical tests as per IS-4031 as shown in Table 4.

Results and Discussions

The VSK cement plant selected for the present study showed a problem of poor clinker quality because it had high free lime content at temperature lower than 1450°C. To get a better insight into this factor, various approaches were adopted which optimize various parameters, i.e., improved homogenization, increased fineness, and optimized raw mix design by maintaining proper modulii value. However, these factors were found to improve only marginally the kiln output and quality of clinker, as free lime was on the higher side. Thus,

TABLE 4
Physical properties of cement.

Sample	Fineness M^2/Kg	Soundness Le-chat. (mm)	Auto. (%)	Compressive Strength (MPa) 3 days	7 days	28 days
Cement-1 (cont.)	31.99	7.0	0.5	21.0	30.5	38.0
Cement-2	32.21	6.5	0.45	31.0	36.9	41.2
Cement-3	32.50	6.7	0.48	34.0	39.1	46.9
Cement-4	32.87	6.1	0.43	32.0	38.9	44.3
Cement-5	32.75	6.8	0.46	32.8	37.6	48.9
Cement-6	31.99	6.1	0.41	33.2	39.7	52.0

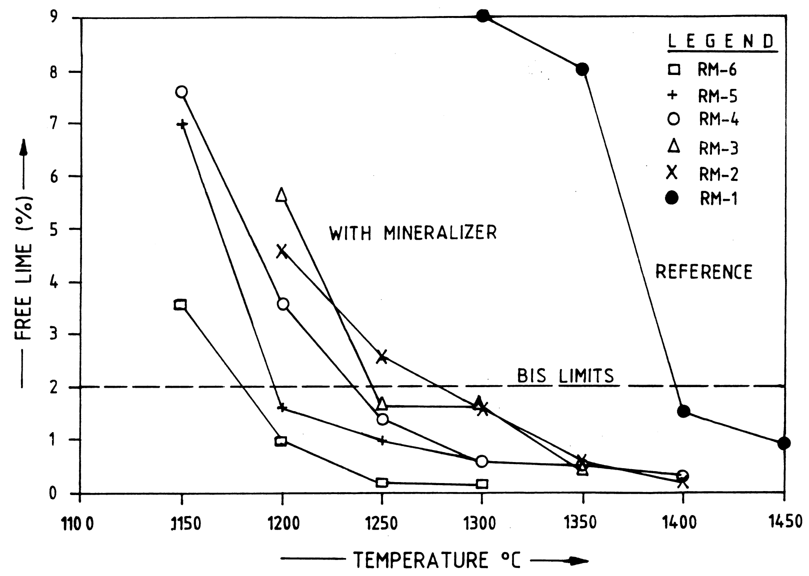

FIG. 3.
Free lime at different temperatures for raw mix with and without mineralizers.

the use of mineralizer was thought to overcome these problems and reveal the effect on the clinkering process.

Compounds, such as $CaSO_4$, CaF_2, and a mixture of the two, when added in economical ranges, provided encouraging results. Figure 3 shows the changes in burnability, expressed by the free lime content, caused by the presence of mineralizer mixed with raw mix. A free lime value of less than 2%, which corresponds to a well-burnt clinker, could be obtained by burning RM-1 between 1400–1450°C. After using mineralizer like $CaSO_4$, CaF_2, and a mixture of $CaSO_4$ and CaF_2 in raw mixes RM-2 to RM-6 respectively, free lime content decreases substantially and the value of less than 2% can be achieved at temperature range 1300–1350°C by using mixture of $CaSO_4$ and CaF_2. It is clear that use of CaF_2 provides significant improvement in clinker quality due to their interaction with the liquid phase during the C_3S formation. Table 3 shows the effect of mineralizers on C_3S formation in clinker burnt for 20 min. at 1350°C. C_3S and C_2S contents were determined by XRD analyses. The comparable addition of gypsum shows relative little effect. This is in conformity with findings by other researches (6). Comparison of complex mineralizer, i.e., a mixture of $CaSO_4$ and CaF_2, when mixed with raw mix (RM-5&6) presents interesting results (Fig. 3) by reducing the free lime content to $<$8% at 1150°C. It is clear that complex mineralizers lowers the temperature of the liquid formation and significantly increases the rate of C_3S formation as shown in Table 3. This is due to following reasons:

1. It is known from literature that $CaCO_3$ decomposes above 1000°C, absorbing a large amount of heat. Most of the heat is consumed for $CaCO_3$ decomposition. The presence of SO_3 and F^- speeds up $CaCO_3$ decomposition at a lower temperature, thus reducing heat consumption or fuel inputs.

2. It is reported (7,8) that low melting point phase, i.e., $3C_2S{\cdot}3CS^{-}$-CaF_2, appears at 1173°C; $2C_2S{\cdot}CS^{-}$ occurs at 1323°C, and both phases disappear at 1300°C. These two intermediate phases play a very important role during firing of raw mix by increasing the liquid phase and reducing the viscosity and surface tension. The dissolution of C_2S and CaO ion diffusion accelerates C_3S formation. The crystal growth of C_3S is also favoured by the liquid phase formation at lower temperature. At the same time SO_3 is able to stabilize $-C_2S$, preventing it from transformation to $-C_2S$ and favouring strength development.

Introduction of fluoride causes an additional phase, $C_{11}A_7{\cdot}CaF_2$, which is formed above 1300°C and begins to decompose at higher temperature. The quality of fluoride-containing compounds was kept low (0.5–1.0%) because of various conflicting reports given in the past. However, it has been made clear from fluoride-bearing SEM data (Fig. 3) that, in the presence of F^{-} content, alite phase changes with more flattened periphery and its amount increases correspondingly. Furthermore, its crystal size becomes smaller. As for belite phase, its amount was decreased with addition of F^{-} to the clinker and the rounded shape was transformed to a finger- or leaf-like shape, turning more and more irregular (9).

When used in small quantity, mineralizers do not have any adverse effect on the property of cement. The effect of mineralizers on the strength of cement is shown in Table 3. Compared to the non-mineralized Cement-1 (control sample), mineralized cement samples, i.e., Cement-2 to Cement-6, exhibit good strength increase with no adverse effect on other properties. This may be attributed to the increase in C_2S plus C_3S contents in the mineralised clinker. Some adverse effects of excess fluorine if any on the properties of cement is minimized due to volatilization of fluoride during the clinkerisation process in vertical shaft kiln technology. The quantity of fluoride emission is too small to cause pollution problems.

Conclusions

The following conclusions can be drawn from the present study:

1. It has been established that both gypsum and calcium fluoride improve burnability of cement clinker. From Figure 2 the CaF_2 effect seems to be stronger than that of $CaSO_4$
2. The study also indicates that a combination of mineralizers show the most promising results.
3. Selection of mineralizer and the mode of addition demand a careful investigation to determine what is appropriate for plant practice, as various processes and material parameters need to be optimised.
4. Clinker produced with mineralizers shows significant increase in C_3S plus C_2S content as compared to non-mineralized clinker. The results therefore indicate the possibility of producing clinker at lower temperature with compressive strength comparable to OPC.

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