Pergamon

Cement and Concrete Research, Vol. 26, No. 9, pp. 1361-1367, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00120-2

INFLUENCE OF SAND NATURE ON BURNABILITY OF WHITE CEMENT RAW MIXES MADE USING CaF_2 AND $CaSO_4$ FLUXING/MINERALIZER PAIR

F. Puertas, M.T. Blanco-Varela, T. Vázquez and A. Palomo
Instituto Eduardo Torroja de Ciencias de la Construcción (CSIC)
P.O. Box 19002, 28033 Madrid, Spain

(Refereed)
(Received October 13, 1995; in final form June 26, 1996)

ABSTRACT

The influence of sand nature on the burnability of white cement raw mixes manufactured using CaF_2 and $CaSO_4$ as flux and mineralizer has been studied. A methodology based on a statistical method called Experimental Design is used to establish a model.

Raw mixes burnability models have been compared depending on sand nature. An Al_2O_3 and CaO rich sand enhances raw mix burnability, favouring clinkering. The enhancement is attributed to the different distribution of clayey material in the raw mix.

Introduction

In a former study (1), a new methodology to model and evaluate cement raw mixes burnability was employed. This methodology was specifically applied to the burnability of a white cement raw mix made with limestone, sand, kaolin and CaF_2 and $CaSO_4.2H_2O$ fluxing/mineralizer pair.

The presence of this fluxing/mineralizer pair in cement raw mixes has economical and technical advantages. On one hand, it allows to obtain white cement clinkers with less than 5%wt. C_3A content; this means that sulfate and sea water resistant cements can be prepared. On the other hand, the presence of the fluxing/mineralizer pair allows raw mixes to clinker at temperatures between 1350-1400°C. White cement clinker can be obtained at approximately 200°C below the normal clinkering temperatures of traditional white cement raw mixes. This leads, obviously, to an important energy saving in the white cement manufacturing process. These described aspects can be applied to grey portland cement manufacturing.

In the proposed model (1), raw mixes were prepared using a SiO_2 rich sand (> 90%) with a relatively low Al_2O_3 and CaO content; this sand was designated Sand II. This sand was used in an industrial test to produce white mineralized clinker. The industrial plant has a semiwet system (LEPOL). The main problem during the test was the breakage, due to poor cohesion, of the nodules in the decarbonation zone of the grate prior to the rotary kiln.

To avoid this problem of nodule breakage and to obtain stronger nodules another sand richer in clayey content (Sand I) was tested.

Sand II was obtained from Sand I by water washing, extracting most of the clayey material, resulting in quartz grains which were mineralogically identical.

The main objective of this paper is to know the influence of sand nature on the burnability of these white cement raw mixes.

The same methodology described in (1) was used for modelling the raw mixes burnability.

Experimental Procedure

The chemical analyses of the raw materials are shown in Table 1.

A two-level factorial experimental design was used for modelling (2). The parameters given in Table 2 were considered to be the most relevant for raw mix burnability assessment. That table also shows the two levels (+ and -) defined for each factor.

LSF selected levels (93 and 98) are in the range usually used in industrial practice. Only one level was selected for silica modulus, M_s= 11. This value is higher than those employed in traditional grey and white clinker production but it is necessary to produce sulfate resistant cements. Clinkerization is possible due to the mineralizing and fluxing effects of CaF_2 and $CaSO_4$. The AR (alumina iron ratio) values in these raw mixes are in the range between 7.3 and 7.6.

Sand I mixes were prepared. A 2^{6-1} design was done; this means 32 different experiments or different clinkerizations. These experiments correspond to the 8 different dosages obtained through the combination of three compositional parameters (LSF, % CaF_2 and % $CaSO_4$) at two levels (2^3).

Also Sand II mixes were prepared. In this case the design corresponded to a 2^6 one.

The preparations and thermal treatments of those raw mixes were done using the same methodology described in (1). Sizes of limestone and sands were selected by sieving,

TABLE 1

Chemical Analysis of Raw Materials

	LIMESTONE	KAOLIN	SAND II	SAND I	GYPSUM	FLUORITE
I.O.	43.21	11.50	2.13	3.25	--	10.54
SiO_2	0.68	53.56	91.78	87.90	1.41	18.80
R.I.	0.12	0.12	--	--	--	--
Al_2O_3	0.05	32.78	4.16	5.91	0.09	--
Fe_2O_3	0.19	0.57	0.14	0.19	--	--
CaO	56.78	1.21	1.40	2.54	32.94	13.43
MgO	--	--	0.03	0.06	0.70	--
SO_3	--	--	--	--	43.86	--
Na_2O	0.02	0.06	0.03	0.02	--	--
K_2O	0.01	0.76	0.04	0.10	--	--
CO_2	--	--	--	--	2.12	--
H_2O Comb.	--	--	--	--	19.30	--
F_2Ca	--	--	--	--	--	51.4

TABLE 2

Relevant Factors and Corresponding Levels

Factors	Factors Identification	Levels (-)	Levels (+)
LSF	A	93 .	98
CaF_2 (%wt)	B	0.65	1.30
$CaSO_4$ (%wt)	C	2.6	3.9
Size Particule of Sand (%wt)	D	100%<45 μm	80% <45 μm 20% <45 μm
Size Particule of Limestone (%wt)	E	100% <125 μm	80% <125μm 20% >125μm
Temperature	F	1350°C	1400°C

LSF = Lime Saturation Factor

kaolinite is very fine having an average size of 6 μm. The measured variable was free CaO in clinkers determined using an ethylene glycol method (3).

Results and Discussion

Burnability of Sand I Raw Mixes. The statistical analysis of free CaO values of the 32 clinkers obtained has been done using the variance analysis method (V.A.), neglecting interactions higher than second order.

Results analysis shows the importance of the main factors (A, B, C, D, F and, G). Significative binary interactions are:

BC, BE and CE

The proposed model for this design is:

$$\% \, CaO_{Free} = 3.36 + 0.37\,X_A - 1.05\,X_B - 0.60\,X_C + 0.003\,X_D + 1.57\,X_E + 0.11\,X_F + 0.34\,X_B X_C - 0.49\,X_B X_E - 0.28\,X_C X_E + \Sigma \quad [1]$$

Where $\Sigma \approx N(0, \sigma)$, $\sigma = 0.41$ by Variance Method (V.A.) neglecting interactions greater than second order. The coefficient of determination (R^2) is 98.87%.

Those interactions with coefficients lower than 0.2 have not been considered as significant. In order to analyze their importance, main factors X_D, and X_F have been considered in spite of having coefficients lower than 0.2.

3.36 %wt is the mean free lime content found in clinkers obtained by burning raw mixes for 30 minutes at pre-established temperatures. X_A, X_B, X_C, X_D, X_E and X_F are assigned a value of -1 or +1 depending upon the level, - or +, that each of these factors have in the raw mixes. The coefficient applied to factors X_A....X_G, is a measure of each one's contribution to raw mix burnability.

The value of coefficients will depend on the range selected for each parameter. It means that the obtained model can be only applied (in the most strict sense) to explain the burnability of raw mixes having their characteristics parameters within the selected ranges. In this study the chosen range of each parameter were the most adequate for producing fluor-sulfate white clinker.

The statistical analysis of experimental data shows that, the considered factors as well as their interactions, explain 98% of the burnability results of those raw mixes. So, it can be considered that the proposed model explains well the behaviour of the raw mixes studied.

Equation [1] analysis leads to the following interpretations:

i) E factor (limestone particle size), B factor (fluorite percentage) and C factor (gypsum percentage) are the most important factors with respect to clinkers final free CaO contribution. These main factors not only contribute to the free lime content of samples at individudal level but they are involved in the main significative binary interactions. In fact the coefficient of the BE binary interaction is higher than the one's of some individual factors as LSF (A), sand particle size (D) or clinkering temperature (F). Then, for example, the effect of limestone particle size (E) on burnability depends not only of its own level but also of CaF_2 and $CaSO_4$ levels.

ii) Fourth factor in significance is lime saturation factor (LSF).

iii) Temperature coefficient is relatively low and sign preceeding temperature coefficient is positive. Then, free CaO content in clinkers, from raw mixes treated at 1350°C is higher that from meals treated at 1400°C.
Analysis carried out in ten different clinkers have shown that clinkers obtained at 1350°C have a SO_3 loss lower than 10% .In those obtained at the highest temperature the loss of SO_3 is around 25-40 %wt. This loss of SO_3 and the consequent increase in effective LSF could explain the increase in final free lime content of clinkers obtained at 1400°C.
Although the loss of SO_3 observed in laboratory clinkering tests is very important, the industrial experience shows that the loss of SO_3 is very much lower. This is because of the high partial pressure of SO_2 in the kiln atmosphere from the fuel combustion and SO_2 capture by the incoming feed. Hence the range at adequate clinkering temperature for these raw mixes can be established as being 1350-1400°C.

iv) Finally, D factor, corresponding to sand particle size influence, is, surprisingly, the factor with the least significant effect. The correlation coefficient for the coarse sand fraction obtained in this work is different from that established by others authors (4). However, the experimental conditions in the studies are quite different, and a direct comparation is not possible.

These raw mixes have five times more limestone than sand. Calculating the final free CaO contribution of 1%wt from the coarse limestone and sand particles, it is obtained that:

1 % sand particles > 45 μm = 0.03 % wt CaO
1 % limestone particles > 125 μm = 0.20 % wt CaO

So, the specific contribution of coarse limestone particles to free CaO is more than six times superior to the coarse sand particles contribution. These results have a great technological importance, because of the expensive process to obtain sand particles finer than 45μm; and grinding processes require an important energy cost.

Finally, from analysing some clinkers after firing, it has been confirmed that the clinker chemistry is close to target, although losses of SO_3 can modify effective LSF as was dicussed before.

Burnability Models Comparison of Sand I and Sand II Raw Mixes. The burnability model of white cement raw mixes prepared with Sand II as raw material, considering the same factors and levels as using Sand I, follows the equation [2]:

$$\% CaO_{Free} = 4.64 + 0.62 X_A - 1.62 X_B - 0.89 X_C + 0.28 X_D + 1.70 X_E - 0.24 X_F - 0.21 X_A X_B + 0.24 X_A X_D - 0.36 X_B X_E + \Sigma \quad [2]$$

Where $\Sigma \approx N(0, \sigma)$, σ estimation is of 0.51, neglecting interactions higher than third order. The coefficient of determination (R^2) is 97.72%.

Comparing equations [1] and [2], some relevant conclusions can be extracted about sand nature influence on the burnability of these white cement raw mixes. In Table 3 the coefficients of main factors in the two models obtained are shown. In burnability equation [1], almost all coefficients and the independent term are inferior, in absolute value, to those in equation [2], and all except temperature retain the same sign. In any case, the absolute value of temperature coefficient in both models is small, confirming its scarce influence on clinkers free CaO.

From these results it can be deduced the better burnability of Sand I raw mixes with respect to Sand II raw mixes. D factor, corresponding to sand particle size, is the greater difference, confirming the positive effect of Sand I on raw mixes burnability.

TABLE 3

Comparison of Coefficient Values in Equations [1] and [2]

	EQUATION [2] SAND II	EQUATION [1] SAND I
Mean Free Lime	4.64	3.36
A LSF	+ 0.62	+ 0.37
B CaF_2	- 1.62	- 1.05
C $CaSO_4$	- 0.89	- 0.60
D θ SAND	+ 0.28	+ 0.003
E θ LIMESTONE	+ 1.70	+ 1.57
F T[a]	- 0.24	+ 0.11

The enhanced burnability for Sand I raw mixes is due to the presence in their composition of a small proportion of clay (mainly aluminous in contact with quartz grains) acting as a flux. This produces, at adequate temperatures, a certain quantity of melt phase around quartz particles enabling reactions to occur at a higher rate. This clayey material can be very advantageous to enhance formation and stabilization of raw mixes nodules before their kiln entrance, confirming that the industry practice of sand washing allows to have a better control of some parameters (dosage, cromophore elements,etc.) but may make calcination and burnability difficult.

Finally, to evaluate the specific effect of sand type, data were analyzed considering a new factor called G, corresponding to sand type, its levels were:

-1 : Sand II
+1 : Sand I

A 2^{7-1} design was done consisting on 64 experiments. Compositions, clinkers obtained and free CaO values were taken from those made in the former models [1] and [2].

Results analysis was done by Variance Method (V.A.) neglecting interactions higher than second order. Conclusions are coherent.

In this design, all factors are significant except temperature, remaining the relative importance order of initial factors, with G factor "sand type" following limestone and fluorite, before gypsum.

With respect to binary interactions, the following are significant:

X_AX_D, X_BX_C, X_BX_E y X_BX_G

The model explaining this design is:

$$\% \text{CaO}_{\text{Free}} = 4.00 + 0.49\, X_A - 1.36\, X_B - 0.74\, X_C + 0.19\, X_D + 1.62\, X_E - 0.09\, X_F - 0.64\, X_G + 0.21\, X_AX_D + 0.25\, X_BX_C - 0.41\, X_BX_E + 0.31\, X_BX_G + \Sigma \quad [3]$$

Where $\Sigma \approx N(0, \sigma)$, $\sigma = 0{,}57$, neglecting interactions higher than third order. The coefficient of determination (R^2) is 97.27%.

From this design analysis, the influence of sand nature (G factor) on this raw mixes burnability is confirmed, being G the fourth more important factor. In these raw mixes studied, an increase of 0.64% in clinker final free CaO is produced if Sand II has been used in raw mixes elaboration; opposite, a decrease of 0.64% in free CaO is produced if Sand I was used.

Conclusions

Composition and nature of sand used in raw mixes preparation has a great influence on their burnability.

Burnability of white cement raw mixes made using CaF_2 and $CaSO_4$ fluxing/mineralizer pair and two sands of the same origin but with different clayey material content has been studied and evaluated.

The equation explaining burnability of these raw mixes when sand has a higher clayey material contain (Sand I) is:

$$\% \, CaO_{Free} = 3.36 + 0.37\, X_A - 1.05\, X_B - 0.60\, X_C + 0.003\, X_D + 1.57\, X_E + 0.11\, X_F + 0.34\, X_B X_C - 0.49\, X_B X_E - 0.28\, X_C X_E + \Sigma \qquad [1]$$

D factor, corresponding to sand particle size influence is the main factor with less significance. In these raw mixes, the specific contribution of coarse limestone particles to free CaO is six times superior to the contribution of the coarse sand particles.

Comparing the proposed models (equations [1] and [2]) to explain burnability of raw mixes prepared with a siliceous rich sand (Sand II) and that with higher clayey material proportion (Sand I), it is concluded that the latter has much better burnability. That enhancenment is due to the different clayey material distribution in raw mix bulk. In the case of Sand I raw mixes, part of the clayey material is given by sand itself and, hence, its distribution among raw mixes particles is near quartz grains and not randomly distributed. This produces, at suitable temperatures, a certain melt phase amount around quartz particles and so, reactions may occur at higher rate.

Not depending on other factors, Sand I incorporation to raw mix involves a mean reduction of 1.28% wt. in clinker final free CaO, for equal raw mixes dosages.

Acknowledgement

The authors wish to thank to J.G. Palomo Sánchez for the statistical data analysis.

References

1. BLANCO-VARELA, M.T.; PUERTAS, F.; VAZQUEZ, T.; PALOMO, A. "Modelling of the burnability of the white cement raw mixes made with CaF_2 and $CaSO_4$". Cem. Concr. Res. Vol 26, No 3, pp. 457-464 (1996)
2. BOX, G.E.P.; HUNTER, W.G.; HUNTER, J.S. "Statistic for Experimenters. An Introduction to Design, Data Analysis and model Building". Ed. John wiley & Sons (1989)
3. UNE Standard 80-243-86. "Métodos de ensayo de cementos. Determinación del óxido de calcio libre; método del etilenglicol" (1986)
4. FUNDAL, E. World Cement Technol. 10, N°6, pp. 195-196, 199-200, 203-204 (1979)