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MODELLING OF THE BURNABILITY OF WHITE CEMENT RAW MIXES MADE WITH CaF_2 AND $CaSO_4$

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ABSTRACT

Burnability of white cement raw mixes made using CaF_2 and $CaSO_4$ as fluxes/mineralizers is studied and modelled. A methodology based on a statistical method called experimental design is used to establish the model.

An equation that explains the burnability of these new raw mixes is established. Through this equation, it is deduced that limestone particle size, fluorite and gypsum content have a major influence on burnability, while silica modulus has little effect.

Introduction

The burnability concept is related to the reaction rate of the CaO component during the high temperature treatment of raw mixes. Burnability of raw mixes depends on the properties of the mixes themselves and on conditions of manufacture. Mix properties include chemical and mineralogical composition, granulometry and degree of contact between the various constituents. Manufacturing parameters include the thermal gradient, maximum clinkering temperature, clinkering time, cooling rate, kiln atmosphere, etc.

There are various ways of evaluating portland cement burnability. (1-12). E. Fundal (6) proposes two empirical equations for raw mix burnability at 1400°C and 1500°C respectively, burned during 30 minutes. Such equations are the result of analyzing 92 raw mixes from different parts of the world.
Their expressions are the following:

$$\% \, CaO_{1400°C}(\text{free}) = 0.31\,(LSF-100) + 2.18\,(M_s - 1{,}8) + 0.73\,Q_{45} + 0.33\,C_{125} + 0.34\,Aq \qquad [1]$$

$$\% \, CaO_{1500°C}(\text{free}) = 0.21\,(LSF - 100) + 1.59\,(Ms - 1.9) + 0.40\,Q_{45} + 0.22\,C_{125} + 0.08\,Aq \qquad [2]$$

where LSF is the lime saturation factor, Ms is the silica modulus, Q_{45} the weight fraction of quartz particles with a size greater than 45 µm, C_{125} is the weight fraction of limestone particles with a size superior to 125 µm and Aq is the clay materials fraction greater than 45 µm. This equation is of general application for grey portland cement raw mixes with traditional compositions.

Mineralizers and/or fluxes are often added to cement raw mixes to accelerate reactions and enhance burnability. In such cases the methods described above for evaluating burnability of raw mixes are inapplicable, rendering evaluation quite difficult.

CaF_2 acts in different ways in the consecutive reactions of the clinkering process, reducing the $CaCO_3$ thermal decomposition temperature, altering the phases in thermodynamic equilibrium, varying the properties and temperature of melt formation, etc. The net result is improved burnability of raw mixes. The alite formation reaction in a clinker occurs at lower temperatures and a much faster rate (in particular in white clinkers) if CaF_2 is present (13, 14).

Since $CaSO_4$, in turn, reduces melt viscosity and consequently increases ion mobility. When the $CaSO_4$ content was increased in the raw mix a decrease on alite rate formation has been observed (15, 16). This decrease can be attributed to the decrease in the driving force for this reaction as well as to the effect of $CaSO_4$ on the C_2S stability range, which widens at the expense of the C_3S stability range (14).

Burnability can be substantially improved by adding the mineralizing pair CaF_2 and $CaSO_4$ to the raw mixes, especially at temperatures between 1300 and 1400° C. The rate of alite formation in this case is even higher than that found for mixes mineralized with CaF_2 only (17). This higher rate is due essentially to the thermodynamic effect of the widened stability range and primary phase field of crystallization of C_3S induced by CaF_2, together with enhanced ion mobility in the melt due to $CaSO_4$ and CaF_2 and the appearance of a new liquid phase at temperatures under 1200° C (18, 19). Fluorellestadite ($3C_2S.3CaSO_4.CaF_2$) is the main compound of such a liquid whose approximate composition is: CaO 54 wt %, Al_2O_3 4 wt %, Fe_2O_3 wt %, SiO_2 11 wt %, CaF_2 4 wt %, $CaSO_4$ 24 wt % .

Some authors (17, 20-24) have reported good burnability for raw mixes mineralized with CaF_2 and $CaSO_4$. In most of these studies, the intention was to optimize the content of such compounds to achieve cements with good burnability or increased mechanical strength.

$CaSO_4$, as well as CaF_2, have low vapour pressures, which makes them to be volatile in the hottest areas of the kiln. This fact, together with thermal gradients, facilitates the transport of the gasses, enabling the vapour condensation in the kiln lower temperature areas and thus producing phases which are, in their turn, able to decompose again in the high temperature areas. In other words, a cycle of the volatile elements takes place in different areas of the kiln.

CaF_2 and $CaSO_4$ can in turn be used to partially replace the traditional fluxes Al_2O_3 y Fe_2O_3, to produce clinkers with low aluminate contents at temperatures between 1300 and 1400° C (18, 25-26). In this type of material the essentially fluorsulfatic liquid phase is composed mainly of molten fluorellestadite (60 -75% by weight), ferrites and aluminates. The low clinkering temperature of these raw mixes reduces the loss of F_2 and SO_3.

The use of this mineralizing pair to partially replace aluminates is particularly useful in the manufacture of white clinker, because of the potential for energy conservation and because seawater- or sulfate-resistant white cements can be produced when such additives are used (27).

To date, naturally, no mathematical model has been able to predict the burnability of these raw mixes. And yet it is of utmost importance to be able to determine burnability when modifying production processes, optimizing thermal performance or changing clinker characteristics.

The main objective of this paper is to propose a mathematical model to predict the burnability of raw mixes made using CaF_2 and $CaSO_4$ as fluxes and mineralizers for manufacturing white clinker.

Experimental Procedure

Starting from some raw mixes containing CaF_2, $CaSO_4$ and Al_2O_3 as fluxes to obtain clinkers with a C_3A content under 5% at temperatures between 1350 - 1400° C, the burnability of these white cement raw mixes has been modelled.

The chemical analysis of the raw materials is shown in Table 1. A two-level factorial experiment design was used for modelling (28). The parameters given in Table 2 were considered to be the most relevant for raw mix burnability assessment. The table also shows the two levels (+ and -) defined for each parameter. The complete design consists in $2^7 = 128$ different experiments. These 128 experiments correspond to 16 different dosages that are shown in Table 3.

The raw mixes were prepared from the corresponding amounts of limestone,sand, kaolin, fluorite and gypsum (the two former with previously selected sizes). The mixes were hand homogenized, taking great care to avoid any modifications of particle size and then dried. The dispersive medium used was ethanol. With each of the raw mixes, cylindrical pellets of 2.5 cm diameter and 1.5-2cm length were prepared.

Temperature treatment of these pellets was done in laboratory kilns at selected temperatures. Heating time was always constant and equal to 30 minutes. The measured variable was free CaO in clinkers through the ethylene-glycol method (29).

Results and Discussion

The statistical analysis of free CaO values of the 128 clinkers obtained has been done using the variance analysis method (V.A.), neglecting interactions higher than third order. This V.A.

TABLE 1
Chemical Analysis of Raw Materials

	LIMESTONE	KAOLIN	SAND	GYPSUM	FLUORITE
L.O.I	43.21	11.50	2.13	—	10.54
SiO_2	0.68	53.56	91.78	1.41	18.80
I.R.	0.12	0.12	—	—	—
Al_2O_3	0.05	32.78	4.16	0.09	—
Fe_2O_3	0.19	0.57	0.14	—	—
CaO	56.78	1.21	1.40	32.94	13.43
MgO	—	—	0.03	0.70	—
SO_3	—	—	—	43.86	—
CO_2	—	—	—	2.12	—
H_2OComb.	—	—	—	19.30	—
CaF_2	—	—	—	—	51.4

TABLE 2
Relevant Parameters and Corresponding Levels

Parameters	**Parameters Identification**	**Levels**	
		(-)	(+)
LSF	A	93	98
Ms	B	11	14
CaF_2 (%wt)	C	0.65	1.30
$CaSO_4$ (%wt)	D	2.6	3.9
Particle Size of Sand (%wt)	E	100% < 45 µm	80% < 45 µm 20% < 45 µm
Particle Size of Limestone (%wt)	F	100% <125 µm	80% < 125 µm 20% > 125 µm
Temperature	G	1350°C	1400°C

LSF = Lime Saturation Factor
Ms = Silica Modulus

method is based on decomposing observations as a sum of terms, each one depending on a factor or an interaction of factors.

Assembling the information of the free CaO analyses obtained from the 128 clinkers, it is deduced that results are completely coherent, observing that factors considered: A, B, C, D, E, F and G are clearly significant. Likewise, the second order AC and CF interactions are also significative.

The proposed model is:

$$\begin{aligned} \%\ \mathrm{CaO}_{\mathrm{Free}} = {} & 4.55 + 0.675\, X_A - 0.08\, X_B - 1.565\, X_C\ - \\ & - 0.765\, X_D + 0.335\, X_E + 1.695\, X_F - 0.135\, X_G\ - \qquad [3] \\ & -0.202\, X_A X_C - 0.301\, X_C X_F + \Sigma \end{aligned}$$

Where $\Sigma \approx N(0, \sigma)$,, σ estimation is of 0.47045, neglecting interactions higher than third order.

Where 4.55 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, X_F and X_G 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.

TABLE 3
Composition of 16 Mixes Prepared

Dosages	LSF	Ms	% CaF_2	% Gypsum
1	98	11	1.3	2.6
2	93	14	1.3	3.9
3	93	11	1.3	2.6
4	98	14	0.67	2.6
5	98	11	1.3	3.9
6	98	14	1.3	2.6
7	93	14	1.3	2.6
8	93	11	0.67	2.6
9	98	14	1.3	3.9
10	98	11	0.67	3.9
11	93	11	0.67	3.9
12	98	11	0.67	2.6
13	98	14	0.67	3.9
14	93	11	1.3	3.9
15	93	14	0.67	2.6
16	93	14	0.67	3.9

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

The statistical analysis of the experimental data shows that the considered factors, as well as their interactions, explain 95%, at 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.

From the analysis of the coefficients multiplying the factors in the equation [3] of the proposed model it can be deduced that:

i) The most significant factors, that is, the ones that contribute most to the clinker free lime are (in ascendent order):

F (limestone particles size)> C (% wt CaF_2) > D (% wt $CaSO_4.2H_2O$)

When 20% limestone particles with size greater than 125 μm are present in the sample, a contribution of 1.695% wt to the total free lime is produced; oppositely, when all the limestone particles are less than 125 μm, the final free lime amount is reduced 1.695%.

This is justified taking into account that limestone is the raw material present in major proportion in the raw mix. The coarser particles of limestone decarbonate and produce CaO particles of great size. As a consequence of that decarbonation, the particles size decrease and the linear reduction in particles diameter is estimated to be 10% (30). Clinkering reactions, in the solid state or in the presence of a melt phase, occur around these CaO grains. When these grain are coarse and with melt phase is scarce, the reaction products are deposited around these CaO grains, acting as diffusion barriers, decreasing the rate of reaction, and always leaving the leaving always CaO cluster unreacted.

The great significance of C and D factors (The greater CaF_2 and $CaSO_4.2H_2O$ amount in the raw mix, the lesser is free CaO proportion in the clinker) confirms the important flux-mineralizer role of the fluorite-gypsum pair.

ii) Lime saturation factor (LSF) is the fourth factor in importance with respect to the burnability of raw mixes. Its contribution to the final free CaO is of +0.675% wt when LSF is 98% or -0.675% wt when LSF is 93.

iii) Sand particle size (E factor) is the fifth factor in importance. This factor, as it is deduced from the obtained model, has less influence than F (limestone particles size) with respect to the final free CaO contribution.

Those raw mixes, at which parameters E and F take the maximum level value (see Table II), have about 15% wt of limestone particles higher than 125 µm, while the proportion of sand particles coarser than 45 µm is 3% wt; that is, the ratio between coarse limestone and sand particles is 5:1 in weight. Supposing that in the variation range studied, there is a linear relation between limestone or sand particles percentage higher than 125 µm and 45 µm respectively, and the free CaO percentage produced, the contribution of 1% in weight of coarse limestone and sand particles to the clinker free CaO can be calculated. This contribution would be:

1% wt sand particles > 45 µm= 0.111% wt in CaO

1% wt limestone particles > 125 µm= 0.113% wt in CaO

Thus, the specific contribution of coarse limestone and sand particles to the free CaO, is practically the same. These results are different to those expressed by Fundal (6), since in equation [1], the coefficient multiplying the factor corresponding to the quartz particles higher than 45 µm is 2.2 times greater than the coefficient that multiplies the factor corresponding to the limestone particles fraction superior to 125 µm. It is known that coarse quartz particles contribute in a significant way to the clinker final free lime. The results obtained indicate the need to carry out a specific research work concerning the effect of sand particle size on the burnability of white mineralized cement raw mixes.

iv) It is significant concerning the effect of that factor G (clinkerization temperature) and especially factor B (silica modulus) were of little importance . Practically, there is no difference between burning temperature 1350° or 1400°C. It should be stressed that traditional white cement raw mixes require clinkering temperature higher than 1500°C, while the new raw mixes are perfectly burned at temperatures of 1350°C.

It is of special interest to point out the results obtained with respect to the low significance of silica modulus, Ms, in these white raw mixes. This means that from the point of view of final free CaO contributions, it is practically irrelevant whether the Ms value is 11 or 14. From the technological point of view, this result is very important since both values are very high (it is worth remembering that an Ms value of about 3-4 is normal for a white raw mix), this means that raw mixes with Ms values of 11 or 14 would be very difficult or impossible to be clinkered. However, due to the CaF_2 and gypsum flux-mineralizer pair, these raw mixes can be clinkered and they are technologically satisfactory.

Finally, a comment is necessary with respect to the two terms in the equation representing second order interactions with a certain influence (X_AX_C and X_CX_F) in the final free lime value. These interactions contain the more important factors individually, sharing X_C factor that corresponds to % wt CaF_2 present in the raw mix.

Conclusions

A new methodology for the study and determination of cement raw mixes burnability is presented. This methodology, based on a statistical tool called experimental design, enables the evaluation of the different chemical and physical factors influencing burnability.

Using this methodology, an equation is proposed that explains the burnability of white cement raw mixes containing CaF_2 and $CaSO_4.2H_2O$ as fluxes and mineralizers. This equation is:

$$\begin{aligned} \%\ \mathrm{CaO}_{\mathrm{Free}} = {} & 4.55 + 0.675\ X_A - 0.08\ X_B - 1.565\ X_C - \\ & - 0.765\ X_D + 0.335\ X_E + 1.695\ X_F - 0{,}135\ X_G - \\ & - 0.202\ X_A\ X_C - 0.301\ X_C\ X_F + \Sigma \end{aligned} \qquad [3]$$

Where $\Sigma \approx N(0, \sigma)$, σ estimation has been of 0.470, neglecting interactions with order higher than three.

For raw mixes within the range of chemistries and finenesses studied, the following conclusions can be deduced from the data analysis:

a) The factor affecting the final free CaO in the clinker to the greatest extent is limestone particle size in the raw mix, followed by fluorite and gypsum content. The flux-mineralizer role of these latter materials is marked.

b) The silica modulus (11 or 14) has little influence on the burnability of these special raw mixes. In spite of those atypical Ms values, these raw mixes are easily burned giving optimum white clinkers at temperatures of 1350°-1400°C.

c) Sand particle size is significant from the point of view of final free CaO. Considering the contribution to the free lime of 1% limestone particles greater than 125 µm and 1% of sand particles greater than 45 µm, both contributions are practically the same.

d) The selected burning temperatures in this study (1350° and 1400°C) have not resulted in differences of practical significance; both have led to similar results.

e) The good reactivity and burnability of these raw mixes have been confirmed, because they are perfectly clinkered at low temperatures of 1350°C: this is about 200°C less than the clinkering temperatures of traditional white cement raw mixes.

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