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A STUDY ON THE GRINDABILITY OF PORTLAND CEMENT CLINKER CONTAINING TRANSITION METAL OXIDES

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ABSTRACT

The subject of this paper is to investigate the effect of transition metal oxides on the grindability of clinker. As it is concluded clinker containing ZnO has the lower grindability while clinker containing MnO or Cr_2O_3 has the higher grindability. The classification of the added oxides, concerning the clinker grindability (descending sort), is: MnO, Cr_2O_3, Ni_2O_3, ZrO_2, CuO, Co_2O_3, V_2O_5, MoO_3, TiO_2, ZnO. The study of the clinker by means of X-Ray diffraction and optical microscopy confirms the results. © *1997 Elsevier Science Ltd*

Introduction

The addition of transition element compounds in the cement raw mix affects the sintering process provoking modifications of the structure and properties of clinker (1, 2, 3, 4, 5).

The cement raw mix sintering is a complicated process involving physical and chemical operations. The main stage is the formation of the liquid phase which is the means to the formation and development of the alite crystals.

TABLE 1

Chemical Comp. of the Raw Meal. Mineralogical Comp. of the Clinker (% w/w)

Raw meal	
SiO_2	13.87
Al_2O_3	3.29
Fe_2O_3	2.50
CaO	43.53
MgO	1.16
K_2O	0.34
Na_2O	0.05
Clinker	
C_3S	71.44
C_2S	7.75
C_3A	6.96
C_4AF	11.80

TABLE 2

Transition Metal Oxides Used

Oxide	Sample code
-	Cl
ZnO	Cl-Zn
Ni_2O_3	Cl-Ni
Co_2O_3	Cl-Co
TiO_2	Cl-Ti
MnO	Cl-Mn
ZrO_2	Cl-Zr
Cr_2O_3	Cl-Cr
V_2O_5	Cl-V
MoO_3	Cl-Mo
CuO	Cl-Cu

The dissolution of additions in the liquid phase modifies its structure and chemical/physical properties, provoking important effects on the clinkerization kinetics. Besides, the incorporation of foreign ions in the crystal lattice of the clinker minerals causes significant changes of the micro and macro structure of the resulting clinker.

The behaviour of the clinker during grinding is directly related to the texture and structure of the crystals. Therefore, it is interesting to examine the grindability of clinker containing transition element oxides.

Experimental

Ordinary Portland cement raw meal of industrial origin was used (Table 1). Transition metal oxides used are chemical grade. 2% by weight of transition metal oxides were mixed with cement raw meal. Table 2 presents the sample codes of the prepared clinkers. Homogeneity was ascertained by dosing the added oxide on samples of the mixtures.

All raw mixes were thermally treated up to 1450°C in an electrical furnace and cooled rapidly in air. Sintering and cooling conditions were simulated to the industrial ones.

The clinker grinding was carried out in a Pascall laboratory mill. The specific surface area, according to Blaine (S_b), of the ground material was measured at different grinding time.

TABLE 3

Specific Surface Area (S_b) of Clinker vs. Grinding Time

Grinding time (min)	Specific surface area (cm^2/g)										
	Cl	Cl-Zn	Cl-Ni	Cl-Co	Cl-Ti	Cl-Mn	Cl-Zr	Cl-Cr	Cl-V	Cl-Mo	Cl-Cu
15	1500	1420	1630	1550	1420	1850	1650	1670	1310	1310	1670
30	2200	2070	2140	2270	2050	2590	2230	2270	2090	1890	2270
45	2790	2600	2900	2840	2620	3200	2860	2530	2700	2530	2730
60	3310	2990	3350	3330	3080	3590	3380	3440	3200	3230	3420
75	3740	3360	3740	3690	3480	3920	3680	3900	3530	3590	3780
90	4200	3570	4070	3980	3920	4360	4060	4730	4200	3980	3920

TABLE 4

Grindability Factor of Clinker

Clinker	Grindability factor ($gf = a_i/a_{cl}$)
Cl-Zn	0.83
Cl-Ti	0.90
Cl-Mo	0.92
Cl-V	0.95
Cl-Co	0.98
Cl-Cu	0.98
Cl-Zr	0.99
Cl-Ni	0.99
Cl	1.00
Cl-Cr	1.09
Cl-Mn	1.11

X-Ray diffraction (XRD) was used in order to identify the mineralogical phases formed during the sintering of the clinker and record the differentiation caused by transition metal oxides.

Optical microscopy (OM) was used in order to study the effect of the added oxides on the texture of the produced clinker.

Results and Discussion

Table 3 presents the results of the grinding tests. Regression analysis was used in order to model the specific surface of the ground clinker as a function of the grinding time and the added transition metal oxide. The statistical evaluation of the data presented in Table 3 led to the equation ($S = a_i \cdot t + b$) where S: specific surface area (cm^2/g), t: grinding time (min), a_i: constant depended on the added transition metal oxide and b: constant (value:1152). It is obvious that the value of a_i is proportional to the clinker grindability.

TABLE 5

Appreciation of the Clinker Grindability in Relation to the Added Oxide

Transition metal	Clinker grindability
Zn	low
Ti Mo V	low-moderate
Co Cu Zr Ni -	moderate
Cr Mn	high

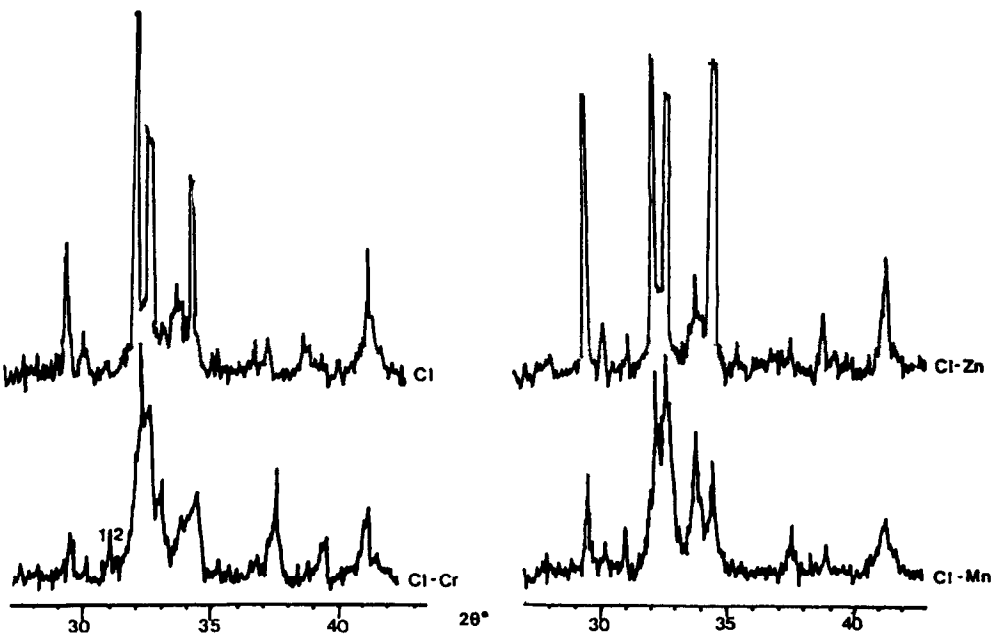

FIG. 1.
XRD patterns of the samples Cl, Cl-Zn, Cl-Cr and Cl-Mn (1: $Ca_5Cr_3O_{12}$, 2: $Ca_5Cr_2SiO_{12}$).

In order to compare the grindability of clinker containing transition metal oxide with the grindability of the pure clinker the ratio a_i/a_{cl} (a_{cl}= 34.6) is used. This ratio is referred as grindability factor (gf). Table 4 presents the grindability factors of the produced clinker. In Table 5 the appreciation of the clinker grindability, in relation to the added oxide, is given. The clinker containing ZnO (Cl-Zn, gf = 0.83) is the most hardly ground while the clinker containing Cr_2O_3 (Cl-Cr, gf = 1.09) or MnO (Cl-Mn, gf = 1.11) are the most easily ground.

The structure of the prepared clinkers was studied by means of X-Ray diffraction and optical microscopy.

FIG. 2.
Photo of sample Cl (x20).

FIG. 3.
Photo of sample Cl-Zn (x20).

FIG. 4.
Photo of sample Cl-Cr (x20).

FIG. 5.
Photo of sample Cl-Mn (x20).

Figure 1 shows the XRD patterns of the samples Cl-Zn, Cl-Cr, Cl-Mn and Cl. As it can be seen, new compounds such as $Ca_5Cr_2SiO_{12}$ and $Ca_5Cr_3O_{12}$ are detected in Cl-Cr, while in Cl-Zn greater peaks of the calcium silicates are recorded.

The examination of the samples using OM led to the photos presented in Figures 2-5. The areas shown were selected to be representative as far as the size and texture of alite or belite crystals are concerned.

The main observations made during the examination of the samples are summarised in the Table 6. The above observations explain the experimental results concerning the increased grindability of the Cl-Mn and Cl-Cr and the decreased grindability of the Cl-Zn in relation to the pure sample.

Conclusions

The following conclusions can be drawn from the present study:

- The addition of transition metal oxides in cement raw meals affects the clinker grindability.
- The classification of the added oxides, concerning the clinker grindability (descending sort), is the following: MnO, Cr_2O_3, Ni_2O_3, ZrO_2, CuO, Co_2O_3, V_2O_5, MoO_3, TiO_2, ZnO.
- The positive effect of the MnO and Cr_2O_3 on the grindability is associated with the increase of the clinker porosity, the decrease of the melt content and the appearance of cracks on the calcium silicate crystals.
- The negative effect of ZnO is connected with the increase of the melt content and the decrease of the clinker porosity.

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TABLE 6

Textural and Structural Characteristics of the Samples Cl, Cl-Zn, Cl-Cr and Cl-Mn

Sample	Observations
Cl	moderate porosity moderate percentage of liquid phase wide distribution of alite and belite size
Cl-Zn	increased amount of liquid phase larger belite crystals with deteriorated edges smaller alite crystals
Cl-Cr Cl-Mn	increased porosity larger pores cracks on the crystals development of the alite crystals in expense of the liquid phase

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