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A STUDY ON THE BURNABILITY AND THE PHASE FORMATION OF PC CLINKER CONTAINING Cu OXIDE

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ABSTRACT

Subject of this paper is to investigate the effect of CuO on the burnability of the cement raw mix and on the phase formation of the clinker. The effect was studied by means of differential scanning calorimetry, X-ray diffraction and optical microscopy. Besides, the rate of fCaO consumption during the sintering of raw meals was measured. As it is concluded the presence of the CuO in cement raw mix promotes the combination of the free lime, especially in the temperature range between 1000 and 1300°C. It also favors the formation of alite and belite at lower temperatures. Furthermore, CuO lowers the temperature of the sintering reactions. *Copyright © 1996 Elsevier Science Ltd*

Introduction

The present study belongs to a series of experiments concerning the effect of transition metal compounds on the formation of clinker and on the properties of cement, [1,2].

The effect of transition elements on the hydration of cement has been the subject in a number of published papers, [3,4,5]. Besides, it is known that these elements affect the sintering process of the cement raw meal, [6,7], as for example, the Zn compounds which are known to be effective fluxes, [2,8,9]. Despite this, the modifications caused by these compounds on each one of the sintering steps has not yet been recorded and clarified.

Since Cu is an element broadly dispersed in nature, it is interesting to study the sintering process of cement raw mixes containing Cu compounds. This paper deals with the incorporation of CuO in the mineralogical phases of the clinker and its influence on the burnability and the sintering process of the cement raw mix.

Experimental

Materials. Ordinary Portland cement raw meal of industrial origin was used. Cu oxide used is chemical grade. 0.5%, 1.0%, 1.5% and 2.0% by weight of CuO was mixed with cement raw meal. The above samples are referred as C1 - C4 respectively, while sample No 1 is the sample with no addition of CuO. Homogeneity was ascertained by dosing the added oxide on samples of the mixtures.

TABLE 1

Chemical Composition of the Raw Meal (% w/w)

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O
43.46	15.84	3.79	2.94	0.86	0.42

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. Table 1 represents the chemical compositions of the raw meal. The fineness of the raw meal was $5050cm^2/g$ and the residue at 90μ was 17%.

Measuring and Monitoring Techniques:

- Differential scanning calorimetry, (DSC): This technique was applied in order to study the effect of the added oxide on the sintering and cooling reactions of the clinker. The temperature was raised at a constant rate (10°C/min.) from ambient to 1450°C. The experiments were conducted in an atmosphere of Ar flowing in $50cm^3/min$. α-Al_2O_3 was used as reference material.
- X-ray diffraction (X-RD): This technique was used in order to identify the mineralogical phases formed during the sintering of the clinker and find out the differentiation caused by CuO.
- Optical microscopy: The samples, thermally treated to 1400°C, were examined by means of an optical microscope in order to study the effect of CuO on the texture of the alite and belite grains.
- fCaO determination: The burning tests were carried out in pellets (weight:5g, d:3cm, h:4mm) which were thermally treated for 15 min. at 5 different temperatures (1100, 1200, 1300, 1400 and 1450°C). After sintering the samples were air cooled, ground and analyzed by the ethylenoglycol method in order to determine the fCaO content.

Results and Discussion

1. Rate of fCaO Consumption During the Thermal Treatment. Table 2 and Figure 1 show the fCaO content of all samples at different temperatures. As it can be seen, the addition of CuO in the raw mix lowers the clinkerization temperature (ranging from about 50° for 0.5% CuO to 50-100° for 1-2% CuO).

The rate of fCaO consumption is higher in the samples containing CuO even at 1100°C. This fact is more clear at 1200°C where an addition of 1.5-2.0% CuO in the raw meal causes a decrease of fCaO by 75-80%. At 1400°C the fCaO is almost completely consumed in

TABLE 2

% fCaO Content of the Samples at Different Temperatures

sample	1100°C	1200°C	1300°C	1400°C	1450°C
1	39.2	31.0	13.5	6.5	1.8
C1	39.0	19.0	6.7	1.1	-
C2	37.7	10.6	3.6	0.8	-
C3	36.0	6.1	3.7	-	-
C4	35.5	8.1	2.9	-	-

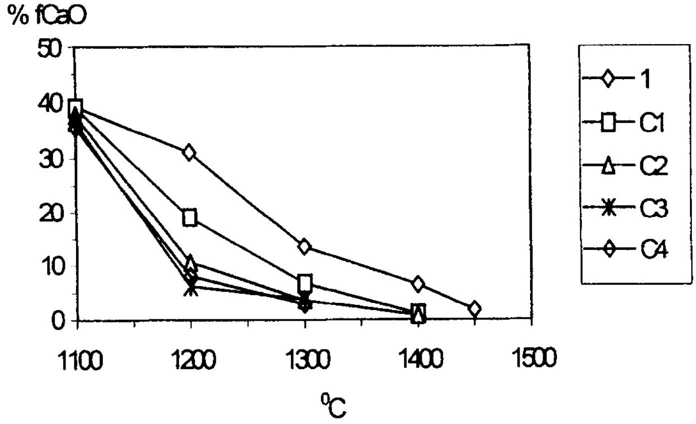

FIG. 1.
% CaO content of the samples at different temperatures.

samples C1 - C4. The increased rates of the sintering reactions are also indicated by the color change of the samples. The color of the samples C1 - C4 has already turned to black after thermal treatment at 1100°C.

2. Thermal Treatment of Samples. The DSC curves of raw mixes are given in Figure 2. The expected endothermic effect between 600°C and 800°C is attributed to the decomposition of $CaCO_3$. The following exothermic reactions are associated with the formation of belite while the endothermic effect at about 1250°C is attributed to the formation of liquid as well as to the formation and development of alite crystals. The exothermic effects appeared in the cooling curve are connected with the crystallization of the liquid phase. Table III shows the temperatures measured by DSC and the associated reactions of all samples studied.

As it can be seen, CuO does not cause any differences as far as the temperature of the limestone decomposition is concerned. On the contrary, the formation of the belite and the liquid phase are strongly affected by the presence of CuO. The peaks between 1000°C and 1200°C become gradually smaller in size and totally disappear when the CuO concentration in raw meal exceeds 1.5%. Besides, the main exothermic peak at about 1200°C shifts towards lower temperatures by 4 - 26°C. These discrepancies are caused by the different reactivity of the raw meals. In materials which sinter easily the formation of belite is extended

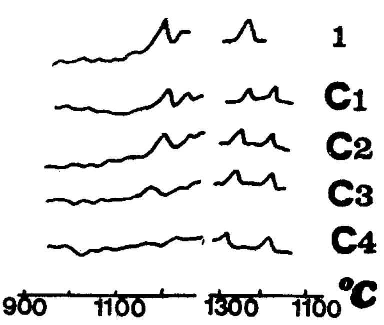

FIG. 2.
DSC curves of the samples.

TABLE 3

Temperatures of Sintering and Cooling Reactions, Measured by DSC (°C).
R1: Cecomposition of $CaC0_3$, R2: Main Formation of Belite,
R3: Formation of Melt, R4: Crystallization of the melt

	R1	R2	R3	R4
1	800	1228	1260	1244
C1	800	1224	1264 1316	1288 1224
C2	800	1216	1256 1316	1296 1224
C3	800	1202	1234 1305	1290 1202
C4	800		1230 1302	1302 1194

over a wide temperature range. In less reactive materials the main formation of belite is assumed to take place in one step. The higher reactivity of the samples containing CuO in these temperatures, has also been confirmed by the determination of the fCaO.

The addition of CuO affects significally the formation of the liquid phase which takes place in two well-defined stages, the former at lower and the latter at higher temperature compared with the liquid formation in the pure sample. The same effect is recorded during the cooling of the samples. These are attributed to the effect of CuO on the CaO-Al_2O_3 reactions and the formation of the alluminates.

3. Crystallographic Examination of Clinkers. All samples were examined by means of X Ray diffraction after the thermal treatment at the various temperatures. Figure III shows the XRD patterns of the pure and the C4 samples.

At 1100°C CaO, SiO_2 and C_4AF are present in both samples. Pure sample, also contains gehlenite (C_2AS) while in C4 CuO and greater amounts of C_4AF are present. It is obvious that the sintering reactions have been promoted in the sample C4, as it has been already confirmed by the fCaO and the DSC measurements mentioned above.

At 1200° C the formation of C_2S begins. In the sample C4 γ-C_2S and C_3A have been also formed.

At 1300°C the main difference is the presence of C_3S in the sample C4 in addition with C_3A_5 and CA_2.

At higher temperatures both samples tend to have the same mineralogical composition. The above differences become more obvious as the concentration of the CuO increases.

4. Examination of the Samples by Optical Microscopy. The examination of the samples 1 and C4, after thermal treatment at 1400°C, has led to the Photos 1 and 2 presented below. The selected sites are representative as far as the size and texture of alite and belite crystals are concerned.

As it can be seen, in the sample C4, the clinkerization has been already completed at 1400°C, since the alite crystals are well developed. In the pure sample only the belite formation has been completed. The alite nuclei have been formed but the crystal development is not promoted.

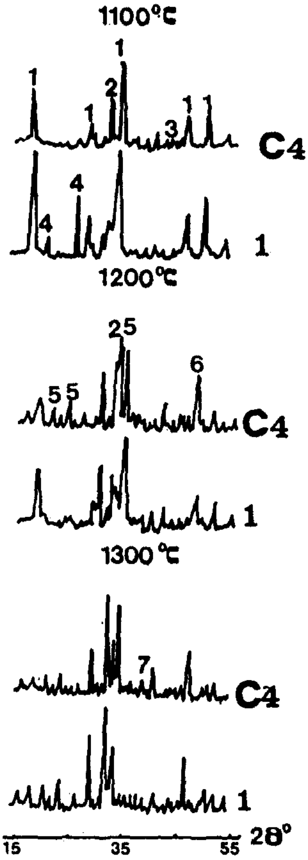

FIG. 3.
XRD patterns of samples. 1: CaO; 2: β-C_2S; 3: CuO; 4: SiO_2; 5: γ-C_2S; 6: C_4AF; 7: C_3S.

PHOTO 1
Sample 1, burnt at 1400°C, (×40).

PHOTO 2
Sample C4, Burnt at 1400°C, (×40).

Conclusions

The following conclusions can be drawn from the present study:

The addition of CuO in cement raw meal lowers the clinkerization temperature by at least 50°C. This stands even for 0.5% addition in the raw meal.

CuO acts as a mineralizer and as a flux. Its action begins already at 1100°C.

The addition of CuO affects the formation of silicates as well as the formation of alluminates. Specifically, CuO promotes the formation and the development of the alite crystals at lower temperature and alters the crystallization process during the cooling of the clinker.

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