Pergamon

Cement and Concrete Research, Vol. 25, No. 1, pp. 79-85, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in the USA. All rights reserved
0008-8846/95 $9.50+.00

0008-8846(94)00115-4

INVESTIGATION OF THE EFFECT OF Zn OXIDE ON THE FORMATION OF PORTLAND CEMENT CLINKER

Kakali G., Parissakis G.

Laboratory of Inorganic and Analytical Chemistry,
National Technical University of Athens,
9 Iroon Polytechniou Str., 15773 Athens, Greece

(Communicated by F. Massazza)
(Received April 20, 1994)

ABSTRACT

Subject of this paper is to investigate the effect of ZnO during the sintering process of cement raw meal. The effect was studied by means of differential scanning calorimetry and X-ray diffraction. Besides, the rate of CaO consumption during the sintering of raw meals was measured. Final discussion concerns the action of the above oxide on raw material sintering and its incorporation in the phases of the clinker.

Introduction

Some investigations have been done on the effect of Zn compounds upon the hydration rate of the cement, [1,2]. Besides, it is well known that ZnO acts as mineraliser during the sintering of the cement raw mix, [3,4,5,6]. However the incorporation of ZnO in the mineralogical phases of clinker and its influence on the reactions kinetics during sintering have not been yet clarified.

The present study belongs to a series of experiments concerning the effect of transition element compounds on the formation of clinker and on the properties of cement, [7].

Experimental

Materials :

Ordinary Portland cement raw meal of industrial origin was used. Zn oxide used is chemical grade. 0.5%, 1.0%, 1.5%, 2.0%, 3.0% and 4.0% by weight of ZnO was mixed with cement raw meal. The above samples are referred as Z1 - Z6 respectively, while sample No 1 is the sample with no addition of ZnO. 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. Table I 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%.

Table I
Chemical Composition
of the raw meal

CaO	43.33
SiO_2	13.40
Al_2O_3	3.13
Fe_2O_3	2.44
MgO	1.13
K_2O	0.27

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 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 ZnO.

- fCaO determination: The burning tests were carried out in pellets (weight:5g, d:3cm, h:4mm) which were thermally treated for 15 min at 6 different temperatures 1000, 1100, 1200, 1300, 1400 and 1450 °C). After sintering the samples were air cooled, ground and analysed by the ethylenoglycol method in order to determine the fCaO content.

Results and discussion

1. Rate of fCaO consumption during the thermal treatment:

Table II and Figure I show the fCaO content of all samples at different temperatures. As it can be seen, the addition of ZnO in the raw mix lowers the clinkerization temperature (ranging from about 50° for 1.5% ZnO to 50-150° for 2-3% ZnO). The addition of more than 3% ZnO in the raw mix does not affect the burnability.

Figure II presents the ratio $[fCaO_{Zi}(T_2)-fCaO_{Zi}(T_1)]/[fCaO_1(T_2)-fCaO_1(T_1)]$ at different temperature ranges in relation to the ZnO content. This ratio indicates the effect of ZnO content on the rate of the fCaO consumption and it is assumed to be 1 at all temperature ranges for the pure sample. As it is observed, ZnO increases the rate of the fCaO reaction in the range between 1000 and 1200°C and especially from 1000 to 1100°C. From 1200 to 1300°C the rate is almost constant in all samples.

At higher temperatures the rate is lowered as the ZnO content is increased

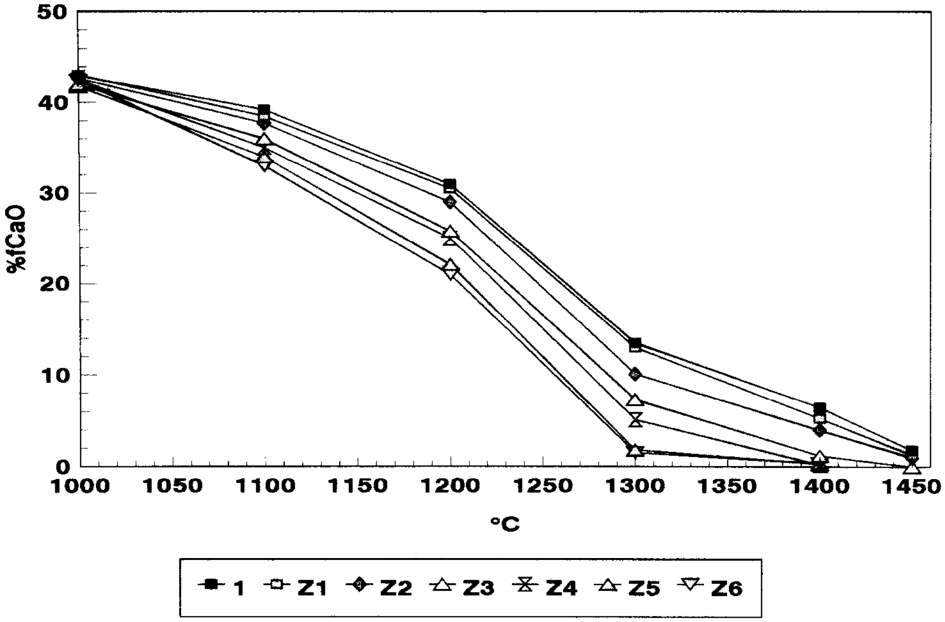

Figure I
% CaO content of the samples at different temperatures

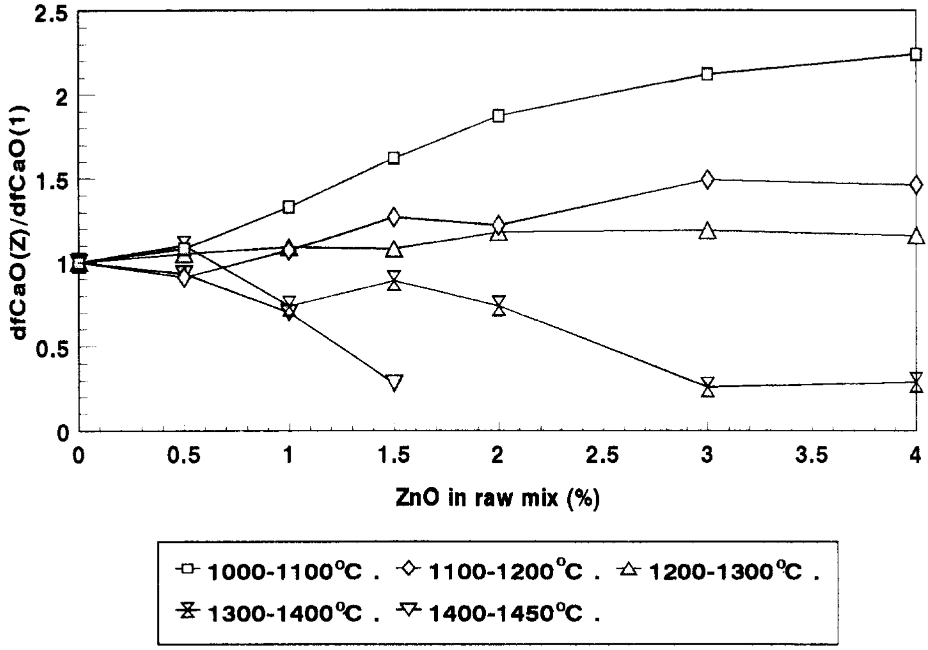

Figure II
dfCaO (Zi)/dfCaO(1) at different temperatures ranges

above 1.5%. That was expected since the major part of fCaO in these samples has already been consumed at lower temperatures. As ZnO is partly volatilized at high temperatures, the content of ZnO is retedermined after the thermal treatment of the samples at 1450^{o}C. Table III presents the obtained results.

2. Thermal treatment of samples :

The DSC curves of raw mixes are given in Figure III. The expected endothermic effect between 600^{o}C and 800^{o}C is attributed to the decomposition of $CaCO_3$. The following exothermic reactions are associated with the formation of belite while the endothermic effect between 1200^{o}C and 1260^{o}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 crystallisation of the liquid phase. Table IV shows the temperatures measured by DSC and the associated reactions of all samples studied.

Table II

%fCaO content of the samples at different temperatures

sample	1000^{o}C	1100^{o}C	1200^{o}C	1300^{o}C	1400^{o}C	1450^{o}C
1	43.0	39.2	31.0	13.5	6.5	1.8
Z1	43.1	39.0	31.5	13.0	5.3	1.3
Z2	42.7	37.7	29.0	10.1	4.0	1.0
Z3	42.0	36.0	25.8	7.3	1.2	
Z4	42.5	35.5	25.6	5.1		
Z5	41.8	34.0	22.1	1.8		
Z6	42.1	33.8	22.0	2.0		

Table III.

% ZnO added in the raw mix and remaining in the clinkers

	Z1	Z2	Z3	Z4	Z5	Z6
% ZnO in raw mix	0.50	1.00	1.50	2.00	3.00	4.00
% ZnO in clinker	0.58	1.12	1.62	2.12	3.03	3.98

As it can be seen, ZnO 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 ZnO. The peaks between 1000^{o}C and 1200^{o}C become gradually smaller in size and totally disappear when the ZnO concentration in raw meal exceeds 1.5%.

The main exothermic peak at about 1200^{o}C shifts towards lower temperatures becoming smaller in size. As it can be seen in Figure III, the formation of belite in sample Z6 has been completed at about 50^{o}C lower than in sample 1. These discrepancies are caused by the different reactivity of the raw meals. In materials which sinter easily the formation of belite is extended 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 ZnO in these temperatures, has also been confirmed by the determination of the fCaO.

The increasing content of ZnO causes a decrease of the melt temperature and an increase of the corresponding peak area. This is due to the formation of an eutectic melt as well as to the higher percentage of the melting material.

The temperature of the crystallisation of the melt during the cooling process, moves towards lower temperatures as the ZnO content increases, following the temperature of the melt formation. When the ZnO concentration exceeds 1.5%, a new exothermic peak is recorded. This is attributed to the solidification of the part of the liquid phase in which the remaining ZnO is dissolved.

Table IV
Temperatures of sintering and cooling reactions measured by DSC.

	R1*	R2*	R3*	R4*	R5*
	800	1228	1260	1244	
Z1	800	1220	1240	1240	
Z2	800	1220	1240	1240	
Z3	800	1216	1240	1240	
Z4	800	1210	1220	1220	1180
Z5	800	1200	1220	1200	1180
Z6	800	1180	1200	1200	1160

* SINTERING REACTIONS:
R1: Decomposition of $CaCO_3$
R2: Main formation of belite
R3: formation of melt
COOLING REACTIONS
R4,R5: Crystallisation of melt

3. Crystallographic examination of clinkers :

The effect of the ZnO on the mineralogical state of the clinker concerns mainly the phases which are crystallised from the melt. Figures IV and V show the XRD patterns of the pure treatment at 1450 and 1300° C respectively.

As it can be seen in Figure IV, there is an increase of the C_4AF content followed by a decrease of the C_3A content. But the most interesting fact is the appearance of a new phase in the clinkers containing more than 1.5% ZnO. This phase has a diffraction pattern similar to the pattern of $2CaO.ZnO.SiO_2$ (d:2.87, 3.09°A).

The parallel study of the DSC and the XRD graphs shows that this phase must be the part of the melt in which the remaining ZnO is dissolved. Figure V shows that at 1300 °C higher percentages of the silicates are formed in the samples containing ZnO. Besides, different forms of alluminates are found to be present.

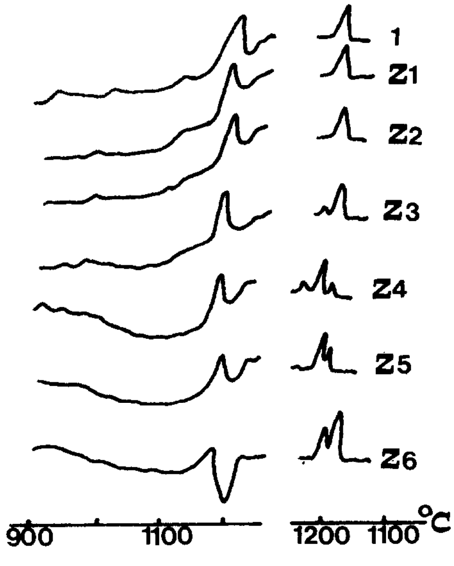

Figure III
DSC curves of the samples

C_3A and $C_{12}A_7$ are mainly formed in the pure sample, while CA and C_2A are also present in samples containing ZnO. This means that ZnO affects not only the reaction kinetics of the silicate formation but the alluminates as well.

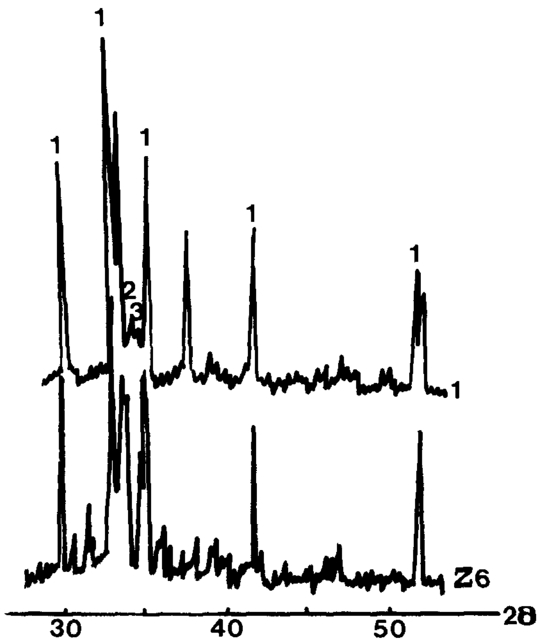

Figure IV
X-RD graphs of samples burnt
at 1450°C

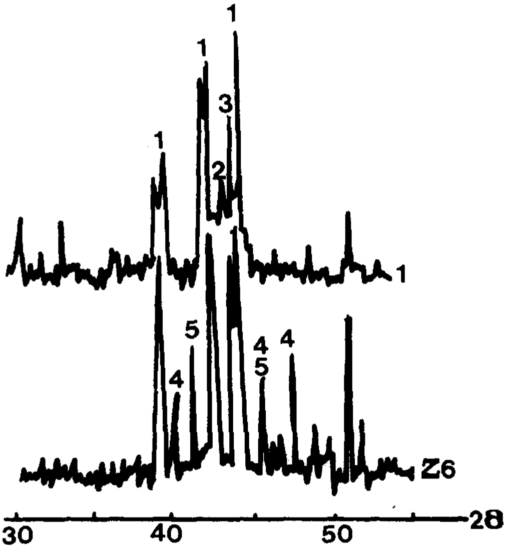

Figure V
X-RD graphs of samples burnt
at 1300°C

1: C_3S - C_2S, 2: C_3A, 3: C_4AF, 4: CA, 5: C_2A

Conclusions

1. The addition of ZnO in cement raw meal lowers the clinkerization temperature. The decrease is varying from 50°C for the sample containing 1.5% ZnO in the raw mix to 100-150°C for the samples containing 2-4% ZnO.

2. The addition of ZnO in the cement raw mix promotes the combination of the free lime especially in the temperature range between 1000-1200°C. This fact leads to the conclusion that ZnO does not affect only the formation of the melt but is capable of promoting the solid reactions as well. The presence of ZnO affects not only the formation of silicates but also the combination of CaO with Al_2O_3.

3. The presence of ZnO alters the kinetics of the crystallisation process. If the percentage of ZnO exceeds 1.5% in the raw mix, a new phase ($2CaO.ZnO.SiO_2$) is formed in which the excess of ZnO is dissolved.

4. It has been found that the addition of more than 3% ZnO in the raw mix does not provoke any further changes on the burnability. However, this is not the solubility limit of ZnO in the clinker, since further increase of the ZnO content changes the colour of the clinker to brown. This is associated with the formation of the new phase mentioned above.

REFERENCES

1. TASHIRO C., Proc. 7th Int.Cong.Chem.Cem., Paris, V.II, II-37, 1980.
2. ARLIGUIE G., GRANDET J., Cem.Conc.Res., 20(1990), pp 517-524.
3. OLDER I., ABDUL-MAULA S., Z-K-G, 33(1980), N.3, pp 132-136.
4. OLDER I., ABDUL-MAULA S., Z-K-G, 33(1980), N.6, pp 278-282.
5. BURGER D., LUDWIG U., Proc. 8th Int.Cong.Chem.Cem., Rio de Janeiro, V.II, pp 372-378.
6. TSUBOI T., ITO T., HOKINOUE Y., MATSUZAKI Y., Z-K-G, 9 (1972), pp 426-431.
7. KAKALI G., KASSELOURI V., PARISSAKIS G., Cem.Conc.Res., 20 (1990), pp 131-138.