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THE EFFECT OF V_2O_5 ON THE C_3S AND C_3A FORMATION

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ABSTRACT

Using pure chemical reagents and varying the V_2O_5 content (0-3.5w/w %) two series of nine compositions, each for C_3S and C_3A phases, were prepared at 1450 °C and investigated in respect of the vanadium effect on the phases formed. Results derived by X-Ray Diffraction (XRD), step by step XRD scanning and DSC analysis reveal that V_2O_5 addition up to 0.5(w/w) % promotes C_3S formation. Also, up to the percentage 3.5(w/w) % examined enhances the C_3A phase.. In both cases V_2O_5 effect increases remarkably the crystal size D.

INTRODUCTION

Minor constituents are chemical species different from the main fundamental oxides which participate in the transformation process of the raw meal into clinker. Among these minor constituents many of the transition metal compounds are involved which act as mineralizers or fluxes during the sintering of the clinker, lowering consequently the energy demand. As a rule, they derive from the accessory minerals of rocks, fuels, refractories, wear parts of equipment. They can also result from admixtures added to the raw meal for specific purposes (1-9).

Blaine (10, 11) reports the distribution frequency of 17 minor elements into 186 Portland cement clinkers and the influence resulted on the cement properties.

The aims on stimulating the research regarding the minor constituents and admixtures for several years are:
- production of more reactive raw mixes
- improvement of particular technological conditions to increase the process efficiency
- increase in the allowable levels of impurities associated with enlargement of the availability of the raw materials and fuel types
- a way out to handle specific industrial wastes for ecological purposes
- improvement of the cement quality

In an extended research programme we attempt to investigate the effect of low additions of the transition metal oxides on the structure and properties of the main phases of the Portland cement clinker. With the present paper we aim to elucidate the effect of V_2O_5 on the formation and structure of the C_3S and C_3A phase, using X-Ray Diffraction (XRD), step by step scanning XRD and Differential Scanning Calorimeter (DSC) techniques. Our results show that the proper addition of V_2O_5 promotes both the C_3S and the C_3A formation, increasing significantly their crystal size (D).

EXPERIMENTAL

Two series of compositions were prepared, each for C_3S and C_3A respectively, containing V_2O_5 varied from 0 to 3.5%, by using pure chemical reagents. Pellets were formed from the well homogenised mixtures, calcined at 1000 °C for 1 hour. Then the C_3S compositions were sintered at 1450 °C for three hours, whilst the sintering conditions of the C_3A series were at 1450 °C for 30 minutes. After sintering the samples were fast cooled in air. The code of the samples and the concrete content of V_2O_5 are referred to the Table I.

Table I
The series of the C_3S and C_3A compositions prepared

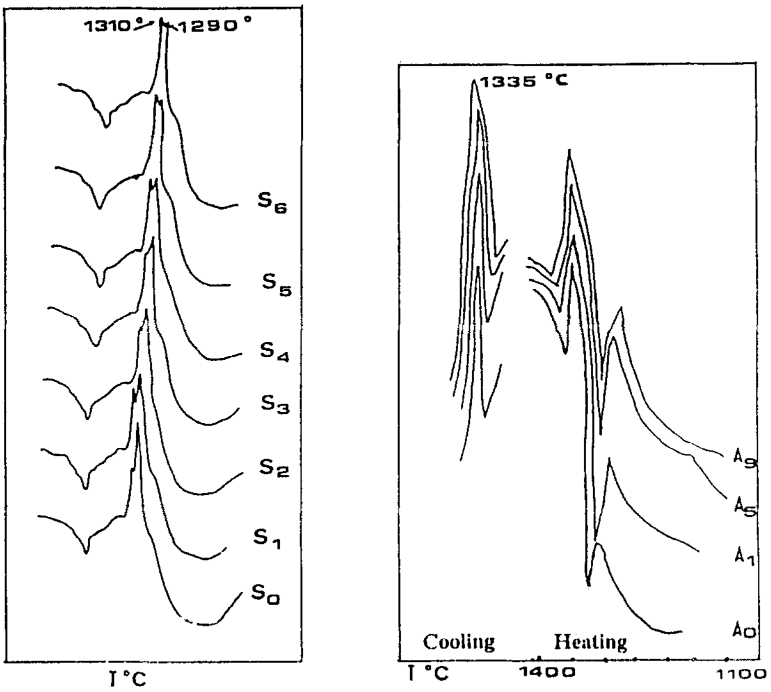
V_2O_5 content (%w/w)	Code of C_3S	Code of C_3A
0.0	S_0	A_0
0.1	S_1	A_1
0.2	S_2	A_2
0.3	S_3	A_3
0.4	S_4	A_4
0.5	S_5	A_5
1.0	S_6	A_6
1.5	S_7	A_7
2.0	S_8	A_8
3.5	S_9	A_9

In order to identify the phases formed, as well as the formation temperatures the samples prepared were studied by means of both DSC and XRD-analysis. In the former, measurements were carried out by means of a Stanton-Redcroft 1500 DSC equipment operated at a heating and cooling rate of 10 °C/min, up to 1500 °C. XRD-analysis was performed by means of a Philips Diffractometer using CuK_α radiation. The diffractometer was operated at 40 kV and 25 mA. The XRD-spectra were obtained by scanning continuously at the rate of 1 °2θ/min.

Furthermore, the integrated intensities for the d-spacing of C_3S (d=2.614 Å) and of C_3A (d=2.698 Å) were calculated using step by step XRD scanning, operated in steps of 0.02° 2θ and measuring the counts per 20 seconds at each step. Integrated intensities obtained were used for the quantitative estimation and the crystal size (D) determination of both the C_3S and the C_3A phases. For the crystal size determination, the integral breadth of the diffraction peaks was used, applying then the Sherrer (12) equation ($D=k\lambda/\beta\cos\theta$, where λ: the wavelength in Å, β: the pure diffraction broadening, θ: the Bragg angle and k: constant, assuming to be 1.0 because the integral breadth is used).

RESULTS AND DISCUSSION

The peaks observed on the DSC-diagrams of the S and A series are summarised in Table II, whilst figure 1 shows some representative thermodiagrams of the two series. The results derived from the DSC-analysis reveal a remarkable increase of the C_3S phase at expense of the β-C_2S phase from the sample S_0 up to S_5, remaining almost at the same level for the rest samples of the series, which contain more V_2O_5. An increase is also observed for both the C_3A and $C_{12}A_7$ phases from the sample A_0 up to A_9. As far as the formation temperature of all the phases formed is concerned, in both the series, it is not observed any remarkable variation, which suggests that vanadium oxide does not actually affect their formation temperature.



(a) (b)

FIG. 1

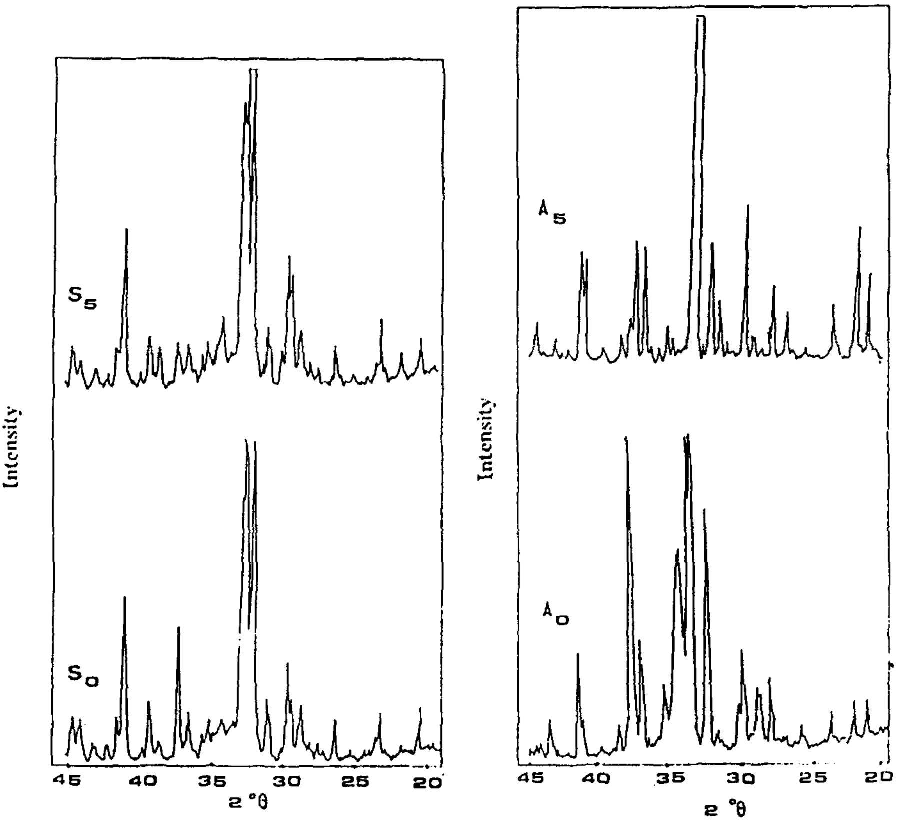
Representative DSC-diagrams of the samples prepared (a) S series, (b) A series.

TABLE II

Reactions observed on the DSC-thermodiagrams of the S and A series.

HEATING			
S Series		A Series	
Temperature (°C)	Reaction	Temperature (°C)	Reaction
1290 exo 1310 exo	β-C_2S formation C_3S formation	1350 endo 1365 exo	C_3A formation $C_{12}A_7$ formation
COOLING			
	No reaction is observed	1335 exo	Devitrification of C_3A

In addition, XRD-analysis confirms the results derived from DSC study and contributes to further clarification of the phases formed. Thus, figure 2 presents some representative XRD-patterns concerned with S and A series. In the former, for all the samples prepared, the phases identified are mainly C_3S, β-C_2S, CaO and some γ-C_2S. In the case of the C_3A series, the phases observed are C_3A, $C_{12}A_7$ and CaO. An evaluation of the peak intensities on the XRD patterns confirms the observations noted by DSC-analysis. A remarkable decrease of the CaO content is also noted.



(a) (b)

FIG. 2

Representative XRD-patterns of the samples prepared (a) S series. (b) A series.

Furthermore, integrated intensities calculated for C_3S (d=2.614 Å) and C_3A (d=2.698 Å) respectively (fig. 3) reveal for the former a remarkable increase of the C_3S phase from the sample S_0 up to S_5, remaining then almost unchanged up to the sample S_9. These comments suggest that the presence of the vanadium oxide promotes the C_3S formation, reducing consequently the CaO content. This promotion appears to take a limit at the addition of 0.5%(w/w) V_2O_5. A significant increase is also observed for the C_3A phase up to the sample A_9, which consequences that V_2O_5 addition enhances the C_3A formation up to the highest percentage of 3.5(w/w) % examined.

In addition, the crystal size (D) for the C_3S and C_3A phases formed were calculated by applying the results derived from step by step XRD-analysis to the Scherrer equation. Plots of the crystal size (D) versus V_2O_5 addition for C_3S and C_3A are shown in figure 4. Firstly, in both the cases, a significant increase of the crystal size is observed up to the percentage of 0.5(w/w) % V_2O_5 content. Further addition of vanadium oxide in the case of the C_3S phase does not affect the crystal size of the phase any more, suggesting that the effect of vanadium takes a limit at this percentage. However, for the C_3A phase, the crystal size is increasing, although in a much slower rate, up to 3.5(w/w) %, which reveals that vanadium influences the C_3A formation up to the percentage examined.

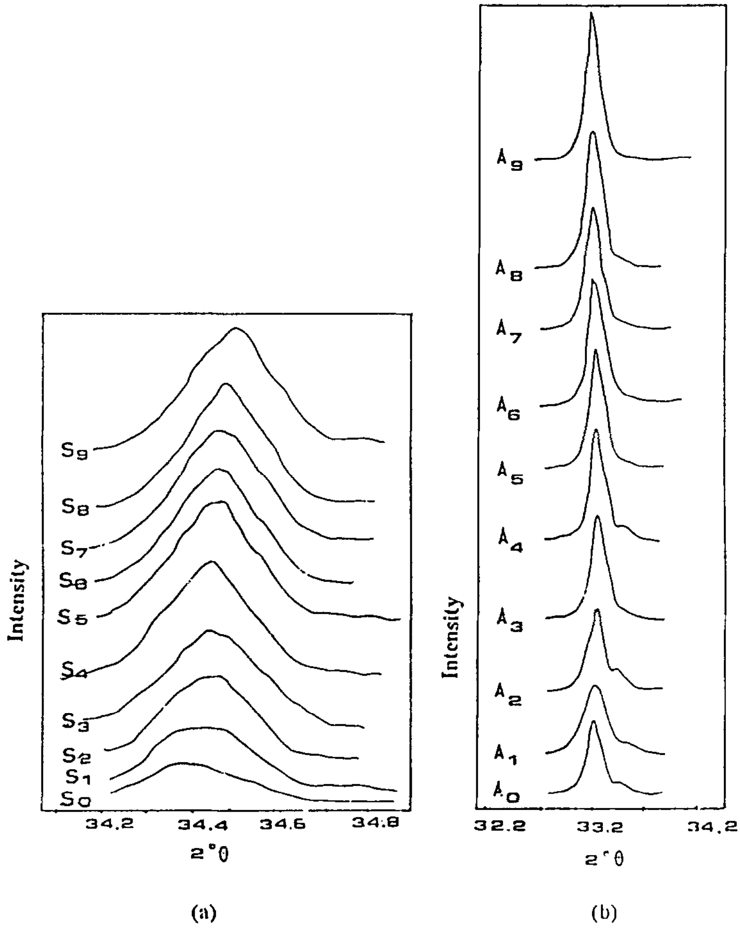
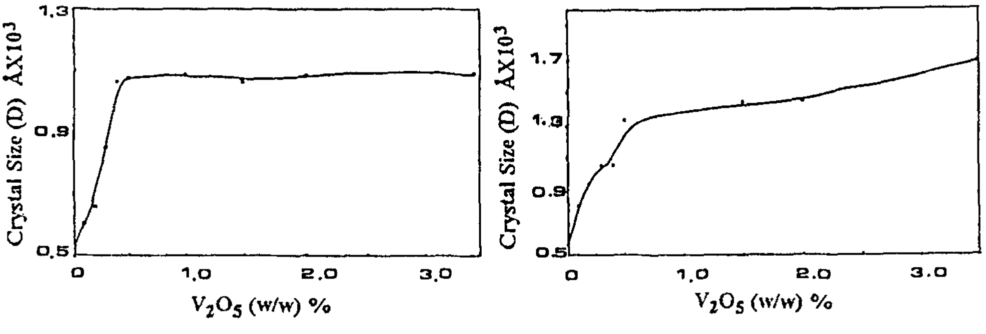


FIG. 3

Step by step XRD Scanning-patterns for (a) C_3S (d=2.614 Å), (b) C_3A (d=2.698 Å).

CONCLUSIONS

Summarising the suggestions derived by the results of the present research work, we conclude that V_2O_5 addition enhances both the C_3S and the C_3A phase formation. In the former, the most effective addition of vanadium oxide is at the region of 0.5 (w/w) %, whilst for the C_3A up to the percentage examined, 3.5(w/w) %. Furthermore, V_2O_5 addition, up to 0.5(w/w) %, brings about a remarkable increase of the crystal size in both the C_3S and C_3A phases.



(a) (b)

FIG. 4

Crystal size v. V_2O_5 content for (a) C_3S, (b) C_3A.

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