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HYDRATION OF ORDINARY PORTLAND CEMENTS MADE FROM RAW MIX CONTAINING TRANSITION ELEMENT OXIDES

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ABSTRACT

The subject of this paper is the study of the hydration process in cements made from raw mixes containing transition element oxides. The oxides used are ZrO_2, V_2O_5, Ni_2O_3, CuO, Co_2O_3, MnO, Cr_2O_3, TiO_2, MoO_3, and ZnO, and their percentage in the raw mixes is 2% w/w. The cement pastes are cured in water for 24 h, 48 h, 7 days and 28 days. Hydration rate and products are studied by means of X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis. As it is concluded, the added oxides provoke, in general, a retardation of the hydration reactions. The effect is stronger during the first 2 days and becomes negligible at 28 days. The addition of CuO strongly delays the hydration even after 28 days. Its action is related to the formation of $Cu(OH)_2$ during the first days of hydration. *© 1998 Elsevier Science Ltd*

Introduction

The use of industrial wastes, such as waste tyres, waste oil, non-ferrous metal slag, or waste molding sand, as alternative raw materials and fuel in cement plants has been established from an environmental and recycling point of view and is expected to increase in the future (1–4). Cement is broadly used, among other hydraulic binders, in the solidification and stabilization of industrial and municipal wastes (5). This tendency to the use of wastes in the cement industry or the utilization of cement for the handling of wastes has led to the presence of several transition element compounds in the clinker and/or in the hydrated cement (6–8).

Transition element compounds exert a remarkable effect on the sintering process, the crystal structure and texture of clinker minerals, and the hydration reactions (9,10). Certain elements, such as Cu and Zn, when added in raw mix, are found to be effective mineralizers (11,12). However, the addition of these elements, as well as V and Pb, in cement, seems to prohibit the early hydration reactions through the formation of amorphous compounds that cover the unreacted cement grains. The hydration reactions start again after the crystallization and sedimentation of these compounds, which take place when the Ca^{+2} and OH^- concen-

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TABLE 1
Chemical and mineralogical composition of the pure clinker

Chemical composition (%)						
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
21.20	5.03	3.82	66.54	1.77	0.52	0.08

Mineralogical composition (%)			
C_3S	C_2S	C_3A	C_4AF
71.44	7.75	6.96	11.80

tration becomes high enough (13–15). The hydration process, however, of clinkers containing these compounds is expected to be different because their incorporation in the clinker phases modifies their dissolution rate during hydration.

In the present paper, thermoanalytical methods (thermogravimetric analysis (TGA), differential scanning calorimetry (DSC)) are used in order to study the cement hydration, whereas X-ray diffraction (XRD) is used for the identification of the hydrated products in cements produced from raw mixes containing ZrO_2, V_2O_5, Ni_2O_3, CuO, Co_2O_3, MnO, Cr_2O_3, TiO_2, MoO_3, and ZnO. This work is a part of a project, developed in our laboratory, concerning the effect of transition element compounds on the formation of clinker and on the properties of cement and aiming to determine the connection between elements' particularity and the way they affect the sintering and hydration processes.

Experimental

Ordinary Portland cement raw meal of industrial origin was used. The ZrO_2, V_2O_5, Ni_2O_3, CuO, Co_2O_3, MnO, Cr_2O_3, TiO_2, MoO_3, and ZnO used are chemical grade. Each oxide (2.0% by weight) was mixed with cement raw meal. The prepared samples are named after the chemical symbol of the added element, whereas sample No. 1 is the pure sample. Homogeneity was ascertained by dosing the added oxide on samples of the mixtures. The fineness of the raw meal was 5050 cm^2/g and the residue at 90 μm was 17%. Table 1 presents the chemical and mineralogical compositions of the pure clinker.

All raw mixes were thermally treated up to 1450°C in an electrical furnace and cooled rapidly in air. The clinkers were coground with 5% w/w gypsum in a laboratory ball mill. The gypsum was of industrial origin (98% w/w $Ca_2SO_4 \cdot 2H_2O$, 46.7% w/w SO_3). The fineness of all samples is between 3500 and 3700 cm^2/g (Blaine).

Pastes were prepared with a water-to-solid ratio of 0.4 using tap water. After a period of 6 h the cement cores where put in sealed polythene containers and wet-cured at 20°C. Samples hydrated for periods 1, 2, 7, and 28 days were subjected to acetone and isopropyl ether treatment and then dried for 24 h in vacuum.

TGA was used for the determination of nonevaporable water and calcium hydroxide content in dried cement paste samples using the thermobalance TGA 2050 of TA Instruments. The samples ($\sim$50 mg) were heated over the range 20°C to 600°C at a constant rate of 15°C/min in an atmosphere of carbon dioxide free nitrogen, flowing in 90 cm^3/min. The

TABLE 2

Nonevaporable water and $Ca(OH)_2$ content of the hydrated cements.

Sample Code	nonevaporable water (%)				$Ca(OH)_2$ (%)			
	1 day	2 days	7 days	28 days	1 day	2 days	7 days	28 days
1	14.63	17.28	17.10	20.27	13.78	16.18	18.88	18.99
Zn	5.34	15.07	16.27	20.02	6.80	14.15	16.95	18.44
Ni	13.75	11.92	12.24	19.64	13.36	16.76	19.26	19.93
Co	12.60	15.42	15.67	21.29	11.53	13.22	16.73	17.01
Ti	11.77	13.89	16.74	18.02	11.39	13.98	17.55	18.54
Mn	11.42	12.15	17.22	19.08	13.44	13.84	15.22	17.89
Cr	10.88	11.03	18.63	19.84	11.67	13.69	15.01	18.65
V	11.13	13.53	17.32	18.60	13.29	13.91	16.75	17.06
Mo	12.95	15.46	15.75	19.96	10.97	13.20	15.18	17.78
Cu	4.97	7.64	15.48	19.96	3.47	12.23	13.57	15.13
Zr	14.71	16.80	17.12	21.21	14.25	16.37	18.67	18.42

samples were also subjected to DSC using a Standon Redcroft HT-1500 calorimeter under the same measuring conditions. A limited number of samples were treated up to 1000°C in order to confirm that there was no transformation of $Ca(OH)_2$ (henceforth termed CH) to $CaCO_3$.

Powdered samples, with particle size less than 54 microns, were measured on a Siemens D5000 diffractometer and the data were evaluated using Siemens "Diffrac Eva" software in order to identify the hydrated products.

Results and Discussion

The TGA and DSC curves of cement paste can be divided into two major parts, representing two different kinds of reactions:

- Up to 300°C. Removal of water from hydrated products, which are likely to include, among others, most of the C-S-H. Several minor steps are likely to take place in this area, attributed to capillary pore water, interlayer water and adsorbed water. The corresponding peaks overlap each other because of the dynamic heating process.
- 400°C–500°C. Dehydroxylation of calcium hydroxide.

The CH and nonevaporable water determined by TGA are shown in Table 2. Both CH and nonevaporable water are expressed as a percentage of weight of the dried paste.

In order to compare the CH content of cements containing transition metal oxide (i) with the CH content of the pure clinker (1), the ratio $(\%CH_i)/(\%CH_1)$ is used. Figure 1 presents the above ratios in relation to the hydration time.

As it is shown, transition elements, in cement raw mix, cause, in general, a delay of the hydration especially during the first 2 days. However, the hydration in modified samples is accelerated afterwards and at 28 days the variations in CH content are almost negligible. More specifically, the studied elements can be divided in three groups. The first one includes only Cu, which is the most effective retarder even at 28 days. The second group consists of

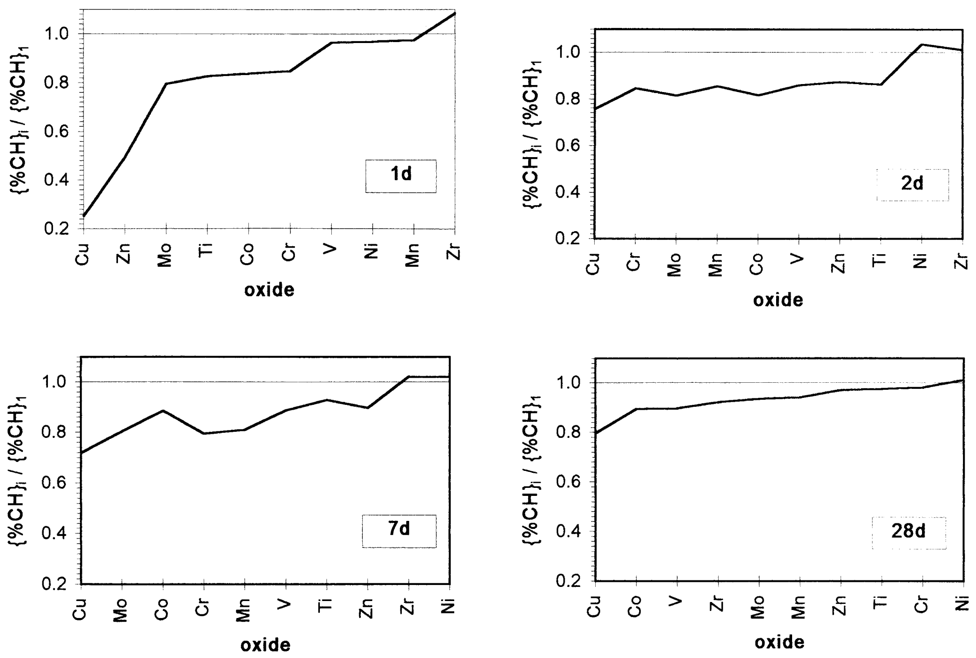

FIG. 1.

$(\%CH)_i/(\%CH)_1$ in relation to hydration time: i, added element; 1, pure sample.

the elements Co, Ti, Cr, V, Mo, Zn, and Mn, which cause a slight delay during the first days but have almost similar degree of hydration with the pure sample at 28 days. The third group includes Ni and Zr, which do not seem to affect the formation of CH even during the first days.

Figure 2 presents the DSC, TGA, and differential thermogravimetric (DTG) curves of Cu samples hydrated for 1 day. The DSC curve shows an endothermic reaction at 117°C, whereas TGA confirms that weight loss is also involved. This reaction is attributed with the decomposition of $Cu(OH)_2$, which is formed during the hydration and probably acts as coating retarder. At later ages, no $Cu(OH)_2$ is detected and the hydration rate is accelerated.

It must be noted that ZnO, which greatly inhibits hydration when added in cement, does not have the same effect when added in cement raw mix. This must be associated with the different dissolution rate of Zn^{2+}. The incorporation of Zn in the crystal lattice of clinker minerals delays the dissolution of Zn^{2+}. If the Ca^{2+} concentration is high enough when Zn enters the solution, crystalline-hydrated zincate salts are formed rather than amorphous zinc hydroxide and the retarding effect is decreased.

Figure 3 presents the XRD patterns of the relative samples. As expected, there is a decrease of anhydrous compounds and an increase of the CH and CSH. An attempt was made in order to identify the cement compounds formed with the incorporation of the transition elements. The first step was to find the peaks present in the patterns of the modified pastes but not in the patterns of the pure samples. The second step was to identify those peaks by means of the software data base. It must be noted that this procedure provides only indications on the existence of new compounds because of their low content and the overlapping with the main cement phases caused by the similarities of the crystal structure.

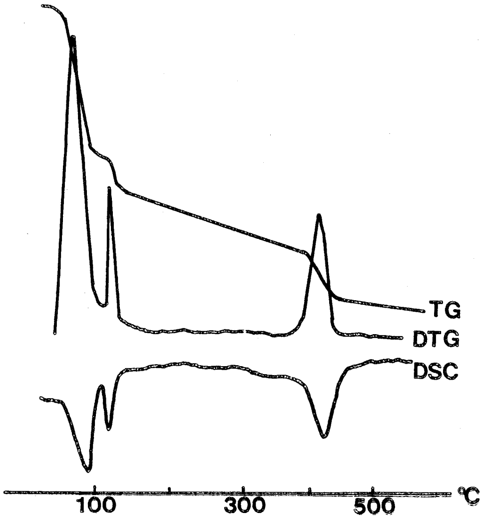

FIG. 2.
TGA, DTG, and DSC of sample Cu hydrated for 24 h.

The following compounds were identified:

- $CaZrO_3$ (d: 2.83, 2.00, 4.01 Å) in samples hydrated up to 7 days;
- $Ca_3Fe_2TiO_8$ (d: 2.69, 2.72, 1.94 Å) in samples hydrated up to 7 days;
- $Ca_2V_2O_7$ (d: 3.10, 3.15, 2.98 Å) in samples hydrated up to 7 days;
- $CuSiO_3·H_2O$ (d: 2.60, 7.26, 4.05 Å) in samples hydrated from 1 to 28 days;
- $Ca_2V_2O_7·2H_2O$ (d: 3.25, 6.99, 2.94 Å) in samples hydrated from 1 to 28 days;

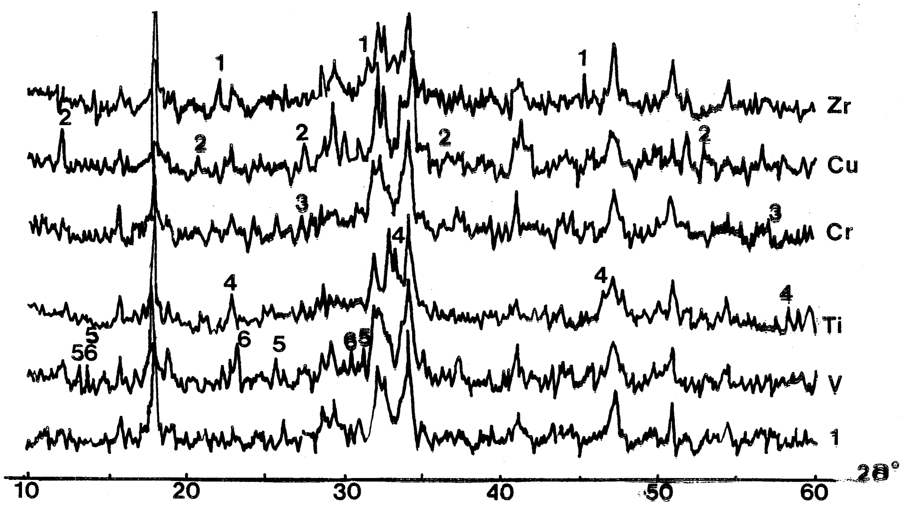

FIG. 3.
XRD patterns of samples 1, Cu, Zr, Cr, V, and Ti hydrated for 7 days: 1, $CaZrO_3$; 2, $CuSiO_3·H_2O$; 3, $CaCrO_4·2H_2O$; 4, $Ca_3Fe_2TiO_8$; 5, $Ca_2V_2O_7$; 6, $Ca_2V_2O_7·2H_2O$.

- $CaCrO_4 \cdot 2H_2O$ (d: 4.30, 3.11, 8.00 Å) in samples hydrated from 1 to 28 days.

It seems that Zr, Ti, and Cr ions preferably substitute Si^{4+}, while Cu^{2+} is probably placed in Ca^{2+} positions.

Conclusions

The following conclusions can be drawn from the present study:

1. Ni and Zr oxides, added in cement raw mix, do not affect the hydration rate of cement;
2. V, Co, Mn, Cr, Ti, and Mo slightly retard the hydration during the first 2 days but their effect on the hydration rate tends to become negligible at 28 days;
3. Zn delays the formation of $Ca(OH)_2$ only during the first day;
4. Cu oxide causes the greater delay of all elements, even at 28 days.

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