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ZINCOPHOSPHATE CEMENTS – HARDENING MECHANISMS

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ABSTRACT. Phosphate binders mostly, and zincophosphate dental cements especially, base their hardening on acid-base reactions, in which the liquid component is an aqueous phosphate solution and the solid component is usually an amphoteric, and only rarely basic one. In the present paper, investigations of the hardening mechanisms of zincophosphate cements were performed using X-ray diffraction analysis, IR spectroscopy, and scanning electron microscopy. The phase evolution of the hardening system and the microstructure of the hardenend binder were highlightened related to the specific mechanisms of the hardening process—specific to phosphate binders.

1. INTRODUCTION

The hardening of phosphate binders, mostly, and of zincophosphate dental binders, especially, takes place based on acid-base reactions between an acid liquid component and a usually amphoteric and seldow basic, solid component. The products in the forementioned chemical reactions undergo a structuring process, which determines the entire mechanical consolidation of the hardened system [1–5].

Dissimilarly from the hardening in the case of hydraulic binders—silicate binders (ordinary portland cement or portland cement with or without admixtures) or aluminate binders, including some phosphate binders with pre-established phosphate linkages within the used solid component—, the chemical reaction issuing zincophosphate binders—the subject of our paper—is not a hydrolysis reaction but—as shown before—an acid-base reaction in the presence of water. Similarly to the case of the hydraulic binders, the products are hydrocompounds with a further composition-structure development. The initially-formed hydrophosphates pass from coagulation structures to polycondensation-crystallisation structures, with corresponding changes of composition, which confer the hardened systems higher mechanical strengths depending on case. In developing hardened systems with adequate strengths, the kinetic conditioning of

The hardening process plays a special role. To this conditioning, not only the intrinsic parameters of the binding system, but also the processing parameters of the binding system are engaged.

The present paper deals with the investigations carried out on hardening mechanism of the zincophosphate cement in general, with particularisation to a zincophosphate cement of Romanian mark.

2. EXPERIMENTAL CONDITIONS AND PROCEDURES

In the our study was used, the zincophosphate cement ROMDENT of Romanian manufacture [6–8], with the chemical composition given in Table 1 and Table 2.

Table 1.

Oxide composition of the raw batch used in preparing the ROMDENT zincophosphate cement powder.

Oxide composition	ZnO	MgO	Al_2O_3	SiO_2
Proportion, %	85.5±1.0	8.5±1.0	2.0±0.5	1.5±0.5

Table 2.

Composition on the liquid component of ROMDENT zincophosphate cement

Liquid component composition	H_3PO_4	$Al(OH)_3$	ZnO	H_2O
Proportion, %	51.5±2.5	10.5±1.0	3.7±1.0	34.0±3.0

Figure 1 shows the X-ray diffraction pattern of ROMDENT cement powder illustrating its phase composition before casting.

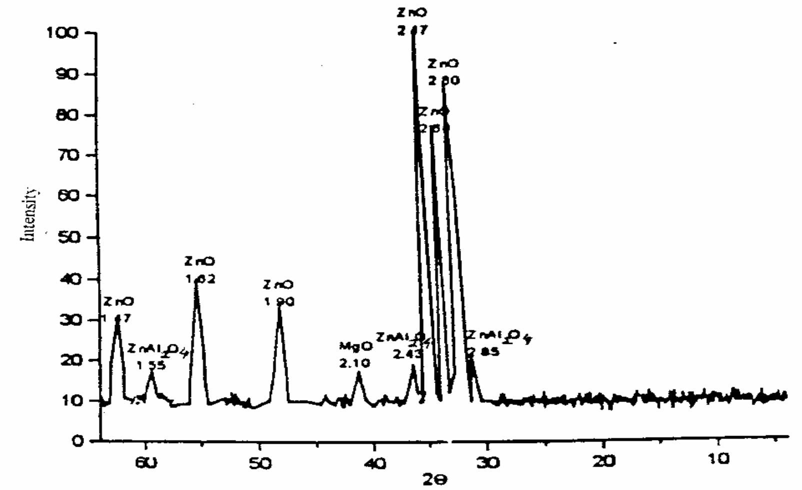


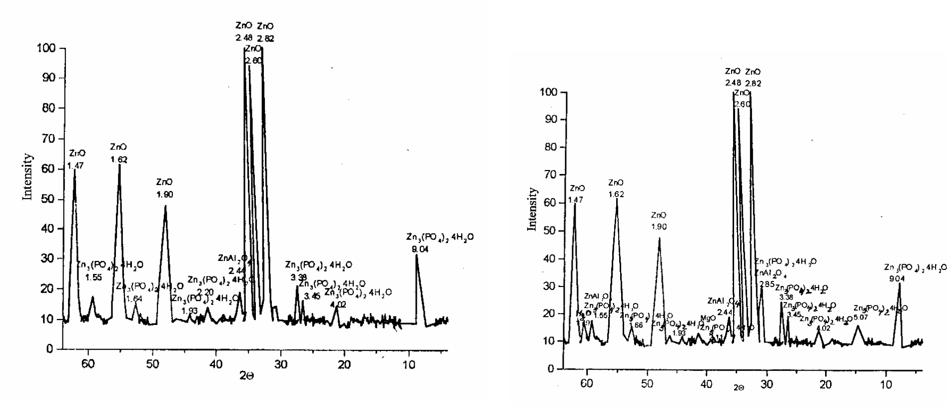
Figure 1. X-ray diffraction pattern of the solid component of ROMDENT zincophosphate Cement

On cement pastes as prepared there mere performed XRD, IR analysis and electron microscopy determinations, as well.

3. RESULTS AND INTERPRETATION

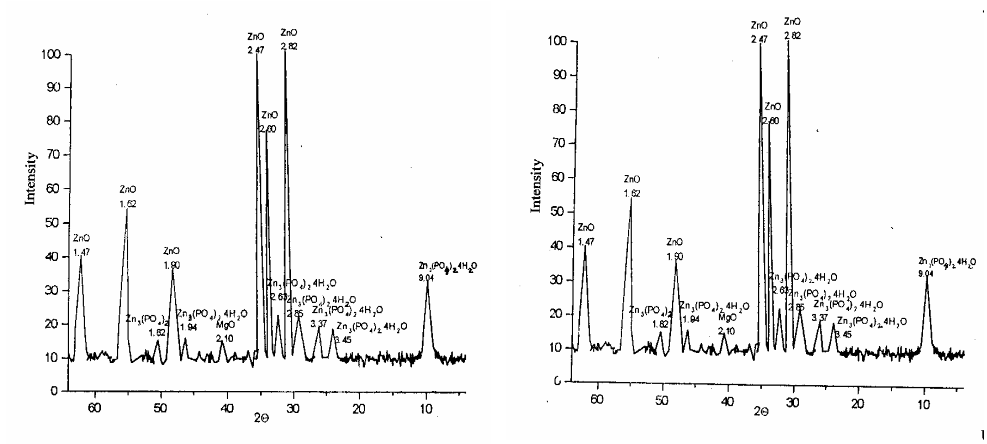
3.1. X-ray diffraction analyses, (XRD)

XRD analysis was performed on the cement pastes during the setting period (after 5 and 15 minutes) and on the cement hardened for 1 and 7 days. The obtained X-ray diffraction patterns are shown in Figures 2 and 3.



(a) (b)

Figure 2. X-ray diffraction patterns of the ROMDENT zincophosphate cement pastes cured (a) 5 minutes; (b) 15 minutes



(a) (b)

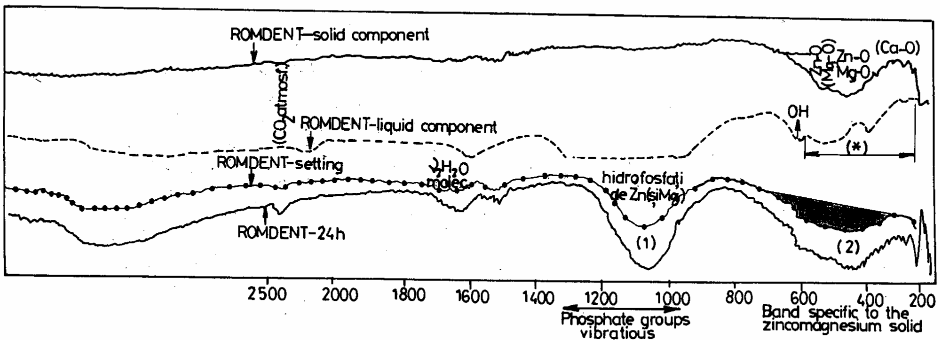
Figure 3. X-ray diffraction patterns of the ROMDENT zincophosphate cements hardened—for (a) 1 day; (b) 7 days

Since from the setting period—even after the first 5 minutes from mixing of the two components of zincophosphate cement—it is emphasized the formation of the neutral zinc hydrophosphate $Zn_3(PO_4)_2{\cdot}4H_2O$, an insoluble compound. Its proportion does not change significantly further if compared with the zinc oxide remained unreacted.

Taking into consideration the relations of phase equilibrium in the ZnO-P_2O_5-H_2O system, the nature of the ternary phases in equilibrium with the corresponding saturated solutions, the features and the stability of the products, and the kinetics of the chemical reactions, it is very likely that the zinc hydrophosphate $Zn_3(PO_4)_2{\cdot}4H_2O$ should be the result of the conversion of some unstable hydrophosphate phases initially, formed, such as the zinc hydrophosphate $Zn(H_2PO_4)_2 \cdot 2H_2O$ [1, 5, 9]. It is suggested a rapid chemical interaction on the surface of the particles of solid component of the zincophosphate cement. The hydrophosphates formed in the early stage of the process feature a higher rate of chemical conversion and transition from coagulation structures to crystallised structures, and constitute the matrix of a composite assemblage which hardens while including and binding the unreacted, anhydrous powder grains (mostly ZnO).

3.2. IR spectroscopy and scanning electron microscopy analyses

Also IR spectroscopy analysis was carried out on the ROMDENT zincophosphate cement pastes during setting and after 24 hours hardening in comparison with those of the two components befor mixing. The obtained results are shown in Figure 4.



(a) (b)

Figure 4. IR absorption spectra of the ROMDENT zincophosphate cements — (a) during setting; (b) hardened after 24 hours

The IR absorption spectra in Figure 4 emphasize two distinct domains: the domain 4000–1400 cm^{-1}—with relatively weaker absorption bands — and the domain 1400–200 cm^{-1}, respectively—with relatively strong, ample absorption bands alongside of weak and very weak peaks.

In the domain 4000–1400 cm^{-1} the following bands are observed —

(i) 3500–2900 cm^{-1}, corresponding to the vibrations of OH in the molecular water (the crystallisation water of the hydrated products, and the molecular water in the phosphate solution respectively—the liquid component of the cement);

(ii) 1650–1600 cm^{-1}, corresponding to the deformation vibrations of the molecular water;

(iii) round a maximum placed at ~2330 cm^{-1}, a meagre band corresponding to the CO_2 absorbed from the environment.

In the domain 1400–200 cm^{-1} the following bands are found:

(i) ~250–650 cm^{-1}, specific to the solid component of the ROMDENT cement and assigned to the Zn-O and Mg-O bondiugs; this band is also found in the hardened or during hardening cement. In the anhydrous cement the band is centered at 460–465 cm^{-1} and exhibits also a maximum at 530 cm^{-1} (Zn-O). Besides, also weak and very weak peaks are visible in the domain of the Me-O vibrations, as follows: 470–480, 430, 405–410, 395–400, and 385 cm^{-1}, and 360, 335, 310, and 285–290 cm^{-1} respectively.

(ii) 800–1350 cm^{-1}, specific to the liquid component of the cement before casting and assingned to vibrations corresponding to the phosphate groups (of type PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^{-}$); these bands are also found in the hardened or during hardening cements as a result of hydrophosphates formation zinc especially.

(iii) 250–580 cm^{-1}, a band labeled with (x) in Figure 4 and which corresponds to the liquid component of the studied cement. The band is assigned to the neutralising agents of the H_3PO_4 solution, to the boudings of type Zn-O, Al-O respectively. Thus, the band superposes the band 250–650 cm^{-1} assigned to the solid component of the zincophosphate cement and is also further refound in the hardened or duringhardening cement pastes.

When compared, the IR spectra of the hardened cement and of the single components (liquid and solid) of the cement before hardening it is suggested the consumption of the phosphoric acid in its reaction with the solid component of the cement and the subsequent disappearance of the bands specific to the liquid component. A band specific to hydrophosphates appears within a frequency domain with a maximum at 1065–1070 cm^{-1}. The consumption of the solid component is supported particularly by the decreasing of the amplitude of its specific band, which is plating out.

The IR absorption spectra also suggest the composite character of the hardened zincophosphate cements, which is consistent with the XRD analysis. The binding matrix consists of the ready-formed hydrophosphates. It includes the unreacted particles of ZnO and other oxides, as well as the particles of the solid solutions of ZnO with other oxides.

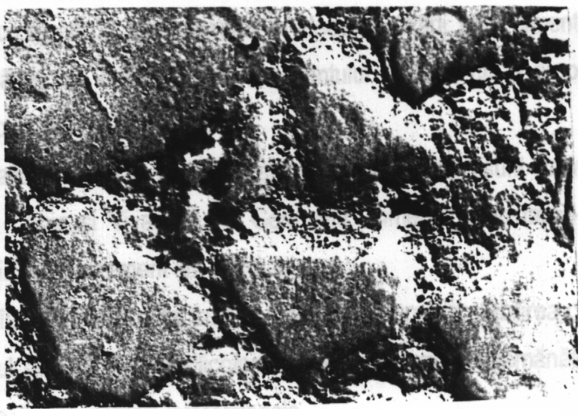


Figure 5. SEM image (x5000) of the ROMDENT zincophosphate cement hardened for 24 hours

The final structure of the zincophosphate cement is such as illustrated by the scanning electron microscopy image in Figure 5: a crystalline structure with a matrix growing from coagulation structures to crystallisation structures and forming interfaces consolidated with the included also crystalline grains.

4. CONCLUSIONS

The results obtained from the investigations carried out and their correlation together with their interpretation may suggest the following comprehensive description of the mechanisms in the processes taking place at hardening of the zincophosphate dental cements, namely: the succesion of processes, the nature of the products and their composition-structure development:

(a) In the early stage of hardening, just upon mixing the two components of the zincophosphate cements, rapid chemical interactions take place on the surface of solid particles, with formation of unstable acid hydrophosphates—such as $Zn(H_2PO_4)_2 \cdot 2H_2O$, in gelous state—, which develop coagulation structures, determining for the beginning of setting.

(b) With their coagulation structure, the acid hydrophosphates formed during the early stage of the hardening process feature a high rate of chemical and structural conversion. Thus, even after 5 minutes from the beginning of the process the integral conversion of the acid hydrophosphates into the stable neutral zinc hydrophosphate ($Zn_3(PO_4)_2 \cdot 4H_2O$) takes place, with transition from the coagulation structures to crystallisation structures.

(c) The phosphate constituent in the liquid component of the zincophosphate cement vanishes rapidly, with formation, upon its entire consumption, of neutral hydrophosphates, with progresive development from chemical and structural point of view. The neutral hydrophosphates evolve towards the anhydrous neutral phosphate, $Zn_3(PO_4)_2$, while the crystalline structure consolidates. The solid component is only partly consumed. The chemical interaction process between the two components of the cement ends up shortly, virtually in less than one day after mixing.

(d) The hardened zincophosphate cement shows itself as a composite material with a final structure of obvious crystalline nature and whose matrix (neutral hydrophosphates and phosphates formed during cement hardening) has evolved structurally up to crystallisation structures and formed interfaces consolidated with the enclosed grains, also crystalline.

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