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DOCTORAL THESIS

Phosphate cements based on calcined dolomite. Obtention, properties and utilizations

Abstract

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Content

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The main objective of this doctoral thesis was to obtain and characterize of phosphate cements in which:

- the basic component was obtained by the calcination of magnesite at 1500°C and dolomite at different temperatures (750°C, 1200°C and 1400°C), and
- the phosphate component was:
  - KH_2PO_4 (MKP) or K_2HPO_4 (DKP),
  - NaH_2PO_4 (NP).

Other components used for the preparation of phosphate cements were borax (setting retarder), fly ash (filler), quartz sand and two types of wastes with heavy metals content (chromium and nickel).

Based on the obtained results, the following conclusions can be formulated:

In the case of cements obtained by the mixing of calcined magnesite with KH_2PO_4 (MKP) or K_2HPO_4 (DKP) with/without fly ash addition, it was found that:

- The main reaction product formed in these cements, assessed by X-ray diffraction, is K-struvite ($KMgPO_4 \cdot 6H_2O$); this crystalline compound is essential for the hardening process of phosphate cements;
- the rate of the hardening process is influenced by the nature of the phosphate salt and dosage of the setting retarder;
- for the preparation of cement pastes with MKP is compulsory to use borax, due to the very fast reaction kinetics of the precursors (magnesia and MKP);
- regardless of the type of phosphate salt used (MKP or DKP), the increase of borax dosage determined, as expected, an increase of the setting time;
- the compressive strengths of phosphate cements prepared with KH_2PO_4 (MKP) were higher as compared with those of cements prepared with K_2HPO_4 (DKP). This may be due to the formation, precipitation and crystallization of a higher amount of K-struvite ($KMgPO_4 \cdot 6H_2O$) in the cements with MKP;
- partial substitution of the calcined magnesite with fly ash (10%wt.) determines an increase of the mechanical strength of phosphate cement pastes with MKP and borax.

The calcination conditions of dolomite (temperature and plateau) lead to the obtention of materials with different compositions and reactivities vs. water:

- the partial calcination of dolomite at a relatively low temperature (750°C) permits the obtention of a mixture of MgO and $CaCO_3$, while its thermal treatment at 1200°C and 1400°C leads to the decomposition of the calcium magnesium carbonate into MgO and CaO;
- the increase in calcination temperature of dolomite, from 1200 to 1400 °C reduces the reactivity of calcium and magnesium oxides vs. water or phosphate salt solution; during the mixing of dolomite calcined at 1200°C with solutions of MKP or DKP an important increase of temperature was noticed; the setting proceeded rapidly, even when a setting retarder addition (borax) is added to the cement mixture and an important expansion phenomenon of the pastes was observed;
- to reduce the reactivity of the solid component (calcined dolomite) vs. phosphate solution, the calcined dolomite was mixed with quartz sand and thermally treated at 1200 °C for 1 h. The XRD patterns of the material resulting from this thermal treatment shows the presence of SiO_2, MgO and CaO, as well as of some calcium and/or magnesium silicates formed by the partial reaction of the previously mentioned oxides.

The calcination conditions of dolomite, as well as the nature and dosage of the components in the phosphate cements, influence ***the nature and amount of the compounds formed in the reaction of calcined dolomite with the phosphate solution***:

- on the XRD patterns of the phosphate cements based on dolomite calcined at 1200°C and MKP or DKP solution, the main compounds assessed by X-ray diffraction are: calcium hydroxide, magnesium hydroxide and hydroxyapatite;
- when water and MKP are mixed with the material resulted by the thermal treatment at1200°C of dolomite and silica mixture (D_{12S}_MKP_2), in the hardened cement paste, are identified (by XRD), the following compounds: SiO_2, MgO and CaO, calcium and/or magnesium silicates and K-struvite;
- in the case of hardened phosphate cements based on dolomite calcined at 1400°C (D_{14}) and a lower dosage of MKP (corresponding to a ratio D_{14}/MKP = 4) the compounds detected by XRD were: with $Ca(OH)_2$ and $Mg(OH)_2$ and hydroxyapatite (HAP). For a higher dosage of MKP (corresponding to D_{14}/MKP = 2) on the XRD patterns of hardened cement paste

are also present the peaks specific for K-struvite ($KMgPO_4 \cdot 6H_2O$), compound which is responsible for increasing the mechanical strength;

- when dolomite calcined at 1400°C was mixed with a sodium dihydrogen phosphate (NP) solution, the compounds identified by X-ray diffraction in the hardened cement binder paste were: MgO, $NaMgPO_4 \cdot 7H_2O$, CaO, $Ca(OH)_2$ and $Na_2CaMg(PO_4)_2$;
- in the case of magnesium-phosphate cements based on dolomite calcined at 750°C (D_{750}) and potassium dihydrogen phosphate on the XRD patterns are present the peaks specific for $CaCO_3$, MgO and K-struvite ($KMgPO_4 \cdot 6H_2O$).

The properties of phosphate cements based on calcined dolomite are influenced by its reactivity vs. phosphate solution used (MKP and NP) and the nature and amount of compounds formed in the hardened cement paste:

- the increase of calcination temperature of dolomite to 1400°C in correlation with the increase of the dosage of phosphate salt (MKP), leads to the increase of the compressive strength of the cement pastes after short curing times;
- the mechanical strengths of phosphate cement based on D_{12S} (mixture of dolomite and silica calcined at 1200°C) and MKP, have low initial values (1.5 MPa after one day of hardening) but compressive strengths steadily increase up to 28 days of hardening;
- in the case of cement pastes based on dolomite calcined at 1400°C (D_{14}) and potassium dihydrogen phosphate (MKP), the only composition that developed mechanical strength was the one with a higher dosage of phosphate salt (D_{14}_MKP_2); an increase of compressive strength was observed up to 7 days of hardening, but at the 28 days cement the values were below the detection limit of the testing machine; this sharp decrease of compressive strength is most probably due to the late hydration of magnesium oxide and calcium oxide, still present in system;
- the calcination of dolomite at lower temperatures (750°C) had a positive effect on the compressive strength of the magnesium-phosphate cements, both at short curing ages (1, 7 days) and at longer curing ages (28 days). The highest compressive strengths were recorded for the composition D_{750}_MKP_B_0,23, i.e. 6.34 MPa after 1 day of hardening and 15.44 MPa after 28 days of hardening;

- the use of sodium dihydrogen phosphate solution (instead of MKP) improved the mechanical strength of cement pastes based on dolomite calcined at 1400°C; the compressive strengths developed by these phosphate cements were around 10 MPa after 28 days of hardening, unlike those where the phosphate salt was MKP, which had no measurable strengths after 28 days.

The studied phosphate cements based on calcined magnesite or calcined dolomite (D_{14} and D_{12S}) and KH_2PO_4 (MKP) or NaH_2PO_4 (NP) solution, were used for ***the immobilization of toxic waste with heavy metals content (Cr or Ni).***

- the cements based on calcined magnesite (M) and MKP can ensure, after 28 days of hardening, a good immobilization of an industrial waste with a high chromium content; the cements based on dolomite calcined at 1400°C (D_{14}) and MKP can be used to immobilize the waste with high chromium content, but only for lower dosages (corresponding to a 0.5% Cr). The phosphate cements based on calcined dolomite (D_{12S} and D_{750}) and MKP do not ensure an adequate chromium immobilization; the amount of chromium leached (according to the SR EN 12457-4:2003 standard) exceed the limit imposed by the current legislation (Romanian Ministerial Order no. 95/2005). This is probably due to the formation of a smaller amount of K-struvite in the hardened cement pastes based on D_{12S} and D_{750} as compared to those based on D_{14} and especially M; K-struvite is the compound with a decisive role both for the development of compressive strength and for the immobilization of heavy metals;
- the phosphate cements based on calcined magnesite (M) or calcined dolomite (D_{14}) and NaH_2PO_4 solution (NP), achieved also a good immobilization of a waste with high nickel content; the concentration of Ni in the leaching solutions did not exceed the limit imposed by the current legislation (OM 95/2005);
- regardless of the phosphate salt used (MKP or NP), the partial substitution of calcined magnesite or calcined dolomite (D_{14}, D_{12S} or D_{750}) with wastes with a high content of Cr or Ni, leads to the decrease of mechanical strength of the studied phosphate cements. This decrease can be due to:

- decrease of the amount of active component (waste partially substitutes calcined magnesite or calcined dolomite) which leads to the formation of a smaller amount of K-struvite;
- the influence of heavy metals on the kinetics and nature of the compounds formed during the hardening process of studied phosphate cements.

The phosphate cements based on calcined magnesite (M) or dolomite calcined at 750°C (D_{750}) and MKP were tested to be used ***as passive fire protection materials, for structural steel.*** For this specific application was assessed the tensile adhesion strength of the hardened phosphate cements on different type of substrates (steel or ceramic); also, the temperature evolution of the metal substrate, covered with a layer of phosphate cement paste, when the cement layer was put in direct contact with a flame, was assessed.

It was found that:

- both cements based on calcined magnesite and dolomite calcined at 750°C show a good adhesion to the metal substrate for short curing ages (2 days); at longer curing ages (28 days) in the case of compositions based on calcined dolomite, the adhesion to the metal substrate decreases;
- the coatings based on phosphate cements pastes applied on a metal (steel) plate ensures a good protection of this substrate in the event of a fire; when the studied phosphate cements (the compositions without setting retarder - borax) were put in direct contact with the flame, the temperature of the steel plate was maintained below 500°C - temperature considered critical for this type of structures; moreover, during the entire test period (45 min) the coating remained well fixed to the surface of the metal plate.

Dissemination of the results obtained in this Thesis:

Articles published in ISI journals

1. **C. A. Vîjan**, A. Bădănoiu, G. Voicu, A. I. Nicoară, Coatings Based on Phosphate Cements for Fire Protection of Steel Structures, Materials, vol. 14, no. 20, p. 6213, 2021. (J.I.F.2021 = 3,748)
2. **C. A. Vîjan,** A. Bădănoiu, G. Voicu, A.I. Nicoară, Phosphate Cements Based on Calcined Dolomite: Influence of Calcination Temperature and Silica Addition, Materials, vol. 14, no.14 p. 3838, 2021. (J.I.F.2021 = 3,748)
3. **C. A. Vîjan,** A. Bădănoiu, A.I. Nicoară, I. Barcan, Effect of lead and nickel on the hardening processes and properties of phosphate cements, Romanian Journal of Materials, vol. 50, no. 4, pp. 510 - 520, 2020. (J.I.F.2020 = 0,563)
4. **C. A. Vîjan,** A. Bădănoiu, The influence of potassium phosphate and fly ash addition on the setting time and mechanical strengths of magnesium phosphate cements, U.P.B. Sci. Bull, vol. 82, no. 3, pp. 21-32, 2020.

Conference presentations

5. **C. A. Vîjan**, A. Bădănoiu, I. Barcan, Calcium magnesium phosphate cements for toxic waste immobilization, RICCCE ediția 21, Constanța - Mamaia, septembrie, 2019.
6. **C. A. Vîjan**, A. Bădănoiu, A.I. Nicoară, I. Barcan New phosphate cement for the immobilization of hazardous wastes with heavy metals content, SICHEM ediția 25, București, septembrie, 2020.
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8. **C. A. Vîjan**, A. Bădănoiu, Mase liante fosfatice pe bază de dolomită calcinată, Sesiunea de Comunicări Științifice, Universitatea Politehnica București, 2021.