Bone cements of calcium-magnesium phosphate and magnesium oxide

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Abstract. The new bone cements were obtained in the calcium phosphate – magnesium phosphate system. The cement powders were synthesized by precipitation method and calcium-magnesium phosphates and magnesium oxide were obtained. The cement liquids based on Na₂HPO₄ and NaH₂PO₄ characterized by pH 3.5-5.5 were used and cements phase composition, microstructure, and mechanical properties depending on pH of cement liquid were investigated. Due to the ability to form high-strength cement stone with compressive strength up to 40 MPa and setting time 10-12 minutes, these materials are promising candidates for use as the bone cements.

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1. Introduction
In the past few years, magnesium phosphate bone cements have become as regarded as an alternative to the calcium phosphate cements [1]. They are characterized by biocompatibility and osteoconductivity, have an optimal bioresorption rate [2]. The main disadvantage of these cements is the exothermic reaction occurring during the setting and hardening of cement [3] which can lead to tissue necrosis. To reduce the thermal effect, composite cements containing magnesium phosphate and calcium silicate [4] or calcium sulfate [5] are being developed.

In our work, calcium phosphates will be used as an additional phase. The creation of the cements containing both calcium phosphates and magnesium phosphates will allow to combine the advantages of both components: high strength, increased bioresorption rate for magnesium phosphate and high biological properties of calcium phosphates.

In the present work, we have synthesized powder and cement calcium-magnesium phosphate materials and have investigated their properties.

2. Materials and method
Cement powder materials were obtained based on the reaction

\[(1-x)Ca(NO_3)_2+4xMg(NO_3)_2+4(NH_4)_2HPO_4+8NH_4OH \rightarrow (1-x)Ca_4P_2O_9+xMgO+xMg_3(PO_4)2+16NH_4NO_3+6H_2O, \text{где } x=0,2; 0,4; 0,6 \] (1)

The synthesis was carried out by the method of precipitation from aqueous solutions. The synthesized materials were evaporated, dried at a temperature of 100 °C, and heat treated at 300 °C to remove...
ammonium nitrate [6, 7]. To form high-temperature phases, heat treatment was performed at 1100–1350 °C. After calcination, they were ground into a planetary ball mill in dimethyl ketone media.

Cement liquids with different pH levels were obtained based on solutions of Na2HPO4 and NaH2PO4 salts.

Cement materials were prepared by manual mixing of synthesized powders and cement liquid on a glass slide in the ratio: liquid to powder = ½. The phase composition, setting time, microstructure, and compressive strength were investigated. X-ray phase analysis (XRD) was performed on a Rigaku D / Max - 2500 diffractometer (Japan) using the JCPDS PCPDFWIN database. FTIR investigations were performed by Nikolet Avatar in KBr tablets. To study the compressive strength of cements, samples of a cylindrical shape 8 * 4 mm in size were prepared. To assess the reproducibility of strength values, 3 to 5 samples were tested. The compressive strength was measured using an Instron 5581 tensile testing machine.

Figure 1. Diffraction patterns of cement powders (a) and cement (b) calcium-magnesium phosphate materials with different ratios of calcium and magnesium, where ● - Mg3Ca3 (PO4) 4, △ - whitlokite, ♦ - hydroxyapatite, ۸ - magnesium oxide, - Ca2.589 Mg0.411PO4, º - (CaMg)3(PO4)2.
The setting time of cement materials was determined by the resistance to penetration into the material of a needle with a diameter of 1 mm of a Vika device under the load of 400 g (standard ISO 1566). The microstructure of the materials was studied by scanning electron microscopy (SEM) on a Jeol microscope.

3. Results and discussion

X-ray diffraction analysis of cement powder materials showed that for 20 mol.% of Mg, the main phases are hydroxyapatite (HA) and whitlokite, magnesium oxide, and for powders 40 and 60 mol.% of Mg, MgO, calcium-magnesium phosphates with different ratios of calcium and magnesium: Mg3Ca3(PO4)4, Ca2.589Mg0.411PO4 and (CaMg)3(PO4)2 (figure 1) was carried out. The formation of phase composition of the cements have occurred with decrease of crystallinity degree and with formation of amorphous phase. At the same time, the amount of the magnesium-enriched phases has increased with decrease of the MgO content.

The FTIR investigation of cement powders has demonstrated the presence of ν1(OH−) at 3576 cm−1 and 632 cm−1 for materials with 20 mol.% of Mg and bands of ν1-ν4 PO43− groups (1050, 1100, 962, doublet at 570, and 600 cm−1, the broad triplet at 420-480 cm−1) what has confirmed the formation of HA (figure 2). The materials with 40 and 60 mol.% of Mg did not demonstrated the OH−, but were characterized by ν1-ν4 PO43− and the intensity of the stretching vibration mode of phosphate group ν3 at 1050 cm−1 and 1100 cm−1 and bending mode ν4 at 570, and 600 cm−1 from the P–O was increased with growth of Mg content. Nitrate residues from reactants were detected as bands at 1380 cm−1 [8].

The formation of the cement materials were linked with significant increase of the intensity and broad of adsorbed H2O regions at 2900-3400 cm−1 and 1780-1525 cm−1. These indicate the formation of crystal-hydrate amorphous phase during the cement materials formation. For cement material with 20 mol.% of Mg the intensity of the (OH−) bands decreases and spectra becomes similar to materials with 40 and 60 mol. % of Mg.

![Figure 2](image-url)  
Figure 2. FTIR spectra of cement powders (a) and cement (b) calcium-magnesium phosphate materials with different ratios of calcium and magnesium.

The setting time and compressive strength after hardening of the obtained cement materials are presented in table 1. The setting time decreases with increasing pH of the liquid for the composition of 20 mol.% Mg, and also monotonically decreases with increasing of Mg content for liquids with pH 3.5 and 4.5.

The maximum strength was obtained on the composition of 60 mol.% Mg and reaches 40 MPa, decreasing with increasing of liquid pH down to 13 MPa are presents in Table 1.
Table 1. Properties of cement materials

| Composition of cement powder | Cement setting time, min | Cement compressive strength, MPa |
|-----------------------------|-------------------------|----------------------------------|
|                             | pH liquid = 3.5         | pH liquid = 4.5                   | pH liquid = 5       | pH liquid = 5.3 |
| 20 mol. % Mg                | 10/11                   | 6/16                             | 3/6                 | 1/9             |
| 40 mol. % Mg                | 6/30                    | 4/32                             | 4/7                 | 7/11            |
| 60 mol. % Mg                | 3/40                    | 1/30                             | 3/19                | 3/13            |

The microstructure of the cement materials were porous and zones with crystal hydrate formation were observed (figure 3). The average sizes of the particles formed the cement materials increased with growth of Mg content and were about 1-3 µm for cement with 20 mol.% of Mg to 10-20 for cement with 60 mol.% of Mg.

Figure 3. The microstructure of cement calcium-magnesium phosphate materials, where a - 20 mol. % Mg, b - 40 mol. % Mg, c – 60 mol. % Mg.

Thus, the formation of calcium -magnesium cements occurs by formation of amorphous phase and crystal hydrate structures. The decrease of the pH level and increase of Mg content led to growth of the strength up to 40 MPa. These new calcium-magnesium phosphate bone cements are promising candidates for medicine for restoration and regeneration of bone tissues.

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