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RESEARCHING OF PHOSPHORUS SLAG FOR PRODUCING ZINC-PHOSPHATE COMPOSITE CEMENT

Abstract
The cements required for dentistry are not produced in our country, and all their types are imported from abroad. The scientific article examines the possibility of producing zinc phosphate dental cement and the composition of the phosphorus slag added to it. Phosphorus oxide and fluoride oxide present in the phosphorus slag play an important role as activators in the production of dental cement. In addition, the chemical composition of the phosphorus slag was determined, their X-ray phase and differential thermal analyses were carried out. In the differential thermal analysis of pseudowollastonite, the exothermic effect is observed at a temperature of 920 °C.

Keywords: phosphorus slag, zinc phosphate cement, microstructure, radioactivity, composite material.

Introduction

Not a single type of cement used in dentistry is produced in Kazakhstan. Our country is forced to import this type of composite material from across the border. For the last 10 years, composite materials necessary for the dental industry have been supplied to Kazakhstan from countries such as Germany, USA, Russia, China, Switzerland, France, Great Britain, Japan, and South Korea [1]. According to the UN, the countries that export dental cements to Kazakhstan are Germany - 54%, USA - 14%, France - 8%, Switzerland - 7%, Russia - 5% and other countries - 12% [2].

Dental materials are composite materials that harden when mixed with a special liquid and are used for temporary tooth restoration, pulp protection, cavity filling, sedation or isolation, as well as cementing of removable prostheses. In modern dentistry, according to the international classification, there are 8 types of cements, which include:zinc phosphate, zinc-eugenol, silicate, polycarboxylate; silicophosphate; glass ionomer, bactericidal, polymeric.

Materials and methods

Zinc-phosphate cement is a material that hardens when reacted with an aqueous solution of phosphoric acid (H_3PO_4) and consists of 90% zinc oxide powder (ZnO), 10% magnesium oxide powder (MgO). When powder and liquid are mixed, an exothermic reaction occurs, resulting in the formation of water-insoluble zinc phosphate. Cement setting time is from 2,5 to 8 minutes, film thickness — 20 μm, water-cement ratio — 0,5, working time after hardening — 5 minutes, compressive strength — 104 MPa, tensile strength — 5,5 MPa (Vishakha, 2020). Cement does not irritate the pulp of the tooth, quickly neutralizing H_3PO_4 [4].

The chemical composition of zinc-phosphate cement includes ZnO, MgO, etc. The powdery components of the oxides are mixed according to their chemical ratio and fired in an electric furnace at a temperature of 950–1300 °C for 4–6 hours. The burnt semi-finished product reacts with orthophosphoric acid, resulting in a reaction [5]. Aluminum phosphate ($AlPO_4 \cdot nH_2O$) was used to slow down the hardening reaction of zinc-phosphate cement and increase its strength. As a result, cement strength is 100,6 MPa. Here % $AlPO_4 \cdot nH_2O$=11,9, ZnO=372, H_3PO_4=50,9 .

Currently, scientists around the world, including John Fisher, Stephen Schwartz, Benjamin Palmer, Lee Howe, and John Hodson, are working on developing new formulations of zinc phosphate cement and improving their properties [6].

In our research work, we consider the possibility of using phosphorous slag to obtain a binding material, fully suitable for zinc-phosphate cement with high stability, strength of adhesion over time, low wear, physico-chemical resistance, high physico-mechanical indicators and high remineralization properties.

Elements P and F, contained in phosphorus slag, play an important role in the composition of zinc-phosphate cement. The inclusion of phosphorus slag in zinc-phosphate cement increases cement strength, water resistance and resistance to atmospheric influences. In addition, phosphorus slag is a production waste and can be obtained at a low price [7].

Zinc phosphate is introduced into cement by activating phosphorous slag. That is, there are thermal, alkaline, acid, mechanical and mixed methods of activation of phosphorus slag. Mechanical activation is the most effective among them. In the process of mechanical activation, phosphorus is enriched by grinding slag particles in a ball mill.

As a result, the implementation and full-scale study of phosphorus slag as an additional additive in the production of zinc-phosphate cement is relevant. In this scientific article, the slag of the "New Zhambyl Phosphorous Plant" located in the city of Taraz is considered as the main object [8].

Results and discussion

Chemical, X-ray phase, differential thermal, and dosimetric analysis of the slag of the Zhana-Zhambyl Phosphorus Plant LLP was conducted. Chemical analysis was performed using a modern XRF Axios FAST multi-element spectrometer located in the central laboratory of the Shymkentcement Plant JSC.

According to the chemical and mineralogical composition, phosphorus slag (%) consists of: SiO_2 – 41,98; Al_2O_3 – 3,06; Fe_2O_3 – 0,74; CaO – 40,92; MgO – 2,30; SO_3 – 2,30; F – 1,5; P_2O_5 – 2,01; CaF_2 – 4,5; Ca_3P_2 – 0,3. The amount of glassy phase in the composition is 90-95%.

X-ray phase analysis of phosphorus slag was carried out at the Scientific Research and Testing Center “SAPA” of the South Kazakhstan University by M. Auezov. The X-ray diffraction pattern of phosphorus slag is shown in Figure 1.

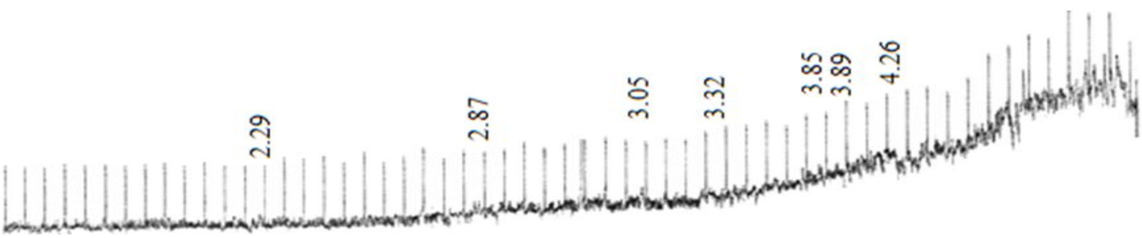

Fig. 1. X-ray of phosphorus slag

As a result of X-ray phase analysis, the following minerals were identified in the phosphorus slag: pseudowollastonite (α-$CaO \cdot SiO_2$) d/n=4,26; 3,85; 3,32; wollastonite (ß-$CaO \cdot SiO_2$) d/n=3,89; 3,05; and melilite [$Ca_2(Al,Mg,Si)Si_2O_3$] d/n=2,87; 2,29. Differential thermal analysis (DTA) was used to study the physicochemical changes occurring in phosphorus slag. The derivative of phosphorus slag is shown in Figure 2.

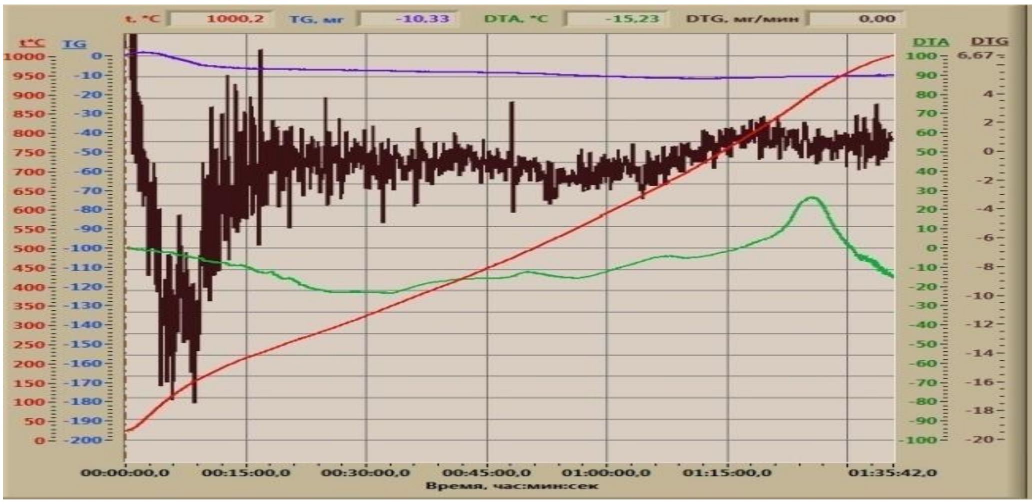

Fig. 2. Derivatogram of phosphorus slag

The DTA curve of phosphorus slag revealed a deep exothermic effect with a maximum at 920°C. The effect process begins at a temperature of 870°C, which indicates the presence of pseudowollastonite mineral in phosphorus slag. The amount of glass phase with a disordered structure in phosphorus slag is 95-98%. With increasing temperature, a slight loss of mass is observed (TG curve) due to the removal of a small amount of adsorbed water.

The structure of phosphorus slag was analyzed by scanning electron microscopy using a JEOL JSM-6490LV device in the regional testing laboratory of the engineering profile "Constructive and Biochemical Materials". Electron-microscopic energy dispersive microanalysis is shown in Fig. 3.

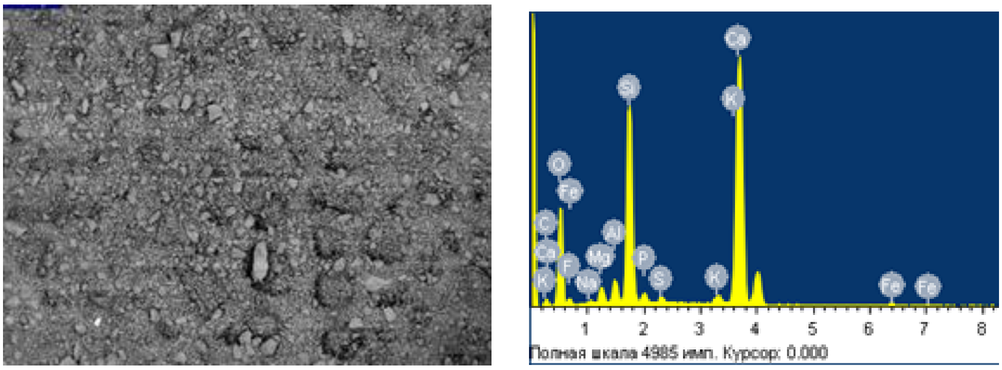

Fig. 3. Raster electron-microscopic energy dispersion microanalysis of phosphorus slag

As a result of scanning electron microscopic analysis, no radionuclides such as harmful radioactive elements U, Th, Ra and their derivatives were found in the phosphorus slag. Also, no toxic, heavy metal elements Zn, Cu, Pb, Be were found, zinc phosphate is recommended for use as an additive in the production of cement.

Table 1. Elemental composition of phosphorus slag

Elements	C	O	F	Na	Mg	Al	Si	P	S	K	Ca	Fe	Total
Weight, %	6,54	42,44	2,22	0,29	1,39	1,62	13,55	0,88	0,46	0,84	29,25	0,52	100

The study of the actual effective activity and radioactivity of radionuclides contained in the phosphorus slag was carried out in the "Radiology" laboratory of the National Expertise Center in Shymkent using the "DKG-02U Arbitr" radiometer-dosimeter.

Conclusion

1. For the first time, the use of phosphorus slag in the production of zinc phosphate cement will be implemented.

2. The chemical and mineralogical composition of phosphorus slag was determined, (%): SiO_2 – 41,98; Al_2O_3 – 3,06; Fe_2O_3 – 0,74; CaO – 40,92; MgO – 2,30; SO_3 – 2,30; F – 1,5; P_2O_5 – 2,01; CaF_2 – 4,5; Ca_3P_2 – 0,3. The amount of glassy phase in the composition was 90-95%.

3. As a result of X-ray phase analysis, the phosphorus slag contained pseudowollastonite (α-$CaO·SiO_2$) d/n=4,26; 3,85; 3,32; wollastonite (ß-$CaO·SiO_2$) d/n=3,89; 3,05; and melilite [$Ca_2(Al,Mg,Si)Si_2O_3$] d/n=2,87; 2,29 were detected.

4. As a result of scanning electron microscopic analysis, no radionuclides such as harmful radioactive elements U, Th, Ra and their related particles were found. Also, toxic, heavy metal elements Zn, Cu, Pb, Be were not found, zinc phosphate is recommended for use as an additive in the production of cement.

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МЫРЫШ-ФОСФАТТЫ КОМПОЗИТТІ ЦЕМЕНТ ӨНДІРУГЕ АРНАЛҒАН ФОСФОР ҚОЖЫН ЗЕРТТЕУ

Түйін

Елімізде стоматология саласына қажетті цементтер өндірілмейді және олардың барлық түрі шет мемлекеттерден импортталады. Ғылыми мақалада цинк фосфатты цемент алу мүмкіндігі және оған қосылатын фосфор қожының құрамы зерттелді. Фосфор қожының құрамында кездесетін фосфор оксиді мен фтор оксиді композициялық цемент алу барысында белсендендіргіш ретінде маңызды рөл атқарады. Сонымен қатар, фосфор қожының химиялық құрамы анықталып, оған рентгенофазалық және дифференциалды термиялық талдау жасалды. Дифференциалды термиялық талдау барысында 920 °С-та псевдоволластониттың экзотермиялық әсері байқалады. Расторлы электронды микроскопиялық талдау нәтижесінде де элементтер адамның денсаулығына зиян келтіретін уран, торий және радий тәріздес радионуклидтердің жоқтығы дәлелденді. Фосфор қожын стоматологиялық мырыш фосфатты цемент алу саласында қолдану экологиялық мәселелерді шешуде ғана емес, сонымен қатар, күйдіру температурасын төмендетуге, стоматологиялық цемент бағасын арзандатуға және мырыш фосфатты цементтің физико-механикалық қасиеттерін жақсартуға мүмкіндік береді.

Кілттік сөздер: фосфор қожы, мырыш фосфатты цемент, микроқұрылым, радиоактивтілік, композициялық материал.

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ИССЛЕДОВАНИЕ ФОСФОРНОГО ШЛАКА ДЛЯ ПРОИЗВОДСТВА ЦИНК-ФОСФАТНОГО КОМПОЗИЦИОННОГО ЦЕМЕНТА

Аннотация

Необходимые для стоматологии цементы в нашей стране не производятся, и все их виды импортируются из-за рубежа. В научной статье исследована возможность производства цинкфосфатного стоматологического цемента и состав добавляемого в него фосфорного шлака. Оксид фосфора и оксид фторида, присутствующие в фосфорном шлаке, играют важную роль в качестве активаторов при производстве стомотологического цемента. Кроме того, был определен химический состав фосфорного шлака, проведены их рентгенофазовый и дифференциально-термический анализы. При дифференциальном термическом анализе псевдоволластонита экзотермический эффект наблюдается при температуре 920 °С. Анализ электронной микроскопии не выявил опасные радионуклиды, таких, таких как уран, торий и радий, которые являются элементами, вредными для здоровья человека. Использование фосфорного шлака при производстве стоматологического цинк-фосфатного цемента позволит решить проблему импортозамещения, экологической проблемы региона, способствует снижению температуры обжига и снижению себестоимости стоматологических цементов, а также улучшить физико-механические свойства цинк-фосфатного стоматологического цемента.

Ключевые слова: фосфорный шлак, цинкфосфатный цемент, микроструктура, радиоактивность, композиционный материал.