

# Refractory Concretes from Waste of Kovdor Mining and Processing Plant by Magnesium Phosphate Cement

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**Abstract:** This work is aimed at using the technogenic raw materials of the Kovdorsky GOK for the production of refractory materials. Currently, many researchers are engaged in the development of technologies for unshaped materials. The most demanded among them are refractory concrete. They are able to set and harden at low temperatures with the formation of structures that retain their characteristics when heated. In our work, concretes were obtained from a briquette based on forsterite concentrate obtained from the waste of the Kovdorsky GOK. Magnesium phosphate cement was used as a binder. As a result of the research, the grain composition of the charge was selected, the ratio of filler and binder to improve the structural properties of concrete was found, the effects of the composition and the temperature of heat treatment of concretes on the physical and technical properties were shown. Concretes have the following characteristics: bulk density 2170-2260 kg / m<sup>3</sup>, strength up to 50 MPa (at 25°C), volume change after heat treatment at 450-1000°C 1-2%. Recovering the waste of the Kovdorsky GOK by manufacture of concrete will lead to a qualitatively new use of non-renewable natural resources, reduce the rate of depletion of mineral raw materials in the subsoil, eliminate sources of environmental pollution and restore land occupied by waste.

**Keywords:** Forsterite Concentrate, Magnesium Phosphate Cement, Refractory Concrete

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## 1. Introduction

Exploitation of man-made mineral formations is explained by environmental aspects. There are two directions: additional extraction of the main useful components and the development of technologies for the use of unconventional raw materials.

Magnetite, apatite and baddeleyite concentrates are isolated during the enrichment of complex ores of the Kovdor deposit. The wastes of this production are, %: forsterite 38 - 48, calcite 21 - 30, phlogopite 10 - 11 and not extracted part of the main products. The development of new technologies for processing these mineral raw materials can lead to the production of demanded products, for example, the involvement of forsterite in the production of refractories and concretes. Efficiency of the extraction of basic minerals will increase and minimize the negative impact on environment.

Non-fired refractories are capable of setting and hardening

at low temperatures, with the formation of structures that retain their characteristics when heated. The advantages of using non-fired refractory concretes in comparison with traditional molded products are as follows: saving up to 50% of energy costs for the manufacture of refractory products; reduction in 2 - 3 times the time of work and a decrease in the labor intensity of work on the lining by 25 - 40%; the possibility of obtaining high-quality lining material - refractory concrete with increased mechanical properties; the universal technology of concrete production allows, by changing the components of the mixture, to give the molded masses the given technological properties; the ability to manufacture lining blocks of complex shape without breaking the tightness of the lining; reduction of downtime during emergency repairs due to the rapid (12 - 24 hours) recruitment of working strength with refractory concrete.

The role of the binder is to impart strength to the material other necessary properties are realized during primary heating of concrete in thermal installations during service.

Currently, preference is given to "green" binders, therefore the most promising and environmentally friendly are magnesium phosphate cements. They have proved themselves in refractory technology, providing high heat resistance and material strength at high temperatures.

Phosphate binders are dispersion of a number of inorganic substances in phosphoric acid. Refractories with their use appeared, thanks to the research of a number of domestic and foreign scientists, who laid the theoretical foundations of the chemical technology of phosphate materials [1-8].

For phosphate binders, the transformation schemes of the cementing part are ambiguous, the compositions contain variable phases, the neoplasms are mostly amorphous and only when heated are prone to crystallization and interaction with filler grains. During heat treatment the microstructure undergoes significant changes.

The study and analysis of new experimental data were required since the complexity of the physic chemical processes that determine the hardening and structure formation of phosphate materials.

The purpose of the work is to obtain materials based on forsterite concentrate with magnesium phosphate cement. Influence of the binder on the properties of the materials and the result phosphate compounds during their interaction are investigating.



with density 1.491-1.556 g/cm<sup>3</sup>.

## 2.2. Methods

The chemical composition of forsterite concentrate was determined using the following methods: the SiO<sub>2</sub> gravimetrically by [9], the MgO, the Fe<sub>2</sub>O<sub>3</sub>, the calcium oxide according to [10-12] respectively. The relative change in mass on ignition was determined by standard method [13]. Content of FeO was determined by titration according to method [14].

The grain sizes of the forsterite concentrate are in a narrow range of values, namely, less than 0.2 mm. Grain size classification was determined by standard method [15].

The phase compositions were investigated by X-ray diffraction at a diffractometer XRD 6000 Shimadzu. The cleavage faces were examined using Scanning Electron Microscopy (SEM) method at a SEM LED 420 microscope.

## 2.3. Preparation of Concrete Samples

Grain sizes of forsterite concentrate are < 0.2 mm. Concrete from a raw forsterite concentrate had bulk density of 1280-1450 kg/m<sup>3</sup> and compressive strength of 1.2 - 1.5 MPa. Concretes from briquettes are investigated further.

Some part of forsterite concentrate for briquettes was ground in vibration mill by fraction <0.063 mm. The magnesite refractory waste was grinding in roller crusher by fraction 3- 0.2 mm.

In the study, briquettes of the following compositions were used: 1- 60% fraction <0.2 mm and 15% fraction <0.063 mm

## 2. Material and Methods of Research

### 2.1. Raw Materials

The chemical composition of forsterite concentrate from processing waste is as follows, %: MgO – 43 - 48; SiO<sub>2</sub> – 33 - 39; FeO – 4.4 - 5.3; Fe<sub>2</sub>O<sub>3</sub> – 0.8 - 5.9; CaO – 0.6 - 2.4; loss on calcination – 0.1- 1.5. Forsterite of the Kovdor iron ore deposit contains, as a rule, from 3 to 8 molecular percent Fe<sub>2</sub>SiO<sub>4</sub>.

The classification by grain size of forsterite concentrate is as follows, %: (>0.2 mm) - 1, (-0.2+0.16 mm) - 7, (-0.16+0.1 mm) - 48, (-0.1+0.063mm) - 25, (-0.063+0.05 mm) - 5, (< 0.05 mm) - 14.

The grain sizes in the charge are of significant importance in the technology of forsterite products, since the parameters of bulk density and mechanical strength depend on it. In the technology of forsterite materials, the grain size composition of the charge assumes the presence of up to 55% fraction 3 - 0.63 mm and up to 40% fraction less than 0.1 mm. Consequently, forsterite concentrate which a particle size distribution of <0.2 mm is required briquette.

Basic magnesium carbonate was used to obtain magnesium phosphate cement, Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O:

forsterite concentrate, and 25% comminuted magnesite refractory waste fraction 3- 0.2 mm; 2- 50% fraction <0.2 mm and 15% fraction <0.063 mm forsterite concentrate, 35% comminuted magnesite refractory waste fraction 3- 0.2 mm.

The briquette is obtaining by technology: a blend of a certain composition from forsterite concentrate and comminuted magnesite refractory waste is mixed, a binder (polyvinyl alcohol) is introduced then samples are pressed under 50-70 MPa and are dried by natural conditions for a day. These are fired at a temperature of 1400°C. The resulting briquette is crushed to obtain fractions < 3 mm. Some part of briquette is subjected to grinding in a vibrating machine IV-1 by a fraction < 0.063 mm.

The main stages in the manufacture of concretes: magnesium phosphate binder was introduced in charge of briquette containing from 80 to 50% fraction <3 mm and 20 - 50% fraction < 0.063 mm. The mixes were carefully homogenized and placed in a mold. After hardening for 2 days, the samples were fired at 450 - 1200°C. Then the bulk density, volume change and cold crushing strengths were determined.

### 2.4. Testing of Concrete Samples

The samples were tested for compressive strengths, bulk density, changes in the volume after temperature treatment. Cold crushing strengths was calculated for cubic specimens from the ratio of the applied load to their cross-sectional area [16]. The bulk density was determined from the sample weight to volume ratio [17]. The change in volume is

expressed as the difference between the volumes before and after heat treatment to the initial volume of the samples and calculated as a percentage [18].

### 3. Results and Discussion

#### 3.1. Investigation of the Process Occurring During Sample Sintering

Magnesium phosphate cements (MPC) are formed through a reaction between MgO and a soluble acid phosphate to form a magnesium phosphate salt with cementation properties.

Complex physic chemical processes occurring during hardening of mixtures by magnesium phosphate cement can be represented as follows: the formation of new magnesium

phosphates; gradual removal of chemically bound water and the transition of mono- and di-substituted phosphates to tri-substituted; slow decomposition of magnesium phosphate binder or phosphoric acid with sublimation of phosphate anhydride; gradual transition of the binder to a ceramic form with the formation of MgO.

Researchers provide contradictory information on the composition of the compounds formed in concretes with magnesium phosphate cement and the transition temperature of one compound to another.

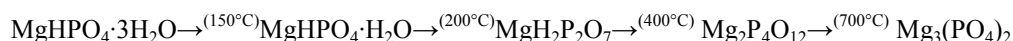
In the table 1 shows the transition temperature and the main lines in the X-ray diffraction pattern for compounds in the MgO - H<sub>3</sub>PO<sub>4</sub> system according to references [1, 3-7, 19].

**Table 1.** Magnesium phosphate compounds formed during heat treatment.

Compounds	The transition temperatures, °C	The main lines of compounds on the radiograph	References number
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	25		
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	95-110	7.57, 3.82, 3.55, 3.40	[5]
MgH <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	240	7.16, 4.33, 4.21, 3.21	
Mg <sub>2</sub> P <sub>4</sub> O <sub>12</sub>	430-650	4.58, 4.24, 3.22, 2.99	
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	25	7.31, 3.79, 2.73	
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	60-120		
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	90-200	7.57, 3.82, 3.55, 3.40	[6]
MgH <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	200-350	7.16, 4.33, 4.21, 3.21	
amorphous (Mg(PO <sub>3</sub> ) <sub>2</sub> ) <sub>n</sub>	400-450		
Mg <sub>2</sub> P <sub>4</sub> O <sub>12</sub>	500-800	4.58, 4.24, 3.22, 2.99	
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	25	5.94, 4.71, 3.46, 3.04	
Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	190	4.14, 3.01, 2.96,	[1, 3]
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	719	3.85, 3.44, 2.41	
MgHPO <sub>4</sub> ·3H <sub>2</sub> O	20	5.94, 4.71, 3.46, 3.04	
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O			
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	100-400	7.57, 3.82, 3.55, 3.40	[4]
MgH <sub>2</sub> P <sub>2</sub> O <sub>7</sub>		7.16, 4.33, 4.21, 3.21	
Mg <sub>2</sub> P <sub>4</sub> O <sub>12</sub>	675-680	4.58, 4.24, 3.22, 2.99	
Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	1200	4.14, 3.01, 2.96,	
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>		3.85, 3.44, 2.41	
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O			
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	115-250	7.57, 3.82, 3.55, 3.40	[7]
MgH <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	160-450	7.16, 4.33, 4.21, 3.21	
amorphous Mg(PO <sub>3</sub> ) <sub>2</sub>	360-600		
Mg(PO <sub>3</sub> ) <sub>2</sub>	600-1000		
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	25		
Mg(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	170	7.57, 3.82, 3.55, 3.40	[19]
MgH <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	230-270	7.16, 4.33, 4.21, 3.21	
Mg <sub>2</sub> P <sub>4</sub> O <sub>12</sub>	400-470	4.58, 4.24, 3.22, 2.99	
Mg <sub>2</sub> P <sub>4</sub> O <sub>12</sub> (ж)	600-1000		
MgO и P <sub>2</sub> O <sub>5</sub> ↑	1200-1800°C	2.43, 2.10, 1.49, 1.27	

In our work, as a result of the interaction of forsterite briquette with Mg(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O newberite was formed.

We were studied the phase composition of the samples depending on the heat treatment of the mixture. Based on the data of X-ray phase analysis, newberite at 150°C was



The principal sources of variation in phase composition among MPC system relate to the quantity of water used, the magnesium/phosphate ratio, the addition of diluents, and the use of setting retarders.

An increase in the strength properties of mixtures based on

converted into monohydrate of hydrogen phosphate MgHPO<sub>4</sub>·H<sub>2</sub>O. At 200°C, MgHPO<sub>4</sub>·H<sub>2</sub>O was converted to dihydropyrophosphate MgH<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. After 400°C, the X-ray diffraction pattern shows the lines of tetrametaphosphate Mg<sub>2</sub>P<sub>4</sub>O<sub>12</sub>, from 700°C - orthophosphate Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>:

a phosphate binder is associated with the identity of the main structural elements of silicates and phosphates (for silicates, the SiO<sub>4</sub><sup>4-</sup> tetrahedron, for phosphates, the PO<sub>4</sub><sup>3-</sup> tetrahedron), the similarity of the tetrahedron sizes (the average Si - O distance in SiO<sub>4</sub><sup>4-</sup> tetrahedron is 0.162 nm, and P - O in the

$\text{PO}_4^{3-}$  0.155 nm tetrahedron), a similar nature of the P - O - P and Si - O - Si bonds, determined by the closeness of the electronic configurations of phosphorus and silicon atoms and the closeness of the sizes of the ionic radii of these elements ( $\text{Si}^{4+}$  - 0.039 nm,  $\text{P}^{5+}$  - 0.034 nm) [19].

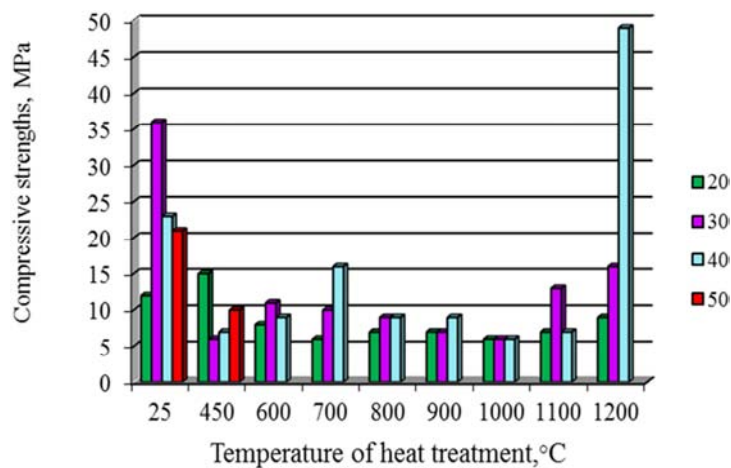
### 3.2. Cold Crushing Strengths of Samples After Heat Treatment

Graphs of changes in the crushing strength of concrete from temperature of heat treatment and fractional composition of briquettes are presented in the Figures 1-3.

The strength of samples at room temperature: from briquette 1 (charge with 30% fraction less than 0.063 mm) up to 35 MPa, from briquette 2 (charge with 40% fraction less than 0.063 mm) up to 50 MPa.

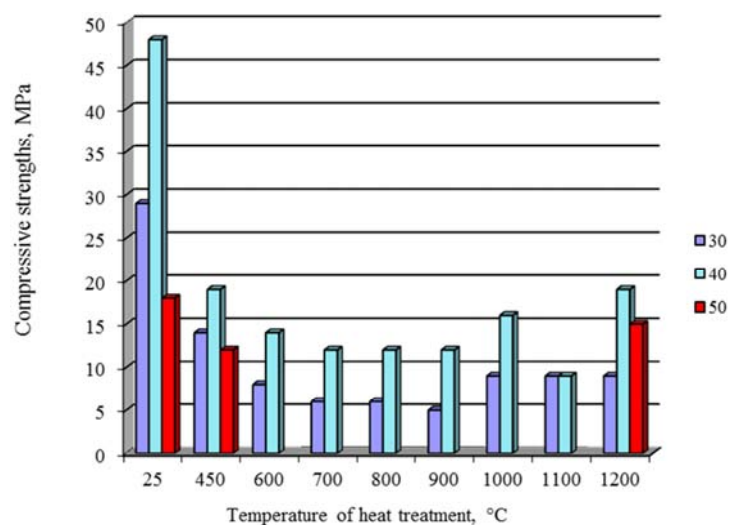
When concretes are heat treated up to 900°C, all compositions are characterized by a decrease in the mechanical strength index, which is smoother for concretes

from briquette 2. This is due to the formation of new compounds by chemical reactions occurring in the system of forsterite - magnesium phosphate cement. At 1000°C and above, the mechanical strength index begins to grow. After firing at 1200°C, the strength is 15 - 20 MPa for samples from both briquettes. The exceptions are samples with 40% of the fine fraction of briquette 1. Their strength increased to 50 MPa. This is probably due to the lesser amount of magnesite refractory waste in the composition of briquette 1, which leads to more intense sintered, when the amount of fine fraction in the batch of concrete is increased. As will be shown below, in this case, a sharp decrease in the sample volume occurs, which complicates the practical application of a material of this composition. The preferred amount of fraction less than 0.063 mm in the composition of the batch for concrete: samples from briquette 1 – 30%, for samples from briquette 2 - 40% (Figures 1, 2).



In charge composition: 20, 30, 40, 50% fraction < 0.063 mm

Figure 1. Dependence of compressive strengths from quantity fraction < 0.063 mm briquette 1 and the temperature of heat treatment.

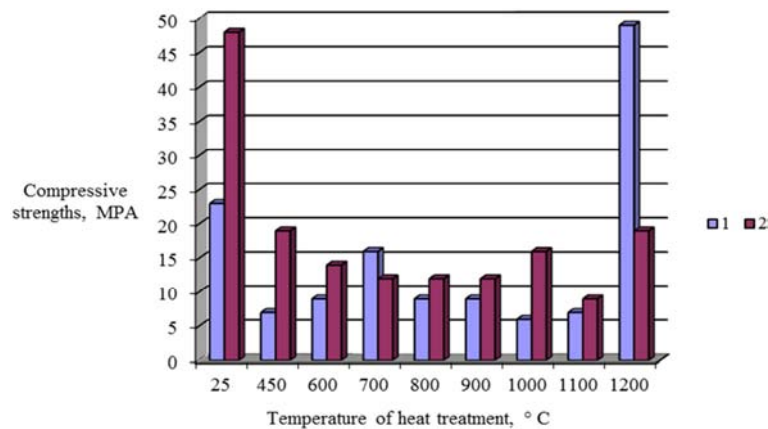


In charge composition: 30, 40, 50% fraction < 0.063 mm

Figure 2. Dependence of compressive strengths from quantity fraction < 0.063 mm briquette 2 and the temperature of heat treatment.

Comparative analysis of samples from a charge of 60% briquette with a fraction of less than 3 mm and 40% less than 0.063

mm showed that specimens from briquette 2 have a higher strength with a change in temperature (Figure 3).

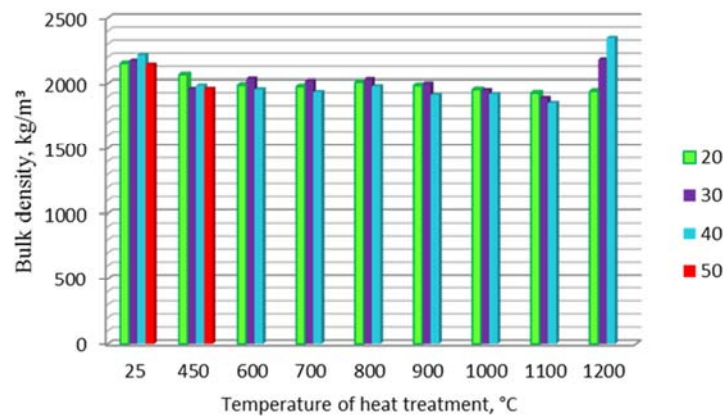


For charge composition: 60% fraction < 3 mm and 40% fraction < 0.063 mm

**Figure 3.** Dependence of compressive strengths from the composition of the briquette (1 or 2) and the temperature of heat treatment.

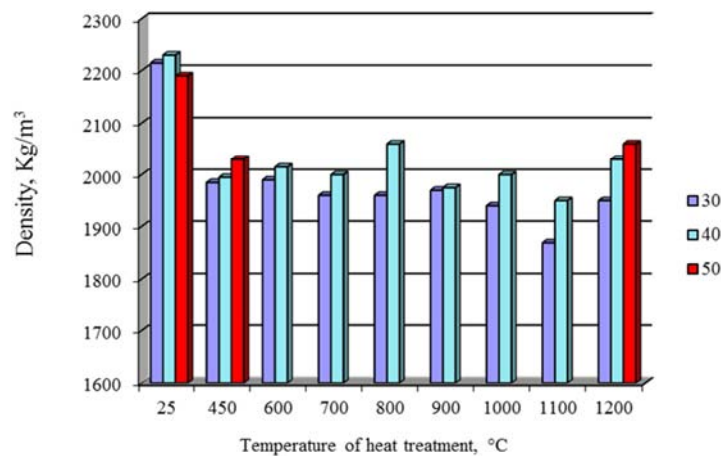
### 3.3. The Bulk Density of Samples After Heat Treatment

Graphs of changes in bulk density of concrete from temperature of heat treatment and fractional composition of briquettes are presented in the Figures 4-6.



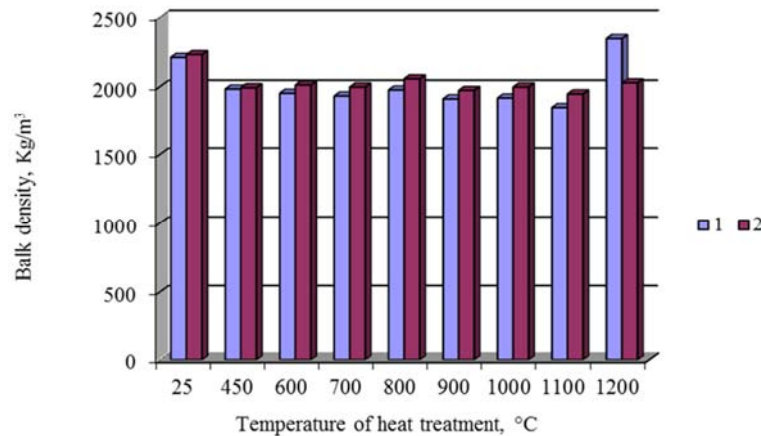
In charge composition: 20, 30, 40, 50% fraction < 0.063 mm

**Figure 4.** Dependence of bulk density from quantity of fraction < 0.063 mm briquette 1 and the temperature of heat treatment.



In charge composition: 30, 40, 50% fraction < 0.063 mm

**Figure 5.** Dependence of bulk density from quantity of fraction < 0.063 mm briquette 2 and the temperature of heat treatment.



Charge composition: 60% fraction < 3 mm and 40% fraction < 0.063 mm

**Figure 6.** Dependence of bulk density from the composition of the briquette and the temperature of heat treatment.

The bulk density of samples at room temperature for compositions with briquette 2 is higher than from briquette 1. For example, indexes of bulk density were 2215 and 2170 kg/m<sup>3</sup> from charge with 30% of a fine fraction, 2220 and 2215 kg/m<sup>3</sup> from charge with 40% of a fine fraction, 2190 and 2140 kg/m<sup>3</sup> from charge with 50% of fine fraction, respectively. By heat treated up to 900°C, the density is about 2000 kg/m<sup>3</sup> for materials from briquette 1 and 2. At 1000-1100°C, the process of softening of concrete from briquette 1 occurs and, accordingly, the volume of the sample increases, which is shown in the following figures. While in materials from briquette 2, this phenomenon is observed at 1100°C. Further processing up to 1200°C leads to strong sintering of specimens from briquette 1. For example, the bulk density of material from a charge with 40% of fraction < 0.063 mm of briquette 1 was 2350 kg/m<sup>3</sup>, a change in the sample volume index was 22%, which is shown below. The bulk density for an identical charge based on briquette 2 was 2030 kg/m<sup>3</sup> and the change in

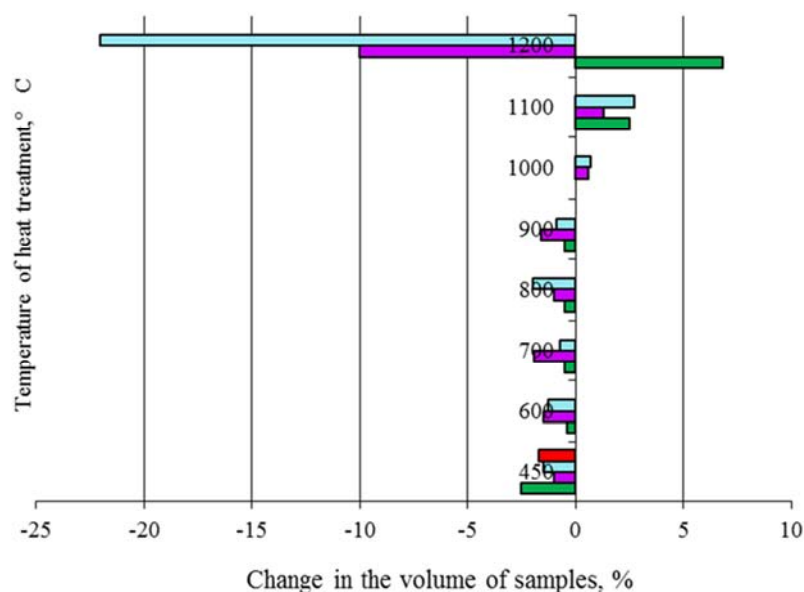
the volume index of the sample was up to 4% (Figures 4, 5).

Comparative analysis of samples from briquettes (60% fraction < 3 mm and 40% fraction < 0.063 mm) showed that specimens from briquette 2 have a higher bulk density when the temperature changes up to 1100°C (Figure 6).

### 3.4. Permanent Change in Dimensions on Heating

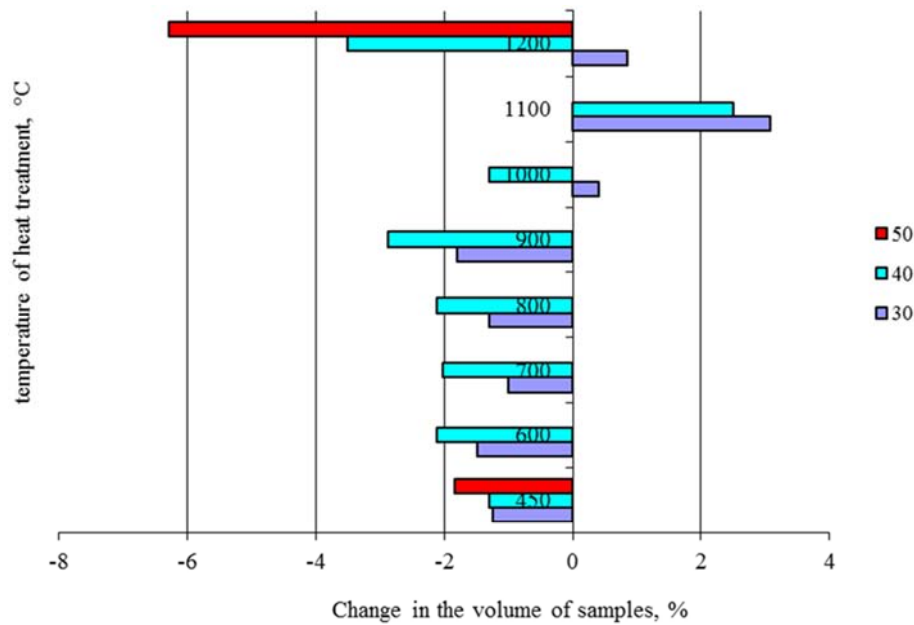
Graphs of permanent change in dimensions of concrete from temperature of heat treatment and fractional composition of briquettes are presented in the Figures 7-9.

Cold crushing strengths and bulk density are depended on volume changes, this fact is indicated above. The volume of the samples decreases to one degree or another when they were heated to 900°C, it depends on the fractional composition of the charge and the type of briquette. The increase in sample volume begins by 1000-1100°C, accordingly, the concrete was softening.



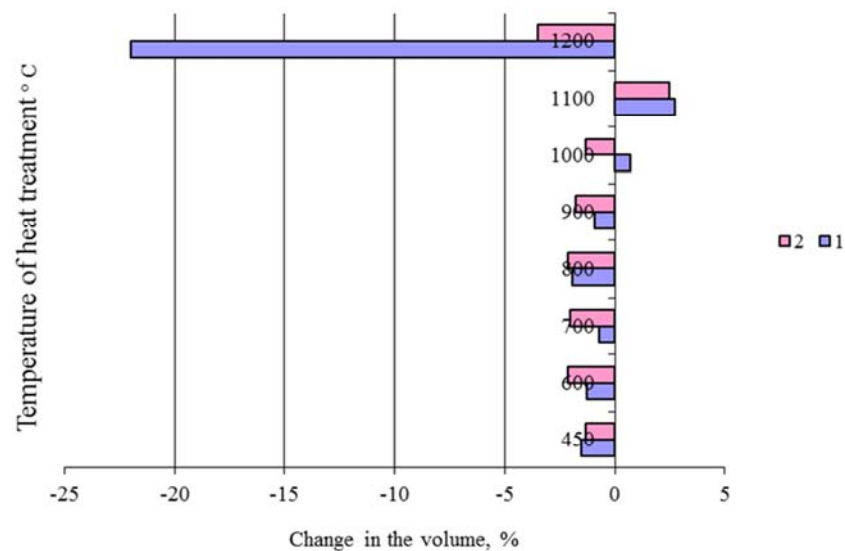
In charge composition: 20, 30, 40, 50% fraction < 0.063 mm

**Figure 7.** Dependence of permanent change in dimensions of samples from temperature of heat treatment and quantity fraction < 0.063 mm briquette 1.



In charge composition: 30, 40, 50% fraction < 0.063 mm

**Figure 8.** Dependence of permanent change in dimensions of samples from temperature of heat treatment and quantity fraction < 0.063 mm briquette 2.



Charge composition: 60% fraction < 3 mm and 40% fraction < 0.063 mm

**Figure 9.** Dependence of permanent change in dimensions of samples from temperature of heat treatment and the composition of the briquette.

For example, volume has decreased by 0.5% for specimens from briquette 1 with a 20% fraction <0.063 mm in charge by the temperature range 450-900°C, and at 1000°C the volume has not changed. Heating to 1200°C leads to an increase in volumetric changes up to 7%. For a charge with 30% fraction <0.063 mm, the volume change index in the temperature range 450-900°C decreased from 1 to 2%, at 1000-1100°C it increased from 0.6 to 1.3%, respectively, at 1200°C it decreased by 10%. Samples from a charge with 40% fraction <0.063 mm at 1200 °C were very strongly sintering, decrease in volume to 22%, which is unacceptable when using concrete.

Up to 900°C, the volume of samples from briquette 2 with 30% fraction <0.063 mm decreases in the range from 1.25 to

1.8%. At 1000, 1100, and 1200°C, the volume increases by 0.4, 3, and 0.9%, respectively. The behavior of the samples slightly changes when 40% fraction <0.063 mm are using in charge. Up to 1000°C the volume decreases by about 2%, at 1100°C the volume increases by 2.5%, at 1200°C the volume decreases again by 3.6% (Figures 7, 8).

Despite the fact that the samples (60% fraction <3 mm and 40% fraction <0.063 mm) from briquette 2 have slightly higher volumetric changes up to 1000°C, but at 1200°C they are not sintered as much as from briquette 1 (Figure 9).

### 3.5. Discussion

In earlier studies of concretes with magnesium phosphate cement was noted that they lost of strength during heat



treatment, due to the loss of chemically bound water and the destruction of the condensation-crystallization structure. Indicators of mechanical strength are reduced, especially for specimens heated to 1000-1100°C. The degree of loss of strength should not increase, otherwise the concrete chipping occurs in service. With further heating, the processes of polycondensation and polymerization of the main structure-forming phosphate compounds occur, which ensure the formation of a wear-resistant structure and volumetric constancy of concrete [1, 4].

The crushing strength of samples at room temperature was 35 MPa (briquette 1) and 50 MPa (briquette 2). After heat treated to 900°C strength indexes of concretes were decreased. New compounds were formed in the system of forsterite - magnesium phosphate cement.

Based on the data of X-ray phase analysis, newberite at 150°C was converted into monohydrate of hydrogen phosphate  $\text{MgHPO}_4 \cdot \text{H}_2\text{O}$ . At 200°C,  $\text{MgHPO}_4 \cdot \text{H}_2\text{O}$  was converted to dihydropyrophosphate  $\text{MgH}_2\text{P}_2\text{O}_7$ . After 400°C, the X-ray diffraction pattern shows the lines of tetrametaphosphate  $\text{Mg}_2\text{P}_4\text{O}_{12}$ , from 700°C - orthophosphate  $\text{Mg}_3(\text{PO}_4)_2$ . After 1000°C, the mechanical strength index begins to grow. The preferred amount of fraction less than 0.063 mm in the composition for concrete, %: 30 (briquette 1) and 40 (briquette 2).

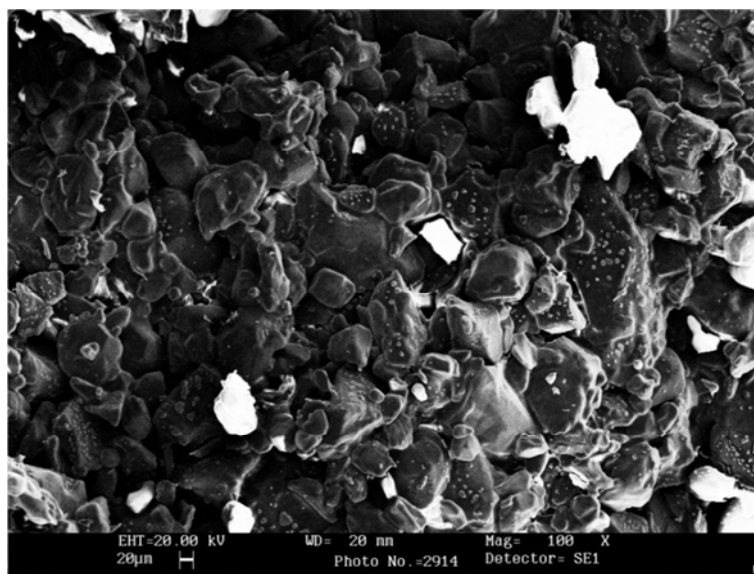
Some modern researches were studied the effect of heat

treatment on the properties of magnesium phosphate cements [20-22]. They were given the changes in the property indicators that similar to ours, but we cannot use them for comparison, since they additionally introduce other substances into the binder, for example,  $\text{KH}_2\text{PO}_4$ , ash or ammonium salts.

The temperature of the initial firing of the briquette affects the rate of change in volume after heat treatment in the range of 450-1000°C. For specimens from a briquette fired at 1300°C, its value is 1.8%, while for specimens from a briquette fired at 1400°C it is 0.5%.

Concrete from briquette 1 is sintered to a greater extent at a temperature of 1200°C than from briquette 2. The change in volume in the first case reaches 22%, in the second - 3.6%.

For specimens from briquette 1 with 20% fraction less than 0.063 mm, the volume change is from 0.07 to 1.8%, in the range of 450-1000°C, the larger this indicator, the higher the density. Softening of concrete at 1100°C leads to a decrease in the density indicator (relative to the sample without firing), but its indicator does not change sharply. An increase in the amount of fraction less than 0.063 mm to 30% leads to an increase in volume change index of concrete at 450-900°C and, accordingly, to an increase in density. At 1000°C, softening occurs, the density index drops, but at 1200°C, the material begins to sinter sharply (Figure 10).



**Figure 10.** SEM-micrograph of the surface structure of the sample from briquette 1 after heat treatment at 1200°C (analyst, Ph.D. Semushin V. V.).

This is probably due to the lower amount of magnesite refractory waste, which is additionally introduced into forsterite concentrate during briquette production. The dependencies above allow us to assume that for briquette 1, the composition of the charge for concrete should contain from 20 to 30% of the fraction less than 0.063 mm, since containing 40% of this fraction the volumetric changes increase at 1100°C and a sharp jump in sintering occurs at 1200°C.

The volume change index of samples from briquette 2

decreases at 450-900°C approximately equally, density and strength change insignificantly, the greatest increase of volume samples is at 1100°C. The decrease in volume at 1200°C is not as pronounced as for concretes based on briquette 1. The dependencies above allow us to assume that for briquette 2, the composition of the charge for concrete should contain up to 40% of a fraction less than 0.063 mm, since the strength and density indicators are high.

As a result of the study, the grain composition of the charge was selected in order to maximize the filling of the



volume; the ratio of filler and binder to improve the structural properties of concrete were found; the effect of the composition and temperature of briquette heat treatment on the physical and technical properties of the materials obtained is shown.

## 4. Conclusions

The production of refractory concrete from waste of Kovdor mining and processing plant was investigated. Materials and technologies developed in the course of research are considered economically viable due to the low cost of the raw materials used in comparison with olivine or dunite.

Concrete from briquette has higher property indices in comparison with samples from raw forsterite concentrate.

The XRD, optical microscopy and SEM studies have revealed the formation of new phases during heat treatment of concrete:  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgHPO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{MgH}_2\text{P}_2\text{O}_7$ ,  $\text{Mg}_2\text{P}_4\text{O}_{12}$ ,  $\text{Mg}_3(\text{PO}_4)_2$ .

The main technology of concretes and their heat treatment parameters have been identified and the key dependencies were found.

In the charge for concrete from briquette 1 is to add from 20 to 30% fraction less than 0.063 mm. By larger amount of fraction < 0.063 mm, volumetric changes increase at 1100°C and at 1200°C a strong decrease in the sample volume occurs due to sintering. We must add up to 40% of fraction less than 0.063 mm in charge of producing concrete from briquette 2, since in this case high strength and density indicators are obtained, and the decrease in the volume of the sample at 1200°C is not so significantly.

Concretes by briquette 2 have the following characteristics: bulk density 2170 - 2260 kg/m<sup>3</sup>, strength - up to 50 MPa (at 25°C), volume change after heat treatment at 450-1000°C is 1-2%.

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