THE INFLUENCE OF THE PHOSPHORIC ACID AND CLAY ON THE PHYSICAL AND MECHANICAL PROPERTIES OF REFRACTORY CONCRETE

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ABSTRACT

In recent decades, the interest in refractory materials which are formed without baking - by chemical bonding - has increased significantly, as their production is less complex and more economical than the production of classical refractory materials, which involves a long baking process. In this work, as a chemical binder, phosphoric acid, which is intensively reacted with refractory oxides MgO, SiO_2 or Al_2O_3, was used, and the resulting mass quickly hardened. Quartz sand of the Bukinje deposit, Tuzla, was used as filler. In the previous researches it has been proved, and this work has confirmed, that the chemical bond between the filler and the binder without the binding agent will not occur. Illite-kaolinite clay from deposit Sočkovac -Gračanica, was used as a binding agent. In this paper, the influence of the amount of phosphoric acid and clay, as an activator of binding, to the physical - mechanical properties of refractory concrete was investigated.

1. INTRODUCTION

In the industry of refractory materials in the last decades, production of refractory materials which are formed without baking - by chemical bonding, is increasing. Representatives of these materials are definitely refractory concrete consisting of an inert refractory filler (mulite, chamotte, quartz sand, etc.) and a binding agent of mineral or organic origin. These concretes differ from the constructional concrete because they have high refractoriness (above 1600 °C) and a certain amount of strength at high temperatures, which is a key requirement for a construction material exposed to high temperatures. The interest in refractory materials of this type in recent decades has increased, since their production is less complex and more economical than the production of classical refractory materials, which involves a long heat treatment process.

In the production of refractory materials without thermal treatment, as well as refractory concrete, the phosphate binder is increasingly used. This is explained by the fact that the phosphate bond allows the use of phosphate bonded material at high temperatures of 400-1000°C without significant loss of strength, as opposed to refractory materials bound to other binders: aqueous glass, as well as magnesium oxisulphate or oxychloride, when the strength of the formed material at these temperatures is significantly lower. Additionally, phosphate-bonded materials are more resistant to melted metals.

The simplest phosphate binder is phosphoric acid, which reacts intensively with refractory oxides: MgO, SiO_2 or Al_2O_3, and the resulting mass quickly hardening. The solidification of alumosilicate products by phosphate bonding is result of the formation of acid phosphate, their polymerization and polycondensation in the process of heating, and also the formation of insoluble phosphates in the reaction of phosphoric acid with oxides from the refractory filler.

There are two types of binding: acidic (through metaphosphate) and chemical binding. With acid binding the binding temperature is low. Binding goes through a hydrogen bond, and at a higher temperature, macromolecules are condensed by the amorphous - polymeric glass. In chemical binding, H_3PO_4 or mono Al phosphate react with low alkaline or amphoteric oxides as well as with glass (neutralization). In this case, at high temperature, a crystalline orthophosphate that acts as a binder is formed.

The phosphate binding process is very complex. In contact with silicate materials there is a partial replacement of silicate groups with PO_4^{3-} groups in which the oxygen connecting the phosphorus atoms is more strongly bound to oxygen in the SiO_4^{4-} tetrahedrons. In addition, PO_4^{3-} ion has a high propensity for polymerization. Also, hydrogen in acid phosphates forms additional hydrogen bonds, and it can be said that the polymerization process of phosphate goes through hydrogen bridges.

However, previous studies have shown that the refractory filler and phosphate binder will not achieve chemical bonding unless they are added to a binding agent. The influence of the binding activator is more significant when it comes to the speed and degree of hardening of phosphate-bound phosphates, and in this sense a range of solutions are offered. However, in practice, there are serious problems in selecting the binding agent. Their chemical character must be in correlation with the composition of the refractory mass that binds to the type of binder. The amount of activator added to the refractory mass is also important. It has been shown that the addition of up to 30% clay, as a binding agent, achieves chemical bonding of refractory concrete at normal temperatures.

2. RAW MATERIAL AND PREPARATION OF SAMPLES

Commercial chemical phosphoric acid (85%, $\gamma = 1.71$ g/cm^3) was used as chemical binder. The quartz sand used in this test is from the Bukinje deposit, Tuzla. The chemical composition of quartz sand produced by XRF analysis is given in Table 1, and the quartz sand rayogram is shown in Figure 1.

Table 1. Chemical composition of quartz sand from Bukinje deposit, Tuzla (XRF)

Component	LOI	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO
Content (%)	1.00	95	1.20	0.60	0.20	0.40

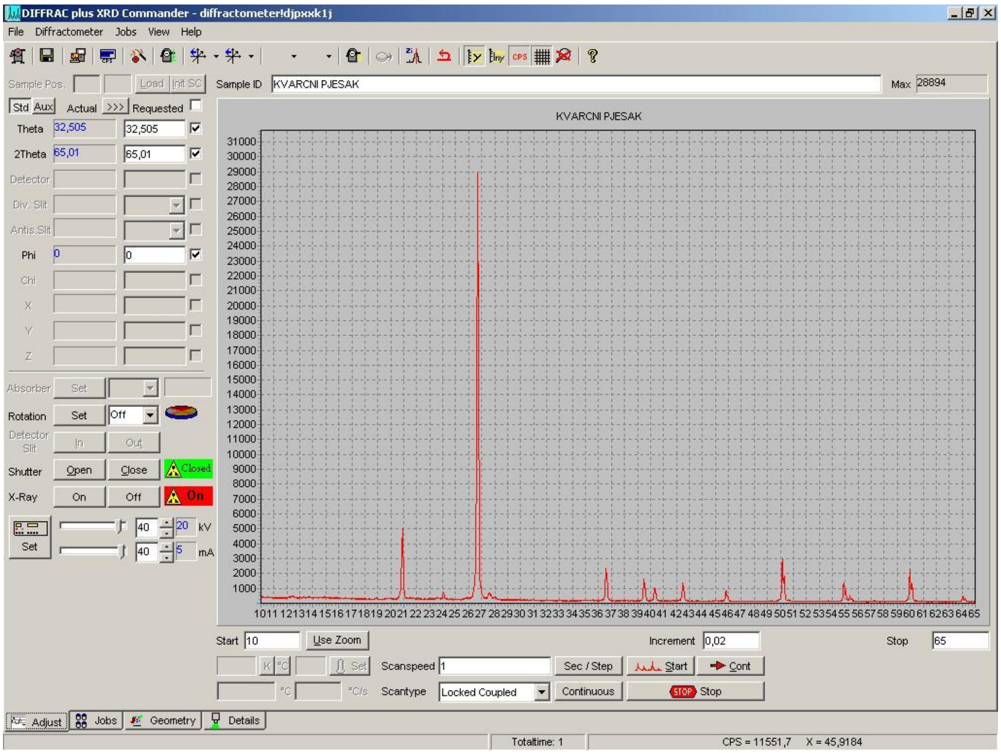

Figure 1. X-ray analysis of quartz sand

Quartz sandis of high purity and consists of not less than 95% alpha quartz. Impurities are negligible. Figure 2 shows the DTA/TG quartz sand. The DTA curve shows an endothermic change with the peak at the temperature of 569.7 ºC showing the transformation of α quartz into β quartz.

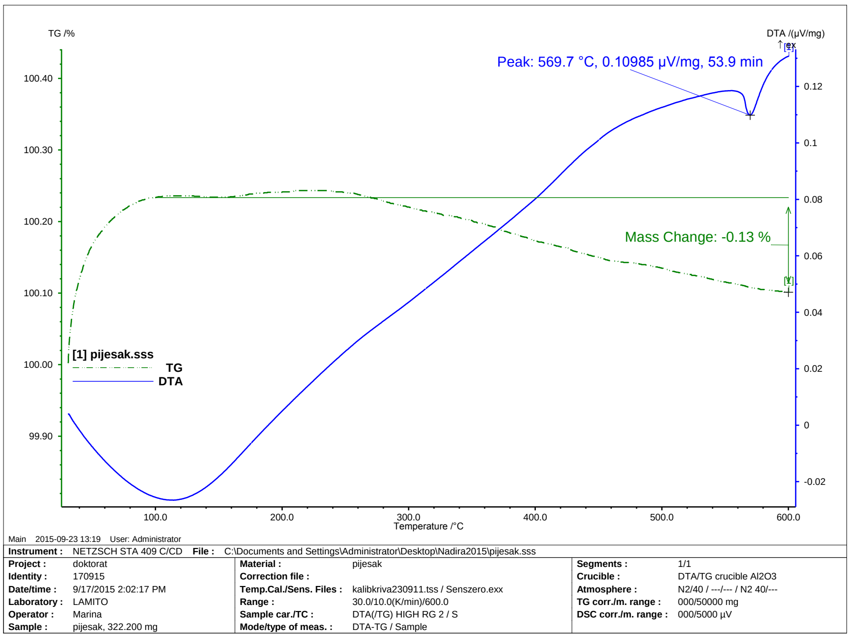

Figure 2. DTA/TG of quartz sand

The clay of the Sočkovac deposit, Gračanica, was added to the refractory concrete in a dry state, particle size below 63 μm. Its chemical composition is given in Table 2, and the corresponding X-ray diagram in Figure 3.

Table 2. Chemical composition of clay from Sočkovac deposit, Gračanica (XRF)

Component	LOI	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O+K_2O	MnO_2
Content (%)	4.7	71.92	14.12	0.98	1.46	3.70	1.55	1.36

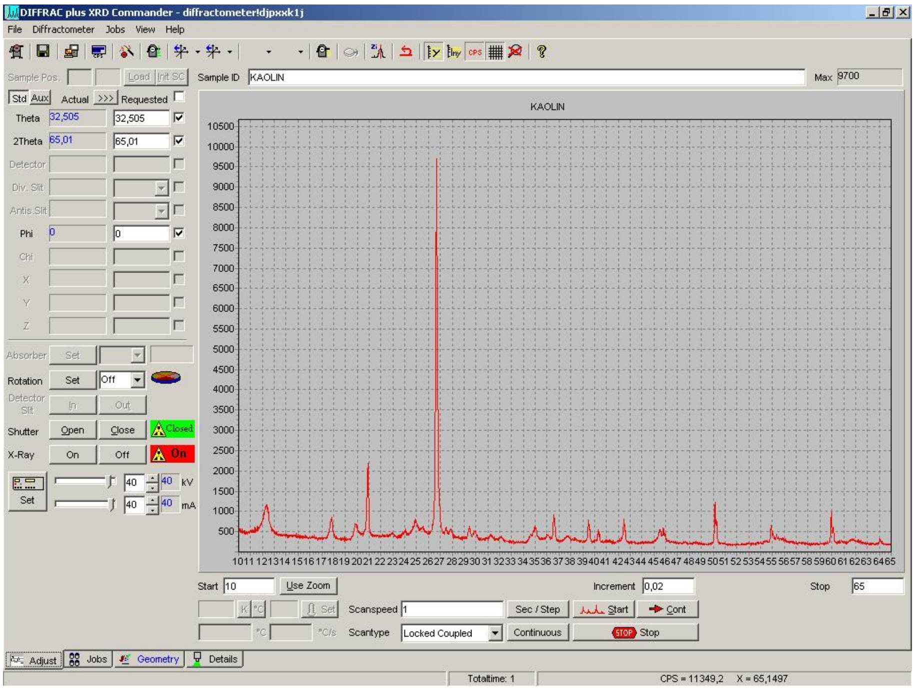

Figure 3. X-ray analysis of clay

Based on the semi-quantitative X-ray analysis of clay from the Sočkovac deposit, it has an approximate mineral composition shown in Table 3.

Table 3. Mineral composition of clay (XRD)

Mineral	α quartz	Kaolinite	Ilite	Feldsparand calcite
Content (%)	40	25	15 -20	5 - 10

The test specimens are formed in such a way that the basic grain component is well mixed with a certain amount of clay in the powder form. Then, a certain amount of binder is added to the solid mixture as well as (if necessary) water to achieve a slightly plastic consistency of the mass. From this prepared, well-homogenized mass, test bodies were formed by compressing the mass in the steel mould, Fig. 4. The prepared mass is placed in the metal cylinder where compaction of the material is performed under the action of three impacts with the weight of 6667 g. The weight drops from a height of 50 mm. In order to achieve uniform strikes, a special device is used where the weight is lifted to a certain height and freely falling on the mixture in the metal cylinder. The obtained test bodies are cylindrical shapes with dimensions: base diameter d = 50 mm and height h = 50 mm.

Preparation and testing of samples was carried out at the Faculty of Metallurgy and Technology, Metallurgical Institute in Zenica and Cement Factory Kakanj.

Figure 4. Sample forming device

3. RESULTS OF THE EXAMINATION

Samples were prepared with quartz sand as filler, phosphoric acid as a binder, and ilite-kaolinite clay as a binding agent. The first mixture contains 80% quartz and 20% clay with 5, 10, 15 and 20 mass % of phosphate binders in regard to total dry mass. The second mixture contain 0, 10, 20 and 30 mass % clay (rest is quartz) with 10 mas % of phosphate binder in regard to total dry mass. The aim of this study is to determine the optimum content of: the base component in the refractory mass; the amount of ilite-kaolinite clay and the amount of phosphate binder. The prepared samples were dried at the temperature of 120 °C for 5 h and then treated thermally at the temperature of 1000 °C for 5 h. Table 4 shows the contents of the components of prepared samples. The physical properties of the prepared samples are shown in Table 5. Figures 5 and 6 show compressive strength dependence of composition and temperature.

Table 4. Composition of the prepared samples

Mixture	Test sample mark	Components (%)		
		Quartz sand	Clay	H_3PO_4 (85 % solution)
I	PGF5	80	20	5
	PGF10	80	20	10
	PGF15	80	20	15
	PGF20	80	20	20
II	PF	100	-	10
	PG10F	90	10	10
	PG20F	80	20	10
	PG30F	70	30	10

Table 5. Physical-mechanical properties of samples

Test sample mark	Thermal treatment	Bulk density (*g/cm*^{3})	Apparent porosity (%)	Compressive strength (MPa)
PGF5	120ºC/5 hours	1.66	26.3	3.93
	1000ºC/5 hours	1.82	22.1	6.88
PGF10	120ºC/5 hours	1.80	12.3	8.84
	1000ºC/5 hours	1.90	12.7	14.74
PGF15	120ºC/5 hours	1.70	22.3	6.38
	1000ºC/5 hours	1.87	18.4	11.79
PGF20	120ºC/5 hours	1.86	18.4	8.84
	1000ºC/5 hours	1.79	16.2	14.74
PF	120ºC/5 hours	1.61	27.0	1.96
	1000ºC/5 hours	1.68	27.3	2.45
PG10F	120ºC/5 hours	1.63	26.3	4.91
	1000ºC/5 hours	1.75	22.8	6.88
PG20F	120ºC/5 hours	1.74	21.1	9.82
	1000ºC/5 hours	1.88	16.9	16.70
PG30F	120ºC/5 hours	1.76	21.1	6.10
	1000ºC/5 hours	1.96	16.9	17.70

From Table 5 it can be seen that samples thermally treated at 1000 ºC have bulk density mostly higher and apparent porosity lower than samples treated at 120 ºC as it could be assumed.

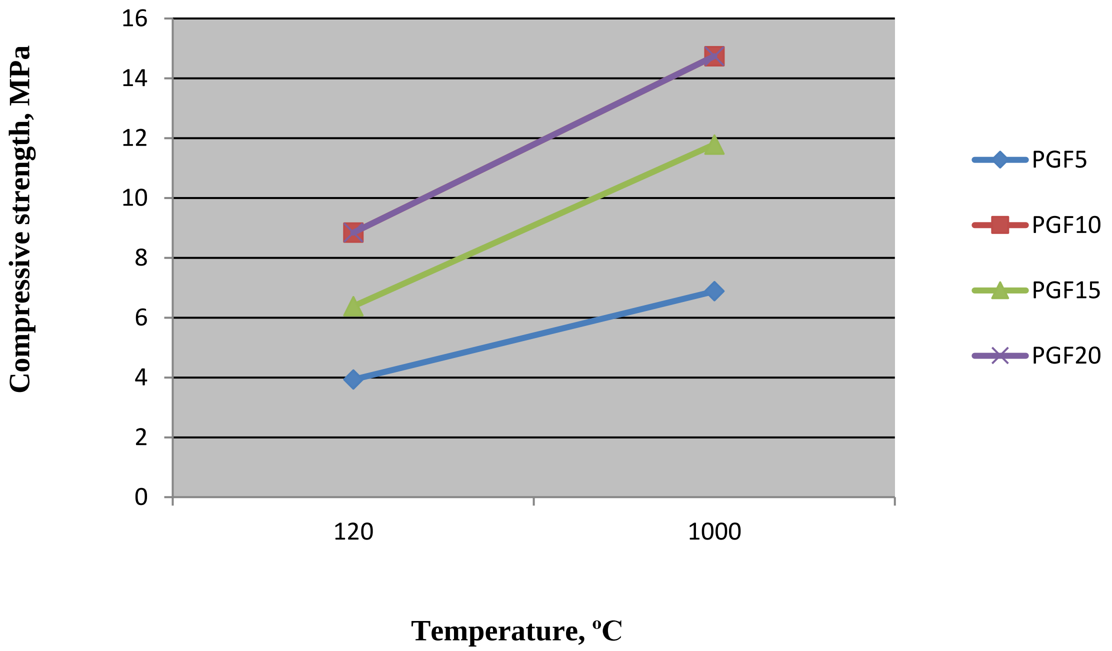

Figure 5. Compressive strength of sample of the first mixture

From Fig. 5 it can be seen that increasing the content of phosphoric acid increases the compressive strength. Increased temperature also increases compressive strength. Samples with 10 and 20% phosphoric acid have the same compressive strength at both temperatures, so that it can be concluded that higher amounts of phosphoric acid than 10% should not be used.

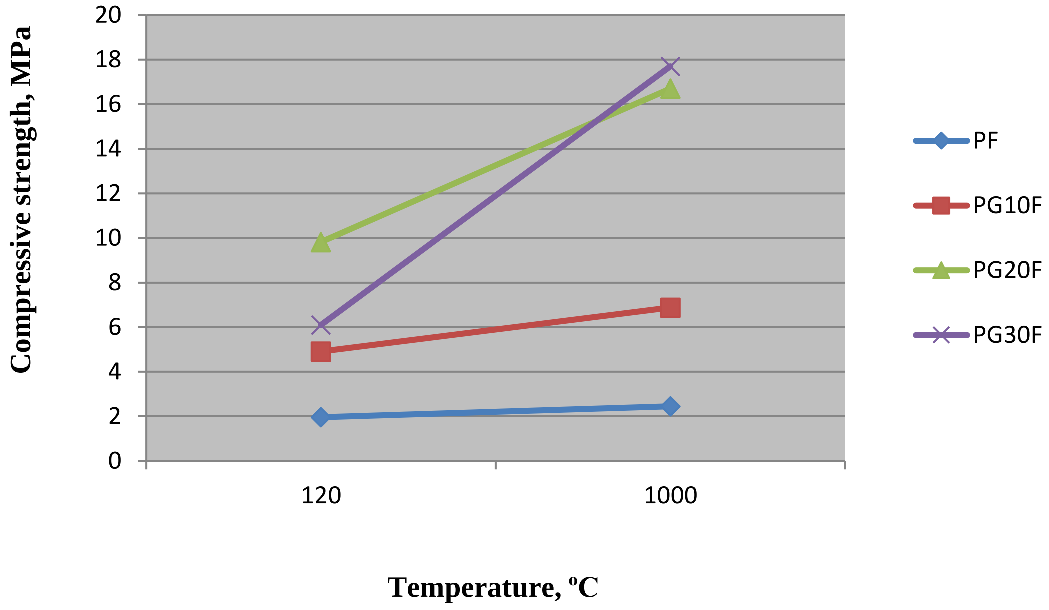

Figure 6. Compressive strength of sample of the second mixture

Figure 6 shows the compressive strength dependence of the temperature of the samples with different clay content and the content of 85% phosphoric acid solution of 10 mass %. It can be seen from the diagram that the sample without clay has low compressive strength which does not change with increasing temperature. This means that without the addition of clay as a binding agent, there can be no transition of the chemical into a ceramic bond. The diagram also shows that the samples with increased clay content have higher compressive strength, i.e. the sample with 30% clay and 10% phosphoric acid reaches compressive strength of about 18 MPa at 1000 °C.

With the addition only phosphoric acid to quartz sand (refractory mass without the addition of the activating agent) the prepared samples after drying at 120 °C and annealing at 1000 °C show very low strength. It is obvious that without the additional binder (in this case ilite-kaolinite clay) the basic refractory material is not possible bonded by phosphate, or because of the inadequate creation of a chemical bond there will be no ceramic bonding during annealing. Also, it can be noted that the addition of 10 mass % of clay to quartz sand (quartz sand : clay = 90 : 10) is not sufficient to activate phosphate bonding. The best results are obtained with the refractory mass of the following compositions: quartz sand : ilite-kaolinite clay "Sočkovac" = 80 : 20 mass %, with addition of 10 mass % of 85% phosphoric acid.

4. CONCLUSION

In this paper the influence of the amount of phosphoric acid and ilite-kaolinite clay on the physical-mechanical properties of quartz refractory concrete was examined.

- It has been shown that when increasing the binder content and increasing the temperature of the thermal treatment, the strength of the samples is increased. However, the samples with 10% and 20% of the binder have the same values of the compressive strengths both at the drying temperature and at the firing temperature, and it can be concluded that the amount of phosphoric acid of 10% is sufficient for chemical bonding.
- A sample without clay (sample of 100% sand) and 10% phosphoric acid does not show significant compressive strength increase at elevated temperature. This means that without the addition of clay as a binding agent, there can be no transition of the chemical into a ceramic bond.
- Samples with an increase in clay supplements have a higher compressive strength, i.e. the sample with 30% clay and 10% phosphoric acid reaches compressive strength of about 18 MPa at 1000 °C.
- The best results are obtained with the refractory masses of the following compositions: quartz sand : ilite-kaolinite clay "Sočkovac" = 80: 20 mass %, with the addition of 10 mass % of 85% phosphoric acid.

5. LITERATURE

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