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PRACTICAL ASPECTS OF THE USE OF PHOSPHATE BINDING MATERIALS  
IN REFRACTORY MIXTURES, MORTARS AND PUTTIES

Blazej Soltysik, Alicja Pawelek, Elzbieta Witkowska

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Polska Akademia Nauk - Oddzial w Krakowie, Prace Komiski  
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16. Abstract  Phosphate binders, particularly acidic phosphates of Al and Cr, are used for binding Al silicate refractories used for lining of burners, SiC refractories, and refractory mortars. The binders have apparent d. 2.13-2.18 g/cm <sup>3</sup> , porosity 21.4-23.8%, compressive strength 223 71 kg/cm <sup>2</sup> , total shrinkage 0.2-0.8%, and refractoriness 1240°.			
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Blazej Soltysik, Alicja Pawelek, Elzbieta Witowska

Refractory Materials Institute, Gliwice

Introduction

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Phosphate binding materials, and particularly the binders containing acid aluminum and chromium phosphates, have been more and more widely used in recent times for the production of refractory lining mixtures, mortars and putties.

Within industrial tests, phosphate binding materials have been used, e.g., in:

- a) alumino-silicate mixtures for lining hot wind nozzles in blast furnaces;
- b) mortars for joining silicon carbide elements in "Thede" furnaces provided for melting zinc-carrying materials;
- c) putties for filling scratches, cracks and fissures in auxiliary refractory materials used in baking ceramics.

Aluminosilicate Mixtures Based on Phosphate Binders Used for Lining Hot Wind Nozzles of Blast Furnaces

For the interior lining of blast furnace nozzles (tuyeres) there are used in present industrial practice, in general, refractory concretes based on alumino-calciferous cements or, relatively more rarely, alumino-silicate mixtures based on water-glass with or without the addition of  $Al_2O_3$ . Nozzles of this kind work without trouble /102

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\*Numbers in the margin indicate pagination in the foreign text.

on the average, at most 1-2 months. The problem of the life extension of refractory linings in blast furnace nozzles is, therefore, of great importance to ensure the continuity of the tuyere connection set's operation.

Some years ago, industrial research was carried out in the "Bobrek" Steelworks on possibilities of using refractory aluminosilicate mixtures based on phosphate binders for lining blast furnace hot wind nozzles. A diagrammatic cross-section of a blast furnace tuyere with a refractory lining is shown in Figure 1.

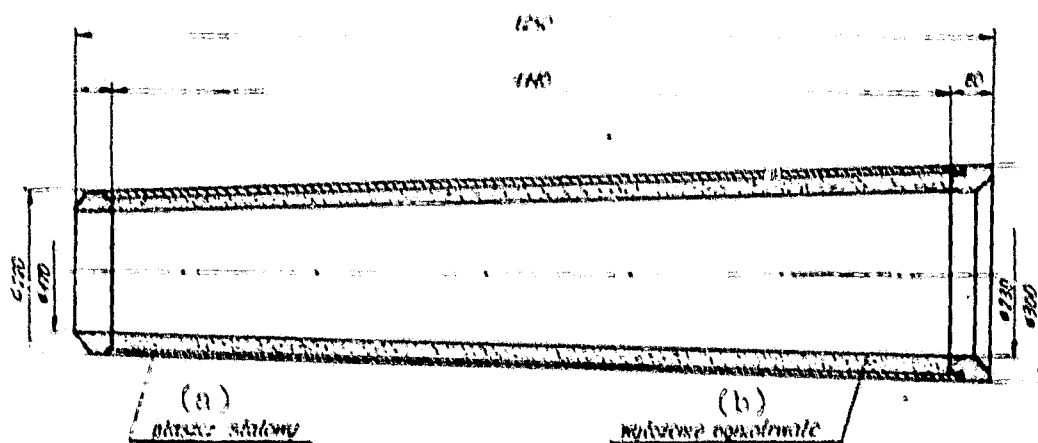


Figure 1. Blast furnace tuyere connection.  
Key: (a) Steel Jacket; (b) Refractory Lining

Based on laboratory experiments, a mixture was selected containing about 80% aluminosilicate raw materials and about 20% refractory silty materials. The addition of green phosphate-alumino-chromium binder was 10-15% and the addition of water did not exceed 3-5%. In order to obtain an adequate degree of mechanical strength and "cold" setting speed, moreover, 1 to 3% MgO was added, preliminarily roasted and then ground to a granulation below 0.2 mm. Green phosphate-alumino-chromium binder produced by TChN "Sulfochem" in Poznan,

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of a density  $1.56 \text{ g/cm}^3$ , was used in both laboratory experiments and industrial tests.

The alumino-silicate mixture provided for ramming, with an addition of 10-15% green phosphate-alumino-chromium binder, used in industrial tests for lining blast furnace hot wind nozzles in the "Bobrek" Steelworks showed, after being baked at a temperature of  $1000-1100^\circ\text{C}$  (working temperature of hot wind nozzles), the following properties:

open porosity	21.4 - 23.8%	
apparent density	2.13 - 2.18 $\text{g/cm}^3$	
compressive strength	223 - 271 $\text{kg/cm}^2$	<u>/103</u>
total contraction (in drying and baking)	+0.2 - +0.8%	
regular refractoriness	156 - 158 sP	
refractoriness under load	1240°C	
resistance to thermal shocks (850°C - water)	more than 10 heat changes	

The blast furnace tuyeres with the above-mentioned alumino-silicate lining based on green phosphate-alumino-chromium binder worked without trouble for about 2-4 months, thus proving that the phosphate-alumino-chromium binder may be used in alumino-silicate mixtures provided for lining blast furnace hot wind nozzles.

Within the scope of laboratory experiments, similar mixtures based on a white phosphate-aluminium binder were also tested. Nevertheless, despite satisfactory results in laboratory experiments, the alumino-silicate mixture based on white phosphate-aluminium binder did not prove useful in industrial conditions. The introduction of such setting accelerating additives as aluminium oxides, hydroxides and fluorides, magnesium salts, boric acid and its salts to the mixtures based on white phosphate aluminium binder also did not give satisfactory results.

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The reason for this is the fact that the phosphate-aluminium binder has an insufficient adherence to steel plates and a too small capacity of binding the alumino-silicate material in the low temperature range, in contrast with the phosphate-alumino-chromium binder which creates with the addition of MgO, even at low temperatures, good set mixtures adhering to the steel jacket of the blast furnace tuyere. This has been confirmed in supplementary laboratory experiments which proved that the adherence of alumino-silicate mixtures based on phosphate-alumino-chromium binder is about 5-10 kg/cm<sup>2</sup> and their compressive strength about 10-20 kg/cm<sup>2</sup> higher than the respective properties of mixtures based on white phosphate-aluminium binder.

Mortars for Joining Silicon Carbide Elements in "Thede" Furnaces  
Provided for Melting Zinc-Carrying Materials

"Thede" furnaces are provided for melting zinc-carrying melting losses and dusts. These furnaces are membrane-heated in the temperature range 400-800°C and they work in a slightly oxidizing atmosphere; the refractory interior lining of silicon carbide is exposed to the action of metallic Zn, Cd and Pb and oxides of these metals and, moreover, to abrasion by the charge. A diagrammatic cross-section of a "Thede" furnace with the refractory lining is shown in Figure 2.

Of essential importance here is the tightness of joints and low porosity of the joined refractory lining elements made of silicon carbide, because otherwise zinc may penetrate to the cast iron drum causing its destruction due to the formation of the "porridge"-like intermetallic combination FeZn<sub>2</sub>. /104

So far, to join the refractory lining elements mortars were used with the addition of silty raw materials or Portland cement, or with the addition of water-glass for reducing the setting temperature.

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Recently, industrial tests on the use of phosphate mortars for joining silicon carbide elements in "Thede" furnaces for melting zinc-carrying materials were carried out in the "Silesia" Ceramic Works in Katowice. The mortar used contained 70-90% silicon carbide and 10-30% refractory materials.

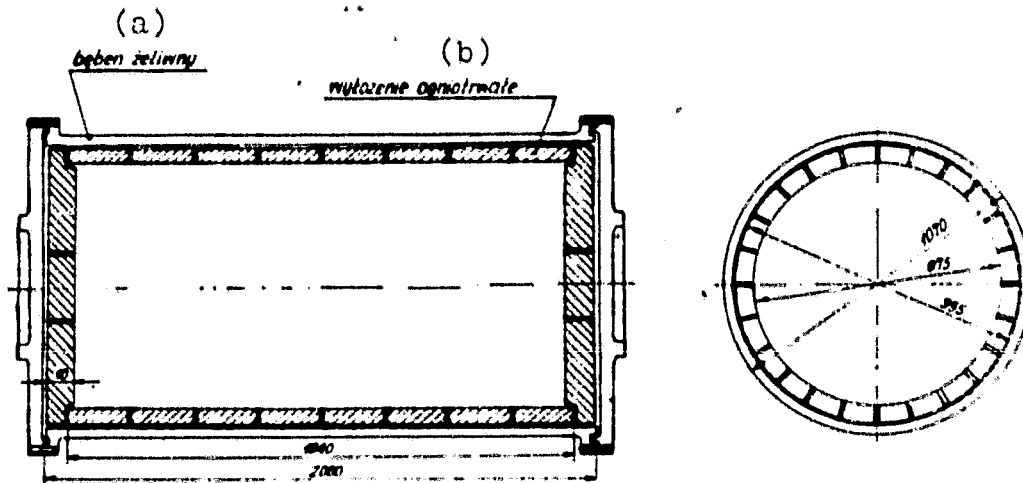


Figure 2. "Thede" furnace for melting zinc-carrying materials  
Key: (a) Cast iron drum; (b) Refractory lining

The addition of white phosphate-aluminium binder was 25-35% and the amount of added water never exceeded 10%. White phosphate-aluminium binder produced by IChN "Sulfochem" in Poznan, of a density  $1.45 \text{ g/cm}^2$ , was used in the test.

The mortar used showed high adherence to the silicon carbide elements and sufficient adherence to the cast iron drum of the rotating "Thede" furnace, both after drying in open air and after supplementary drying by means of electric lamps.

The "Thede" furnaces in which mortars based on white phosphate-aluminium binder were used proved to have a service life of about 90-95 days, whereas the average working time of those furnaces with



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"non-phosphate" mortars was only 70-80 days. The obtained results confirmed, thus, the possibility of using mortars based on white phosphate-aluminium binder for joining elements made of silicon carbide in the "Thede" furnaces provided for melting zinc-carrying materials. It should also be mentioned that the upper limit of the lifetime of a "Thede" furnace also depends to a high degree on the durability of the /105 cast iron drum, partly "limiting" the life of the whole set.

The industrial tests were preceded by broad laboratory experiments which proved that the mortars based on white phosphate-aluminium binder distinctly increase their binding properties after roasting in the temperature range 400-500°C. This results from the dehydration process occurring in two phases:

- a) at the beginning in the temperature range 200-400°C, in conformity with the reaction:
- $$2\text{Al}(\text{H}_2\text{PO}_4)_3 = \text{Al}_2(\text{H}_2\text{P}_2\text{O}_7)_3 + 3\text{H}_2\text{O}$$
- with a strong endothermic effect,
- b) then in the temperature range 400-600°C, in conformity with the equation:
- $$\text{Al}_2(\text{H}_2\text{P}_2\text{O}_7)_3 = 2\text{Al}(\text{PO}_3)_3 + 3\text{H}_2\text{O}$$
- with a poor endothermic effect.

The process of white phosphate-aluminium dehydration with the eduction of an adequate quantity of water provides for compaction of the grains of the mortar filling agent, thus creating a joint that makes a monolithic unit of the joined elements. The roasted mortars also did not show any tendency to repeated dehydration, even after a longer contact (up to 30 days) with a humid ambient atmosphere.

The laboratory experiments also covered mortars based on green phosphate-alumino-chromium binder. The results of these experiments are to be recognized as rather negative, because in the temperature range above 600-800°C the green phosphate-alumino-chromium binder lost its cohesion somewhat in the presence of Zn+ZnO, thus enabling the penetration of liquid zinc into the interior of tested samples made of silicon carbide to a depth 2-3 mm already after 4 hours of action.

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In such a situation the green phosphate-alumino-chromium binder has been excluded from industrial tests on mortars for the "Thede" furnaces for melting zinc-carrying materials.

In order to increase the life of the ceramic lining, the interior of the "Thede" furnace was additionally coated with a special protective mixture, containing fine-grained silicon carbide and white phosphate-aluminium binder in an amount up to 50%. This mixture gave, after drying, a compact coat reducing the penetration speed of the "Thede" furnace's melted charge into the interior of the silicon carbide refractory lining.

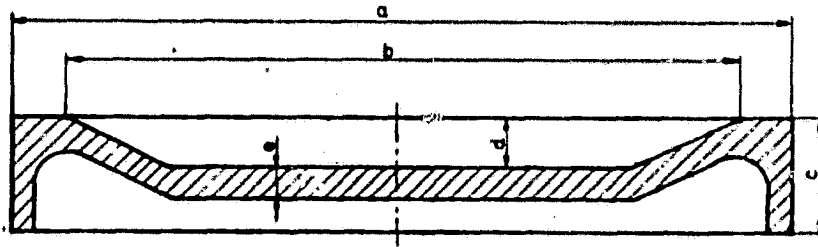
Putties Based on Phosphate Binders for Filling Scratches, Cracks and Fissures in Auxiliary Refractory Materials Provided for Baking Ceramics

The method of filling scratches, cracks and fissures in refractory materials depends, e.g., on the method of putting on the putties and the size of the filled scratches and cracks. The putties can be put on in various ways, the best method proved to be, however, to "lute". /106 After the putty has been put on, the products are once more baked in a temperature range not less than 400-600°C, in order to prevent the possible dehydration of the phosphate binder.

The luted putty layer shows high adherence to the base, giving a uniform potsherd without any effects. No flaking off or loosening of the putty layer was noticed in the filled places.

At present, the ZMO of Gliwice uses this kind of putty based on white phosphate-aluminium binder for filling cracks and fissures, as well as scratches on some thin walled products and refractory materials for baking ceramics, including refractory casings for baking table ceramics. A diagrammatic cross-section of a silicon carbide casing for baking table china is shown in Figure 3.

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- a - 157-300 mm
- b - 129-332 mm
- c - 28-75 mm
- d - 9-40 mm
- e - 7-14 mm

Figure 3. Silicon carbide casing for baking table china.

The laboratory experiments carried out proved that for products working in a changeable atmosphere it is more favorable to use white phosphate-aluminium binder, but in the case of an oxidizing atmosphere or in low temperature ranges very good results are obtained when using green phosphate-alumino-chromium binder that shows, moreover, very favorable binding properties also in a lower temperature range. Nevertheless, independently of the kind of phosphate binder used, each putty layer has to be roasted in a temperature range not less than 400-600°C, in order to eliminate the tendency to dehydration. In the temperature range 400-600°C there also occurs a total dehydration of acid aluminium phosphates with formation of anhydrous aluminium metaphosphate, thus increasing the durability of the joint joining the elements in a monolithic unit.

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