

Mechanical properties of chemically bonded phosphate refractory castables

Propriedades mecânicas de concretos refratários quimicamente ligados a fosfatos

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ABSTRACT

The knowledge of the phase transformations and the role of different parameters in the performance of phosphate-bonded systems are of utmost importance for the refractory field. The effect of the setting agent, phosphoric acid concentration and additives on the setting time, cold crush strength, hot modulus of rupture, abrasion resistance, and thermal shock resistance of the phosphate chemically bonded refractory systems was evaluated. The setting time was shorter for mixtures containing cement (CaO) and a lower acid concentration. Mixtures with a higher acid concentration presented better mechanical, abrasion and thermal shock resistance. In spite of increasing the cold mechanical resistance and abrasion of the materials, the Buditec 6H negatively impacted the hot properties. For Fabutit761, there was no liquid phase formation at intermediate temperatures and this additive increased the cold mechanical strength, but it also negatively impacted the hot mechanical strength. Compositions containing cement as a setting agent, 40°Be phosphoric acid and Fabutit761 additive as an extra source of phosphate presented a better set of properties.

Keywords: Refractory materials, Monolithic refractories, Repair, Chemically bonded castable, Phosphate, Phosphoric acid

RESUMO

O conhecimento das transformações de fase e o papel de diferentes parâmetros no desempenho de sistemas ligados a fosfato são de extrema importância para o campo refratário. Os efeitos do agente de endurecimento, da concentração de ácido fosfórico e dos aditivos no tempo de endurecimento, resistência ao impacto a frio, módulo de ruptura a quente, resistência à abrasão e resistência ao choque térmico dos sistemas refratários quimicamente ligados ao fosfato foram avaliados. O tempo de endurecimento foi menor para misturas contendo cimento (CaO) e uma menor concentração de ácido. Misturas com maior concentração de ácido apresentaram melhor resistência mecânica, à abrasão e ao choque térmico. Apesar de aumentar a resistência mecânica a frio e a abrasão dos materiais, o Buditec 6H impactou negativamente as propriedades quentes. Para o aditivo Fabutit761, não houve formação de fase líquida em temperaturas intermediárias e esse aditivo aumentou a resistência mecânica a frio, mas também impactou negativamente a resistência mecânica a quente. As composições contendo cimento como agente endurecedor, ácido fosfórico a 40° Be e aditivo Fabutit761 como fonte extra de fosfato apresentaram um melhor conjunto de propriedades.

Palavras-chave: Materiais refratários, Refratários monolíticos, Reparação, Calcínvel ligado quimicamente, Fosfato, Ácido fosfórico.

1. INTRODUCTION

Refractory materials can be classified into two groups: shaped refractory materials and monolithic refractory materials [1]. Monolithic refractories have a lower cost than shaped refractories, since molding, pressing, and burning are not required.

Monolithic concretes may contain hydraulic or chemical binders. Hydraulic castables use calcium aluminate cements [2], CAC, as a binder, and the setting mechanism is related to the hydration of the cement particles. However, the use of CAC is limited because it has a high CaO content and forms low melting phases together with silica, such as anorthite and gehlenite, damaging the performance of the material at high temperatures [3]. In addition, these refractories have low permeability after the consolidation of the hydraulic bond, which generates the need for a long drying time so that the water can be released without risk of explosion [4].

In this context, the evolution of the castables is closely related to the development of low cement [5] or non-cement castables containing other binders which increase the availability of equipment, reducing the drying time. The chemically bonded castables are an alternative to replace the hydraulic castables and are formed by mixing a refractory aggregate, binders and additives such as accelerators and inhibitors, which are prepared at room temperature and provide structural integrity to the material at low temperatures. Currently, nanoscale binders such as hydratable alumina (HA), colloidal alumina (CA), and colloidal silica (CS) have been used to improve the thermo-mechanical properties of refractory materials [3, 5].

Among the chemically bonded castables, the phosphate bonds, or CBPC, chemically bonded phosphate ceramics [6-8], and especially those produced from the reaction of aluminates and phosphates are of particular interest, as they have good mechanical resistance as well as presenting a high decomposition temperature superior to 1700°C [6]. This temperature is high enough to promote ceramic sintering in substitution of the chemical bonding which is broken with the decomposition of the phosphate phases.

Currently there is a strong incentive for the development of monolithic materials which can be easily applicable in situ for repairing damaged lining. In the cement and petrochemical [8] industries, the lining is subjected to an extremely aggressive environment, therefore it needs periodic maintenance. One possibility would be the removal of the damaged lining replacing it by a new one, but this would lead to several problems, such as high cost of refractory material and workmanship, in addition to long maintenance time. One of the benefits of chemically bonded monolithic castables is precisely that castables can be applied in situ and subjected to high heating rates without risk of explosion, which greatly reduces downtime, making it possible to return to the equipment operation more quickly.

CBPC's can be classified into heat-setting or cold-setting. The heat-setting is an $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5$ system that requires a temperature increase to get harden. In the case of the cold-setting system, a setting agent is necessary such as an alkaline or alkaline earth oxide (MgO or CaO) forming an $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5\text{-M}_x\text{O}$ system so that the hardening occurs at room temperature. In this case, the product is supplied in two components: the dry material composed by the aluminous aggregate with the setting agent, and the phosphoric acid solution as the liquid binder. The setting at room temperature occurs due to acid-base reactions that take place between the setting agent and the liquid binder. The phases formed between the phosphoric acid and the oxides will function as cement giving the cohesion necessary to keep the particles agglomerated, providing the mechanical strength at room temperature.

During application, the most important characteristic of the material is its rheological properties followed by adherence to the substrate to be repaired and hardening at room temperature in the range of 60 and 300 minutes [8]. Considering rheological properties, LOPES *et al.* [8] reported that mixtures containing Budit 6H showed free-flowing results above 80% (condition defined as the most suitable one to cast the samples without requiring any external energy source).

An important factor in the choice of the setting agent is its reactivity. A very reactive material reacts by precipitating compounds with low cohesion between the particles, and the resulting material exhibits a very low strength. On the other hand, larger amounts of a less reactive material are required to harden at the desired time [9]. Due to the violent reactions between MgO/CaO and phosphoric acid, it is necessary to use less reactive forms of these oxides [8]. Normally, sintered magnesia and calcium aluminates are used as sources of MgO and CaO, respectively.

After the material hardening at room temperature, the material is subjected to a heat treatment. At elevated temperatures the unreacted phosphate will react with the alumina particles to consolidate the phosphate bonds and ensure the properties of the materials at high temperatures. During operation, the

material will be in contact with solid / liquid abrasive materials and will be subjected to temperature fluctuations. Therefore, in order to guarantee the optimal condition of the equipment, the refractory material must have a high thermal stability and adequate mechanical properties at the service temperature.

Thus, the aim of this paper is to study the hardening and the mechanical strength development of the chemically bonded phosphate castables, and to understand how some variables interfere in the properties such as setting time, cold crush strength (CCS), hot modulus of rupture (HMOR), abrasion and thermal shock resistance. The variables studied were the concentration of phosphoric acid (20 and 40°Be), the type of setting agent (Dead Burned Magnesia or Calcium Aluminate Cement) and the type of additive used in the formulations (Budit 6H, FFB761 or Monocalcium phosphate). The choice of these variables was based on previous research developed at RHIMagnesita.

2. MATERIALS AND METHODS

A white fused alumina from Almatiss (85.5 / 87.0 wt.%), and a calcined alumina from Almatiss (10 wt.%) were used. As setting agents, a CaO source (CAC Secar-71® from Kerneos) and a MgO source (DBM <212 µm with 98 wt.% of MgO from RHI MAGNESITA) were used, in concentrations of 2.5 wt.% and 1.0 wt.%, respectively. Three different commercial phosphates were studied: Budit 6H and Fabutit 761 from Budenheim and Mono Calcium Phosphate (FMC) from ICL Brasil Ltda. All additives were used in the concentration of 2.0 wt.%. Formulations with no additives were also tested. Phosphoric acid was added in two different concentrations: 20°Be (28 wt.% of H₃PO₄) and 40°Be (57 wt.% of H₃PO₄). Both solutions were prepared by dilution of the concentrated solution (85 wt.% H₃PO₄ from Samaritá).

Considering all the variables tested, 16 compositions were obtained. Three replicates were performed for each composition, totalizing 48 formulations that were randomly mixed according to the order generated by the Minitab16 software. As the errors recorded were less than 10%, the authors chose not to insert error bars or present standard deviation. The selection of the composition to be tested and the concentration of each compound was supported by previous studies in Research Center of a refractory industry.

Each composition (12 kg) was homogenized in Amadio planetary mixer for approximately 1 minute; the phosphoric acid solution was gradually added over the dry material and the product was mixed for 5 minutes. After mixing, samples of 160 x 40 x 40 mm³ and 114 x 114 x 20 mm³ dimension were vibrated in acrylic mold and the setting time was measured. The final setting time was considered when the sample was no longer deformed by applying pressure on its surface using the fingers.

The material was aged at room temperature for 24 hours and then the samples were removed from the molds and sent for cure in a pre-heated oven at 200°C (Palley Model H595) for 5 hours. The samples which did not present a cold-setting behavior (setting-time at room temperature) were molded again in an iron mold and placed directly in the oven at 200°C.

After this curing, all the samples were measured for further evaluation of permanent linear and volumetric changes. Then, the samples were heat treated at 815°C, 1200°C and 1400°C for 5 hours. After curing and/or heating of samples, the cold crush strength (CCS), hot modulus of rupture (HMOR), abrasion resistance and thermal shock resistance were evaluated.

The CCS tests were performed according to the ASTM C133-97 (2015) standard using Kratos equipment. The samples, with nominal dimensions of 160 x 40 x 40 mm³, were tested after curing and heating.

The HMOR test was performed at 815°C and 1200°C using cured samples according to the ASTM C133-97 (2015) standard. The samples were put in the oven at room temperature and then heated up to the test temperature and kept in the oven for 3 hours before applying the load.

The abrasion resistance was measured after curing and heating according to the ASTM C704 standard. The result is expressed in eroded volume, given in cm³. For the evaluation of thermal shock damage, the Young's modulus of each specimen was first measured using the ultrasound apparatus. After ultrasound measurement, the samples were placed inside an electric oven pre-heated to 1200°C for 30 minutes. The samples were removed from the oven and placed on a refrigerated plate for 30 minutes, with continuous water flow. After this cycle, the Young's modulus was determined and this procedure was repeated for nine times, totalizing 10 cycles. The objective of the test was to compare the residual modulus of elasticity for each composition after those 10 cycles. For a better analysis of the effect of these variables, the DOE (Design of Experiments) statistical tool of the MINITAB16 software was used.

3. RESULTS AND DISCUSSION

In this section each response variable was evaluated in order to verify how the factors studied interfere in these properties.

3.1- Setting-Time

Of the 48 formulations tested, 11 took more than 420 minutes (7 h) to harden. As it was not possible to identify the exact setting-time for these formulations, a fixed number of 600 minutes was used. Another 12 formulations showed no hardening at room temperature. For these formulations a setting-time of 4320 minutes (3 days) was stipulated. These values were specified at a theoretical level, and a value of the response variable is required to feed the MINITAB software. The short setting time is one of the main advantages of the chemically-bonded refractories. LOPES *et al.* [8] defined that 4 hours would be suitable for attaining the complete hardening of phosphate-bonded refractory castables. Figure 1 shows the main effect of the variables tested on the setting time of the formulations. The variables that most interfered in the results were the acid concentration and the setting agent. Mixtures with cement and a lower acid concentration showed a lower setting time. Although a short setting time reduces equipment downtime, fast hardening can impair the adhesion of the material to the substrate.

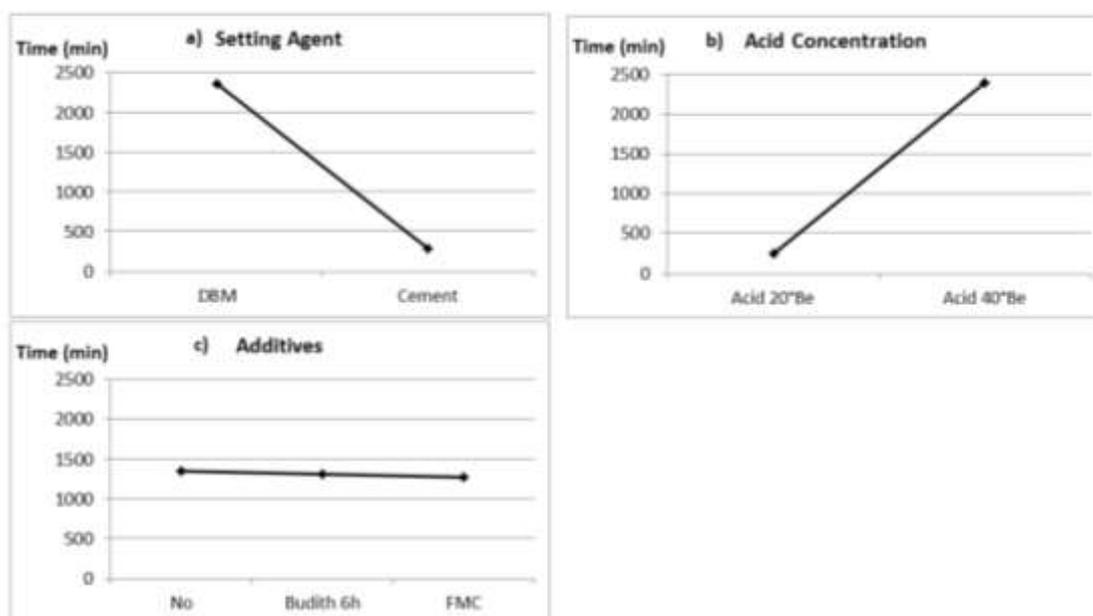


Figure 1: Main effect plots for the effect of cement (CaO source) or DBM (MgO source), (a), acid concentration (b), and type of additives (phosphate source), (c), on setting-time

Related to the type of setting agent, the formulations containing CaO as a setting agent showed a shorter setting time than the formulations containing MgO. This result is not expected since the amount of CaO from the addition of 2.5 wt.% of Secar Cement 71 (0.75 wt.%) is lower than the amount of MgO in the system due to the addition of 1 wt.% of DBM98 (0.98 wt.%), and it was expected that a lower amount of setting-agent would react more slowly with the phosphoric acid providing a longer setting-time. Despite the fact that thermodynamics [9] predict that both Ca^{2+} and Mg^{2+} ions have high concentration in solutions with low pH value (Eq. 1), the kinetics of the CaO dissolution is faster than the MgO dissolution, thus the setting time is shorter when the cement is used.

$$\log(\text{Mg}_{(aq)}^{2+}) = 16.95 - 2pH \quad (1)$$

The higher the acid concentration, the longer the setting-time. This effect is related to the different amount of water in the two systems and the ion dissolution that controls the reactions of setting time.

According to Wagh [9], the hardening of the chemically bonded phosphate ceramics (CBPC) is a result of three steps: (1) The acid phosphates dissolve in water, release phosphate anions, and form an acid phosphate solution of low pH; (2) The oxides dissolve gradually in the low pH solution and release cations; (3) The phosphate anions react with the newly released cations and form a coordinated network and consolidate into a CBPC. The right conditions to form a CBPC are governed by the reaction rate that controls each of these three steps. Since acid phosphates selected for use in the CBPC process are soluble, their dissolution rate is comparatively high and, hence, uncontrollable. The phosphate reaction between dissolved cations and anions described in step 3 is also inherently fast and, again, cannot be controlled. Thus, the only reaction that can be controlled is the dissolution of oxides given in step 2 [10]. The lower the amount of water in the system (concentrated solution), the lower the rate that step 2 is processed. Making some stoichiometric calculations, it can be seen that the amount of water in the system containing 10.5% of phosphoric acid 20°Be is 8.4 wt.% against 6.1 wt.% in the system containing 10.5 wt.% of 40°Be phosphoric acid.

3.2- Mechanical and Abrasion Resistance

The effect of the variables tested on CCS of samples is shown in Fig. 2. After curing at 200°C, the factor that most affects mechanical resistance is the phosphoric acid concentration; the higher the phosphoric acid concentration, the higher the content of aluminum phosphate phases formed. When the curing temperature reaches 150°C, the $AlH_3(PO_4)2.5H_2O$ and $AlH_3(PO_4)2.3H_2O$ are formed. When the curing temperature is higher than 175°C, the main reactions still produce $AlPO_4$ [11]. At higher temperatures, the type of additives influenced the strength of the refractories.

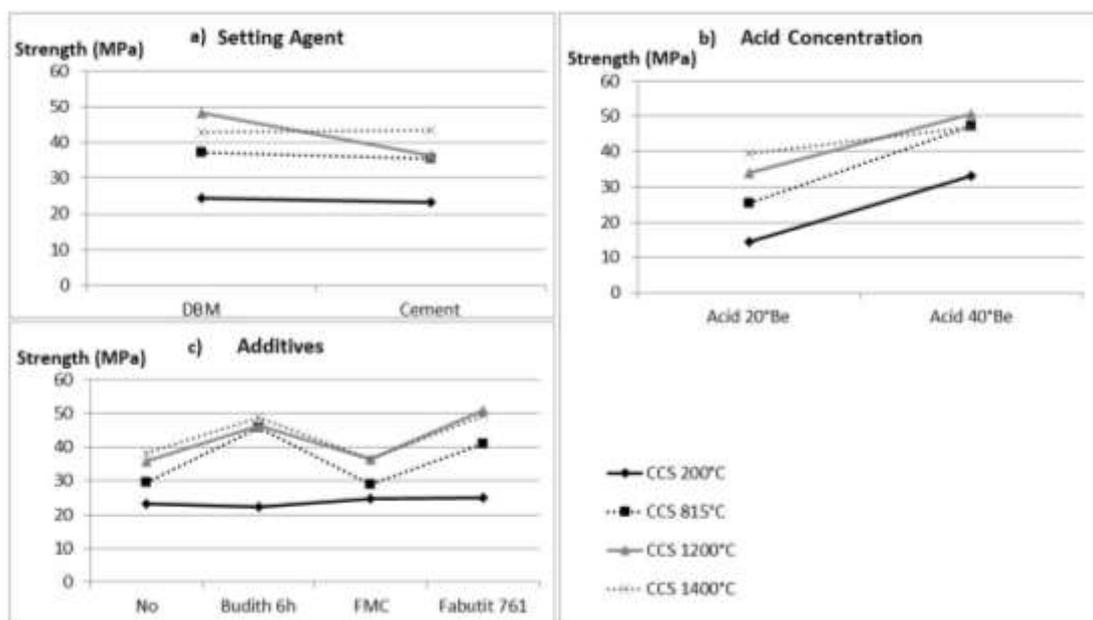


Figure 2 : Main effect plots for the effect of cement (CaO source) or DBM (MgO source), (a), acid concentration (b), and type of additives (phosphate source), (c), on cold crush strength (CCS)

The type of setting-agent does not affect the cold crush strength of the materials, except at 1200 °C as shown in Fig.2, but the MgO source was beneficial to the HMOR and abrasion resistance of samples (Figure 3). HMOR values for phosphate-bonded castables found in literature [8] are in the range of 8-10 MPa for mixtures with phosphoric acid and BUDIT 6H, which agrees with the results obtained. Calcium cement reduced the HMOR of castables at 815°C.

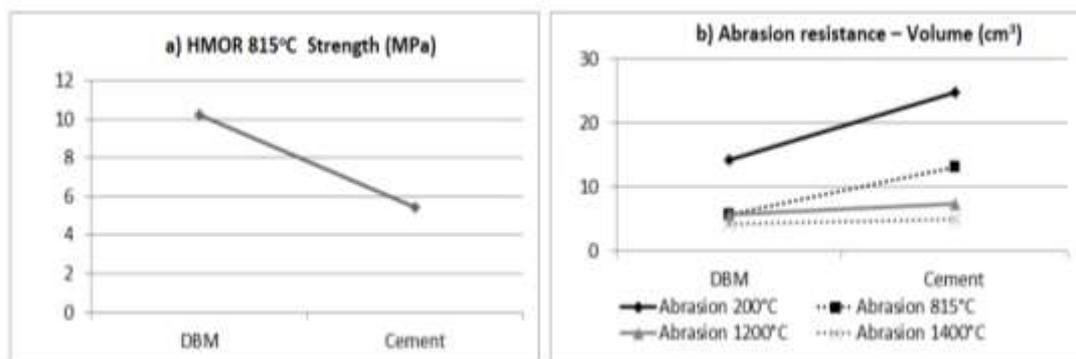
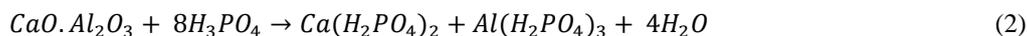


Figure 3: Main effect of the effect of cement (CaO source) or DBM (MgO source) on hot modulus of rupture – HMOR (a), and abrasion resistance (b)

Considering that Secar71 cement, used as a setting agent, has only the CA phase (CaO.Al₂O₃), and that during the dissolution of this compound in the phosphoric acid solution the release of Ca²⁺ and Al³⁺ ions occurs, a mechanism of hardening involving the four stages presented by Wagh [9] can be proposed (Eq. 2). Comparing the Eq. 2 with the Eq. 3 that shows the mechanism of hardening involving the DBM as a setting agent [12], when DBM is used, the phosphoric acid consumption for hardening at room temperature is lower. Thus, a greater amount of P₂O₅ is available to react with alumina at high temperatures and form phases responsible for the mechanical properties. As a result of this phenomenon, the HMOR and the abrasion resistance of materials containing DBM98 (MgO source) were superior to the materials containing cement. This same effect was not observed for the CCS values, except for mixtures cured at 1200°C.



Regarding the acid concentration, the increase in phosphoric acid concentration from 20°Be to 40°Be significantly improved the CCS of the products for all temperatures tested (Fig.2).

This is essentially due to the different amounts of phosphate available in the two systems. From stoichiometric calculations, the amount of P₂O₅ in the formulations containing 20° Be acid is 2.1 wt.%, against 4.4 wt.% in the formulations containing a more concentrated acid. For the cold-setting system, part of the P₂O₅ available reacts with the setting-agent at room temperature and the remainder reacts with the alumina at higher temperatures. By increasing the acid concentration, and consequently the amount of P₂O₅ in the system, a higher amount of that oxide will be available to react with the setting-agent at room temperature, increasing the MO-P₂O₅ phases responsible for the mechanical strength up to 200°C. With the white fused alumina, increasing the Al₂O₃-P₂O₅ phases, the mechanical resistance of the materials was improved at high temperatures. Analyzing the X-ray diffraction of two compositions (with 20°Be and 40°Be phosphoric acid), the peak intensity of AlPO₄ was actually higher for the sample prepared with a more concentrated phosphoric acid (Fig. 4). Considering all the phases that can be formed, aluminum orthophosphate (AlPO₄) is known to have the highest thermal stability, providing adequate properties to the material [13, 14]. The same behavior can be observed for the HMOR and abrasion resistance tests (Fig. 5). The higher the acid concentration, the better the properties.

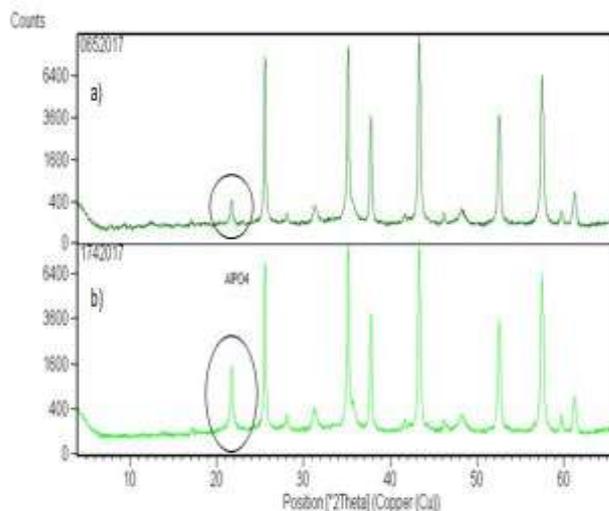


Figure 4: X-ray diffraction pattern for samples heated at 1400°C: a) 20°Be phosphoric acid and b) 40°Be phosphoric acid

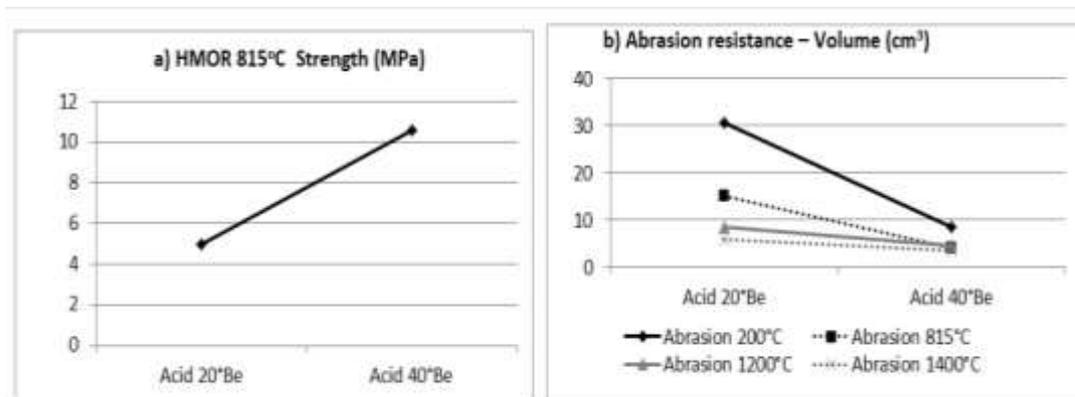


Figure 5: Main effect of acid concentration on HMOR (a), and abrasion resistance (b)

Regarding the types of additives used, at low temperatures (200°C), the presence and type of the additive do not statistically interfere in the CCS value of the products. It is known that, at such temperature, there is the formation of monobasic aluminum phosphate ($Al(H_2PO_4)_3$), but, from the result obtained, the reaction occurs only by the interaction between phosphate from phosphoric acid and alumina from the matrix. The additive, which acts as an extra source of phosphate, was not involved in the reaction. At higher temperatures (equal to or greater than 815°C) Budit 6H and Fabutit 761 stood out. The higher mechanical strength found for compositions using Budit 6H was related to the excessive formation of a liquid phase, since the softening temperature of this additive is 552°C. Actually, by the simulation performed by using the FactSage Software, the composition containing cement, 40°Be acid, and Budit 6H has a liquid phase of 2.3 wt.% (Fig. 6). The liquid phase formed at high temperatures creates a path of high diffusivity, allowing the rearrangement of the material between different parts of the surface, which generates pore closure and densification of the structure when the material returns to room temperature. The abrasion resistance is superior for the material using Budit 6H, since the test was also performed at room temperature. However, the HMOR result for this additive was extremely low as the test was performed at high temperature and the formation of a liquid phase is detrimental. The addition of Budit 6H reduced by 60% the HMOR values at 815°C of the formulations studied (Fig. 7).

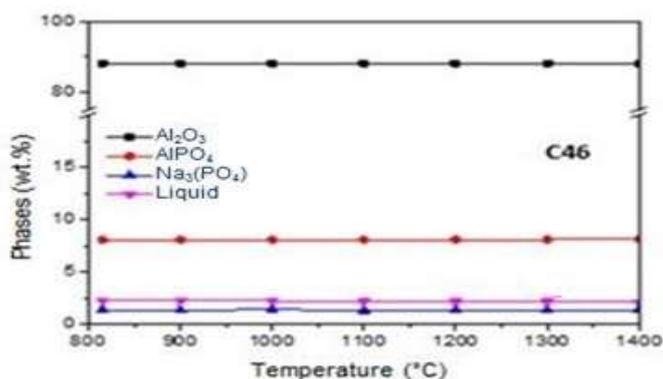


Figure 6: Phase diagram generated by FactSage Software for composition containing cement, 40°Be acid and Budith 6H, heated at 1400°C

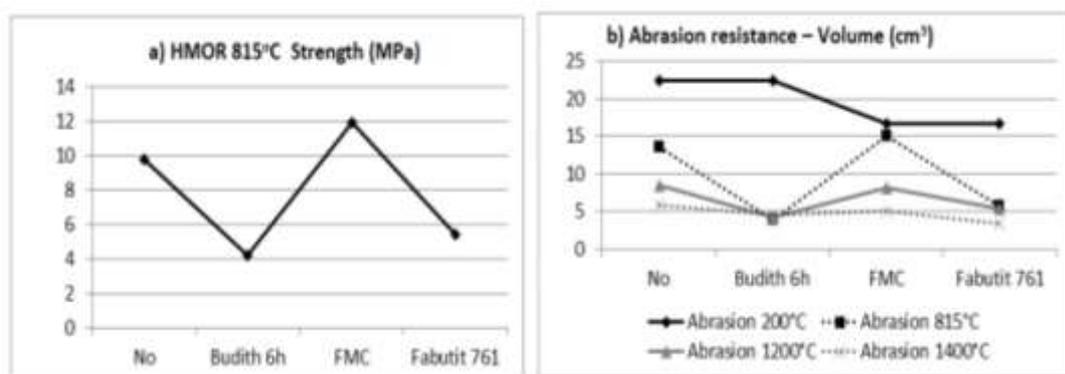


Figure 7: Main effect of additives (phosphate source) on HMOR (a), and abrasion resistance (b)

The high CCS values of the refractories containing Fabutit 761 at 815°C cannot be explained by the formation of a liquid phase, since the softening temperature of that additive is above 900°C. Under these temperature conditions, the Fabutit 761 acted as an extra phosphate source, contributing to the formation of the Al₂O₃-phosphate phases that impart positively in mechanical resistance of the material. However, the HMOR values for the formulations containing Fabutit 761 were very low. The phosphate phases formed by this extra phosphate source would be amorphous phases such as Al(PO₃)₃ - aluminum metaphosphate - formed at temperatures between 500°C and 625°C, which are detrimental to the mechanical resistance at high temperatures, justifying the low values of HMOR at 815°C. At temperatures of 1200°C and 1400°C, in addition to the Al₂O₃-phosphate phase formation, high values of CCS may be associated with the effect of the liquid phase formation and the consequent sintering since these temperatures are above the softening temperature of the additive.

3.3- Thermal Shock Resistance

Thermal shock test compares the residual elastic modulus for each composition after 10 cycles. However, not all the compositions supported the ten cycles and the samples broke before the end of the test. For this reason, the data that was fed into the Minitab16 software was the number of cycles supported by each composition.

Figure 8 shows the results of the main effects of each factor on thermal shock resistance. The type of setting agent was the main factor in relation to the thermal shock resistance of CBPC's. Cement-containing formulations supported a higher number of cycles than the samples containing DBM98.

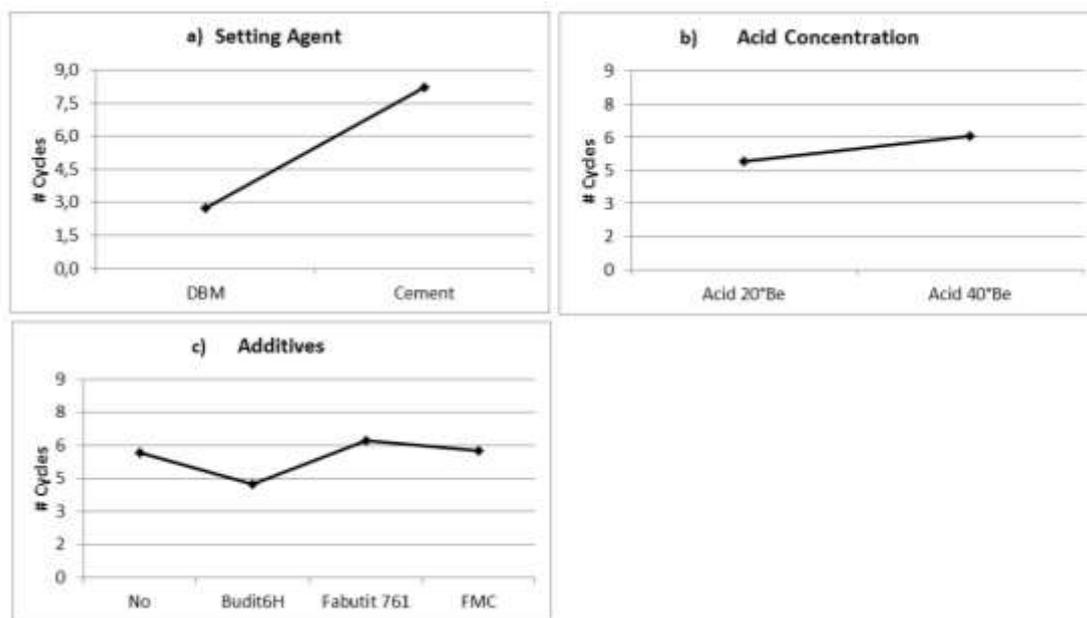


Figure 8: Main effect plots for the effect of cement (CaO source) or DBM (MgO source), (a), acid concentration (b), and type of additives (phosphate source), (c), on thermo shock resistance at 1200°C

Crack nucleation was observed for all samples during the cycles. The higher thermal shock resistance was reached for samples in which the propagation of cracks was inhibited. In this case, Eq. 4 is used to express the thermal shock resistance.

$$R''' = \frac{MOE}{\sigma_t^2 \cdot (1-\mu)} \tag{4}$$

The initial elastic modulus for compositions containing sinter and cement is similar. The Poison modulus (μ) is the same for the refractory materials, the difference found for the thermal shock damage can be related to the thermal stress (σ). In materials with a low mechanical resistance, the stress generated by the crack formation are relieved, which maximizes the R''' factor and reduces the damage by thermal shock. Indeed, the mechanical strength of cement-containing products was lower than that of products containing DBM98, and therefore better results were found in thermal shock tests for CaO as a setting agent.

Compositions containing cement as a setting agent, 40°Be phosphoric acid and Fabutit761 additive as an extra source of phosphate presented a better set of properties, as shown in Table 1.

Table 1: Optimal composition of chemically bonded phosphate castables

	Setting Agent	Acid (°Be)	Additive	Setting Time (min)	CCS 815 (MPa)	HMOR 815 (MPa)	Abrasion 815 (cm³)	Thermo Shock 1200 (#Cycles)
C1	Cement	40	761	405	48	8	3	10
C2	Cement	40	761	600	45	7	6	8
C3	Cement	40	761	400	47	9	5	9
	Average			468	46	8	5	9

It is difficult to optimize all properties. However, it is extremely important to know how each factor affects the concrete properties and to verify which property is more important for each type of application. From this knowledge, the best composition to use can be selected.

4. CONCLUSIONS

The effect of the setting agent ($\text{MgO} \times \text{CaO}$), the concentration of phosphoric acid ($20^\circ\text{Be} \times 40^\circ\text{Be}$), and the presence of different additives as a phosphate source (Budit6H \times Fabutit761 \times FMC) on the properties of chemically bonded phosphate castables was evaluated and discussed.

Analyzing the type of setting agent, the compositions containing cement had a shorter setting time. Cement-containing compositions consume a greater amount of phosphate during the setting reactions, providing a smaller amount of P_2O_5 to react with alumina at high temperatures, which impacts the formation of Al_2O_3 -phosphate phases and, consequently, the mechanical and abrasion resistance of the product. In addition, the formulations containing cement exhibit superior liquid phase formation to sinter-containing formulations, which again impact on the mechanical strength and abrasion resistance of the product.

In relation to the acid concentration, the compositions containing 40°Be acid presented better mechanical, abrasion and thermal shock resistance due to the greater amount of P_2O_5 available in the system, responsible for the formation of phases that will guarantee adequate mechanical properties for the material. However, the use of concentrated acid prolonged the setting time of the products due to the lower amount of water in the system, which affected the dissolution process of the ions in the phosphoric acid.

Analyzing the presence and the type of additives used, the Budit 6H was very efficient to increase the cold mechanical resistance and abrasion of the materials, but it negatively impacts the hot properties due to the excessive formation of a liquid phase from 600°C . For Fabutit761, there was no liquid phase formation at intermediate temperatures and this additive increased the cold mechanical strength by acting as a source of extra phosphate for the system, but also had a deleterious effect on the hot mechanical strength. The FMC did not significantly interfere with any of the measured properties.

Compositions containing cement as a setting agent, 40°Be phosphoric acid and Fabutit761 additive as an extra source of phosphate presented a better set of properties.

5. ACKNOWLEDGMENTS

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