

Advantages of Liquid Phosphate Bonded Refractories

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Liquid phosphate bonded refractories are two-component monolithic products with a binder system belonging to the class of acid-base cements. In the last 15 years liquid phosphate bonded LPB refractories have found wide acceptance as furnace linings in industries like aluminium, power generation and hydrocarbon processing due to the unique characteristics of this material group. LPB refractories show setting characteristics at ambient temperatures and are available for different installation methods such as casting, pumping or gunning and therefore are not just restricted to ramming applications like heat setting mono-aluminium-phosphate (MALP) based products. In this article properties of LPB refractory materials, including non wetting against molten aluminum, fast heat-up and dry-out, bond to existing refractory materials and CO- resistance, are discussed based on documented scientific theory and real world industrial applications.

1 Introduction

A great number of works have reported about the reaction between alumina and phosphoric acid [1, 2, 3]. Alumina reacts with phosphoric acid above 127 °C to form aluminium phosphate and shows considerable strengths above 350 °C. The most often applied phosphate binder in the refractory industry is monoaluminium phosphate (MALP) in liquid or spray-dried form. If setting properties at ambient temperature are desired, an additional setting agent is needed. This can be an alkali- or alkali-earth metal oxide component (MxO) like sodium, magnesium, calcium or compounds thereof. The disadvantage of a spray dried MALP additive in a single component material is the poor shelf life due to the strong hygroscopic behaviour. Other dry mono-phosphate refractory binders such as mono-magnesium phosphate do not show hygroscopic behav-

our, but due to the lack of solubility in water the resulting strengths of the material is often low at the higher water additions necessary for vibration casting. It can be concluded the use of dry phosphate based refractory products that can be mixed with water is limited. Alternately, phosphoric acid can be used as a liquid in two component products where the setting agent and acid component are separated – the so-called liquid phosphate bonded refractories. Phosphoric acid is a tri-basic acid and reacts with different metal oxides to form hydro-gel salts. Some of these salts function as a refractory binder, like the aforementioned mono-phosphates of aluminium and magnesium. In an aqueous solution the phosphoric acid reacts in three stages according to the molar ratio MxO / P2O5 of 1:1, 2:1 or 3:1. In liquid phosphate bonded refractory products those reactions occur at ambient and elevated temperatures and lead to advantages that are unique and often not attainable with conventional materials and other phosphate binder based materials. These advantages include:

- Extremely fast dry-out and heat-up with no need for curing or long setting times

- Non-wetting properties against molten metal, in particular aluminium and its alloys, reducing furnace operating costs and increasing clean metal output
- Excellent repair properties due to the ability of LPB refractories to bond to existing fired refractories, reducing overall refractory costs and furnace downtime
- Resistance against CO attack
- Excellent thermal shock properties.

Liquid phosphate bonded refractory products demonstrate significant advantages over conventional monolithic products and have been successfully used in many industries, including aluminium production, power generation and petroleum and hydrocarbon processing, resulting in substantial net savings to a plant through reduction of maintenance costs and improvements in plant productivity. LPB refractory advantages are presented here based on the theoretical background, test results, and industrial applications.

2 Heat-up and dry-out behaviour of liquid phosphate bonded refractories

LPB refractory materials are two-component products comprised of a premeasured liquid and a dry component. The reaction with liquid phosphoric acid is exothermic, generating temperatures up to 65 °C. In most cases LPB materials are totally set in 1 to 3 h after placement with no additional curing time required, comparing favourably against the 24 h of curing required of conventional refractories. The susceptibility of cement bonded refractory materials for steam explosions during heat-up is also dependent on the associated hydration reactions because low temperature curing leads to higher density calcium aluminates and a much lower micro-porosity [4]. In particular, dense cement-bonded materials with low liquid content and small pore diameter suffer from susceptibility to explosive spalling during dry-out. The degree of critical tensile stresses caused by steam pressure during dry-out is impacted by the lining material, its liquid content,

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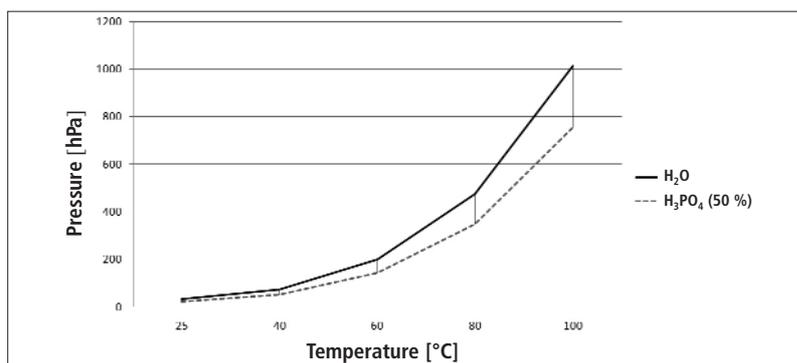


Fig. 1 Steam pressure of diluted phosphoric acid

lining thickness and state of hydration. In contrast the LPB binder technology improves heat-up properties (and reduces downtime) by reducing occurring steam pressure in the material during heat-up. Table 1 compares the occurring steam pressure of water used in conventional castables and the phosphoric acid solution used in the LPB binder system.

Fig. 1 demonstrates the vapour pressure of phosphoric acid solution is 20 % lower than water at 100 °C. Lower vapour pressure leads to a significant reduction of occurring stresses within a refractory lining during heat-up [5]. Since the setting reaction of LPB refractories generates heat and releases moisture it is also part of the "firing in" process, and reduces steam pressures even further. Depending on the lining thickness and overall lining geometry, LPB refractories can be heated-up at rates of 250 °C/h without any holds. Another factor that contributes to the fast firing properties of LPB refractories is the conversion of mono-phosphate hydrates to polyphosphate and meta-phosphate during the heat-up process. The condensation process leads to phosphate

types that possess ring (meta-phosphates) and chain structures (polyphosphates) that resemble organic polymers. As a result, the phosphate bond is very flexible, particularly in the important temperature range between ambient and 600 °C and this is the reason for LPB refractories' excellent thermal shock properties [6]. Fig. 2 shows the difference in heat-up time for a conventional cement bonded refractory and LPB refractory. With a 230 mm lining, the vibration cast LPB refractory is up to operating temperature and on line after 28 h. Because of the lower steam pressure generated by phosphate-bonded refractories, mono-aluminium-phosphate bonded plastics have been preferred in applications such as burner throats. As it relates to heat up however, the disadvantage of phosphate bonded plastics is the migration of phosphates into the lining after the installation. This requires a unit start-up shortly after the installation to avoid a concentration of phosphates in the lining and the potential consequence of explosive spalling during heat-up [7].

Additionally, the release of moisture in phosphate-bonded plastic is still considerably

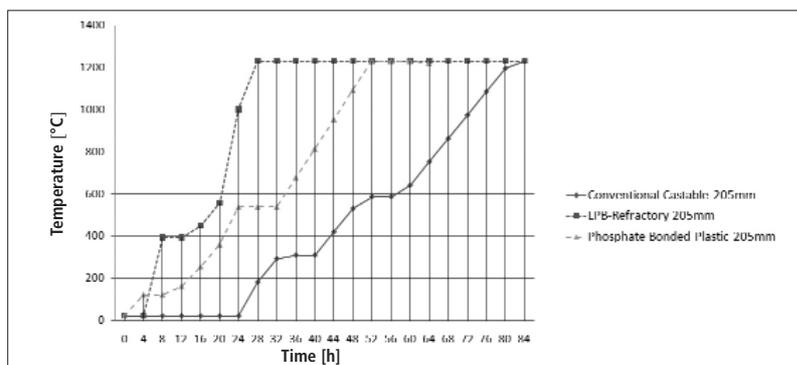


Fig. 2 Heat up time for conventional cement-bonded refractory, phosphate-bonded plastic, and LPB refractory.

slower than in LPB refractories as Fig. 2 illustrates.

3 Non-wetting properties against molten aluminium and its alloys

One of the major wear problems in aluminium melting and holding furnaces is the interaction between the refractory lining and the molten metal. Depending on the furnace conditions cement bonded conventional monolithic materials and also brick linings offer limited resistance against molten aluminium. The most comprehensive studies with regard to this problem were conducted by *Siljan* and *Schonig* [8]. According to these authors, a cardinal condition for an initial reaction between refractory and aluminium is wetting of the lining by molten metal. Experimental studies have shown that the resistance of a refractory lining increases with the alumina content and the addition of anti-wetting additives and decreases with increased silicon oxide content and alloying elements like silicon and magnesium. Furthermore, it has been demonstrated that the presence of sodium from fluxes and a highly reducing atmosphere contributes to the deterioration of aluminosilicate refractories [9]. It is clear from these studies that anti-wetting additives play an important role in diminishing wetting of cement bonded refractory linings. However, the mechanisms of wetting agents are not well defined and experience has shown that the lifetime of anti-wetting agents like BaSO₄, AlF₃ and CaF₂ are limited, particularly if low viscosity flux salts are used at high furnace temperatures. Higher temperatures however are oftentimes necessary to increase the furnace melting efficiency. This weakness of cement bonded materials with non-wetting additives led to the use of LPB materials in particular when furnace conditions are harsh because the binder component in LPB materials (P₂O₅) is a non-wetting additive that does not decompose up to temperatures of 1500 °C. The liquid phosphoric acid is evenly distributed in the refractory matrix after mixing and reacts to create a strong bonding system at ambient temperatures. Based on thermodynamics, aluminium and alloying elements like Mg, Ca, and Si reduce phosphate resulting in corundum growth. In LPB refractory materials however, P₂O₅ occurs as alkali and aluminium-phosphate compounds and the reaction kinetics allow excellent stability and

non-wetting properties in operation. This is not only true for LPB materials but also for phosphate bonded bricks and calcium phosphate bone ash slurries that have been used for centuries in molten aluminium applications. Due to the lack of thermodynamic data available for alkali-earth metal mono-phosphate and di-phosphate compounds it is not yet possible to show clear evidence of the thermodynamic behaviour of the binder system.

4 Case study – non-wetting properties of a 50-t aluminium scrap melting furnace

Fig. 3 shows a 50-t side well furnace used for scrap melting of high Mg containing aluminium alloys at operating temperature. The furnace lining previously failed after only one year in operation due to refractory corrosion in the so-called belly band area where the aluminium bath level interacts with the furnace atmosphere and the refractory. The furnace owner decided to install a LPB refractory lining in this area and a smaller test panel of a conventional non-wetting additive containing cement bonded monolithic material next to it. After only 5 months in operation severe corrosion was visible on the conventional material whereas the LPB refractory does not show any corrosion at all. As a consequence, furnaces at this plant have been lined with LPB materials below the metal line and in critical areas with aluminium contact since 2007.

5 Bond of LPB refractories towards existing refractories

Unexpected damage on furnace linings can lead to a time bottleneck with total replacement of damaged areas not possible to the lack of replacement materials, extended demolition and installation time required. Monolithic materials are advantageous over



Fig. 5 Testing equipment used to determine the bond strengths

bricks because of the wide variety of installation methods and short lead times. However, the adherence property of the repair material determines the long term performance of the lining. Therefore tests have been conducted to show the adherence performance of liquid phosphate bonded materials. Fig. 4 shows a scanning electron microscope analysis on a polished section of a liquid phosphate bonded material cast on a conventional cement bonded high silica containing material. In this case the composite was fired at 800 °C prior to sample preparation. Each colour represents an element present in the sample. It is evident from the P_2O_5 distribution (blue) that phosphoric acid penetrated the cement bonded material. Since phosphoric acid reacts with alkalis like CaO at ambient temperatures, the bonding mechanism can be explained by a reaction between the phosphoric acid of material "A" with the CaO content from the cement of the substrate material "B." Therefore, the bonding mechanism is a chemical bond due to a neutralization reaction. In contrast to cement bonded materials that only bond mechanically on existing materials, the chemical bond possesses much better adherence properties. Other tests have shown that infiltrated phosphate also reacts with alumina to form aluminium-phosphates, explaining the bond with bricks or refractory materials with low or no alkali content. The chemical bond generated in the repair has superior adherence properties as demonstrated in the following bond strength testing. Fig. 5 shows the testing set-up used to determine the bond strengths between a liquid phosphate bonded material and conventional castable refractories. It is a modified ASTM C 133 test that uses four-point loading. Fig. 6 shows the samples after the four-point load test. The red colour represents the LPB material bonded to the white 95 % alumina conventional cement bonded refractory.

The test was conducted on request of a refinery maintenance group that wanted to simulate and evaluate the repair properties of a LPB refractory for a sulfur recovery plant.

The break line does not go directly through the bond-interface but passes through part of the existing lining and part in the veneer. This is typical for LPB products and a further indication of the bond mechanism described in Fig 3.

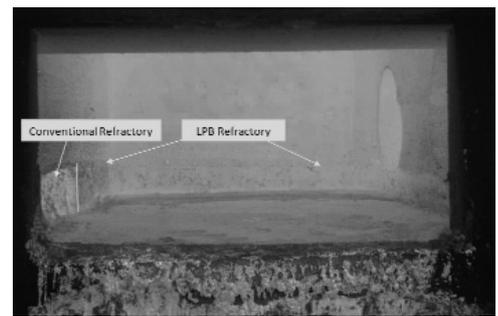


Fig. 3 50-t side wall furnace

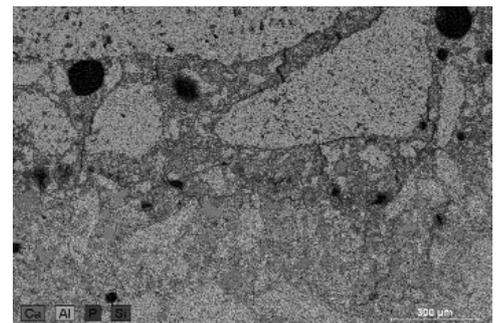


Fig. 4 SEM analysis of phosphate bonded material cast on cement bonded material after 800 °C

Multiple tests using a variety of conventional castables and a variety of LPB refractory formulations show bond strengths between cement bonded products and the phosphate bonded material in the range of 90 % of the average modulus of rupture of the monolithic material.

That in essence means such a veneer repair leads to monolithic properties of the entire lining.

6 Case study - veneer repairs of aluminium melting furnaces

The lifetime of aluminium furnaces can be significantly increased by applying veneer repairs with liquid phosphate bonded refractories. The outcome is less refractory waste because up to 80 % of existing linings can be



Fig. 6 Samples after the four-point load test



Fig. 7 Aluminium round top melting furnace veneer lined with LPB refractory materials

maintained indefinitely rather than torn out and disposed of repeatedly. For example the refractory installation of a 100-t round top melting furnace with monolithic side wall and bricked floor takes usually more than 20 days – heat-up not included. By applying a veneer repair of the existing refractory lining with a liquid phosphate bonded refractory, the downtime can be reduced to less than 5 days with a 24 h heat-up included and the lifetime of the conventional lining can be extended by another two years.

Fig. 7 shows such a round top melting furnace after a veneer repair with an average thickness of 10 cm on the existing lining. This particular furnace undergoes side wall veneer repairs and floor replacement every two years.

7 Resistance against CO attack

Carbon monoxide is a gaseous product that occurs in many thermal processes. For example fuel gas compositions in the refinery and petrochemical industry often contain high percentages of CO. Thermal pyrolysis processes used in waste treatment convert organic materials into CO that is used as a fuel gas for power generation. CO is also a byproduct in coke furnaces and in coal pre-heater in the steel and non iron metal industry. In many of these applications coke or CO gas is in direct contact with refractory products at process temperatures above 400 °C. Above 400 °C CO gas converts to solid carbon in presence of iron or iron-oxide particles in the refractory material. As a consequence the crystallization pressure of local carbon precipitation in the refractory lining can cause cracking and destruction of the refractory lining. The mechanism well known as Boudouard equilibrium can be described as follows:



The role of iron or iron-oxides is still not clear but some literature describes that iron functions as a catalyst rather than a part of the chemical reaction. The iron content can be the result of the crushing and sizing process of the refractory raw materials or is an impurity of the natural raw materials. In many CO applications, synthetic iron free raw materials are required. Tabular alumina, in dense or bubbled alumina as insulating materials are ex-

amples of synthetic iron free raw materials. CO attack is often not recognized as a failure mode because in many thermal processes carbon occurs alongside CO and after the lining has failed it is hard to distinguish between carbon from CO decomposition and solid carbon from the process itself. As already discussed, carbon bursting is predominantly a matter of free iron or iron-oxide and very likely also organic ingredients in monolithic refractory material that may function as germs for carbon growths. Tests have shown that refractory materials with higher porosity show more likelihood of carbon bursting compared to more dense materials with the same iron content. The reason is that the CO access to iron or an iron-oxide particle is easier than is CO access to dense materials [10]. As a consequence insulating materials with high porosity and iron impurities often show poor performance in CO applications. Those materials also demonstrate low strengths and very often higher iron contents compared to dense materials. Therefore CO applications require insulating materials with ultra low iron content in order to avoid carbon bursting.

8 Behaviour of LPB refractories in CO atmosphere

In contrast to conventional monolithic refractories mixed with water, LPB materials are mixed with phosphoric acid. This reaction converts reactive iron or iron-oxide particles into iron-phosphates at ambient temperature. Therefore LPB products are not susceptible to CO attack because the resulting iron-phosphate does not function as a catalyst in presence of CO anymore. As demonstrated in a series of CO tests, a light-weight LPB refractory material showed only minor attack on 3 out of 10 samples compared to a 100 % failure rate in the conventional cement bonded insulating material with a similar density of 1300 kg/m³. Three dense LPB materials with alumina contents between 60 % and 90 % showed no attack whatsoever in this test series. The result of the ASTM 288 CO resistance test is based on a rating: A = no attack, B = minor attack with less than 0.5" pop outs and C and D rating with more than 0.5" pop outs and destructive bursting. All samples of the comparable cement bonded materials showed C and D ratings whereas the LPB refractory materials had only A ratings and 3B ratings

on the light weight material. Liquid phosphate bonded refractory materials are an excellent choice for CO exposure.

9 Summary

The performance of refractory lining materials often dictates the lifetime of furnaces and thermal processes. Any reduction in downtime for refractory repairs can lead to huge cost savings exceeding the investment for the refractory material and installation. By utilizing liquid phosphate bonded (LPB) monolithic materials, these savings can be obtained by avoiding curing with fast heat-up, excellent repair characteristics and in some industries due to unique thermochemical behavior such as CO resistance and non-wetting towards molten metals. LPB refractory technology has been successfully used in furnaces across many industries for more than 15 years with wide acceptance and popularity.

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