Thermbond® - A New Development in Refractory Technology

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Introduction

The evolution of the refractory industry has been characterized by efforts to replace bricks with various forms of monolithic materials. Since the 1980s, the primary evolutionary focus has been on the development of castable monolithic refractories with better installation and performance characteristics (e.g. higher strengths due to lower water content and faster installation rates). In some industries this has significantly lowered installation costs and increased the lifetime of the refractory lining.

However, the advancements in high strength low porosity monolithic refractories have come with a downside. These new monolithics are more vulnerable to fast heat-up, dry-out and thermal shock during operation due to brittleness and high density. In many applications controlled start up procedures are not possible due to equipment restrictions such as burner capacity and control. In order to overcome these problems a new refractory product line, Thermbond Refractories, was developed in the mid 1990s. The technology used in the new refractory material demonstrates significant advantages over conventional monolithic products and is being successfully used in many industries, resulting in substantial net savings to a plant through reduction of maintenance costs and improvements in plant productivity.

Thermbond® Technology Overview

Thermbond Refractories are an entire product line of alumina-based refractories that use a dry refractory component mixed with a specially blended liquid phosphoric acid, or "activator" to achieve properties and characteristics not found in conventional materials:

1. **Fast setting and rapid heat up**
2. **Bonds to existing fired refractories**
3. **Thermal shock resistance**

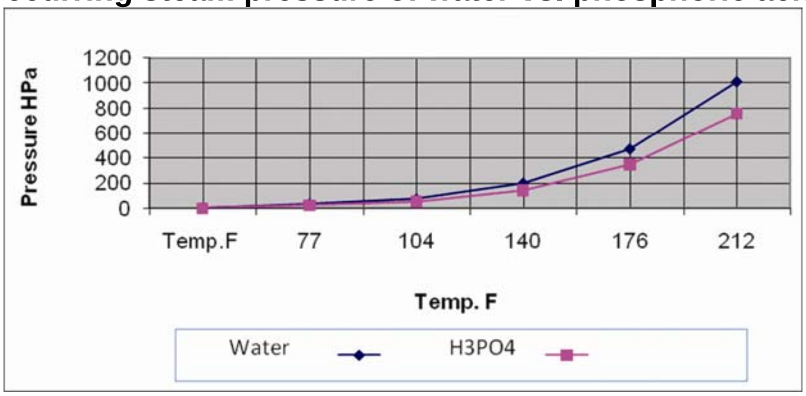
The setting process of cement bonded refractory materials is characterized by the hydration of the binder component, calcium aluminates. This hydration process dictates the material properties after placement. Most manufacturers of conventional castable refractories recommend 24 hours minimum hydration or curing time.[i]

In comparison, Thermbond refractory materials are two-component products comprised of a premeasured liquid and a dry component. A typical formulation is based on CaO, MgO, BaO or other alkali in the dry formulation that act as setting agents. The reaction with liquid phosphoric acid is exothermic, generating temperatures up to 150°F. In most cases, Thermbond products are cured in 1-3 hours after placement, comparing favorably with the minimum of 24 hours 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.[ii] In particular, dense cement-bonded materials with low liquid content and small pore diameter, and insulating materials with very high water contents suffer from susceptibility to explosive spalling during dry-out. The degree of critical tensile stresses caused by steam pressure is impacted by the lining material, its liquid content, lining thickness and state of hydration.

The Thermbond binder technology improves heat up properties (and reduce 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, or "activator" used in the Thermbond binder technology.

Table 1: Occurring steam pressure of water vs. phosphoric acid solution

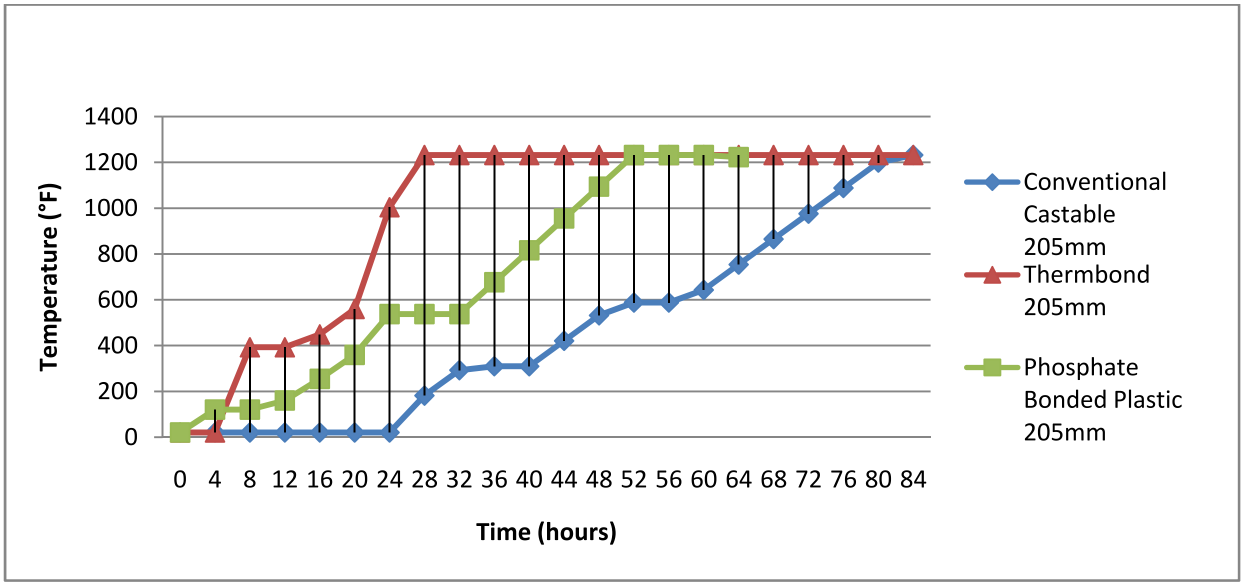


This graph demonstrates the vapor pressure of phosphoric acid solution is 20% lower than water at 100°C (212°F) Lower vapor pressure leads to a significant reduction of occurring stresses within a refractory lining during heat up.[iii] Since the curing of Thermbond generates heat and releases moisture it is also part of the "firing in" process and steam pressures are reduced even further.

Lower steam pressures make heating up Thermbond safer and allow for faster heat-up rates. Depending on the lining thickness and overall lining geometry, Thermbond can be heated up at rates of 100°C per hour without any holds. Another factor that contributes to the fast firing properties of Thermbond refractories is the conversion of mono-phosphate hydrates to polyphosphate and metaphosphate during the heat up process. The condensation process leads to phosphate types that possess ring structures (metaphosphates) and chain structures (polyphosphates) which resemble organic polymers. As a result, the phosphate bond is very flexible, particularly in the important temperature range between ambient and 1100°F. [iv]

Table 2 shows the difference in heat-up time for a conventional cement bonded refractory and Thermbond. With a 230mm lining Thermbond is up to operating temperature and on line after 28 hours.

Table 2: Heat up rate of conventional castables, phosphate bonded plastics, and Thermbond



Because of the lower steam pressure generated by phosphate-bonded refractories, mono-aluminum-phosphate bonded plastics have been used particularly in applications such as burner throats. As it relates to heat up, the disadvantage of phosphate bonded plastics is the migration of phosphates in 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 consequence of explosive spalling during heat up. (Plibrico, Technology of Monolithic Refractories, page 238, 1999). Additionally, the release of moisture in phosphate-bonded plastic is still considerably slower than Thermbond as **Table 2** illustrates.

Thermbond's rapid curing and firing in properties result in:

- **Reduced downtime for curing of refractories**
- **Safer heat-up of refractory linings because of lower internal steam pressures**
- **Faster heat-up rates and less control required to fire in refractory linings**

Thermbond® Bonds to Existing Fired Refractory

Damage to refractory linings reduces operating efficiency and can lead to unexpected shutdowns. Total replacement of damaged areas is not always possible. Material availability, limited work force, or lack of time for an complete reline are all factors affecting the decision. Performing a partial lining repair is often the best solution to minimize downtime, but not always the most reliable in terms of long-term performance.

Thermbond refractories have the ability to adhere to existing fired refractories linings. This is another advantage of the patented phosphate binder technology not found in conventional cement bonded refractories.

During installation, the liquid "activator" component of Thermbond refractories penetrates the existing fired refractory lining and chemically reacts with components of the material. This reaction creates a chemical bond that possesses strengths comparable to the existing refractory material and to Thermbond.

Figure 1 shows a Scanning Electron Microscopy (SEM) analysis of a polished section of Thermbond cast onto a conventional cement bonded alumina/silica castable material. In this case, the composite was fired at 815°C prior to sample preparation. Each color represents an element present in the sample. The P_2O_5 distribution (blue) shows the phosphoric acid contained in the "activator" penetrated the cement bonded material. Since we know phosphoric acid reacts at ambient temperatures with alkalis like CaO, the bonding mechanism can be explained by a reaction between the phosphoric acid, or "activator", of Thermbond with the CaO from the cement of the conventional castable. The bonding mechanism is a chemical bond due to a neutralization reaction.[v]

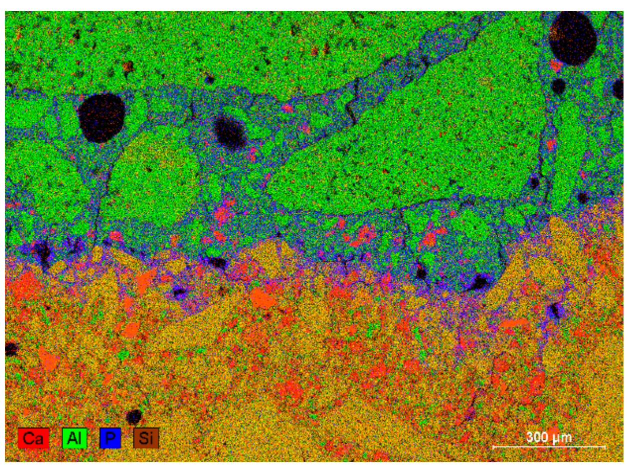


Figure 1: analysis showing phosphate penetration of existing lining

In contrast, cement bonded materials only bond mechanically on existing materials. Making repairs with conventional refractories requires anchoring or repair construction that incorporates a mechanical means of holding the repair material in place. Repairs with Thermbond restore the lining back to its full monolithic configuration.

The chemical bond generated in the repair has superior adherence properties as demonstrated in the following bond strength testing.

Figure 2 shows the testing set up used to determine the bond strengths between Thermbond and conventional castable refractories. It is a modified ASTM C 133 test that uses four-point loading rather than three point loading. The use of four point loading is more representative of how forces are applied to refractory linings in actual application. **Figure 3** shows the sample after the four-point load test. It can be seen that 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 Thermbond products and a further indication of the bond mechanism described in Figure 1.

Multiple tests using a variety of conventional castables and a variety of Thermbond formulations show that the bond strengths between cement bonded products and Thermbond is in the range of 90% of the average modulus of rupture of the monolithic Thermbond material. In essence a veneer repair using Thermbond leads to monolithic properties of the entire lining.

Figure 2: Four point loading test

Figure 3: Interface of sample after break

With Thermbond's unique ability to bond to existing fired refractories the following advantages can be gained:

- **Less downtime required for tear out and repair**
- **Real bonding to existing lining creating a monolithic repair**
- **Less waste generated because the existing lining remains in place**
- **Longer service life on existing refractory material**

Thermal Shock Resistance

Sudden temperature changes in dense refractory materials can lead to thermal stresses. Stresses occur because the relatively low thermal conductivity of dense refractory materials can cause a large temperature gradient between the surface and interior of the refractory material when it is heated or cooled too quickly. Temperature is also correlated with thermal expansion exhibited by refractory when heat is applied. When heated too rapidly, a refractory material develops large expansion stresses on the surface resulting in thermal shock.

One solution to overcome thermal stresses is to choose a refractory containing material with a low thermal expansion and high thermal conductivity such as mullite or silicon carbide. However, even low thermal expansion will not deliver the desired result if the binder phase of the monolithic material is too brittle.

An important property of thermal shock resistant materials is the plastic elastic response during local temperature impact. This can be expressed as “modulus of elasticity”. Thermbond liquid phosphate bonded materials possess a very flexible binder matrix. The binder matrix resembles a polymer structure with a low modulus of elasticity (e.g. a binder matrix with high elasticity). This elasticity allows a high temperature change; heat flux and temperature increase at the surface without exceeding failure stresses over a wide temperature range. **Figure 4** shows a flame impingement test that every Thermbond material undergoes in the R&D process. After curing (approximately 1-4 hours) a 50kg - 100kg block of Thermbond is exposed to two opposing propane flames for 50 minutes. The purpose is to provoke steam spalling and expansion stresses.

All Thermbond materials used in fast heat-up and thermal shock applications have to pass this test successfully without cracking and spalling.

Figure 4: Heat being applied to two sides of a cured Thermbond material

Figure 5: After 50 minutes of firing; no cracking or spalling of sample

Case Study 1

A minerals processing facility in the western USA, operating a captive coal fired power plant, chose to use Thermbond refractories for burner throats, ash hopper and wind boxes. The plant was upgrading burners and doing other maintenance within a very tight turnaround schedule. Thermbond allowed the facility to shorten the turnaround schedule because the firing in rate of Thermbond refractories was dramatically shorter than one using conventional refractories. In addition to the reduction in turnaround days, the customer estimated they saved over US$60,000 in fuel costs that would have been consumed in a conventional refractory heat-up schedule. The fuel savings easily offset the additional cost of Thermbond.

Thermbond Formula 15R was installed in 8 burner throats. Formula 6AG, a gunning grade of Thermbond, was installed in a complete reline of the wet bottom ash hopper and Formula 8B, an insulating material, was installed in 4 wind boxes.

Figure 6: Steel form to properly contour burner throat. This gives the proper shape to the burner throat for efficient burner operation

Figure 7: 15R is laid out on a mortar board prior to being installed

Figure 8: Burner throat with conventional refractory trimmed back to good refractory and ready for a Thermbond overlay

Figure 9: Thermbond Formula 15R being rammed in burner throat bring it back to its proper profile

Figure 10: Wet bottom ash hopper with anchors in place and ready for gunning

Figure 11: Completed ash hopper installation

Case Study 2

A mid-sized coal fired public utility power station in the US needed to redesign and repair existing eight existing burner throats. I addition the new refractory and tubes were to be coated with an energy savings emissivity coating. Based on a recommendation from the Emissivity coating company, the power station chose to use Thermbond Formula 15R repair and reconfigure the burner cones and Formula 8B in the seal cans for over-fire air. The value to the customer of using Thermbond in both areas was the ability to bond to existing refractories and the ability to be placed into service in poorly controlled firing-in conditions.

Another advantage Thermbond provided in the application was rapid curing. Once Thermbond was cured, typically in less than 3 hours, the burner throats were available for the emissivity coatings to be applied.

The power station operators and refractory contractor were very impressed with the workability of Thermbond and its installation characteristics.

Figure 12: quart "Hobart" or bakery mixer used to mix Formula 15R

Figure 13: Formula 15R properly folding into itself and ready to be discharged

 **Figure 14: Thermbond Formula 15R partially installed in burner throat**	 **Figure 15: Completed burner throat**

**Additional installation information, customer references, and customer testimonials are available upon request.

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