New Refractory Technology Provides Advantages in Monolithic Refractories

There have been a number of different refractory binder systems introduced and utilized over the last 100 years. The most long-standing systems, and the ones employed through today, are based on aluminous cements or phosphates and water that chemically combine to form hydrates, which eventually harden. These traditional systems have limitations that refractory consumers have had to take into consideration when using refractory monolithics.

Stellar Materials developed and patented an aggregate binder system that eliminates most of the limitations of traditional systems. It is sold under the brand name Thermbond®. The John Zink Company LLC is an exclusive distributor of this unique line of refractory materials.

**Traditional Binder Systems**

The most popular traditional refractory binder systems currently in use are:

- Calcium aluminate cement and water
- Phosphoric acid and reactive alumina
- Dry phosphates and water

High purity calcium aluminate cement combined with water is a very popular refractory aggregate binder system. When the cement and water are combined a reaction takes place that eventually hardens the monolithic refractory. Under normal ambient conditions, the reaction or "set" time for this binder system is 24 hours or longer. After the refractory hardens it has moderate strengths in this green state. This limitation makes the refractory vulnerable to mechanical damage and care must be taken in handling the refractory.

Prior to being put into service for the first time, refractories using this binder system must be fired in, or brought up to operating temperature, very carefully because of the existence of mechanical water in the hardened refractory. If the hardened refractory is heated very rapidly too much mechanical water is converted to steam which can’t escape from the refractory fast enough. Since steam occupies 1000 times more volume than the water it was converted from, the excess steam will rupture and spall the hardened refractory. Lengthy and expensive heat-up procedures are required to prevent this dangerous phenomenon.

Finally, the calcium aluminate cement and water binder system has no bonding characteristics and requires mechanical means of support to keep it in place when used to repair existing refractory linings. There is no reaction between the new refractory being placed and the existing lining which would bond the two structures together. Placing new refractory over old will normally result in delamination when the refractories are heated and put into service.

A second traditional binder system is phosphoric acid and reactive alumina. This system combines phosphoric acid and reactive alumina to form a bonded aggregate structure with very stable properties. This binder system is typically found in "plastic" refractories. Since this system lacks a cement component that hardens at ambient temperatures, it has no green strength. Until the refractory is fired to at least 600° F, it has no strength, and is susceptible re-hydration.

One advantage of not having the cement component is this binder system has no "set" time requirements and formwork is not always required for placement. The "plastic" consistency allows you to contour the lining to the desired shape by "ramming" the refractory into place.
There are numerous disadvantages to this binder system. While no set time is required, the binder system has a considerable amount of mechanical water associated with it so a lengthy and deliberate heat-up schedule is required to fire the refractory in. Once fired-in, the phosphoric acid and reactive alumina binder system loses a considerable amount of strength at operating temperatures above 2500° F.

This binder system has no ability to bond to existing fired refractories. In addition extreme care must be taken on initial placement to insure the refractory is properly knitted together. If not placed properly, laminations can occur resulting in an inferior lining.

The third traditional binder system is dry phosphate and water. This system relies on dry phosphates, mixed in with the refractory aggregate, to dissolve in water, react, and cause the refractory structure to harden.

This system produces a refractory that has reasonably quick set times and moderate green strengths because of the dry phosphate/water reaction. At operating temperature this system will have poor hot strengths. Bringing the refractory to operating temperature with the dry phosphate binder system also requires a deliberate heat up schedule because of the mechanical water remaining in the refractory mass. Without the proper heat-up schedule the potential for explosive spalling exists.

It is very difficult to control the mesh size of dry phosphates and proper mesh size is an important aspect of phosphate solubility. This complicates a process that is already difficult because, in general, dry phosphates are difficult to put back into solution, especially under field conditions. The reaction is also sensitive to impurities that may be present in the water used for mixing. With the dissolution and distribution of phosphates within the mix erratic, physical properties are also erratic. Inconsistent cast, fired, and bonding characteristics of refractories using this binder system typically results.

**Thermbond® Binder System**

A new binder system has been developed that is a hybrid of the traditional systems. The Thermbond® binder system utilizes liquid phosphoric acid or “Activator”, calcium oxides, and other ingredients as the basis for the unique binder system. The Thermbond® binder system was patented in March 1999 under patent 5888292.

When the liquid “Activator” and dry aggregate materials are mixed together a reaction takes place that hardens or “sets” the refractory in a very short time. Once hardened, the Thermbond® binder system develops extremely high green strengths within the refractory structure. Because of the binder technology, the refractory structure will also have good strengths at operating temperatures.

The Thermbond® binder system also has the ability to withstand very rapid initial heat-up. The binder system releases chemical water gradually, which dramatically reduces the risk of explosive spalling.

Since liquid phosphate or “Activator” is used in the binder system, the dispersal of phosphates is complete and uniform throughout the mix. This generates a mix with consistent qualities and gives it the ability to bond permanently to existing fired refractories.
**Thermbond® Product Characteristics**

The Thermbond® binder system provides Thermbond® refractory products with unique product characteristics not available in other refractories. These unique product characteristics are:

- Rapid Mixing
- Fast Setting/Curing
- Fast Heat-up Capabilities
- Bonding Strength
- Thermal Shock Resistance

The Thermbond® Activator and dry bagged aggregate come in pre-measured components that eliminate measuring errors. Pre-measured components also ensure consistency from batch to batch. The dry aggregate is added to the Liquid Activator and mixed for 45 to 60 seconds. The two components blend together much more rapidly than traditional materials. Mixing Thermbond® can be done in paddle mixers, pan mixer, or with a bucket, “Jiffler” blade, and industrial drill.

Once mixed and placed, an exothermic reaction begins that hardens or “sets” the Thermbond® very quickly after placement. Once the chemical reaction is complete the refractory is totally set and has very high green strengths. Thermbond® does not require outside heat sources to set, and in most applications, the Thermbond® lining is ready for heat-in one to three hours after placement (Figure 1).

![Comparative Green Strengths](image)

**Figure 1:** Thermbond® setting characteristics compared to conventional castable materials
After curing Thermbond® refractory products can be put into service with a very rapid bake-out schedule. In many applications heat-up rates of 500°F per hour can be achieved. Thermbond® can be heated up rapidly because the chemical water in Thermbond® is released slowly through chemical reactions as the refractory is setting and being fired in. From initial mixing:

- During initial exothermic reaction moisture is released from castable
- At 500°F moisture is released from Orthophosphoric acid (H₃PO₄) leaving Pyrophosphoric acid (H₄P₂O₇)
- At 1000°F moisture is released from Pyrophosphoric acid leaving solid Metaphosphoric acid (H₃P₀₃)

Many hours of downtime and the costly expense of slow deliberate heat-up procedures are eliminated with the unique feature (Figure 2).

Because of the uniqueness of the Thermbond® binder system, Thermbond® products bond to themselves, either green or fired. In addition Thermbond® products permanently bond to existing fired refractories and not delaminate upon firing. When Thermbond® is initially poured and placed on the surface of an existing refractory, the chemical reaction taking place in Thermbond® also creates a chemical bond with the existing fired refractory. Thermbond® will permanently bond to the existing refractory whether the installation is a veneer, patch, or near full thickness repair. As long as the refractory being bonded to is mechanically sound, Thermbond® can be placed over it eliminating the need for an entire lining replacement (Figure 3-4).
The Thermbond® binder system also creates a refractory product that is extremely resistant to both wide swings in temperature and repeated thermal cycling. Thermal cycling can easily destroy a refractory material long before other destructive service conditions wear out the refractory (Figure 5).

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Figure 5: Modified ASTM test C 1176-96. Thermbond® cycled between 1500° F and ambient every 15 minutes. Strengths measured before/after and then compared to determine strength loss.
Using a liquid Activator eliminates the introduction of impurities through water as in the dry phosphate mixes. Using a liquid Activator results in a complete reaction and no free water. The liquid phosphoric acid, or Activator, is the foundation of the Thermbond® binder system and the unique characteristics of Thermbond® refractories.

Another significant feature of Thermbond’s® unique binder system is the aggregate matrix, coated evenly with phosphate throughout, forms a hot face which resists penetration from molten metals, organics, and other materials. Ordinary refractory binder systems are highly susceptible to penetration by molten metals, hydrocarbons, and other impurities typically present in refractory environments.

Some traditional refractories combat this weakness through the addition of non-wetting additives to their refractory mix. These additives, while initially very effective, burn out of the refractory system over time or when exposed to temperatures in excess of 2000°F, rendering them just as susceptible as refractories with no such additives. Once penetrated, the refractory life is greatly diminished, both as a result of the difference in the coefficient of linear expansion between the refractory product and the penetrating material, and also as a result of mechanical abuse due to the attempted removal of the penetrating material.

Since there are no additives in the Thermbond® binder system to burn or wear out, Thermbond® linings remain clean for the life of the lining, even after exposure to temperatures of 2000°F and above. Since the lining stays cleaner, there is far less maintenance and mechanical abuse, resulting in significantly longer refractory life.

Despite the phosphate content, the Thermbond® binder system is capable of achieving upper temperature limits of more than 3000°F. This is explained through the combination binder system, which by chemical reaction eliminates the typical limitation of phosphates at higher temperatures and allows ceramic bonding to take place. Although a phosphate bond is technically incorporated in this system, it is not classified as merely another phosphate-bonded refractory. The unique binder system used in Thermbond® does not have the shortcomings typical of other phosphate systems.

The Thermbond® binder system is available in over fifty different refractory formulations. Thermbond® products are available in alumina contents from 57% to 95%, dense and insulating products as well as specialty aggregate mixes. Thermbond® refractory products can be installed by casting, gunning, ramming, and troweling (Figure 6).

Figure 6: Thermbond® Formulations are packaged in pre-measured components and come in a wide variety of alumina content, densities, and installation variations.
**Application Review**

The use of Thermbond® refractory technology has become widely accepted, and used in thousands of applications in most major refractory consuming industries. Those industries include:

- Refining/Petrochemical
- Chemical
- Primary/Secondary Aluminum
- Power
- Rock Products
- Steel

Attached are reports representing a variety of Thermbond® applications in your specific industry. They provide excellent examples of how Thermbond® can provide value in installation, cure-out, firing-in, and performance.

**Summary:**

The above referenced application reviews provide a brief overview as to the value of Thermbond Technology in phosphate applications. The advantages of using Thermbond® can be obtained in new linings as well as repairs.

The John Zink Company LLC is an exclusive world wide distributor of Thermbond® Refractory Products.

Thermbond® is a registered trademark of Stellar Materials, Inc.
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