Better, stronger, faster, and lasts longer

Jens Decker and Ted S. Hagberg, Stellar Materials Inc., USA, explore the advantages of liquid phosphate bonded refractory materials in the refining and petrochemical industry.

The hydrocarbon and petrochemical processing industries operate a variety of refractory lined equipment. Because of the equipments' interdependency, an unplanned shutdown of one unit can have a major impact on the entire production process. Minimising equipment downtime presents unique challenges to the maintenance engineer, production planner, and reliability engineer.

This article explores the advantages of using liquid phosphate bonded refractory materials for equipment maintenance. Operating processes are described based on field experience with Thermbond® refractories in combination with analysis from controlled lab tests.

Two component liquid phosphate bonded refractory products have found wide acceptance in the refining and petrochemical industry thanks to unique features including:

- Fast setting and rapid heat up that reduces downtime costs.
- Tenacious bond to existing refractories that allows for repairs instead of full lining replacement.
- High CO resistance that delivers longer service life.

Use of liquid phosphate bonded refractory products generally results in substantial net savings to a plant through reduction of maintenance costs and improvements in plant productivity.

Fast setting and heat up properties: cement bonded versus phosphate bonded monolithic materials

The setting process of cement bonded refractory materials is characterised by the hydration of the binder component, calcium aluminates. This hydration process dictates the material properties after placement and depends greatly on ambient temperature conditions. Most manufacturers recommend 12 - 24 hours minimum hydration or curing time.[1] The susceptibility of cement bonded refractory materials for steam explosions during heat up is also dependant on the associated hydration reactions because cold temperature curing leads to higher density calcium aluminates and a much lower microporosity.[2] In particular, dense cement bonded materials with low liquid content

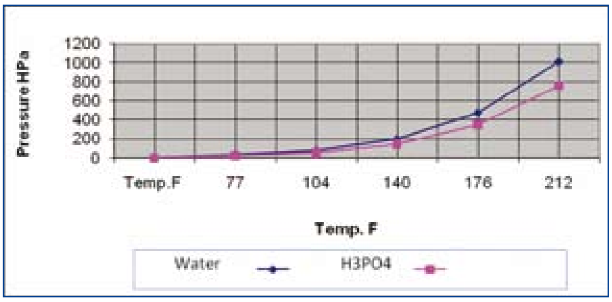

Figure 1. Occuring steam pressure of water versus phosphoric acid solution.

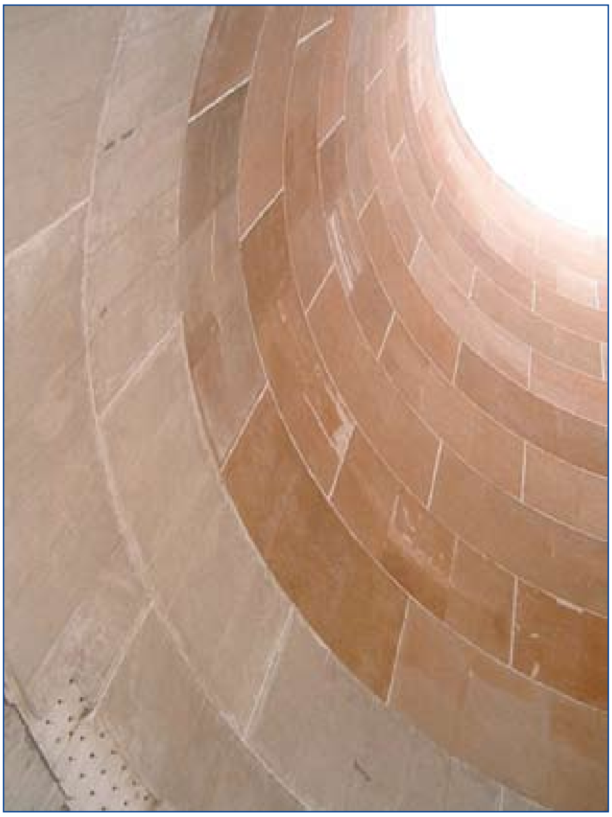

Figure 2. Completed ground flare.

Figure 3. Preparation of composite samples for bond strength test.

and small pore diameter, and insulating materials with very high water contents suffer from susceptibility to explosive spalling during dryout. 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.

One approach to improve heat up properties of refractory material (and reduce downtime) is to reduce occurring steam pressure in the material during heat up. Figure 1 shows the occurring steam pressure of water and a phosphoric acid solution typically used in a binder for liquid phosphate bonded refractory materials.

This graph demonstrates the vapour pressure of phosphoric acid solution is 20% lower than water at 212 ˚F. Lower vapour pressure leads to a significant reduction of occurring stresses within a refractory lining during heat up.[3]

Liquid phosphoric acid bonded refractory materials are two component products comprising 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. The exothermic reaction is already part of the 'firing in' process since liquid is being released. The reaction process depends on the availability of reactants. For example, if the ratio of alkali to phosphoric acid is only 1:1 by molar weight, only mono phosphates can be formed. The setting process needs to be well adjusted to obtain an acidity that leads to the desired low steam pressure.

Other phosphate bonded materials are based on a prereacted monophosphate salt, and an additional alkali component in the mix. After mixing with water, the monosalt reacts with alkali to form a diphosphate salt that is practically pH neutral. In contrast, the monophosphate reaction stays in a range of pH 3 - 4 after setting, and that is important for obtaining the low vapour pressure of the retained liquid in the lining during heat up.

Another factor that contributes to the fast firing properties of liquid phosphate bonded refractories is the conversion of monophosphate 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) and resemble organic polymers. As a result, the phosphate bond is very flexible, particularly in the temperature range between ambient and 1100 ˚F.[4]

Field experience: fast setting and fast heat up properties of liquid phosphate bonded refractory materials

Liquid phosphate bonded refractory materials have been installed in numerous hydrocarbon and petrochemical processing units where fast setting and rapid heat up properties are required.

In February 2006, over 120 t of Thermbond® Formula 8-G liquid phosphate bonded medium weight refractory was installed 8 in. thick in a fluidised coking environment. This application required a rapid heat up refractory capable of withstanding a temperature increase from 300 - 900 ˚F in 90 minutes. The temperature rise occurred during the charging of fluidised coke into the vessel. Using conventional castable refractory would have required a prestartup thermal dry out to eliminate the risk of explosive spalling. This dry out procedure would have added days to the turnaround schedule.

In this example, liquid phosphate bonded refractory eliminated the need for any prestartup dryout, and the turnaround schedule was improved by 3.5 days. The time savings realised by the refinery allowed the turnaround to be completed on time.

Sulfur reactors, fluid catalytic cracking units, thermal combustors, cracking furnaces, reformers, heaters and boilers all benefit from the fast setting and fast heat up properties of liquid phosphate bonded refractories. Figure 2 is a photo from a field installation.

Tenacious chemical bond to existing refractories provides excellent repair opportunities.

Damage to refractory linings will reduce operating efficiency and can lead to unexpected shutdowns. Total replacement of damaged areas is not always possible whether due to a lack of material availability or extended installation time. Partial lining repair is often the best solution to minimise downtime.

Long term performance of a repaired refractory lining depends upon adherence properties of the material used for repair. Independent tests were conducted to measure

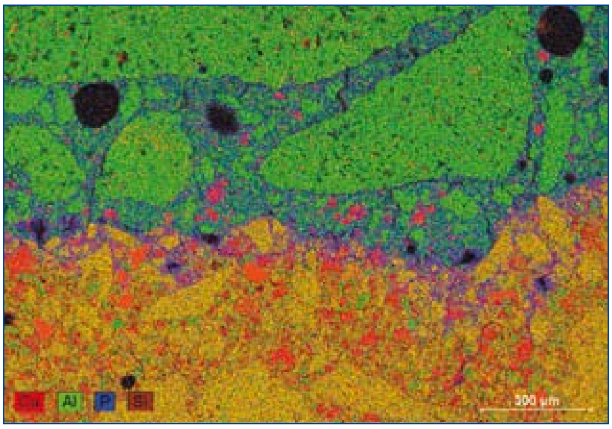

Figure 4. SEM analysis of Thermbond bonded to conventional refractory.

Figure 5. Incinerator side wall, gunning overlay.

the adherence performance of liquid phosphate bonded materials on existing linings.

The bonding properties between an existing lining and the repair material can be simulated by the ASTM C133 modulus of rupture test with a 4 point fixture.

For this test, samples of an abrasion resistant refractory material, considered an industry standard for use in hexmesh anchored linings in FCC units, were prepared by ramming/ handpacking 2in. x 2in. x 9in. bars. The bars were then fired to a typical operating temperature in FCC units. After firing, the bars were cracked in two pieces and Thermbond® Formula 12W, a two component liquid phosphate bonded repair material, was cast on one half of the sample to simulate a repair situation (Figure 3). The resulting composite bars were fired again at 1100 ˚F and MOR testing according ASTM C133 with a 4 point fixture was conducted.

Testing demonstrated the resulting bond strengths of Thermbond Formula 12W (washcoating) to the existing lining (industry standard material) was 2000 PSI, as good as published modulus of rupture data for the existing material. Therefore, the repair produces composites with monolithic properties.

In addition to excellent adherence properties, abrasion resistance is also an important factor for repairs in cyclones of FCC units since the repair coating is exposed to the catalyst and temperature during operation. The abrasion resistance of Formula 12W was measured after firing at 1100 ˚F in accordance with ASTM C704. The resulting abrasion loss was 4.6 cc, which is considered excellent as a washcoat and sufficient enough to provide an extended lifetime of another 5 years.

In order to get a better understanding of how liquid phosphate bonded refractory materials bond to existing refractories, scanning electron microscope (SEM) analysis was carried out on the composite interface that was prepared in the same way as the above referenced sample.

Figure 4 shows the SEM 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 1500 ˚F prior to sample preparation. Each color 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 from the cement of material B. Therefore, the bonding mechanism is a chemical bond due to a neutralisation reaction.[5] In contrast to cement bonded materials that only bond mechanically on existing materials, the chemical bond possesses much better adherence properties as demonstrated in the aforementioned bond strengths test.

Field experience: tenacious bond to existing refractories provides excellent repair opportunities

Since 2002, quality repairs have been completed in high temperature sulfur furnaces by gunning liquid phosphate bonded refractory over existing 70% alumina brick. Thicknesses up to 4 in. have been installed successfully on walls and arches, and the strong chemical bond eliminated the need for any additional anchors. This method of repair has extended the life of the brick lining and greatly reduced the overall cost of the shutdown. Whether caused by mechanical or thermal stress, a permanent repair to damaged refractory can be accomplished using the proper liquid phosphate bonded refractory formulation. Field installations include repairs in FCCU's, thermal oxidisers, convection ducts, stacks, and burner throats in all types of furnaces and boilers. Figure 5 is a photo from a field installation.

High CO resistance provides longer service life

Carbonmonoxide occurs in a variety of processes in the hydrocarbon and petrochemical industry. When in contact with refractory, CO from the process atmosphere can result in serious lining damages due to carbon precipitation. Catalytic operant impurities such as iron and ironoxides can result in carbon bursting of the refractory lining. This phenomenon can be explained by pressure and temperature dependent Boudouard equilibrium reaction:[6]

$$2CO \rightleftharpoons CO_2 + C$$

The Boudouard reaction takes place in the temperature range between 700 ˚F and 1500 ˚F, typical for refinery and petrochemical furnaces. The sources of iron and ironoxide are from impurities within the refractory raw materials and from the crushing process of the raw materials. Even high iron content in the mixing water can be a potential risk

Figure 6. FCCU cold wall reactor riser.

for impurities that can affect the CO stability of refractory materials.

Although iron content is a major factor, it is not possible to predict the stability of a refractory product based only on the iron content in the chemical analysis. It is much more dependent upon whether the iron or ironoxide is accessible for CO. For example, iron incorporated in the glassy matrix of a refractory aggregate is not accessible, whereas iron from the crushing process on the surface of the aggregate very likely contributes to carbon precipitation. Another important factor is open porosity. Porous materials allow better access of CO and therefore show higher reactivity.[7] Insulating monolithic refractory materials are much more susceptible to carbon bursting compared to dense materials.

Liquid phosphate bonded materials possess an important advantage over conventional monolithic products with regards to CO resistance. Although the dry refractory raw materials are similar, the liquid phosphate binder converts most of the ironoxides and all metal iron into ironphosphates based on the following reactions:

$$6H_3PO_4 + 2Fe = Fe_2\,(H_2PO_4)_6 + 3H_2$$
$$6H_3PO_4 + Fe_2O_3 = Fe_2\,(H_2PO_4)_6 + 3H_2O$$

In order to prove the occurrence of the above mentioned reactions, two different lightweight 75 lbs/ ft^3 insulating castables were tested. A conventional cement bond and one with a liquid phosphate bond were compared in a CO resistance test per ASTM C 288. Both materials show low iron content and are recommended by manufacturers for CO applications.

10 samples of each material were prefired at 1000 ˚F prior to CO exposure according to ASTM C 288. All tests were carried out at an independent testing lab. The test results are based on a rating system from A - D. An 'A' rating represents unaffected samples, 'B' samples show small surface popouts, 'C' samples show cracks and 'D' samples show destructive conditions.

The results of this test confirmed the positive impact of the ironphosphate conversion on CO resistance.

- Liquid phosphate bonded samples: 'A' rating - seven samples, 'B' rating - three samples.
- Conventional cement bonded samples: 'C' rating - 10 samples.

The results indicate that the iron content in the chemical analysis of conventional materials is not necessarily a valid criterion for CO resistance. Liquid phosphate bonded insulating refractories possess a much lower risk for carbon bursting than cement bonded materials.

Field experience: high CO resistance provides longer service life

Most ethylene cracking furnaces are designed with refractory lined transfer line exchangers (TLE's) that are exposed to severe service conditions due to the high coking environment and thermal cycling conditions. Since 1999, liquid phosphate bonded refractories have been providing superior performance versus conventional refractory castables in TLE's. The high CO resistance of the liquid phosphate binder system has significantly improved the refractory service life, and subsequently provided dramatic reduction in overall maintenance costs. There are numerous applications where CO resistance is valuable in the refining and petrochemical industries. Field installations include fluid cokers, FCCU reactors and risers, catalytic reformers, and hydrocracking. Figure 6 is a photo from a field installation.

Conclusion

On the basis of the above mentioned experimental results and field experiences, the following can be summarised.

Liquid phosphate bonded refractory materials, both dense and insulating, have advantages over conventional cement bonded monolithic materials with regards to fast heat up, repair properties, and CO resistance.

These features can lead to a significant reduction in downtime and overall cost savings, which should interest maintenance engineers, or anyone else involved in a process unit shut down.

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