Alkali attack as refractory wear mechanism

The increasing use of alternative fuels in cement production has led to increased wear on kiln refractories. Infiltration of sulphur oxides, alkali sulphates, and chlorides require more frequent attention to the state of the refractory to ensure continued safe operation of the kiln line.

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While alternative fuels in cement manufacturing offer significant advantages, including cost savings and reductions in carbon emissions, they also present unique challenges, particularly their impact on kiln operation and durability.

Understanding wear

Infiltration of SO_x gas, alkali sulphates, and chlorides, commonly introduced via industrial fuels, is known to be detrimental to the structural integrity of magnesia-spinel refractories. SO_x gas reacts with magnesia and, to a lesser extent, lime in the brick to form $MgSO_4$ and $CaSO_4$. These compounds then react with other sulphates and chlorides, most often K_2SO_4 and/or KCL, to form complex compounds. Reactions such as these weaken the bond structure of the basic brick and alter the thermo-physical properties of affected portions of the lining. Consequently, the lining is rendered prone to thermal shock after a loss of coating and damage by thermal stresses induced during kiln rotation.

The effects of alkali and chloride attack on high alumina refractories are similar. Alkali- and chloride-containing gasses penetrate the refractory body, where the gases cool and condense. This wear mechanism is generally present in the lower portion of the preheat tower and at the kiln inlet. In this area of the process line, solids containing high levels of chlorides and sulphides attach themselves to the refractory lining of the inlet housing, riser, lower cyclone, or calciner, creating build-ups and blockages.

At this point, the builds detach due to their own weight or are mechanically removed and fall into the kiln inlet. As these low melting point solids travel down the kiln, vaporise, and are entrained in the kiln exit gases where, once they condense, become attached to the refractory lining again. This cycle results in an enrichment of the volatile compounds (Cl, K_2O, Na_2O, and SO_3). Evaporation and condensation take place, resulting in increased amounts of build-ups and alkali attacks of the refractory.

Vessel damage caused by refractory growth due to alkali penetration and expansive growth phases


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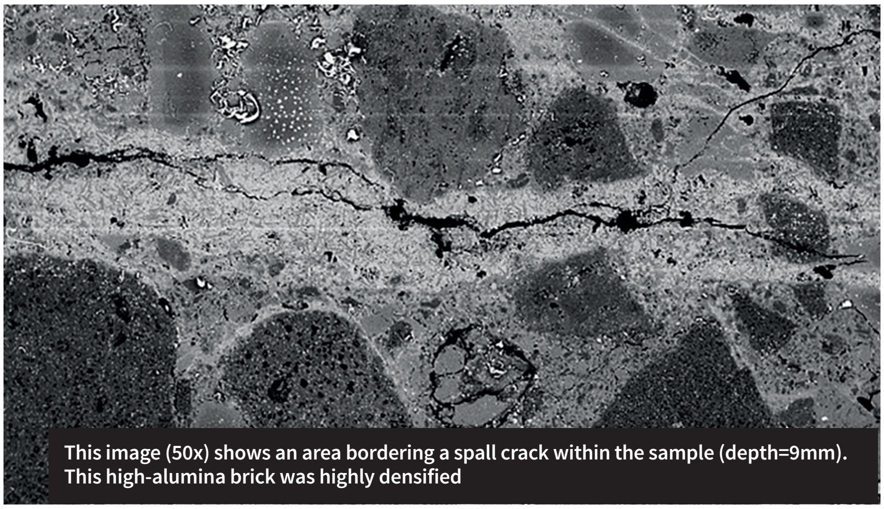
The attack on the high-alumina refractory generally results in densification of the refractory, weakening the refractory bond system and making it prone to thermal shock and spalling. Often, the spalling of refractories is not visible from the hot face surface, which leaves inspectors with a false sense that the refractory, due to its thickness, is satisfactory and can remain in service.

Furthermore, the densification negatively impacts the refractory body's refractoriness, resulting in potentially higher shell temperatures. A dense material, although thick enough once evaluated during a tear-out, does not reduce shell temperatures satisfactorily. The effects could mean added stress on metallic components and increased heat losses.

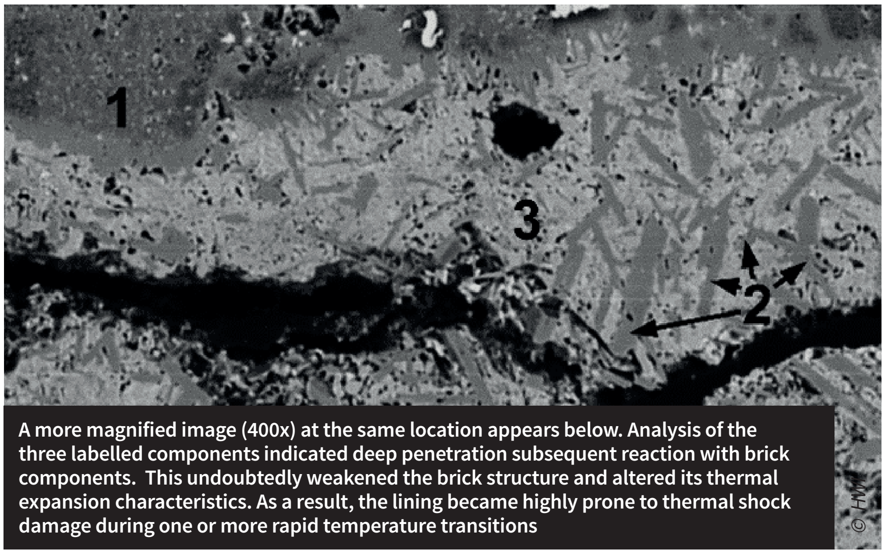
Finally, many of these compounds and phases are expansive and can result in a "bloating" effect on the refractory. Depending on the compounds present, expansion can result in a volumetric increase of up to 30 per cent. This amount of expansion can play havoc on calciners and cyclones. Weld seams and supports are often incapable of containing the pressure of the dimensionally-growing refractory, which can result in cracked weld seams and support beams.

Planning ahead

When faced with the proposition of using alternative fuels for the first time, or increasing the amount currently being used, a good understanding of the current state of the refractories is essential to improving their future state and avoiding unnecessary, unplanned shutdowns. This understanding enables the cement producer to manage its refractory needs from a proactive stance rather than



This image (50x) shows an area bordering a spall crack within the sample (depth=9mm). This high-alumina brick was highly densified



A more magnified image (400x) at the same location appears below. Analysis of the three labelled components indicated deep penetration subsequent reaction with brick components. This undoubtedly weakened the brick structure and altered its thermal expansion characteristics. As a result, the lining became highly prone to thermal shock damage during one or more rapid temperature transitions

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reacting to unforeseen circumstances.

Gaining an understanding of the current state of the refractories should not only include postmortem analysis of refractories as they are removed and replaced, it should also include “half-life” samples. Typically, samples of materials that have failed are analysed to determine the mode of failure. By taking a proactive approach to this methodology one can gain valuable insight into the wear mechanisms at play.

Samples taken and evaluated during their half-service life can provide information that can impact future decisions and highlight accelerated chemical wear of the refractory body. Brick samples can be removed from a ring or course from within a vessel, while monolithic samples can be cut, core drilled, or carefully removed with a hammer. Samples should ideally be full lining thickness with hot face and cold face intact and large enough to perform zonal chemistry on the refractory. Physical tests are difficult to conduct and often provide less insights once a refractory has been in service.

Zonal chemistry analysis can shed light on the story of the refractory. By recognising the compounds present and the depth at which they have penetrated the refractory, the cement producer can begin to plan refractory replacement to avoid unwanted emergency shutdowns to replace refractory. Laboratories will use a series of techniques to get a clear picture of what is happening within the refractory. An x-ray fluorescence (XRF) spectrometer is utilised for chemical analysis, looking for typical compounds and any process-induced compounds such as chlorine, sulphur, or potash (K_2O). An x-ray diffractometer (XRD) will be used to identify the mineralogical phases and phase changes within the sample. It can clearly show whether the mineral phase is major, minor, or trace concentration. Finally, using a scanning electron microscope (SEM) can bring to light things such as the refractory and feedstock bonding and interaction zones, and identify areas of densification within the refractory body.

Transitioning to increased amounts of alternative fuels or alternate raw materials presents many challenges for plant operations, including refractory performance. However, with some forethought and understanding of how refractories behave in alkali-rich environments, decisions can be made to help avoid production interruptions and maintain a smoother transition.

Research-based support

As the largest supplier of refractory products and services in the United States with a history of more than 150 years, HWI is home to North America’s largest refractory industry research facility. Its deep network of technology specialists and application engineers provides a range of products, services, insights, and technical support to many of North America’s leading cement producers. As part of Calderys, HWI can offer an extended portfolio for existing customers, and Calderys’ global customers benefit from more products, knowledge transfer, and research and analytics capabilities. This evolution to greater reach is particularly significant in supporting the increasing energy transition needs of the cement industry globally.

As cement plant operators transition from traditional to alternative fuels, new and perhaps unusual wear mechanisms can impact existing refractory linings. When this situation arose with a large North American cement manufacturing customer, the HWI team provided an understanding of these wear mechanisms and helped the customer effectively plan to stay ahead of these during the company’s energy transitions. This knowledge and the steps taken to address these issues became vital to optimising refractory linings and meeting production goals.

For the company’s kiln engineers and operators, transitioning to alternative fuels (in this case, tyres and car fluff) became a daunting task from a process control point of view. As they transitioned to alternative fuels, they recognised that the increased wear potential on refractories could result in a negative payback through poor reliability. With deep refractory knowledge, HWI was able to help the customer more fully recognise and identify the effects of chlorides, sulphides and alkalis on refractories. This expertise allowed the manufacturer to ease negative impacts during initial trials and as they increased current quantities of alternative fuels. ■