Dear Friends,

We have just stepped on to a new financial year that seems quite eventful. It’s already very hot all around us, be it weather or politics. By the time we communicate next, hopefully the monsoons should cool down the climate and the political dust settled down too.

Kerneos has crossed another milestone on 26th March 2014 in our century old history. Kerneos ownership has changed hands from Materis Group to Astorg Partners, a French Investment Fund. During the past 13 years as part of the Materis Group, Kerneos aggressively expanded internationally, intensified its R&D efforts to bring new products to the market and to secure its supplies of raw materials through acquisition of a majority stake in the Greek bauxite producer Elmin.

"Working alongside us, the Astorg investment fund will be instrumental in helping us deliver continued growth. All of us here at Kerneos are excited at the opening of this new era with Astorg, a highly motivated and agile shareholder that shares our core values and with a decision-making centre close to Kerneos: the key elements of our growth strategy will be new geographical horizons and innovative new products for our customers," said Jean-Marc BIANCHI, Kerneos CEO.

"Thanks to the qualities of its leadership team, the historic shareholders Lafarge and then Materis, and also to the staunch loyalty of generations of employees, Kerneos has won its place as world leader in its sector. We are full of admiration for this outstanding business success story. We are only too well aware of the legacy handed on to us, and of our responsibility to perpetuate the culture of innovation, commitment to quality and respect for stakeholders for which Kerneos is known. Now with fresh room for manoeuvre, Kerneos is more than ever inspired by a will to win, which we will unhesitatingly support." said Thierry TIMSIT, Astorg Managing Partner.

I would like to personally thank each one of our valued customers for their continued and unstinting support over the years. You have propelled Kerneos to global leadership and recognition. Thanks again.

Kerneos was the Platinum Sponsor of the recently concluded IREFCON 2014 and it was indeed gratifying to receive a steady stream of enthusiastic visitors / customers to our booth at the IREFCON exhibition. We also made a couple of technical presentations during the event which received critical acclaim.

Safety has the highest priority in whatever we do at Kerneos and to share related information, we are introducing a new section, "Safety Wall" in SECAR® Gazette. Further, this issue carries an article on “Degradation of structure of calcium aluminate cement based castables in ambient condition” besides other regular columns. We welcome your comments and feedback.

Segi P. Idicula, Managing Director Kerneos India & Middle East Operations

Castable structures are sometimes reported to degrade and the reasons are not always very obvious. In this article, several such degradation routes and their mechanisms are discussed. The necessary conditions for such structure deterioration and possible counter measures are detailed.

(Full Paper on Page 3)
INDIAN STEEL INDUSTRY NEEDS TO ADAPT LATEST TECHNOLOGIES

With open trade policy for steel, Indian steel industry faces global competition, hence to remain competitive and profitable, it has to adapt latest and efficient technologies. Indian steel industry today is fragmented and a mix of large number of small to large scale producers. Use of steel making technologies varies among different steel making units. With overall low level of advanced technological exposure, Indian steel industry faces issues of quality, efficiency, hazards and process standards. This leaves a broad scope for process improvement through introduction of latest and efficient technology. Using of latest technologies can boost steel companies business with advantages of scale, quality, productivity, safety and higher margins. Also with development and use of technologies suitable for steel making using iron ore fines and low grade Indian coal, Indian steel industry can have advantage of raw material security and sustainability. Following issues can be addressed efficiently through technological exposure towards using of Indian raw materials and steel making process:

**Raw Material Supply**
- Low mechanization level and latest technological input towards mining and processing of raw materials.
- Inadequate facility for use of iron ore fines using palletisation and sintering technology.
- Lack of coal processing and washing technology to make higher use of low grade Indian coal.
- Inadequate facility towards raw material loading and transportation.
- Lack of facility for use of raw material rejects.

**Steel Making Process**
- Most of the steel making technologies are old and less efficient.
- Expenditure on research and development is considerably low.
- Present steel making technologies are not suitable for Indian iron ore fines and high ash coal.
- Very few plants are having facility to make complex steel products.

In gasifiers carbon feedstock such as lignite reacts with oxygen and water to produce a synthetic gas between 1300 to 1600°C under pressure (20-40 Bar) in reducing atmosphere. The refractory lining of gasifier must protect the gasifier shell from high temperature and pressure and withstand thermal shock, erosion of solid carbon particles, creep and corrosion against reactive gasifier slag high in oxides of alkali, alkaline earth and sulphur. It has been found that addition of MA-Spinel cement (CMA 72) to spinel-rich alumina castables improves corrosion resistance against molten slag remarkably.

**Tech Edge**

**Technical News:**
The following publication last year in the *Journal of European Ceramic Society* discussed the effect of spinel and cement of spinel-containing refractory castables on their thermo-mechanical properties, phase formation and corrosion resistance against attack by molten coal gasification slag.

Improved spinel-containing refractory castables for slagging gasifiers.

P. Gehre, C.G. Aneziris, D. Veres, C. Parr, H. Fryda, M. Neuroth


Kerneos Corner

**The new Kerneos R&D center in Teda, China to go operational soon!**

This is a significant change as we will move from a small local application laboratory towards a more globally acting R&D center for the Refractory market and with a significant upgrade of capabilities for the Construction market in China and Asia-Pacific. The new laboratory, together and in very close cooperation with KRTC in France, will become a fully integrated part of the global Kerneos R&D network. It will also service as Application training and Seminar Center for customers and applicators.

The 15th of May 2014 is an important day as it will mark the official opening of the new Kerneos Research Center Asia (KRCA). On the following day a seminar will be organized with presentations by Kerneos and external experts from the Chinese Refractory & Construction industry.
DEGRADATION OF STRUCTURE OF CALCIUM ALUMINATE CEMENT BASED CASTABLES IN AMBIENT CONDITION

G. Bhattacharya*, C. Wöhrmeyer and C. Parr, *Kerneos, Kolkata, India

Introduction:
Alkalis are known for their negative effects on high temperature properties of castables. However, their influence on destruction on castable structure is discussed less frequently. The high temperature property requirement of a castable for some refractory applications may allow limited tolerance of alkali use. However, it has also to be tested for structural durability of the castable in ambient condition. With the increased use of alternative raw materials often in combination with alkali-containing additives the risk of degradation on structure may increase. This paper discusses different types of structural degradation, their mechanism, influencing factors and possible preventive measures.

Alkali efflorescence of castables:
Instances of sodium efflorescence are not uncommon, although their severity can vary leading to effects from cosmetic to destructive. Here soluble alkali (sodium oxide or salt) co-exists with water, leading to diffusion of sodium ions in the solution, reacting with aerial carbon dioxide to form sodium carbonate, which reacts with calcium aluminate hydrates and form calcium carbonate, shown as follows:

\[ \text{Na}_2\text{O} + \text{H}_2\text{O} \leftrightarrow 2\text{Na}^+ + 2\text{OH}^- \]

\[ 2\text{Na}^+ + 2\text{OH}^- + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O} \]

\[ \text{Na}_2\text{CO}_3 + \text{CAH}_x \rightarrow \text{CaCO}_3 + \text{Na}_2\text{O} \cdot \text{AI}_2\text{O}_3 + (10-x)\text{H}_2\text{O} \]

Sodium carbonate is regenerated by reaction of sodium aluminate with carbon dioxide.

\[ \text{CO}_2 + \text{Na}_2\text{O} \cdot \text{AI}_2\text{O}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{AI}_2\text{O}_3 \]

The overall reaction depends on the nature of calcium aluminate hydrate as shown in the following three reactions for CAHx, C4AH8 and C3AH6. The end products of the reactions are the same – sodium and calcium carbonate and alumina gel [1].

\[ 2\text{CO}_2 + 2\text{NaOH} + \text{CAH}_x \rightarrow \text{Na}_2\text{CO}_3 + \text{AI}_2\text{O}_3 \cdot x\text{H}_2\text{O} + \text{CaCO}_3 + (11-x)\text{H}_2\text{O} \]

\[ 3\text{CO}_2 + 2\text{NaOH} + \text{C}_4\text{AH}_8 \rightarrow \text{Na}_2\text{CO}_3 + \text{AI}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 2\text{CaCO}_3 + (9-x)\text{H}_2\text{O} \]

\[ 4\text{CO}_2 + 2\text{NaOH} + \text{C}_3\text{AH}_6 \rightarrow \text{Na}_2\text{CO}_3 + \text{AI}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 3\text{CaCO}_3 + (7-x)\text{H}_2\text{O} \]

Although the equations indicate that sodium carbonate is present in anhydrinous form, in reality it is present with 1, 7 or 10 molecules of water of crystallisation, which varies widely in terms of density and therefore, their effects on destruction of castable structure can be quite different. Na2CO3, 7H2O and Na2CO3, 10H2O, depending on their quantity and location can destroy the castable structure (Table 1), whereas Na2CO3, H2O can only cause surface efflorescence without affecting the structure, although it may lead to poor aesthetics. As the reactions indicate, efflorescence requires carbon dioxide and a source of alkali. The extent of reaction depends on the amount of soluble alkali present in the wet mix. Water moves along the moisture gradient taking alkali to the surface of evaporation, whereas carbon dioxide diffuses into castable. A fine white powder of carbonates deposited on the surface is called efflorescence (Figure 1), formation of which is facilitated by with high % of sodium based additive together with highly porous structure due to high casting water addition.

![Figure 1: Example of non-destructive sodium efflorescence arising from a conventional concrete with 80% chamotte, 20% SECAR® 80 with sodium based set modifier and 12% water](image)

**Table 1: Hydrated sodium carbonate salts, their specific gravities and effects on destruction of castable structure**

<table>
<thead>
<tr>
<th>Increasing risk of destructive efflorescence</th>
<th>Specific Gravity</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2CO3 - H2O</td>
<td>2.26</td>
<td>Surface efflorescence only</td>
</tr>
<tr>
<td>Na2CO3 - 7H2O</td>
<td>1.51</td>
<td>Rupture and bursting from within castable (depending upon the quantity and location)</td>
</tr>
<tr>
<td>Na2CO3 - 10H2O</td>
<td>1.44</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2: Condition for destructive efflorescence and their results**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble alkalis from: Aggregates (eg. Andalusite, pyrophyllite)</td>
<td>Source of highly mobile alkali cations</td>
</tr>
<tr>
<td>Casting water</td>
<td></td>
</tr>
<tr>
<td>Additives</td>
<td></td>
</tr>
<tr>
<td>Cold weather</td>
<td>Favours higher hydrates (CAHx) due to more reactivity and also when converts to C3AH6 creates porosity aiding efflorescence</td>
</tr>
<tr>
<td>Dense &amp; deflocculated castables</td>
<td>Low permeability and therefore diffusion is more difficult, hinders efflorescence</td>
</tr>
</tbody>
</table>

**Surface efflorescence after:**
- Air curing for 1 week
- Immersion in water for 24h

**Phases Detected:**
- K2CO3 . 1.5 H2O
- AH3 (gibbsite)
- CaCO3 . 7 H2O
- Na2CO3 - H2O 2.26 Surface efflorescence only
- Na2CO3 - 10H2O 1.44
- Na2CO3 . 7H2O 1.51
- Na2CO3 - 10H2O 1.44

**Carbonation within castables**
Carbonation of castables can be broadly categorised in two types - direct carbonation - in the absence of alkalis and carbonation in presence of alkalis, which is also called alkaline hydrolysis.

**Direct carbonation in absence of alkalis**
Aerial carbon dioxide reacts with calcium aluminate hydrates to form carbonates such as mono-carbo aluminate (C2ACaCO3, 11H2O) and calcium carbonate. Mono-carbo aluminate fills the porosity increasing surface hardness and mechanical strength. The rate and extent of carbonation depends on several factors [2]:
- Type of calcium aluminate C4AH8, C2AH8, C3AH6
- Humidity/moisture accelerates carbonation
- Type of castable: light weight castable>dense due to presence of higher cement, water and porosity

**Carbonation catalysed by alkalis (Alkaline hydrolysis)**
The presence of Na+ increases the solubility of carbon dioxide in solution (CO32-), which leads to carbonation leading to surface degradation and peeling of the castable from the exterior and eventually the destruction of calcium aluminate hydrates [3].

**Influencing conditions for destructive efflorescence** are listed in the following table (Table 2).

**Figure 1**: Example of non-destructive sodium efflorescence arising from a conventional concrete with 80% chamotte, 20% SECAR® 80 with sodium based set modifier and 12% water
The catalysing role of Na\(^+\) ion can be explained by the following schemes of reactions:

\[
\begin{align*}
\text{Na}_2\text{O} + \text{H}_2\text{O} & \rightleftharpoons 2\text{Na}^+ + 2\text{OH}^- \\
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}
\end{align*}
\]

\[
\begin{align*}
2\text{Na}^+ + \text{CO}_3^{2-} + \text{CaO.Al}_2\text{O}_3\cdot10\text{H}_2\text{O} & \rightarrow \text{CaCO}_3 + 2\text{Na}^+ + 2\text{AI} (\text{OH})_3 + 8\text{H}_2\text{O} \\
2\text{Na}^+ + 2\text{AI} (\text{OH})_3 + \text{CO}_2 + 3\text{H}_2\text{O} & \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} + 2\text{AI} (\text{OH})_3 + 7\text{H}_2\text{O} \\
\text{CO}_2 + \text{CaO.Al}_2\text{O}_3\cdot10\text{H}_2\text{O} & \rightarrow \text{CaCO}_3 + 2\text{AI} (\text{OH})_3 + 7\text{H}_2\text{O}
\end{align*}
\]

Calcium carbonate may be formed as aragonite, vaterite or calcite, whereas aluminium hydroxide may be as bayerite, nordstrandite or gibbsite.

The necessary conditions of reaction may be listed as:

- Alkalies
- Carbon dioxide
- Humidity - including long periods between mould stripping and casting
- CAC type

Internal Lafarge studies (1970-1983) with Ciment Fondu\(^\circ\) concretes have shown the dominant effect of porosity. A clear relationship between the porosity and water/cement ratio was identified (Figure 3).

Since alkalies play a catalysing role their presence is a precondition for this type of carbonation reaction. Internal studies indicate that Na\(_2\)O is more detrimental than K\(_2\)O. Li salts do not appear to have the same negative effect, as hydrate radius of Li is too big for effective diffusion due to low mobility for Li\(^+\).

Atmospheric as well as pore humidity accelerate alkaline hydrolysis. The following (Figure 4) is an example of an insulating castable based upon a medium alumina cement (bauxite cement) kept under different humidity conditions. High humidity with sample 2 (relative humidity 100\%) leads to significantly more carbonation than sample 1 kept at low humidity (relative humidity 50\%). Analysis of sample 2 shows formation of calcite (35\%), vaterite (10\%), bayerite (12\%), nordstrandite (18\%) and Na\(_2\)CO\(_3\)\_12\_H\(_2\)O (1.4\%).

Different alumina cement types have different susceptibility to follow certain course of reaction. Bauxite cements favour carbonation via alkaline hydrolysis, whereas higher alumina cements generally tend to show carbonation of alkali. Free lime accelerates the reaction.

The following measures are found to limit alkaline hydrolysis:

<table>
<thead>
<tr>
<th>Action</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prefiring/drying (100-400\°C) to ensure conversion of hydrates</td>
<td>Delays alkaline hydrolysis</td>
</tr>
<tr>
<td>Surface sealing by</td>
<td></td>
</tr>
</tbody>
</table>
- Coating
- Organic membrane coating
- Reduce transport mechanism by using cellulose
- Rapid hardening | Delays alkaline hydrolysis |
| Alkali ‘fixing’ | 
- Removal of soluble alkalies by washing and / or firing of aggregates
- ‘Pozzolonic’ effect using high surface reactive fillers eg. alumina or clean fume silica or metakaolin
- Addition of a complexing additive | Inhibits alkaline hydrolysis |

**Conclusion:**

Different types of structural degradation have varying degree of severity from cosmetic to destructive. In most cases, alkali together with water/humidity plays a major role in accelerating this degradation. The end products are generally carbonates. These different types of structure degradation can be limited by appropriate choice of raw materials, water addition level, curing conditions of castable and early drying.

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