Dear Friends,

The economic and industrial scenario in the country does not look very bright in the short term though the Government is trying out various measures to revive the situation. Sharp depreciation of Rupee has added to the woes of the industrial community that depends on imported high quality raw materials; leave aside the country’s obsession with gold and hunger for oil. Despite passing through such a challenging economic scenario, it was pleasing to see an overwhelming response to the one day workshop on “Calcium Aluminate Technology for New Generation Monolithics” jointly organized by Kerneos India and the Gujarat Chapter of the Indian Ceramic Society on Tuesday, 9th April 2013 at Ahmedabad.

The workshop was inaugurated by Mr. Rajiv Bhatnagar, Director - Hazira Facility, Essar Steel. Technical sessions that followed evinced keen interest and lively dialogue between the gathered delegates from more than 50 organizations. You will find further details elsewhere in this edition.

Kerneos is committed to continuing the process of engagement with the customers. In line with this global policy, Kerneos India and CGCRI Kolkata have planned to jointly organize another seminar on 12th and 13th November 2013 on “Advances in Refractory Raw Materials and Monolithics” at the CGCRI complex in Kolkata. You will get the first circular of this seminar very soon, if not received already. Please block your diary for attending and active participation in this seminar. The need for sourcing quality raw materials and finding alternate raw materials have assumed so much significance today that the right strategy in securing raw materials can immensely impact the bottom line of highly price sensitive businesses like that of refractories.

This edition of Secar Gazette shares an article on “Effect of additives on placing and hardening properties of castables” besides the usual Market Pulse, Technical Tips and Kerneos Corner.

Please feel free to get in touch with us with your comments or request for additional information on topics that are in our domain of expertise.

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

The additives constitute a vital part of the castable matrix. They influence castable placing and hardening properties directly and the effect can be significant even with very little addition. However, the additives are often specific to castable types, particularly the dispersing additives (such as phosphates, polyacrylate, polycarboxylate ether etc.) have strong specificity on the filler type (silica fume or alumina). Optimisation of additives in terms of their choice and dose is essential to get desired castable properties. This article discusses the role of different additives in controlling castable properties.

(Full Paper on Page 3)
Market Pulse

FREE-FALL OF INR, HITS RECORD LOW VS US$  

The rupee’s fall is the latest blow to the stuttering growth story of Asia’s third largest economy, which has been beset by sharply slower growth, worsening public finances and political turmoil.

Asian currencies are depreciating led by the Yen. Since most Asian economies are competing for the same export markets and the view on the US dollar is positive due to signs of revival there, currencies such as the South Korean Won and Taiwanese Dollar have also fallen. The Indian rupee already caught in the tsunami of Asian currencies’ depreciation.

The rupee is down by more than 13% in July beginning compared to May beginning, despite record foreign fund flows as the country imported far more than what it exported. That pushed the current account deficit - the excess of consumption overseas than earnings - to a record high of 6.7% of the gross domestic product. The rupee ended at 60.35 on June 28, it is all time low as Oanda data shows.

Analysts say that while other emerging market currencies have been affected by the dollar’s increasing strength, the rupee is particularly hard hit due to the country’s troubled public finances and string of corruption scandals.

The widening of India’s current account deficit (CAD) — the broadest trade measure — to almost 5% of gross domestic product in the last financial year has also weighed on the rupee. India’s CAD stood at 6.7% of its GDP in the October-to-December quarter. India’s gross domestic product (GDP) grew 5% year-on-year in the past fiscal year, which ended March 31. The growth rate was lowest in a decade. There have been loud calls from business for an interest rate cut to spur the economy.

The depreciation of the rupee could add to the government’s problems of financing a widening current account deficit (CAD), analysts said. The negative real interest rates worsened the CAD as people imported gold as a hedge.

A sticky inflation, as supply failed to keep pace with the demand induced by government splurge on welfare and subsidies on fuel, has made the economy fragile. The weaker currency makes imports costlier, especially of foreign oil on which India heavily relies, and will fuel already high consumer inflation.

Foreign exchange traders reported that there is no sign of the Reserve Bank of India (RBI) intervening in the currency market to support the beleaguered rupee. Analysts say the central bank cannot intervene heavily to buttress the currency as it must retain enough foreign reserves for imports.

Kerneos Corner

Kerneos will participate in the 12th Biennial worldwide congress on refractories - UNITECR 2013 - Unified International Technical Conference on Refractories to be held between 10-13 September this year at the Fairmont Empress and Victoria Conference Centre in Victoria, British Columbia, Canada. The following technical presentations have been planned to be delivered by Kerneos:

**WEDNESDAY, SEPTEMBER 11, 2013**  
**Session:** Advanced Installation Techniques and Equipment  
11:40 AM - 12:00 PM; Location: Sidney  
Title: The Next Generation of Monolithic Application Technology: Continuous Mixing of Low Cement Castables for Wet Shotcreting,  
Authors: Josh Pelletier; Charles Alt; Chris Parr; Jim Farrell;  
**Session:** Monolithics II  
1:40 PM - 2:00 PM; Location: Lecture Theatre:  
Title: Novel Calcium Magnesium Aluminate bonded castables for steel and foundry ladles,  
Authors: Christoph Wöhkmeyer; Jean-Michel Auvray; Bin Li; Herve Fryda; Magali Szepizdyn; Dirk Poerzgen; Nan Li; Wen Yan  

**FRIDAY, SEPTEMBER 12, 2013**  
**Session:** Advanced Testing of Refractories II  
2:40 PM - 3:00 PM; Location: Oak Bay  
Title: Dry out simulation of castables containing calcium aluminate cement under hydrothermal conditions,  
Authors: Carl Zetterstrom; Jean-Michel Auvray; Herve Fryda; Magali Szepizdyn; Goutam Bhattacharya; Chris Parr  

**Kerneos Corner**  
Kerneos India and the Indian Ceramic Society, Gujarat Chapter jointly organised a Workshop on Calcium Aluminate Technology for New Generation Monolithics at Ahmedabad on 9th April, 2013. The workshop was inaugurated by Mr. Rajvikumar Bhatnagar, Director Hazira Facility, Essar Steel.  

The workshop focused on:  
- The role of calcium aluminate cement to obtain the desired performance of castables  
- Optimisation of castable compositions with calcium aluminate cements adapted for Indian climate, installation and cost environment  
- Quality of calcium aluminate cements and what it means for castable manufacturers  
- Innovations in calcium aluminate cements for corrosion resistance and anti-aging

Dr.S.N. Misra, Sr. Principal Scientist and Scientist-in-Charge, CGCRI, Naroda Centre, Ahmedabad welcomed the gathering comprising 130 plus delegates from over 50 companies. Mr. Segi P Idicula-MD of Kerneos India, delivered the key note address. Mr. Thierry Fradin-Executive Vice President of Kerneos SA, Mr. Benoit Valdelievre-Sr. Technical Director of Kerneos SA and Dr. Goutam Bhattacharya-Technical Developer of Kerneos India, Mr. Prashanta Dutta-Regional Manager, Kerneos India, presented papers on technology, quality and innovations.

The sessions were interactive, lively and vibrant.
EFFECT OF ADDITIVES ON PLACING AND HARDENING PROPERTIES OF CASTABLES

Introduction:

The additives are small additions to the castable composition, which can influence the placing and hardening properties of the castables to a big extent. The additives can be accelerators or retarders, which can directly modify the cement hydration reaction kinetics. The other additive type, which is essential to fluidify the fine particles and ensure satisfactory placing properties with low water demand for low cement or ultra low cement castables (also called deflocculated castables), is the dispersing or fluidifying additive. The dispersing additives (deflocculants) support the development of initial flow of castables, whereas the accelerator and retarders control the working time and influence the hardening profile of castables. A list of common additives is shown in Table 1 [1]. Although the additive dosage is very low, its effect on the placing and hardening properties can be remarkable. Hence, it is essential to mix the additives homogeneously in the castable mix. It is also essential to ensure stability of additives during their use in castables. Many additives are strongly hygroscopic and they tend to lose their effectiveness (called aging) with time, particularly in warm and humid conditions, which prevails in most part of India for a considerable duration. Additives need to be stored carefully to prevent moisture ingress before they are added to the castable mix and the castable drymix must be packed and stored appropriately to limit aging as much as possible. It is always better to use high purity additives, which are commonly called chemical grades, than the low purity commercial grades. Commercial grades often vary in terms of their impurity levels leading to inconsistency in castable properties. In this article the roles of different additives are discussed.

Common additives and their impact on CAC hydration:

Calcium aluminate cement hydration takes place in 3 steps – dissolution, nucleation and massive precipitation of calcium aluminate hydrates. The additives may influence these steps, chemically or physically. The chemical effect is shown in Figure 1. The example of chemical acceleration effect is the addition of time which increases the concentration of Ca⁺⁺ ions and thus enhances the nucleation and precipitation. Li⁺⁺ salts exert very strong accelerating effect even with very low dose (Figure 2). Li⁺⁺ ions accelerate the nucleation of Al₂O₃·3H₂O (AH₃) by providing suitable surface for nucleation. Nucleation being the slow step in cement hydration reaction, the cement hydration gets accelerated rapidly with Li salt addition.

Most common retarders for calcium aluminate cements are carboxylic acid based small molecules (sodium citrate, citric acid, sodium gluconate etc.). They can cause large increase in time to massive precipitation with increase of their concentration (Figure 3). These retarders create a film of a gel-containing calcium, aluminium and citrate on the cement grain surface blocking dissolution of cement.

Fluidifying additive for silica fume-containing deflocculated castables:

The most common dispersants for silica fume-containing low cement castables are phosphates, such as sodium hexa-metaphosphate (SHMP) and sodium tri-polyphosphate (STPP). The effect of different phosphates on flow and flow decay with time are shown with a model silica fume-containing low cement castable composition (Table 2) with addition levels of 0.1% (Figure 4) and 0.2% (Figure 5). The setting and hardening properties (exo peak times, set time by cup testing and CCS after 6h) are listed in Table 3 for 0.1% phosphate addition and Table 4 for 0.2% phosphate addition. The initial flow values were not very different for both 0.1% and 0.2% phosphate addition levels. However, additive C (SHMP) partly hydrolyses and becomes sticky and difficult to disperse during dry mixing. The STPP based additives (A, B, D and E) showed rapid flow decay, relatively quicker setting and strength development when their addition level was increased from 0.1% to 0.2%.

<table>
<thead>
<tr>
<th>Table 1: List of different additives commonly used in castables</th>
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<tbody>
<tr>
<td>Accelerator</td>
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<tr>
<td>Calcium formate</td>
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<tr>
<td>Lithium salts (LiOH, Li₂CO₃)</td>
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<tr>
<td>Alkaline salts</td>
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<tr>
<td>Sodium aluminate</td>
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<tr>
<td>Ordinary Portland cement</td>
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<tr>
<td>Lewis bases: Ca(OH)₂, KOH</td>
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<tr>
<td>Sodium silicate</td>
</tr>
<tr>
<td>CaSO₄/plaster/gypsum</td>
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Figure 1: The steps of chemical effect of additives on cement hydration

Figure 2: Set time of EN 14670 mortar (27% Secar® 71, 73% sand and w/c = 0.4) at 20°C as a function of lithium carbonate/cement addition.

Figure 3: Set time of Secar® 71 (W/C=5) as a function of tri-sodium citrate addition

Figure 4: Set time of Secar® 68 V (5.0%) (Table 2) with addition levels of 0.1% (Figure 3).

<table>
<thead>
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<th>Table 2: Model composition of a silica fume-containing low cement castable (LCC) for testing placing and hardening properties of different phosphates</th>
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<tbody>
<tr>
<td>Raw materials</td>
</tr>
<tr>
<td>Calcined Gujarat Bauxite -3-5mm</td>
</tr>
<tr>
<td>Calcined Gujarat Bauxite 1-3mm</td>
</tr>
<tr>
<td>Calcined Gujarat Bauxite 0-1mm</td>
</tr>
<tr>
<td>Calcined Gujarat Bauxite 0-170mesh</td>
</tr>
<tr>
<td>HGRM 30</td>
</tr>
<tr>
<td>Micrasilica 955U</td>
</tr>
<tr>
<td>SECAR® 68 V</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>Deflocculant</td>
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Fluidifying additive for silica fume free pure alumina castables:

Phosphates are not suitable additives for silica fume free pure alumina castables. Substitution of silica fume with reactive alumina in polyphosphate deflocculated castables results in rapid flow decay and very short working time. The dispersion mechanism in silica fume-containing castables is through electrostatic repulsion [2], which is affected severely by variation of ionic activity and pH of the solution, eg. cement dissolution. For pure alumina castables the suitable dispersants include polyacrylate and polycarboxylate ether (PCE) based additives, which deflocculates by electrostatic repulsion and thus remain unaffected by ionic activity change. PCE based additives have stronger activity than the polycrylates. Figure 6 shows the vibration flow of a model pure alumina castable composition (Table 5) as a function of water addition for two deflocculant types – PCE (Peramin®AL200 and AL 300) and polycrylate. The latter shows lower flow for all water addition levels than the former. PCE based additive could develop appreciable flow with very low water addition (3.5%) [3], whereas polyacrylate based additive could achieve similar flow with 4.5% water. The effect of PCE type additives on LCC systems can be very specific. The backbone with carboxylate anionic charge introduces electrostatic repulsion between particles in a liquid phase, whereas the grafted side chains (polyethylene glycol - PEG) with anchors at the backbone induce steric repulsion between particles. Increasing the number of carboxylate groups gives better flow, however, the setting gets prolonged, whereas increasing the number of PEG groups causes higher dispersion efficiency, which means lower dose requirement to obtain similar fluidity and thus the effect on setting is relatively less.

Conclusion:

Since a small dose of additive develops pronounced effect on castable placing and hardening properties, it is important to use a stable additive source and store the additives to avoid aging. The dispersing additive choice depends on the type of castable composition – whether it is silica fume-containing or silica fume-free pure alumina castable. The phosphates, such as sodium hexametaphosphate and sodium tripolyphosphate are suitable for silica fume-containing or silica fume-free pure alumina castable. The polycrylates and polycarboxylate ether based additives are used for pure alumina castables. The additive dose also influences the castable placing properties. Accelerators and retarders change the cement hydration kinetics leading to alteration of castable placing and hardening properties. Castable placing and hardening properties are optimised to have good fluidity with low water addition, sufficiently long working time to complete casting and a rapid hardening for quick demolding using clever use of combination of dispersing additive and accelerator and/or retarder.

References:

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