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Kerneos Calcium, ----- Nancy Bunt
Aluminate Cement Inc. ----- Charles Alt

October 31, 2007
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Subject: Alkali Hydrolysis (Sometimes referred to as Carbonation)

Dear Ms. Bunt and Gentlemen:

Broach has experienced what we feel is an unacceptable increase in Alkali Hydrolysis, in our API refinery heater insulating refractory castable linings. We have spent a great deal of time agonizing as to why we have experienced the significant increase in the last 8-10 years, out of our 47 years of applying gun mix insulating castable refractories.

One of our observations is that the failures occur in proprietary bag mixes where polypropylene fibers are present, and it seems more prolific when castable sealer is applied to prevent the absorption of atmospheric CO2!

Our suspicions regarding the causes of the increased occurrences of Alkali Hydrolysis are based upon our theory of CO2 being internally generated within the castable refractory, rather than by atmospheric absorption; or by polypropylene fibers reacting in the first stage of the Alkali Hydrolysis reaction equation. **We have zeroed in on these theories, due to the number of failures we have had with sealers applied.** We feel confident that the sealers prevented atmospheric CO2 from entering into the equation for Alkali Hydrolysis; leaving only internally generated CO2; or a new first stage Alkali Hydrolysis reaction as the source.

We would like to get others, like yourselves, involved so this mystery can be solved.

Our main suspicions are as follows, in order of greatest suspicion:

1. Polypropylene Fibers

The increased use of polypropylene fibers in the cement mix. These fibers are added to reduce the chance of spalling the castable during the first initial heating of the castable lining. In all cases that we have seen Alkali Hydrolysis, our shop indicated they saw polypropylene fibers in the bag mixes. It is our understanding that these fibers are nearly always mixed into the ingredients of high temperature proprietary bag mix castable cement during packaging.

Polypropylene is organic matter composed of Carbon and Hydrogen (C3 H6). These fibers could be decomposing into CO2 internally inside the castable lining, or reacting directly in the first stage reaction in Alkali Hydrolysis as follows:



(Refer to the attached Babcock & Wilcox Tech Notes.)

If decomposition into CO2 is the mechanism, then decomposition of the organic matter into CO2 could be happening at an accelerated pace because of the application of sealers used to keep atmospheric CO2 out. The reasoning behind this theory is that the sealer traps the humidity and water inside the castable, making a nice environment for rotting and decomposition of organic matter.

2. Mold Or Mildew

Aggregate with excessive mold or mildew (more than ever see in the past).

3. Soluble Alkalis Or Salts

Aggregate, or calcium aluminate cement, with excessive soluble alkali(s) or salts (more than normally seen in the past).

It seems that accelerated use of polypropylene fibers and accelerated use of castable sealer happened simultaneously with our observation of increased Alkali Hydrolysis; I would welcome feedback and alternate theories that could explain the sudden increase.

Sincerely,

THE G. C. BROACH COMPANY

Brian Broach

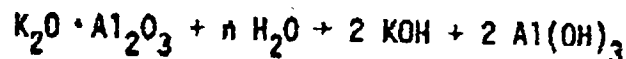
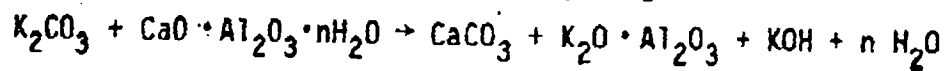
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AUGUST 16, 1985

THE PHENOMENON OF ALKALI HYDROLYSIS IN REFRACTORY CONCRETES

When refractory concretes are left exposed in their "as cast" or "as gunned" state for more than a few weeks a thin layer of loosely held material can form on the surface of the lining eventually reducing the effective thickness of the lining. This phenomenon is known as carbonation - or more appropriately - alkali hydrolysis.

The alkali hydrolysis reaction is a very complex reaction which can be controlled if properly understood. In calcium aluminate concretes the phenomenon of alkaline hydrolysis is due to the cyclic reaction in which the alkalis (specifically potassium-K) act as a catalyst in the following reactions:



As you can see by following the chemical reaction progression, there is regeneration of the alkali hydroxide which can be carbonated once more and thereby bring about the decomposition of further calcium aluminate hydrate (calcium aluminate cements).

This cyclic progression will continue until all the calcium aluminate hydrate is consumed. The end result is complete loss of cohesion in the hydrated cement paste.

It has been found that alkaline hydrolysis leads to the formation of:

CaCO_3 in the form of aragonite or vaterite, which transforms into calcite.

$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (alumina trihydrate) in the form of bayerite, which also transforms towards the stable form, gibbsite.

The phenomenon of alkaline hydrolysis can make its appearance only if the following four conditions occur simultaneously:

1. Presence of alkalis
2. Presence of water
3. Presence of CO_2
4. High level of porosity in the cement paste.

These four conditions must be met for alkali hydrolysis to occur. If any one of these conditions are not met then the chemical reaction will not occur.

Several things can be done to reduce the alkali hydrolysis reaction:

1. Insure that the concrete is made with low water-cement ratio.
2. Place a good curing compound to seal the concrete minimizing atmospheric CO₂ transport into the concrete.
3. Remove the water by drying out the castable at approximately 1200°F.

The chemical reaction does not care where the alkalies come from - water, aggregate or cement - the end point will be the same. The key to using calcium aluminate bonded light weight castable is to understand the controlling conditions and promote an environment which would deter the alkali hydrolysis reaction.

K.J. Moody/A.C. Ferguson