ALKALI ATTACK ON CEMENT PLANT REFRACTORIES,
-AN ALTERNATIVE PERSPECTIVE.

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INTRODUCTION

This problem has been around a long time, but has certainly been exacerbated by the arrival of high efficiency coolers such as the IKN. Conventional alumino-silicate refractories, especially castables have proven unable to cope with the increased aggressiveness of the alkali attack, which now occurs in areas of the process train previously unaffected. In Australia, the CSIRO, in cooperation with a major local cement plant, has devised a laboratory test which seeks to quantify the effect of potassium salts on a range of refractories which may be used in various effected areas of the plant, e.g. precalciner, cooler, dust settler, kiln hood etc. These tests confirmed that there are other materials available, outside the conventional alumino-silicate range, which should provide resistance against this type of attack(1).

THE PROBLEM WITH POTASSIUM.

This issue has been well discussed in recent years, (2) and the effect of Potassium salts well documented. The reactions of Potassium with Mullite seem to be the main issue, since the formation of feldspars (Leucite etc) results in an expansion of +29%(linear). This is largely the cause of the typical eggshell effect often seen in areas lined with high alumina bricks and castables. One conventional approach is to use a lower alumina mix, with higher silica/alumina ratio, attempting to promote the formation of Kaliophilite etc, which can form a siliceous barrier layer preventing excessive alkali penetration. This is certainly one instance where higher alumina content is not necessarily better. Much of the success of Silicon Carbide containing materials relates to their low alumina/fireclay type base. Many materials, including some SiC mixes attempt to use the 'barrier' method described above, with mixed success.

It should be noted that similar expansion is generated when sodium ions attack corundum. This is easier to eliminate, even within the Alumino-silicate system, by choosing a clay based material of composition to the left of the Mullite line (<70% alumina), as corundum is not a stable phase in this zone of composition. However, some materials are not homogenous, and include components containing corundum, even if in small quantities, that can cause problems. Thus a clay based material would be preferred. This would restrict the alumina content to below 50%. Although not proven by this testwork, theoretically, the materials under discussion above could also alleviate the problems associated with Sodium ion attack. The worst case scenario for a kiln system, is where there are significant levels of both alkali species present. In this case it will be necessary to avoid alumino-silicates altogether.

OTHER MATERIALS

Two materials submitted for testwork were not conventional alumino-silicates, nor contained SiC/clay etc. One was based on Forsterite, the second on Zircon. The former, of Norwegian origin, was tested as both brick and castable. While there was some expected differences in their physical properties, neither form showed significant chemical attack, while retaining the original dimensions of the test block.

Forsterite is a mixture of magnesium silicate and fayalite. The refractories tested had a typical chemical composition as follows:

MgO : 52%, **$Si0_2$** : 40%, **FeO** : 6%

The test report (3) on the Forsterite materials stressed that, although extensively penetrated by alkali species, no deleterious phases were formed, thus no expansion was measured.

A very similar result was obtained with a Zircon based Low Cement castable of Australian manufacture. This material is a mixture of naturally arising zircon and other synthetic alumino-silicate materials. The product's chemistry (typical) is as follows:

$A\ l_20_3$: 56%, **$Si0_2$** : 18%, **$Zr0_2$** : 23%, **FeO** :<O.2%, **CaO** :<3%

Here again no deleterious reactions were noted, in the CSIRO testwork, although some penetration of the test sample by alkali species, was evident (4).

Both materials avoided deleterious reactions, and they kept their physical integrity.

PRACTICAL CONSEQUENCES

Both materials are currently under trial at separate Australian plants. Both are showing positive indications in service. The zircon castable is also available in a variant, containing a different alumino-silicate component of lower Corundum content, which is claimed to be resistant to Sodium ion attack.

The Forsterite is the lower cost material, but has limitations in areas were the lining is subject to abrasion, or in contact with a liquid phase. In these applications, the Zircon material would be preferred. Both are significantly cheaper than the SiC type products.

These alternative materials also have significant thermal and mechanical design advantages over SiC containing products, in that the thermal conductivities and Reversible Expansion values are much lower than for those containing SiC.

The Forsterite castable, available in a similar gunning grade, is chemically bonded and thus applicable for use where calcium aluminate cement content needs to be minimised.

CONCLUSIONS

Unique test procedures developed for an Australian cement plant have confirmed that both Olivine/Forsterite and Zircon based products are suitable for use in high alkali (Potassium) environments. These products showed no deleterious reactions, as would be found with high alumina materials. Specifically, no excessive expansion was produced under the test conditions, indicating unwanted reactions were not occurring. These materials also possess thermal properties which make them more user friendly than those containing SiC.

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