

# Autogenous crack healing in composite cementitious barriers using calcium borate binders

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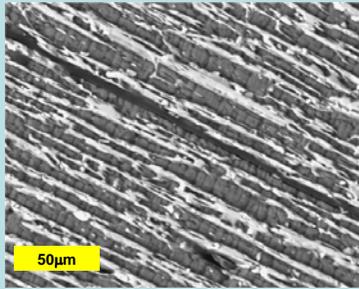
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## 1 Introduction

Reactive, self-sealing binders are attractive materials for many waste containment systems. The concept is a simple one; as a material degrades, the ions released react with those from an adjacent material to form a new phase, which in fills the porosity opened by the dissolution of others. If this reaction product is highly insoluble, its potential for use in a self-sealing barrier is also high, owing its propensity to close developing porosity.

During the MIRO/ENTRUST project "Novel Composite Landfill Liners", such a phenomenon was investigated in which calcium (from by-product calcium carbonate) and borate (from a metallurgical borate slag) react to form calcium diborate dihydrate.



## 3 Borate material

The borate slag is a by-product of silver-zinc refining, initially introduced as a borax flux into which residual zinc is partitioned by solvent extraction. On cooling, it is comprises alternating layers of zinc oxide saturated, borax glass and free zinc oxide (zincite). The ground material is cementitious, largely due to the re-hydration of the borax to form a salt cake containing zinc borate.

## 5 Field Experiment

During the MIRO / ENTRUST project "Novel Composite Landfill Liners", a cementitious, three-layer barrier was constructed, in which the upper layer concrete was bound by ground borate slag. This was emplaced over a clay layer, itself compacted against a lower layer of concrete, comprising metallurgical slag aggregates bound by alkali-activated fly ash. In this way, the entire containment system was made from industrial by-products; in effect, using...  
*waste to contain waste.*

The photograph below (left) shows emplacement of the borate slag-bound concrete, containing spent foundry sand and chrome-alumina slag aggregates. Below, right are shown the reaction products, in colour is the hexahydroborite encrusting limestone and the SEM micrograph (inset) shows smithsonite ZnCO<sub>3</sub>.



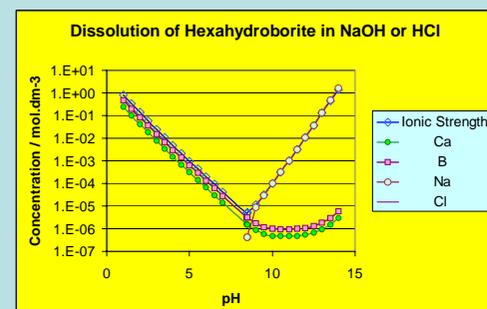
## 8 Solubility relationships

Experimental determination of the solubility of Ca[B(OH)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O shows it to be 1.77 E-6 molal at 25°C, which is close to that in the literature<sup>[1]</sup> of 1.62E-6 molal at 25°C. This suggests at log K<sub>(Dissolution)</sub> of 0.06 using the following dissociation reaction:



Equilibrium calculations were performed using the simulation package PHREEQC (v2.6.01) with thermodynamic databases supplied with the code and compared to predictions from the HATCHES [V16] data set, both supplemented with the new data above.

[1] Casabonne-Masonnave, J.M.(1990) Env. Sci. Technol. 24(6) pp 867-873

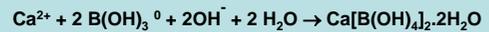


## 9 Predicted solubility as a function of pH

Hexahydroborite phase solubility was predicted as a function of pH in a solution buffered by HCl and NaOH. The graph indicates a solubility minimum between pH 9 and pH 13, suggesting the phase will remain stable in the cement liner environment

## 2 System Chemistry

Under alkaline conditions (the equilibrium pH of the water-saturated borax slag powder is around pH 9.5) borate ions will react with calcium ions in solution to produce a highly insoluble solid; calcium diborate dihydrate. The reaction scheme is a simple precipitation:



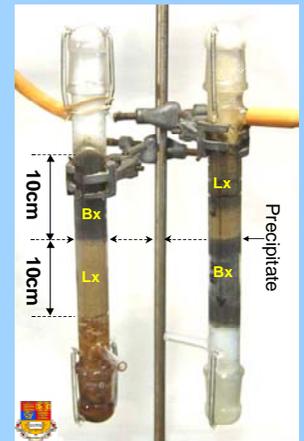
The reaction product is well characterised and occurs naturally in boron-rich lime skarn deposits (Type locality: Solongo B deposit, Vitim Plateau, Buriatia, Eastern Siberian Region), with the mineral name "hexahydroborite".

4 Although borate ions have been known to retard Portland cement hydration for many years, the possibility of using this reaction as a means of crack healing has not, so far, been investigated. The hypothesis was raised that by making both calcium and borate ions available to the pore solution of concrete liners, the potential exists for closure of porosity and autogenous sealing of cracks. In order to test this, two experiments were performed; one, a field-scale trial cell at a licensed waste disposal site (Risley, UK) and the other, a laboratory investigation into pore closure reactions.

Standard laboratory measurements showed that the ground borate slag successfully binds a range of industrial slag aggregates to produce concrete with an unconfined compressive strength of 35-45 MPa at 28days and permeabilities around 10<sup>-10</sup> ms<sup>-1</sup>. It was noted that these materials offer a greater resistance to organic acid attack than do conventional Portland cement concretes, making them attractive liner materials.

## 6 Laboratory Experiments

A range of column experiments was conducted in which cementitious pore solutions were eluted or diffused into the hydrated borate slag and *vice versa*. In all cases, the reduction in permeability during the experiment was marked, as precipitation occurred in the mixing zone between the calcium-rich cement or limestone conditioned pore solution and that dominated by the borate slag.



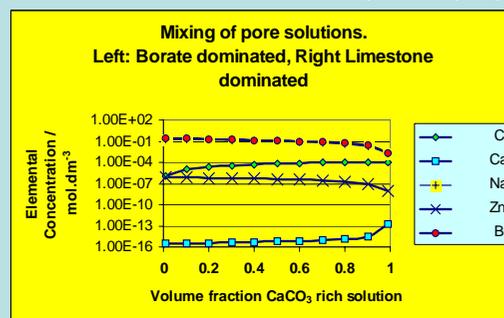
## 7 Phase characterization

Using apparatus similar to that shown above, pore solutions were allowed to interdiffuse to produce a reaction product in the middle flask. This allowed comparison of the material produced by the industrial by-products with model systems formed from Borax and a range of calcium salts or cements. The reaction product in each case was Ca[B(OH)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O

## 10 Prediction of porosity closing reaction

The precipitation of hexahydroborite will be determined by both the availability and mobility of calcium and borate ions. In a composite liner system, both the diffusion gradient and the flow direction (advection) are downwards, *i.e.* the leachate contained by the barrier will slowly migrate through the pore structure.

In the model system (borate slag solution flowing into cement-bound limestone flour) equilibrium in solution is established between the hydrated borax phase, zincite and a minor reaction product; zinc borate Zn(BO<sub>2</sub>)<sub>2</sub>. Subsequent reaction with the calcite-dominated solution results in hexahydroborite precipitation.



Simulated mixing of the two pore fluids shows an almost complete removal of calcium ions from solution in regions where alkalinity and borate activity are high.

The photograph of the columns above illustrates the zone of phase precipitation.