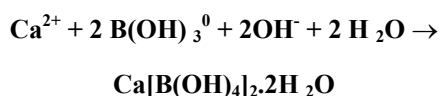


Calcium Borate Binders - A summary of experiments by Mark Tyrer and Essie Ganjian

Reactive, self-sealing binders are attractive materials for many waste containment systems. The concept is simple; as a material degrades, the ions released react with those from an adjacent material to form a new phase, which has a greater molar volume than either of the original components. If this reaction product is highly insoluble, its potential for use in a self-sealing barrier is high.

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 (which has the mineral name "hexahydroborite"). The reaction scheme is a simple precipitation:



Initial experiments showed that the borate slag is hydraulic: it reacts with water and sets hard in a matter of 30 minutes. It has a modest resistance to organic acid attack and was therefore used as the cementitious binder in one of the field trials of these liner systems constructed near Risley, Cheshire. It readily leaches residual borate ions to solution. The slag comprises alternating layers of zinc oxide (light phases in the figure below) and glassy borax (dark, fractured phase).

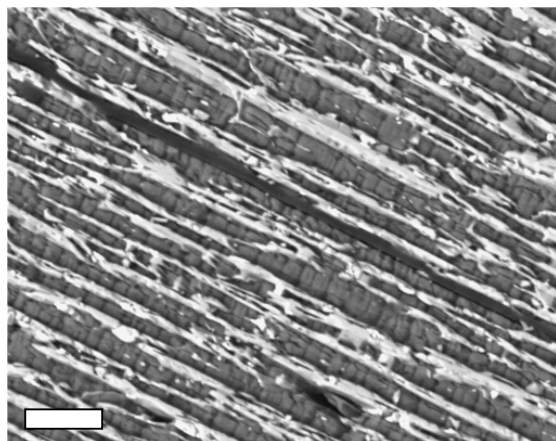


Figure 1 Backscattered SEM micrograph of polished borate slag. Scale bar = 50 μm

The source of calcium ions is a by-product calcium carbonate ("Limex-70"), produced by sparging gaseous CO_2 through a calcium-rich alkaline solution. The precipitate is finely divided, but contains well crystalline calcite and residual organics; principally sugars. X-ray diffraction shows strong reflections for calcite and figure 2 compares the measured pattern with that calculated

for pure calcite. The lattice structure is shown to the left of the figure.

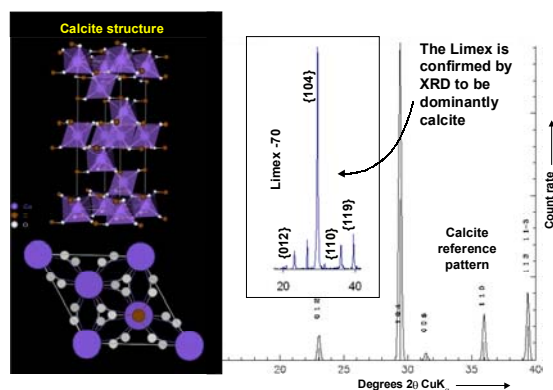


Figure 2 Theoretical calcite lattice and reference pattern compared with that measured for Limex-70 (inset, centre).

Considering next the thermodynamics of the system, the leached slag released borax and a small quantity of zincite to solution. If these two phases are equilibrated with water, we may expect zinc borate $\text{Zn(BO}_2\text{)}_2$ to precipitate, further limiting the availability of zinc ions. Considering these three phases at equilibrium with water, the resulting solution would be expected to contain the following dissolved elements:

| Element | Concentration / mol.dm^{-1} |
|---------|--------------------------------------|
| B | 3.90 e-1 |
| Na | 2.42 e-1 |
| Zn | 1.38 e-7 |
| pH | 9.096 |

Table 1 Solution composition following aqueous equilibration of $\text{Na}_2\text{B}_4\text{O}_7$, ZnO and $\text{Zn(BO}_2\text{)}_2$ [PHREEQC(v2.6) Lawrence Livermore database]

Similarly, leaching of the Limex-70 is calculated to release $1.39\text{e-}4 \text{ M}$ [Ca and CO_3] at pH 9.3.

Considering a solution which contains a mixture of the two pore solutions it is possible to calculate the quantity of $\text{Ca[B(OH)}_4\text{]}_2 \cdot 2\text{H}_2\text{O}$ which is predicted to precipitate from 1 dm^3 of solution. Figures 3 to 5 show respectively, the change in pH, solution composition and yield of $\text{Ca[B(OH)}_4\text{]}_2 \cdot 2\text{H}_2\text{O}$ as the volume fraction of the mixture changes from chemistry dominated by borax (on the left) to a calcite-dominated solution (on the right).

This suggests that the greatest yield of hexahydroborite will be close to the limex and this is indeed observed in the column experiments described below.

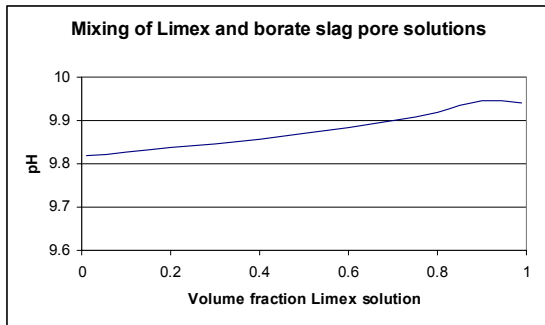


Figure 3 Variation of pH in a mixed pore solution of variable composition between borax slag dominated (left) and Limex dominated (right)

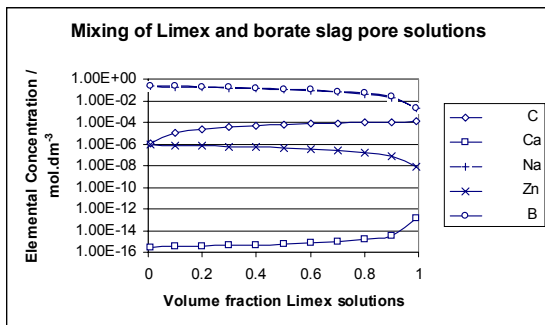


Figure 4 Composition of a mixed pore solution of variable composition between borax slag dominated (left) and Limex dominated (right)

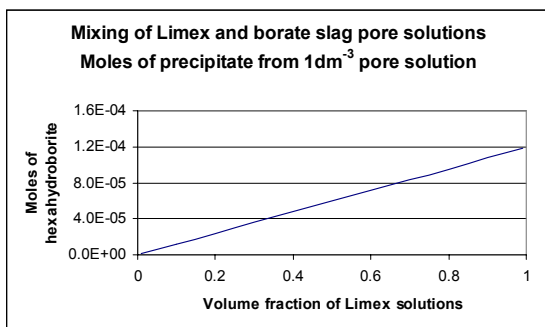


Figure 5 Yield of $\text{Ca}[\text{B}(\text{OH})_4]_2 \cdot 2\text{H}_2\text{O}$ precipitated from a mixed pore solution of composition varying between borax slag dominated (left) and Limex dominated (right)

Column experiments in which ground borate slag and Limex-70 were packed as two layers, were subjected to low flow rates of both deionised water and a synthetic landfill leachate (a mixed electrolyte of Na, K, Cl, SO_4 and organic acids). The eluting solution rapidly formed an expansive reaction product between the two layers which effectively reduced the columns' permeabilities.

The pure water columns were subject to a 1.3m head and remained impermeable for the duration of the experiment (four months). The leachate columns were subject to more aggressive testing (3.0m head) and whilst a little solution eluted over the first few days, the columns satisfactorily self-

sealed and remained impermeable for three months. At the end of the experiment, these columns were split and the reaction product at the interface was analysed by x-ray diffraction and electron microscopy.

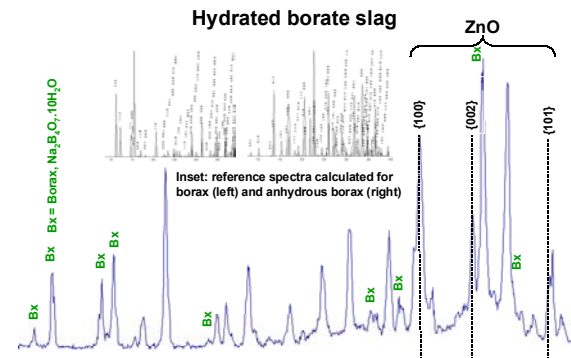


Figure 6 X-ray diffraction pattern of material from the interface formed in the column experiments.

Given confidence that the reaction product is indeed hexahydroborite, the next concern must be for its stability as a function of pH. Again, recourse was made to thermodynamic calculations. Figures 7 and 8 show the effect of changing solution pH on the stability of this phase. By calculating its solubility in solutions where the pH is adjusted by addition of sodium hydroxide or hydrochloric acid, it can be shown that the phase is likely to be stable in any alkaline environment.

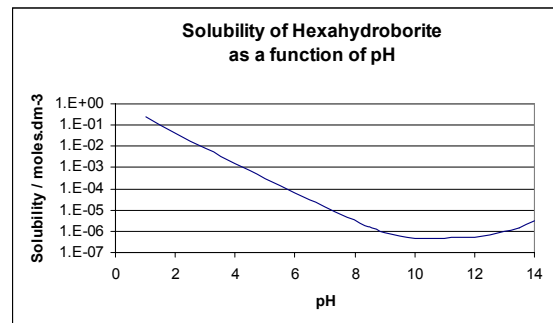


Figure 7 Solubility of Hexahydroborite as a function of pH, adjusted by NaOH or HCl.

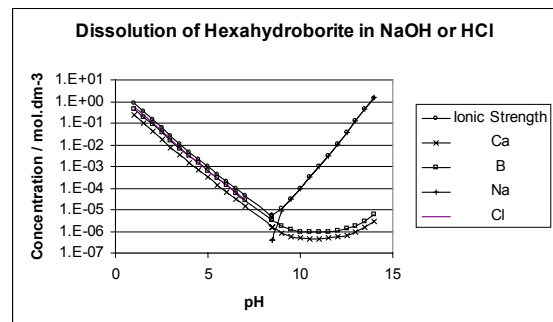


Figure 8 Solution composition on dissolving hexaborohydrite in NaOH or HCl

In conclusion, the use of two industrial by-products in combination shows the potential for producing a reactive barrier composition, which will promote self-sealing of preferential flow paths.

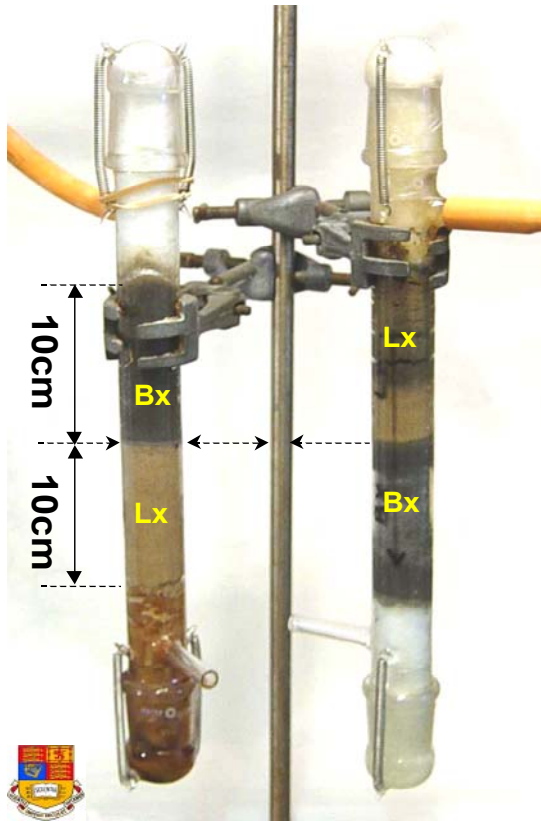


Figure 9 Pure water columns.(Imperial College)

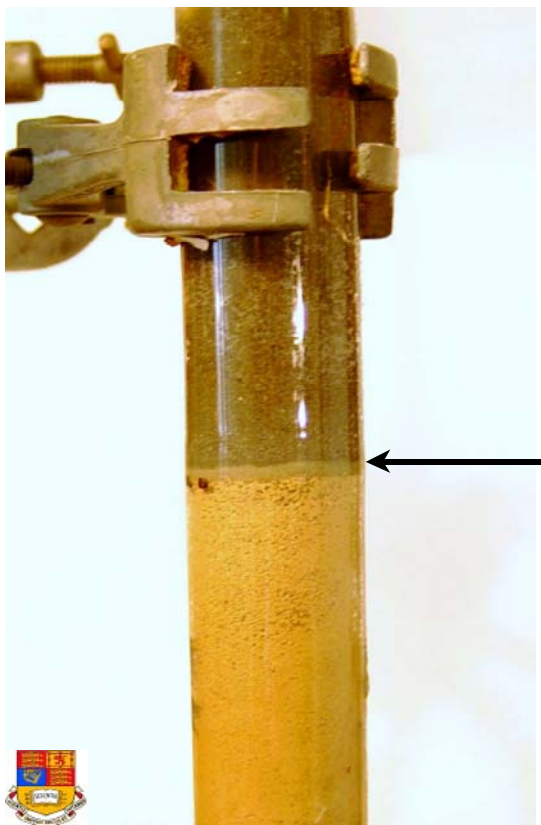


Figure 10 Pure water columns (detail)

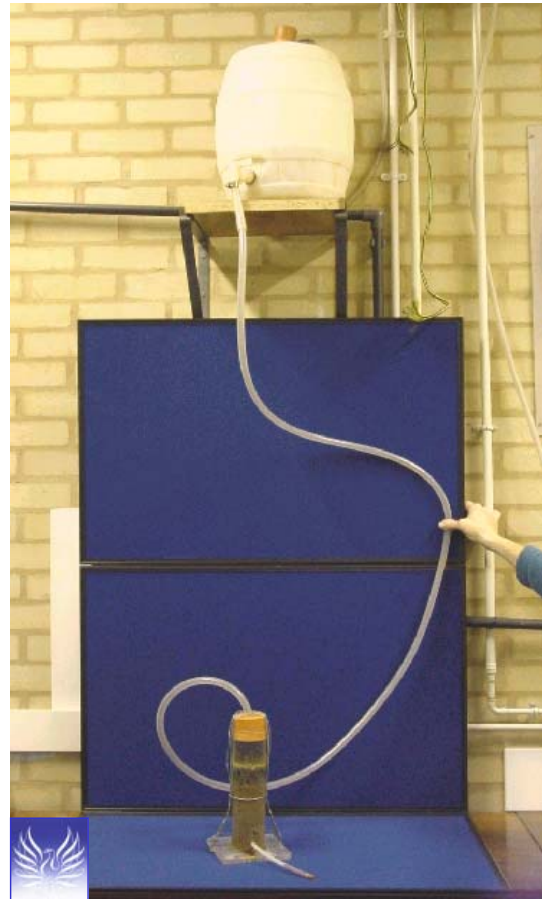


Figure 11 Synthetic leachate columns (Coventry University)

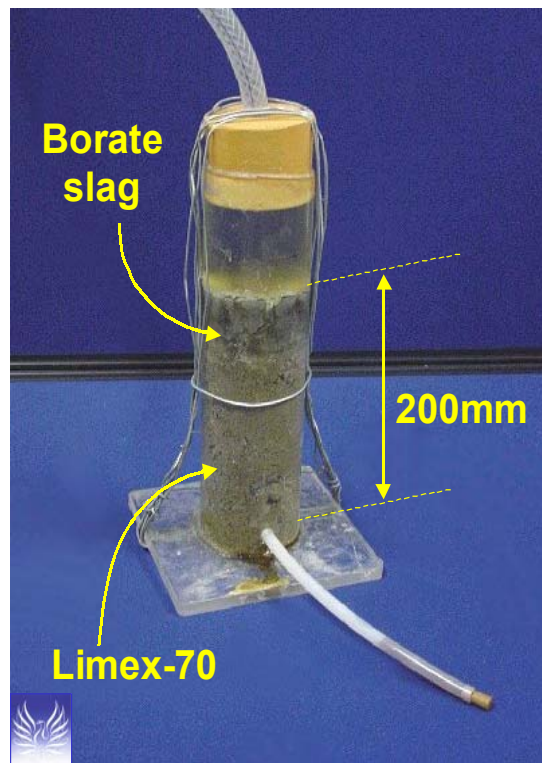


Figure 12 Synthetic leachate columns (detail)