Electronic Supporting Information for:

Hydroxyapatite on cement: insights into the mineralisation processes of a new surface treatment

Ronald Turner[a]*, Pieter Bots[a]*, Alan Richardson[b], Paul A. Bingham[c], Alex Scrimshire[c], Andrew Brown[d], Mark S'Ari[d], John Harrington[d], Susan Cumberland[a], Joanna Renshaw[a], Matthew Baker[e], Paul Edwards[f], Cerys Jenkins[g] and Andrea Hamilton[a]*.

[a] *Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, G1 1XJ, UK. Email: ronald.turner@strath.ac.uk, pieter.bots@strath.ac.uk, and andrea.hamilton@strath.ac.uk*
[b] *Department of Mechanical and Construction Engineering, University of Northumbria, Newcastle upon Tyne, NE1 8ST, UK.*
[c] *Department of Engineering and Mathematics, Sheffield Hallam University, Sheffield, S1 1WB, UK.*
[d] *School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK.*
[e] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1BX, UK.*
[f] *Department of Physics, University of Strathclyde, Glasgow, G4 0NG, UK.*
[g] *Department of Physics, Swansea University, Swansea, SA2 8PP, UK.*

Electronic supplementary information with 3 pages and 4 figures.

Supporting Figures

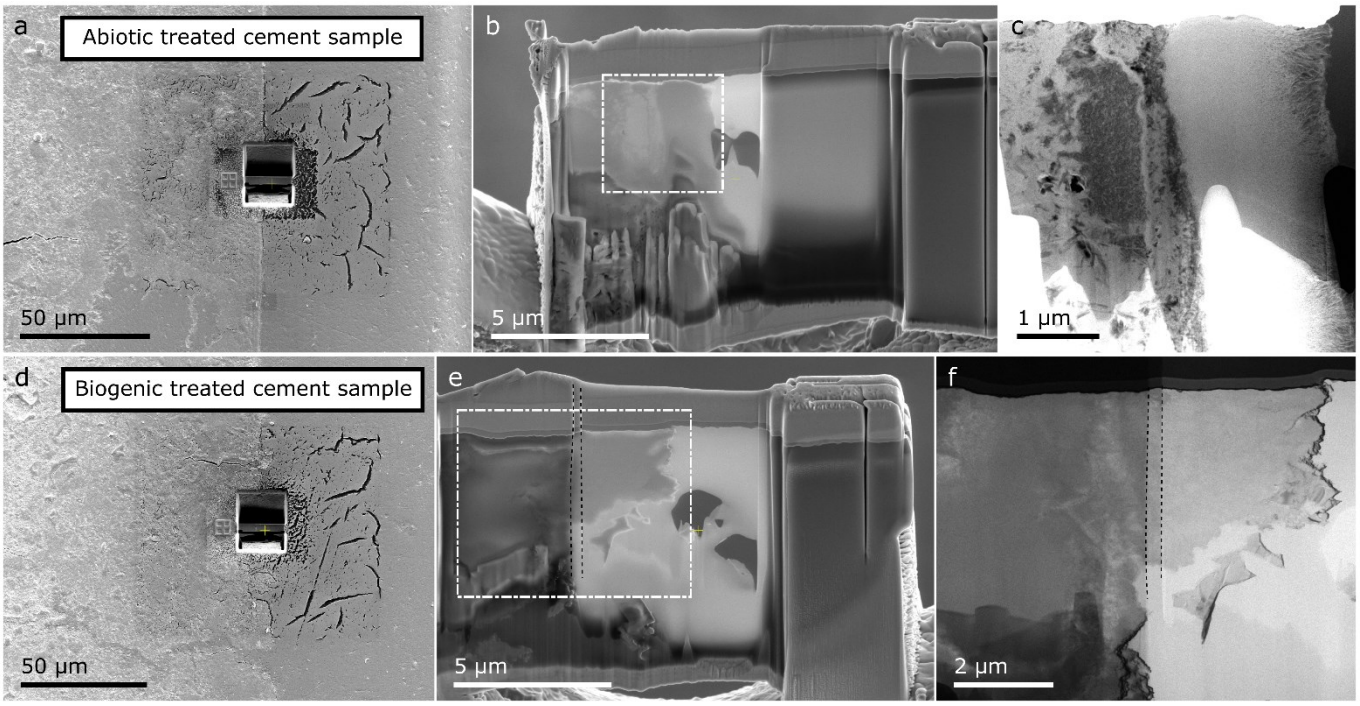

Fig. S1 Summary of the preparation of the FIB-SEM lamellar lift-outs for subsequent TEM analyses of the abiotic treated cement sample (a-c) and the biogenic treated cement sample (d-f). a and d are secondary electron images of the area of the lift-out once the lamellar had been prepared, b and e are the secondary electron images of the liftouts. The areas highlighted by dash-dotted squares were imaged using TEM (b and e). The dash-dotted squares represent the area of the overview TEM images shown in c and f. The dashed lines highlight where the lift out-from the biogenic treated sample stepwise thickens (this region was deliberately not FIB-thinned further to protect the thin lamellar from breaking on transfer to the TEM; e and f).

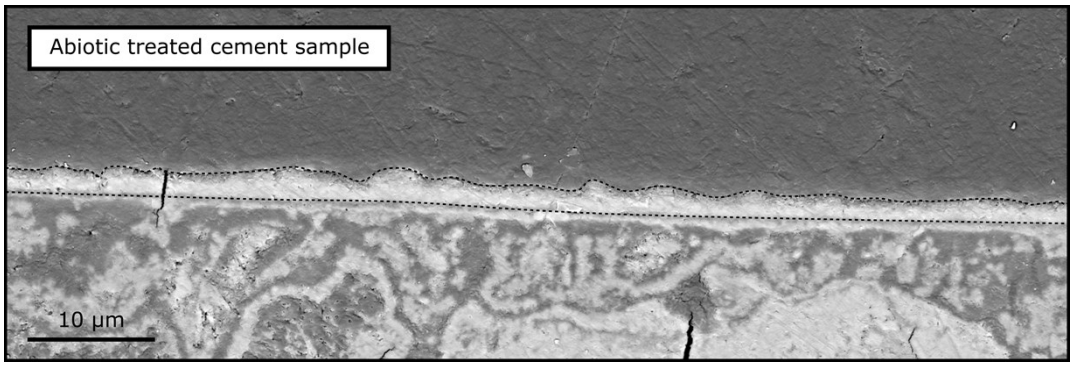

Fig. S2 Higher resolution SEM backscatter electron image of the cement surface of the abiotic treated cement sample to highlight the surface of the cement sample (dashed black lines)

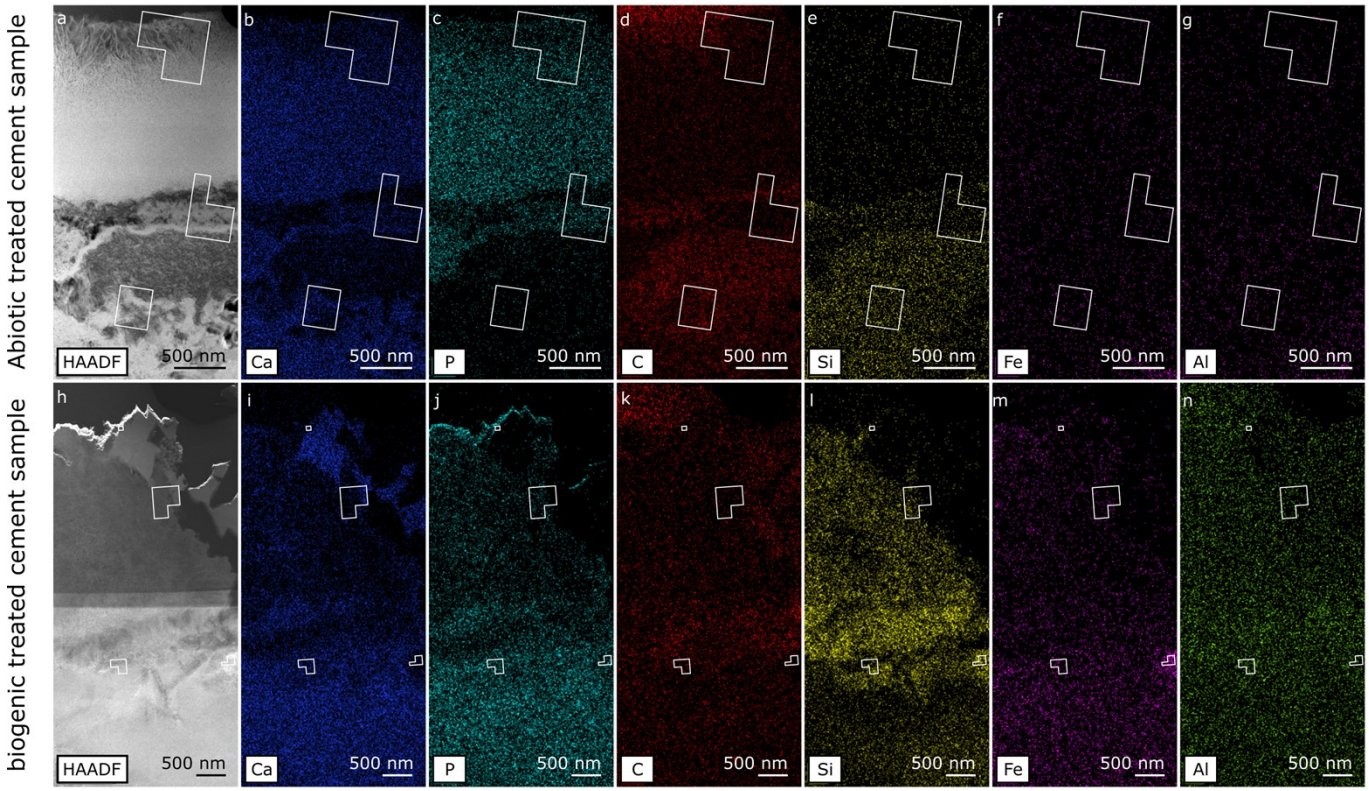

Fig. S3 Overview of the STEM EDS elemental maps on the FIB lift-outs including the respective high-angle annular dark-field imaging (HAADF; a and h) for the abiotically treated cement sample (a-g) and the biogenic treated cement sample (h-n); the outlined regions correspond to the HR TEM images shown in Fig. 6d,e,f,h,l,j and k.

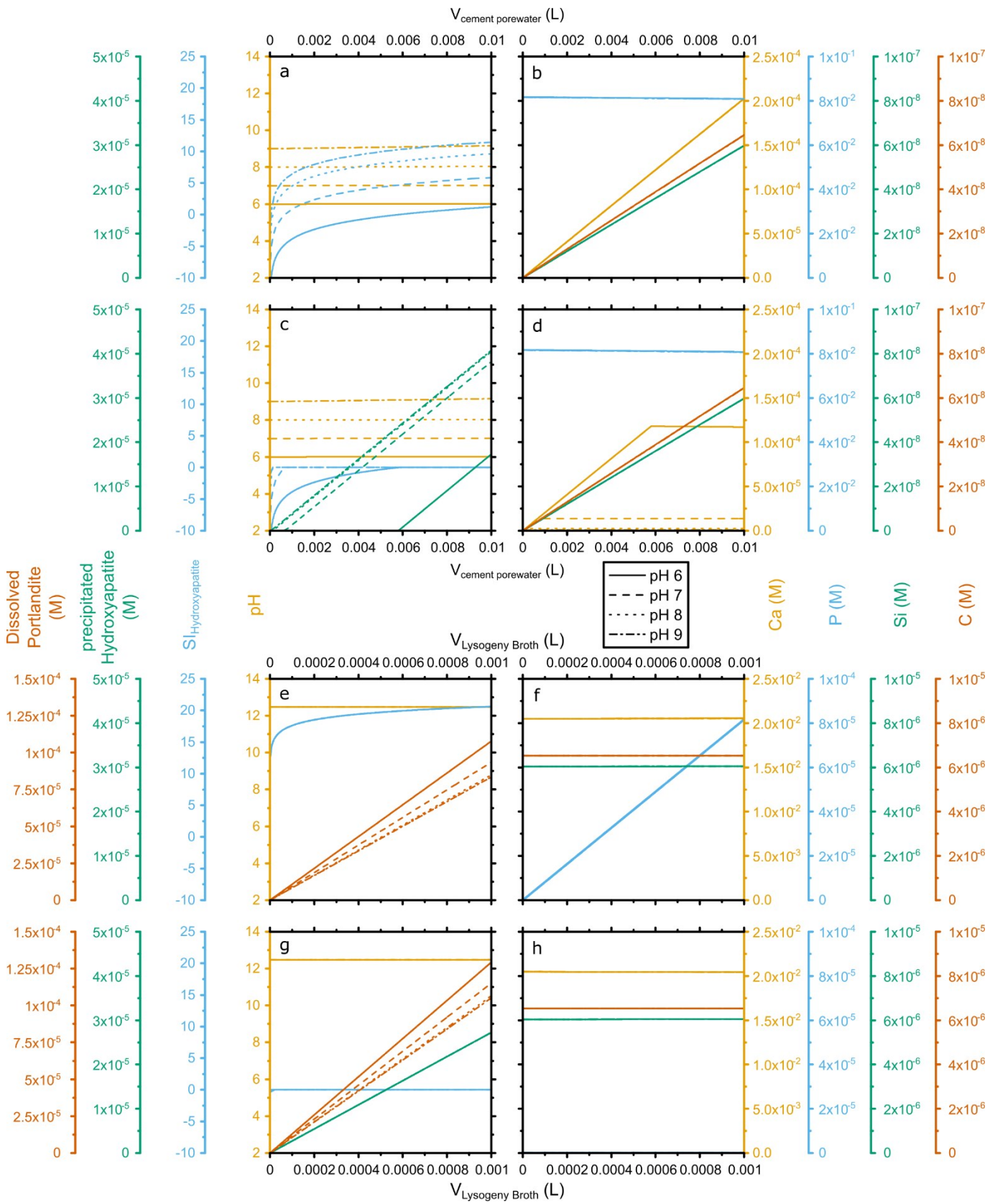

Fig. S4 Summary of the results from the qualitative PHREEQC modelling to mimic the impacts of diffusion of the ions from cement porewater on the geochemistry and hydroxyapatite saturation state and precipitation in the phosphate amended LB broth (a-d) and vice versa (e-h), without (a,b and e,f) and with (c,d and g,h) allowing for the precipitation of hydroxyapatite. These qualitative models were performed by mixing small volumes of a portlandite, C-S-H and calcite equilibrated solution (to mimic cement porewater) with a 1 L, pH 6-9 phosphate solution, containing 69.1 mM KH_2PO_4, 12.6 mM K_2HPO_4 and 85.6 mM NaCl (simulating the phosphate amended LB broth) (a and b) in order to mimic the impact of ion diffusion from a cement equilibrated solution into the phosphate amended LB broth (and the impact of pH in the LB broth on this), and vice versa. Plots show the modelled saturation index (SI) of hydroxyapatite; the pH; the moles of hydroxyapatite precipitated and the moles of portlandite dissolved (a,c,e and g); the moles of Ca, P, Si and C in the aqueous phase (b,d,f and h) as a function of the volume (as a qualitative measure for the amount of diffusion) of the cement equilibrated solution into 1 L of the phosphate amended broth (a-d); the volume (as a qualitative measure for the amount of diffusion) of the phosphate solution into 1 L of the cement equilibrated solution (e-h).