Aluminium Content in Polymorphs of Calcium Silicate Hydrate

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Disrupting challenge for improving cement durability pass today through understanding its atomic scale properties. After the hydration, the key phase of cements is the Calcium-Silicate-Hydrate gel (C-S-H gel), that gives its strength, glue its structure and retains water. The C-S-H gel models are built from the structure of the polymorphs of the Calcium-Silicate-Hydrate mineral called tobemorite. We study tobermorite, which is an inosilicate mineral formed by stacking CaO layers rived by silicates chains (see figure 1). Three different polymorphs are distinguished by their layer thickness 14 Å, 11 Å or 9 Å. To pass from one to the other polymorph, Si-O-Si bonds are broken or formed; this is normally induced by temperature. Experimentally, an unexpected feature was observed: the 9 Å can not be reached for some compositions[1]. For these compositions, tobermorite is called "anomalous" in opposition to "normal" tobermorite. It is noteworthy that the transition mechanism in "normal" tobermorite may be similar to the one responsible of the loss of durability of cements. Consequently, fully understanding the differences between "normal" and "anomalous" tobermorite would lead to an improvement of the thermal and mechanical properties of cements.

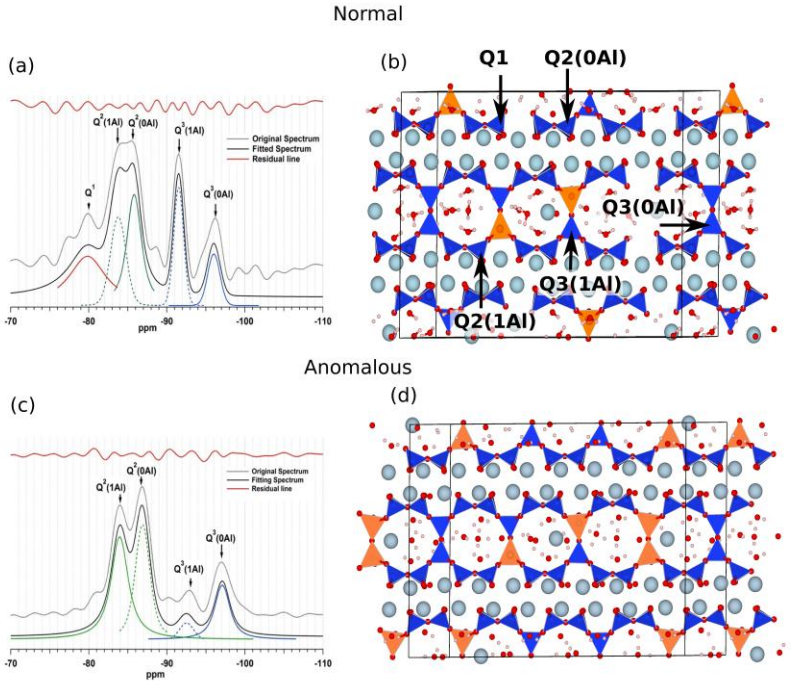

Figure 1. Left panel: silicon Nuclear Magnetic Resonance (NMR) signals obtained for "normal" and "anomalous" tobermorite 11 Å. Right panel: corresponding models are extracted from NMR signals and used to understand the main differences between "normal" and "anomalous" 11 Å tobermorite. Blue tetrahedra denote silicate SiO_4^{4-} unit; orange tetrahedron, aluminate AlO_4^{5-} units.

Apart from temperature effects, we focus in our study on the effect of pressure for the 11 Å tobermorite polymorphs[1]. This work combines advanced experimental methods, Nuclear Magnetic Resonance and synchrotron high pressure XRD, and atomistic calculations. We built two models according to the experimental measures as shown in figure 1. We observed that the tobermorite containing less Al atoms amorphizes at pressures of about 2 GPa. This supposes that the differences between the two compositions result into structural changes that block the transition to the 9 Å polymorph. In particular, substituting Si atoms by Al atoms could have a positive effect by increasing the length of silicate chains[2] and making stronger bonds. In the models, we found that the structure is more regular when the content of Al is higher and the Si-O-Al bonds are stronger than Si-O-Si ones[3]. The lack of Al atoms in the "normal" tobermorite weakens the structure and leads to its amorphization. These findings are in agreement with previous hints saying that the addition of Al atoms could increase the microscopic stability of C-S-H gels.

References:

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[2] H. Manzano et al. , J. Phys. Chem. B 113, 2832 (2009)
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