Poster

Multi-method study of calcium-aluminate cement hydration and its crystal structures

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Calcium aluminate cement (CAC) presents several advantages in comparison to other types of cement. Its fast-setting, high-temperature and sulphate attack resistance make it a valuable choice for projects where quick strength development and heat-resistance characteristics are needed. Despite these advantages, CAC does have some limitations. One notable drawback is its initial setting strength is higher than the strength once dry. This occurs because during its hydration, metastable hydrates are formed [1]. These hydrates are formed as metastable intermediates which, depending on the storage conditions and, crucially, CO_2 availability, convert faster or slower into their stable counterparts hydrogarnet $3CaO•Al_2O_3•6(H_2O)$ or (C_3AH_6), gibbsite $Al_2O_3•3(H_2O)$ or (AH3) [2] and, carbonates such as calcium hemicarbo-aluminate $Ca_2Al(OH)_6[(CO_3)_{0.25}OH_{0.5}·2H_2O]$. These transformations are associated with a decrease in volume and therefore increase in cement porosity, which leads to a corresponding decrease in cement strength. At the moment, since the structures of the metastable products are not yet well known, the difficulty to predict their amount, leads to difficulty in predicting the strength development of the cement, and therefore to narrow use of this low carbon producing alternative. Structure solution of these metastable phases would allow their quantification and therefore, the development of accurate strength prediction routines of CAC strength overtime, leading to a more widespread use of this type of cement.

In this study several analytical and sample preparation techniques have been used and tested to gain understanding of CAC's hydration process. Special focus was put on the unknown C_2AH_x and C_4AH_x phases which are the main hydrates that appears during CAC's early hydration. The analytical methods used include: XRD, In-situ XRD, EDX, SEM and TEM (PED, STEM, HRTEM and cRED). Since these metastable layered materials form as intergrowing, disordered, often twinned and preferentially oriented hexagonal platelets, and, due to their small crystallite size, methods such as single crystal XRD and XRPD have not been entirely successful in the structural elucidation of these types of materials. This is why, electron diffraction has been chosen as the main method of structural investigation. The following sample preparation methods have been tested to optimize sample preparation for 3DED investigation: Graphene encapsulation, cryo-TEM, vitrification, microtomy, focused ionic beam milling (FIB) and cryo-FIB milling. Because of the modifications that occur in air due to CO_2 incorporation into their structure and their tendency to dehydrate rather quickly, especially when exposed to vacuum, the samples need to be kept under strict environmental control at all times. Furthermore, to protect from dehydration and reduce electron beam damage, cryo-protection is needed. To cope with these requirements, a nitrogen glove box is used during synthesis and sample preparation. To further protect the sample, the crystals are frozen on transmission electron microscopy (TEM) grids, which are kept at liquid nitrogen temperature and cryo-transferred into a TEM for 3D ED data collection.

Different synthesis paths have been tested with XRD and In-SituXRD in order to produce pure CAC-hydrates and minimize the amount of carbonate and byproduct formation. The tested synthesis represents the reaction of the powdered component/s in addition to water, and include the following: $C_{12}A_7$ (mayenite) + CH (portlandite), CA (krotite) + CH (portlandite), C_3A (alite) + CA. These hydration reactions have shown to lead to rapid formation of C_2AH_8 with minor amounts of $C_2AH_{7.5}$.

When trying to identify the correct space group of the metastable hydrate's issues are encountered due to their morphology, which leads to preferential orientation perpendicular to c*. When investigating non-oriented individua, the crystals become too thick for the electron beam to penetrate, impeding the collection of diffraction data. Therefore, the critical information of the extinction rules along the c axis is lost. However, methods such as FIB and Microtomy have been really helpful to identify the correct space group and cell of these types of materials. Notably, significantly better data can be achieved when measuring under cryogenic conditions. Thanks to the cryo-protection, the information about the water content in the structure remains, leading to superstructure reflections that reflect a 2-fold modulation along a* direction when described in a monoclinic centered system and 4-fold along a* when described in a hexagonal system.

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