MS15-2-3 Crystal chemistry of extracted brownmillerite from sulfate-resisting Portland cement #MS15-2-3

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Abstract
Brownmillerite, the so-called ferrite phase, is the iron bearing phase of ordinary Portland cement clinker and represents typically 7-8% wt% of the its total mass. It is a wide solid solution between $Ca_2Fe_2O_5$ and $Ca_2Al_{1.3}Fe_{0.7}O_5$, often written $Ca_2Al_xFe_{2-x}O_5$ with 0<x<1.4. The crystal structure is orthorhombic with two distinct space groups: Pnma for 0<x<0.4-0.6 and Ibm2 for 0.4-0.6<x<1.4 [1-3]. In usual Portland cement, it is well established that brownmillerite crystallizes in space group Ibm2, with Al/Fe ratio in the range 1 to 2 approximately [4]. At the present time, only few studies have analyzed brownmillerite phase of more specific sulfate resisting Portland cements (SRPC) [5-7]. It is known that the brownmillerite phase is richer in iron [4] but there is a lack of recent and accurate crystal structure parameters on industrial brownmillerite, that are of particular importance for further study of cement reactivity.
Brownmillerite, resulting from the crystallisation of the liquid phase, is one the less abundant of the four major phases of Portland cement clinker. It constitutes the interstitial phase in which calcium silicates are embedded. Its crystals are with small sized particles (~1 µm), frequently dendritic, eventually mixed with tricalcium aluminate. Studying the crystal chemistry directly from the cement leads to an overly complex interpretation due to the Bragg lines overlap and the lack of accuracy of chemical analysis (SEM/EDS). The proposed approach to overcome this drawback is to extract brownmillerite by selective chemical dissolution.
Four SRPC (A-D samples) were used to extract brownmillerite, then systematically studied by powder X-ray diffraction (XRD), electron microprobe (EPMA), X-ray fluorescence spectroscopy and ^{57}Fe Mössbauer spectroscopy. Two extraction steps were used: the first is the salicylic acid/methanol (SAM) protocol that leaves a residue rich in brownmillerite, tricalcium aluminate and sulfate phases. The second, which was developed in this study, uses acetic acid (AcA) to dissolve tricalcium aluminate and sulfates phases. On the other hand, eight synthetic brownmillerite samples with similar Al/Fe ratio were used to compare their crystal chemistry with the industrial ferrites.
The selective extraction clearly appears of particular importance to obtain a correct estimation of Al/Fe content in ferrite phase, consistent with EPMA analysis. The influence of the extraction protocol is deeply discussed. The Rietveld refinements show that all the brownmillerite samples of this study crystallize in space group Ibm2. Two families of brownmillerite (A&C and B&D) are distinguished by their cell parameters and aluminium content (Figure 1), depending on the presence or the lack of tricalcium aluminate phase in cement. Mössbauer spectroscopy is used to evaluate the iron repartition in octahedral and tetrahedral sites in extracted and synthetic brownmillerite.

References
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Figure 1: Brownmillerite unit cell volume