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DISCUSSION

DISCUSSION OF THE PAPER "NEUTRON POWDER DIFFRACTION INVESTIGATION OF MODEL CEMENT COMPOUNDS" BY R. BERLINER ET AL.[1]

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Rietveld refinement of cement x-ray diffraction patterns for quantitative analysis promises to be a solution for resolving the problem of sorting out the peak overlaps that occur between the various phases found in clinker and Portland cement. However, when attempting a rietveld refinement using the crystal structure data as presented in the tables from the article by Berliner et al. (1), several problems were encountered. Problem 1 is relatively minor; however, problem 2 has some serious ramifications for those doing rietveld refinement of portland cement compounds.

Problem 1

The wrong space group is listed for the triclinic Ca_3SiO_5 in Table 2a. The space group for triclinic Ca_3SiO_5 is P1bar (#2) of the triclinic space group, not the monoclinic space group P21/n (#14).

Problem 2

The second problem involves the subject of partial atom occupancies in the monoclinic Ca_3SiO_5 structure. Nishi et al. (2) proposed, in their model of monoclinic Ca_3SiO_5, three orientations of the silicon tetrahedrons with respect to the pseudorhombohedral threefold axis as shown in their Figures 3 and 4. To model the different tetrahedron orientations, they labeled the oxygen associated with the silicon tetrahedrons as U-up, D-down, and G-tilted with respect to the pseudorhombohedral threefold axis. To accommodate the three tetrahedron orientations they gave the oxygen atoms associated with the silicon atom partial occupancies as listed in their Table 1b and also shown in Figure 5. Although Berliner et al. (1) discuss the silicon tetrahedron disorder problem, they concluded that it is outside the scope of the article and assigned occupancies of 1.0 for all atoms listed in their Table 1b.

Monoclinic Ca_3SiO_5 contains nine atoms in its formula weight. The Z-factor for this structure is 36. Multiplying the number of atoms in the formula weight by the Z-factor gives

[1]Cem. Concr. Res. 27, 551–575 (1997).

324 atoms in the unit cell. Berliner et al. (1) in their Table 1b list 190 unique atom sites in the unit cell. Using the P1bar space group site multiplicity factors, a total of 518 atom sites are defined in the unit cell. A discrepancy exists between the number of atoms in the unit cell (324) and the number of atom sites (518). The only way to accommodate the 324 atoms into the 518 atom sites is to have partial occupancies for some or all of the atoms. Nishi et al. (2) assigned partial occupancies to the oxygen atoms associated with the silicon tetrahedrons because of the tetrahedral orientations. However, Berliner et al. (1) clearly state in the footnote of their Table 1b "that the occupancy of all of the atom sites have been taken as 1.0." This occupancy of 1.0 for all 190 unique atom sites gives the unit cell 518 atoms, not 324 atoms as dictated by the formula weight times the Z-factor calculation. These additional 194 atoms substantially increase the calculated grain density of the structure.

The rietveld refinement program, RIQAS (3), and others calculate the grain density of each phase based on the unit cell parameters, crystal system, space group, crystal site multiplicity, and crystal chemistry. Using RIQAS, a rietveld refinement of the monoclinic Ca_3SiO_5 crystal structure with the unit cell parameters, atom coordinates, isotropic thermal factors, and occupancy values taken from Table 1 of Nishi et al. (2) calculates a grain density 3.11 g/cm^3, whereas a rietveld refinement using the above authors' suggested occupancy values of 1.0 for all atoms, the calculated grain density is 4.28 g/cm^3. The accepted value for the grain density of Ca_3SiO_5 is 3.1 to 3.2 g/cm^3.

In general, multiphase rietveld refinement programs incorporate the grain density value into the weight percent calculation of each phase in a mixture. Thus erroneous results would be obtained when using the authors' full occupancy values in rietveld programs that internally calculate the grain density. It is suggested that cement researchers performing rietveld refinement using the Table 1b data of Berliner et al. (1) set the occupancies of the oxygen atoms associated with the silicon tetrahedrons to those values listed in Table 1b of Nishi et al. (2). It is hoped that the authors' rietveld refinement work on the monoclinic Ca_3SiO_5 structure will be clarified in the near future with respect to the problem of partial occupancies of the oxygen atoms.

References

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