Pergamon

Cement and Concrete Research, Vol. 27, No. 4, pp. 551–575, 1997

0008-8846/97 $17.00 + .00

PII S0008-8846(97)00028-8

NEUTRON POWDER DIFFRACTION INVESTIGATION OF MODEL CEMENT COMPOUNDS

R. Berliner and C. Ball
Research Reactor Center
University of Missouri, Columbia, MO, 65211

Presbury B. West
Construction Technology Laboratories, Inc.
Skokie, IL, 60077-1030

(Refereed)
(Received January 3, 1997; in final form February 4, 1997)

ABSTRACT

A series of synthetic cement compounds: mono- and triclinic-tricalcium silicate, β-dicalcium silicate, cubic- and orthorhombic-tricalcium aluminate and tetracalcium alumino-ferrite have been analyzed with neutron powder diffraction followed by Rietveld refinement. Generally good fits have been obtained and the results form the basis for analysis of cement hydration using neutron diffraction. © *1997 Elsevier Science Ltd*

Introduction

The practical properties of portland cements, their rate of setting, heat of hydration, resistance to chemical attack and development of strength are primarily dependent on the phase abundance of the principal cement compounds in the clinker. For this reason, methods for assessing the mineralogic constitution of cements have been the subject of considerable research. Portland cement phase compositions are investigated using quantitative analysis of oxide composition followed by calculation of phase fractions, quantitative X-ray diffraction analysis (QXDA), and methods based on differences in optical properties. Taylor (1) has provided a comprehensive discussion of methods for assessing phase composition as well as a review of the crystallography of the principal cement compounds with numerous references. An intercomparison of QXDA analyses of cement phase compositions from various laboratories has been given by Aldredge, (2) and a discussion of the state of the art for QXDA has been provided by Struble. (3)

We have undertaken a program to evaluate the use of neutron powder diffraction as a method for the analysis of cement clinker minerals. Although superficially similar to QXDA, neutron methods enjoy several distinct advantages for this problem. First, neutrons are highly penetrating and are only weakly scattered or absorbed by most materials. Typical 1/e penetration depths for neutrons in (dry) cement are ~3 cm in comparison to the case for (Cu-Ka) X-rays, 30 μm. The weak scattering and high penetration power for neutrons leads to the use of large specimens (0.2g-10g) in neutron diffraction experiments. This is an advantage for the analysis of cement clinkers as it provides a more representative specimen. Neutron powder diffraction specimens typically require little preparation and need not be ground to a fine powder of uniform particle size as is essential for QXDA. Second, it is important to note that the strength of scattering for neutrons is dependent on the details of the nuclear configuration of each isotope, appearing to vary randomly from element to element. This is in contrast to the strength of scattering for X-rays which varies as the number of electrons. The effect of this difference is to make neutron diffraction much more sensitive to the configuration of oxygen in the cement compounds than is the case for X-rays. Figure 1 compares the scattering strength of neutrons and X-rays for the common elements found in portland cements. Third, the form factor for neutrons is constant as a function of scattering angle so that diffraction at large scattering angles provides important data. Finally, the incident neutrons for a powder diffraction experiment form a monochromatic beam with a simple gaussian lineshape and the analysis of the diffraction pattern is not complicated by the presence of paired α-β lines with Lorentazian components as from standard X-ray sources. These effects combine to make possible reliable full profile analysis of neutron powder diffraction patterns by comparison to crystal atomic models. This analysis method, Rietveld refinement, (4) has been extended from relatively simple, small unit cell materials, as described by Rietveld's original paper, to the multi-phase analysis of complex, large unit cell substances including the effect of disorder, crystalline defects, absorption and preferred orientation. Nominally, the process of Rietveld refinement consists of the comparison of the data from an observed powder diffraction to the calculated pattern of diffraction that is obtained from a model of the specimen crystalline material-a model that contains not only the space group and lattice parameters (which determine only the location of the diffraction peaks), but the positions of atoms in the unit cell, the effects of thermal vibrations, substitutional disorder, preferred orientation, extinction, and diffractometer resolution that determine the intensity of the observed diffraction peaks. Extension of the model to encompass specimens consisting of multiple crystalline phases is now routine. The difference between the data and the calculated diffraction pattern is used in a non-linear minimization process, to obtain best-fit values of the atomic model parameters. In a multi-phase model, the fraction of each phase present is thus quite naturally obtained.

As a first step in the development of neutron powder diffraction as a tool for the evaluation of cement clinkers, it is essential to examine the structure of phase-pure portland cement compounds. This paper reports the results of the Rietveld refinement of neutron diffraction data from synthetic cement compounds: monoclinic and triclinic tricalcium silicate, β-dicalcium silicate, cubic and orthorhombic tricalcium aluminate, and tetracalcium

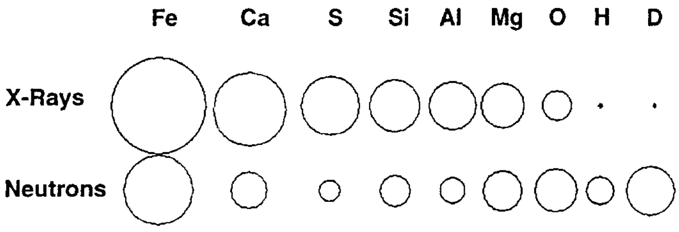

FIG. 1.

Graphical comparison of scattering strength for the principal elemental constituents of portland cements for neutrons (λ = 1Å) and x-rays (λ = 1.54 Å).

alumino-ferrite. The purpose of this investigation was to determine how well the neutron diffraction data could be modeled by the current knowledge of the structure of pure cement compounds as obtained from single crystal X-ray diffraction investigations. This paper also serves to bring together in one place the structural data of these complex minerals-information which is currently scattered throughout the cement and crystallographic literature.

Experimental

Specimens for this experiment were phase-pure synthetic cement compounds. All compounds were prepared from reagent-grade materials using platinum dishes to hold the materials which were sintered in an electrically heated high-temperature furnace. A low alkali reagent grade calcium carbonate was used as the calcium source for all the compounds.

The triclinic tricalcium silicate was made from a 3:1 molar ratio of the calcium carbonate and reagent grade SiO_2 which was ground to a fine powder in a ceramic ball mill, pelletized and then sintered in air at 1500 C for two hours. This material was reground, pelletized, and sintered two more times until no free CaO was detected by X-ray diffraction. Monoclinic tricalcium silicate was made with sufficient amounts of reagent alumina and magnesium carbonate to make a product that contained 0.82% Al_2O_3 and 0.33% MgO and corresponds to Jeffrey's alite formulation (8) except that 1/3 the molar amounts of MgO and Al_2O_3 were substituted for SiO_2 giving a final formula of $C_{162}S_{52}AM$, using the nomenclature of cement chemists (7). The dry materials were ground in a similar manner in a ceramic ball mill, pelletized and sintered at 1480C for 90 minutes. If necessary, the material was reground and the process repeated.

Dicalcium silicate was prepared from a 2:1 molar ratio of calcium carbonate and silica with 0.4% of B_2O_3 added to stabilize the beta form. The pelletized powder was sintered at 1390C for 1 hour and promptly removed from the furnace to rapidly cool.

Tricalcium aluminate (cubic form) or C_3A was made from a 3:1 molar ratio of the calcium carbonate and reagent grade alumina. Pellets were made from the finely ground material and sintered in the furnace at 1450 C for 3 hours. The product was checked by XRD to determine if the reaction was complete. Orthorhombic tricalcium aluminate was made in a similar manner using sodium carbonate, low alkali calcium carbonate, and alumina in molar proportions of 1:8:3, respectively. Blending and grinding was done in a ceramic jar mill and the resulting fine powder was pelletized. The pellets were sintered for three hours at 1450 C and an XRD pattern of the product was obtained to verify formation of the proper phase.

Tetracalcium alumino-ferrite ($4CaO.Al_2O_3.Fe_2O_3$), or C_4AF, was made starting with calcium carbonate, reagent grade alumina, and reagent grade Fe_2O_3 in molar proportions of 4:1:1, respectively. After blending and grinding to a fine powder, pellets were made. The pellets were sintered in air at 1370 C for 90 minutes and an XRD pattern was obtained to verify formation of the compound.

Neutron powder diffraction data over a range of 15°-105° two-theta was obtained using the MURR PSD powder diffractometer at 1.478 Å wavelength. Data acquisition typically lasted 12 to 18 hours per sample. The specimens required no special preparation but were merely loaded into 0.3 cm diameter by 5 cm long 0.07 mm wall thickness vanadium specimen cans and placed on the diffractometer. The sample cans were tightly sealed, but were not air tight.

The GSAS (5) code was used to perform the Rietveld refinements. Typically, the parameters corresponding to the scale factor, lattice parameters, profile parameters (U, V and W), (6) and a 4- or 6-term Chebyshev polynomial background were refined. Additional elements of the refinement are described in conjunction with the discussion of the individual compounds.

Tricalcium Silicate

Tricalcium silicate, $3(CaO).SiO_2$, or C_3S, in the common cement-chemist shorthand, is the major constituent of portland cement and one of the most important for the development of long-term strength in cements and concretes. Taylor's comprehensive work on cement chemistry notes that it is known in a variety of polymorphic forms: two rhombohedral, 2 monoclinic and two triclinic. (1) Complete structure solutions suitable for use as a structural model for neutron powder diffraction refinement are available only for some of the polymorphs. In addition, the structural analysis of tricalcium silicate is further complicated by the fact that the impure forms of this compound (typically found in real portland cements) assume slightly different structures than those of pure C_3S. Nevertheless, each of these structures is the result of a slight distortion of a basic rhombohedral pseudo-structure first described by Jeffrey (8). The pseudo-structure is characterized by the alignment of SiO_4 tetrahedra along the 3-fold axis and the different forms of C_3S differ primarily in terms of the grouping and orientation of these tetrahedra. Jeffrey notes that if the tetrahedra are given alternative orientations, the structure still packs in an almost exactly equivalent fashion as regards the Si and O ions, with negligible changes in the z-coordinates of all the atoms. Nevertheless, our attempts to analyze C_3S in terms of the Jeffrey pseudo-structure failed yielding fits with $\chi^2 = 6.5$ if the standard atom coordinates are used and $\chi^2 = 4.9$ if the atom coordinates are refined.

3.1 Monoclinic C_3S. After reviewing the state of knowledge concerning the various polymorphs of C_3S, Taylor (1) concludes that the most common form is the monoclinic M_3 structure that was studied by Nishi and Takeuchi (9). Data for a specimen of monoclinic C_3S denoted Alite (1/3J) (CTL Lot #MJC50) was obtained and analyzed using this structure solution as a starting point.

The unit cell of this polymorph is so large ~ $33 \times 7 \times 18.6$ Å^3 and contains so many atoms in the asymmetric unit cell (Z = 36) that refinement of atom positional parameters is not reasonable. In addition, the structure is further complicated by statistical disorder and the use of "split atoms". Nishi and Takeuchi describe the position of the calcium atoms in the structure in terms of two closely separated sites, each with occupancy of 0.5. It is unclear if they have proceeded in this fashion to avoid using a description based on anisotropic thermal factors or if the calcium atoms statistically occupy these positions. In addition to the split calcium atoms, there are split oxygen sites associated with these calcium ions. Finally, the structure requires a description of the position and orientation of 18 SiO_4 tetrahedra. In their structural solution, Nishi and Takeuchi discovered that while the orientation of some of these tetrahedra were fixed in position with their apex aligned on the c-axis of the rhombohedral pseudo-cell (as in the pseudo-structure), some were oppositely oriented and still others were tilted off the pseudo-three-fold axis. The three types of tetrahedra were designated as U, D and G. This disorder was included in the crystal model by using statistical occupations of the different tetrahedral atom positions, adding additional sets of atom coordinates to the unit cell description. The end result is that the cell is described by 228 atom sites and this is insufficient to fully describe all of the positions of the tetrahedra-those tetrahedra orientations not observed in Ref. 9 are not included in this list.

In order to describe this crystal for the Rietveld analysis, it was necessary to make some approximations-228 atom sites is too many for GSAS. To reduce the number of atom sites considered, we have taken the average of the atom coordinates for the 36 paired split calcium ion positions. For 11 of the calcium-sites, the splitting is so small that it can easily be neglected ($\delta r \leq 0.1$ Å). Eleven others have a splitting that is somewhat larger ($\delta r \leq 0.2$ Å). The remaining 10 sites have still larger splitting ($\delta r = 0.3$ Å ~ 0.5 Å). It is this latter group that most likely contributes to the modest quality of the Rietveld fit, $\chi^2 = 1.44$ and a weighted residual $wR_p = 0.074$ with a minimum possible $wR_p = 0.062$.

Data and refinement results for the monoclinic C_3S are shown in Fig. 2. Atom coordinates have not been refined. In the refinement of the isotropic thermal factors, the Uiso for all silicon ions was constrained to be the same. In like fashion, Uiso for all of the calcium ions was constrained to be the same. The oxygen ions were split into two groups. Those associated with the calcium ions were constrained to one value while those incorporated into the SiO_4 tetrahedra were all constrained to a separate value.

It is reasonable to expect that the relative orientation of the SiO_4 tetrahedra may be strongly dependent on the amount and species of impurities present in the C_3S. For this reason, several attempts were made to refine the occupancy of the various SiO_4 tetrahedra

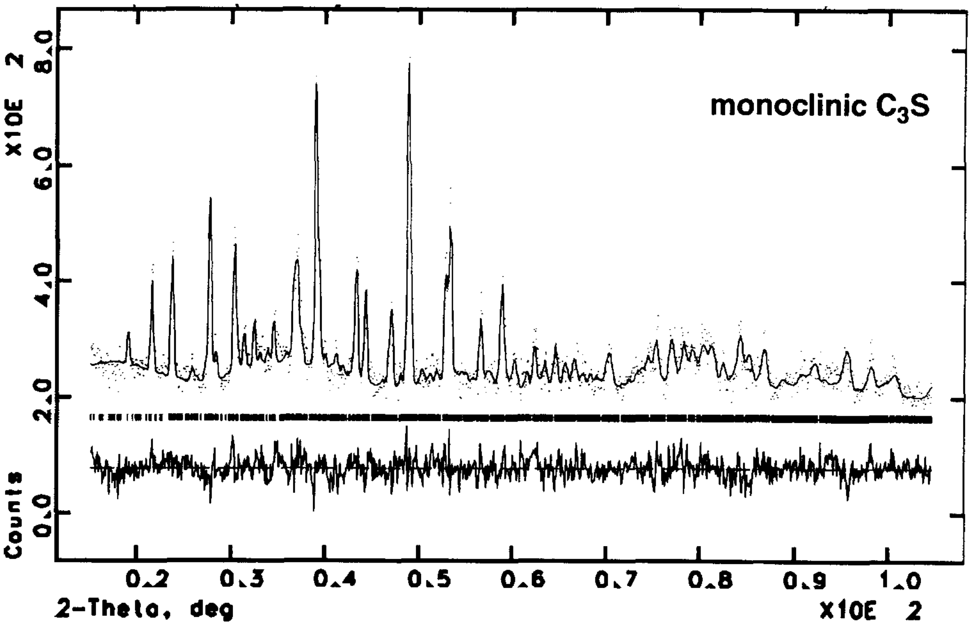

FIG. 2.

Data and refinement results for monoclinic C_3S. Four different Uiso parameters have been used in the refinement; one each for the Ca-atoms, Si-atoms, O-atoms on the SiO_4 tetrahedra and the O-atoms associated with the Ca-atoms. The position of allowed diffraction lines are indicated by the vertical bars below the data (dots) and fit (full line). The difference between the diffraction data and model fit is shown in the lower part of the figure. The refinement obtains a $\chi^2 = 1.44$ and $wR_p = 0.074$.

TABLE 1a

Structure Data for Monoclinic C_3S

Formula	Ca_3SiO_5
Space Group	Cm (#8)
Lattice Parameter	a =33.3594(84)Å b=7.0800(12)Å c=18.6823(36)Å β =94.231(18)
Formula Units/Cell	36

TABLE 1b

Atom Coordinates and Isotropic Thermal Factors Used in the Refinement of Monoclinic Ca_3SiO_5*

Atom	x	y	z	Uiso
Ca(1)	0.0050	0.0000	0.0073	0.023(2)
Ca(2)	0.6673	0.0000	0.1746	0.023(2)
Ca(3)	0.3216	0.0000	0.3318	0.023(2)
Ca(4)	-0.0056	0.0000	0.5008	0.023(2)
Ca(5)	0.6636	0.0000	0.6705	0.023(2)
Ca(6)	0.3365	0.0000	0.8283	0.023(2)
Ca(7)	0.5942	0.0000	-0.0651	0.023(2)
Ca(8)	0.2590	0.0000	0.0908	0.023(2)
Ca(9)	-0.0805	0.0000	0.2656	0.023(2)
Ca(10)	0.5865	0.0000	0.4380	0.023(2)
Ca(11)	0.2568	0.0000	0.5982	0.023(2)
Ca(12)	-0.0742	0.0000	0.7693	0.023(2)
Ca(13)	0.7385	0.0000	-0.0997	0.023(2)
Ca(14)	0.3991	0.0000	0.0749	0.023(2)
Ca(15)	0.0640	0.0000	0.2465	0.023(2)
Ca(16)	0.7279	0.0000	0.4026	0.023(2)
Ca(17)	0.3994	0.0000	0.5693	0.023(2)
Ca(18)	0.0670	0.0000	0.7420	0.023(2)
Ca(19)	-0.0819	0.2833	-0.0858	0.023(2)
Ca(20)	0.5825	0.2538	0.0949	0.023(2)
Ca(21)	0.2435	0.2503	0.2485	0.023(2)

*The coordinates for the Ca atoms are an approximation of the results of ref. 9. Only the isotropic thermal factors have been refined, constrained so that the Ca and Si atoms each have a single Uiso Value. The Uiso for the O atoms been constrained so that SiO_4 tetrahedra sites and the sites associated with the Ca rings each have a different value. The U, D and G designations indicate the orientation of the SiO_4 tetrahedra as up, down or tilted with respect to the pseudo-rhombohedral three-fold axis. The occupancy of all of the sites has been taken as 1.

TABLE 1b *Continued*

Atom	x	y	z	Uiso
Ca(22)	-0.0913	0.2558	0.4202	0.023(2)
Ca(23)	0.5764	0.2562	0.5897	0.023(2)
Ca(24)	0.2452	0.2419	0.7499	0.023(2)
Ca(25)	0.0052	0.2341	-0.1545	0.023(2)
Ca(26)	0.6737	0.2312	0.0109	0.023(2)
Ca(27)	0.3360	0.2321	0.1792	0.023(2)
Ca(28)	-0.0014	0.2410	0.3453	0.023(2)
Ca(29)	0.6659	0.2290	0.5122	0.023(2)
Ca(30)	0.3355	0.2379	0.6788	0.023(2)
Ca(31)	0.8300	0.2735	-0.0109	0.023(2)
Ca(32)	0.4873	0.2512	0.1583	0.023(2)
Ca(33)	0.1515	0.2702	0.3312	0.023(2)
Ca(34)	0.8196	0.2641	0.4896	0.023(2)
Ca(35)	0.4917	0.2808	0.6577	0.023(2)
Ca(36)	0.1606	0.2712	0.8240	0.023(2)
Si(1)	0.0833	0.0000	0.4288	0.007(3)
Si(2)	0.2384	0.0000	-0.0838	0.007(3)
Si(3)	0.4292	0.0000	0.7460	0.007(3)
Si(4)	0.5699	0.0000	0.7506	0.007(3)
Si(5)	-0.0943	0.0000	0.0741	0.007(3)
Si(6)	-0.1015	0.0000	0.5918	0.007(3)
Si(7)	0.0966	0.0000	-0.0851	0.007(3)
Si(8)	0.1637	0.0000	0.1591	0.007(3)
Si(9)	0.1628	0.0000	0.6629	0.007(3)
Si(10)	0.2340	0.0000	0.4118	0.007(3)
Si(11)	0.4214	0.0000	0.2509	0.007(3)
Si(12)	0.5008	0.0000	0.0039	0.007(3)
Si(13)	0.4975	0.0000	0.5004	0.007(3)
Si(14)	0.5682	0.0000	0.2442	0.007(3)
Si(15)	0.7600	0.0000	0.0882	0.007(3)
Si(16)	0.7563	0.0000	0.5803	0.007(3)

TABLE 1b *Continued*

Atom	x	y	z	Uiso
Si(17)	-0.1748	0.0000	0.3338	0.007(3)
Si(18)	-0.1693	0.0000	-0.1575	0.007(3)
O(1A)	0.9900	0.0000	0.2450	0.022(5)
O(1B)	0.9880	0.0000	0.2450	0.022(5)
O(2A)	0.0380	0.0000	0.1190	0.022(5)
O(2B)	0.0520	0.0000	0.1240	0.022(5)
O(3A)	0.0300	0.0000	0.5990	0.022(5)
O(3B)	0.0380	0.0000	0.6100	0.022(5)
O(4A)	-0.0040	0.0000	0.7530	0.022(5)
O(4B)	-0.0050	0.0000	0.7540	0.022(5)
O(5A)	0.3720	0.0000	-0.0770	0.022(5)
O(5B)	0.3730	0.0000	-0.0470	0.022(5)
O(6A)	0.3290	0.0000	0.0750	0.022(5)
O(6B)	0.3310	0.0000	0.0770	0.022(5)
O(7A)	0.2890	0.0000	0.2110	0.022(5)
O(7B)	0.2890	0.0000	0.2230	0.022(5)
O(8A)	0.3620	0.0000	0.4410	0.022(5)
O(8B)	0.3620	0.0000	0.4420	0.022(5)
O(9A)	0.3250	0.0000	0.5830	0.022(5)
O(9B)	0.3340	0.0000	0.5950	0.022(5)
O(10A)	0.2820	0.0000	0.7240	0.022(5)
O(10B)	0.2930	0.0000	0.7320	0.022(5)
O(11A)	0.6660	0.0000	-0.0930	0.022(5)
O(11B)	0.6750	0.0000	-0.0810	0.022(5)
O(12A)	0.6270	0.0000	0.0490	0.022(5)
O(12B)	0.6340	0.0000	0.0670	0.022(5)
O(13A)	0.7060	0.0000	0.2850	0.022(5)
O(13B)	0.7040	0.0000	0.2900	0.022(5)
O(14A)	0.6480	0.0000	0.4210	0.022(5)
O(14B)	0.6550	0.0000	0.4140	0.022(5)
O(15A)	0.6080	0.0000	0.5640	0.022(5)

TABLE 1b *Continued*

Atom	x	y	z	Uiso
O(15B)	0.6220	0.0000	0.5670	0.022(5)
O(16A)	0.7050	0.0000	0.7630	0.022(5)
O(16B)	0.7090	0.0000	0.7710	0.022(5)
O(17A)	0.9490	0.0000	0.3760	0.022(5)
O(17B)	0.9570	0.0000	0.4010	0.022(5)
O(18A)	0.9600	0.0000	0.8970	0.022(5)
O(18B)	0.9650	0.0000	0.9070	0.022(5)
O(D11)	0.1110	0.0000	0.3570	0.018(2)
O(D12)	0.0350	0.0000	0.4080	0.018(2)
O(D13)	0.0960	0.1870	0.4740	0.018(2)
O(U24)	0.2150	0.0000	-0.0110	0.018(2)
O(U25)	0.2860	0.0000	-0.0630	0.018(2)
O(U26)	0.2260	0.1840	-0.1330	0.018(2)
O(D31)	0.4500	0.0000	0.6680	0.018(2)
O(D32)	0.3790	0.0000	0.7300	0.018(2)
O(D33)	0.4430	0.1830	0.7910	0.018(2)
O(U44)	0.5490	0.0000	0.8300	0.018(2)
O(U45)	0.6160	0.0000	0.7670	0.018(2)
O(U46)	0.5550	0.1880	0.7040	0.018(2)
O(U54)	-0.1180	0.0000	0.1490	0.018(2)
O(U55)	-0.0440	0.0000	0.0930	0.018(2)
O(U56)	-0.1070	0.1870	0.0270	0.018(2)
O(U64)	-0.1230	0.0000	0.6690	0.018(2)
O(U65)	-0.0540	0.0000	0.6080	0.018(2)
O(U66)	-0.1170	0.1860	0.5420	0.018(2)
O(D71)	0.1190	0.0000	-0.1610	0.018(2)
O(D72)	0.0480	0.0000	-0.1030	0.018(2)
O(D73)	0.1100	0.1890	-0.0380	0.018(2)
O(U74)	0.0740	0.0000	-0.0090	0.018(2)
O(U75)	0.0550	0.0000	-0.1380	0.018(2)
O(U76)	0.1250	0.1890	-0.0730	0.018(2)

TABLE 1b *Continued*

Atom	x	y	z	Uiso
O(G81)	0.1410	0.0500	0.0800	0.018(2)
O(G82)	0.1340	-0.1230	0.2080	0.018(2)
O(G83)	0.2050	-0.1230	0.1510	0.018(2)
O(G84)	0.1760	0.1970	0.2020	0.018(2)
O(D91)	0.1850	0.0000	0.5870	0.018(2)
O(D92)	0.1140	0.0000	0.6450	0.018(2)
O(D93)	0.1760	0.1890	0.7100	0.018(2)
O(U94)	0.1400	0.0000	0.7390	0.018(2)
O(U95)	0.2120	0.0000	0.6810	0.018(2)
O(U96)	0.1410	0.1890	0.6270	0.018(2)
O(G91)	0.1400	0.0500	0.5840	0.018(2)
O(G92)	0.1330	-0.1230	0.7120	0.018(2)
O(G93)	0.2040	-0.1230	0.6550	0.018(2)
O(G94)	0.1750	0.1970	0.7060	0.018(2)
O(D101)	0.2550	0.0000	0.3350	0.018(2)
O(D102)	0.2680	0.0000	0.4800	0.018(2)
O(D103)	0.2060	0.1890	0.4150	0.018(2)
O(D104)	0.2120	0.0000	0.4870	0.018(2)
O(D105)	0.2830	0.0000	0.4300	0.018(2)
O(D106)	0.2210	0.1890	0.3650	0.018(2)
O(D111)	0.4440	0.0000	0.1750	0.018(2)
O(D112)	0.3720	0.0000	0.2330	0.018(2)
O(D113)	0.4350	0.1890	0.2980	0.018(2)
O(U114)	0.3990	0.0000	0.3270	0.018(2)
O(U115)	0.3820	0.0000	0.1930	0.018(2)
O(Ui16)	0.4500	0.1890	0.2570	0.018(2)
O(U124)	0.4780	0.0000	0.0800	0.018(2)
O(U125)	0.5500	0.0000	0.2200	0.018(2)
O(U126)	0.4870	0.1890	-0.0430	0.018(2)
O(G121)	0.4780	0.0500	-0.0750	0.018(2)
O(G122)	0.4660	-0.1230	0.0400	0.018(2)

TABLE 1b *Continued*

Atom	x	y	z	Uiso
O(G123)	0.5420	-0.1230	-0.0040	0.018(2)
O(G124)	0.5130	0.1970	0.0470	0.018(2)
O(D131)	0.5200	0.0000	0.4250	0.018(2)
O(D132)	0.4480	0.0000	0.4830	0.018(2)
O(D133)	0.5110	0.1890	0.5470	0.018(2)
O(G131)	0.5200	0.0500	0.5800	0.018(2)
O(G132)	0.5260	-0.1280	0.4510	0.018(2)
O(G133)	0.4560	0.1230	0.5080	0.018(2)
O(G134)	0.4810	0.1970	0.4630	0.018(2)
O(D141)	0.5910	0.0000	0.1690	0.018(2)
O(D142)	0.6020	0.0000	0.3120	0.018(2)
O(D143)	0.5400	0.1890	0.2480	0.018(2)
O(U144)	0.5460	0.0000	0.3200	0.018(2)
O(U145)	0.6170	0.0000	0.2620	0.018(2)
O(U146)	0.5550	0.1890	0.1970	0.018(2)
O(D151)	0.7820	0.0000	0.0130	0.018(2)
O(D152)	0.7110	0.0000	0.0700	0.018(2)
O(D153)	0.7730	0.1890	0.1350	0.018(2)
O(U154)	0.7380	0.0000	0.1640	0.018(2)
O(U155)	0.7260	0.0000	0.0200	0.018(2)
O(U156)	0.7880	0.1890	0.0850	0.018(2)
O(D161)	0.7780	0.0000	0.5050	0.018(2)
O(D162)	0.7070	0.0000	0.5650	0.018(2)
O(D163)	0.7690	0.1910	0.6260	0.018(2)
O(U164)	0.7340	0.0000	0.6560	0.018(2)
O(U165)	0.7170	0.0000	0.5220	0.018(2)
O(U166)	0.7870	0.1800	0.5940	0.018(2)
O(U174)	-0.1970	0.0000	0.4090	0.018(2)
O(U175)	-0.1260	0.0000	0.3520	0.018(2)
O(U176)	-0.1880	0.1890	0.2870	0.018(2)
O(G171)	-0.1970	0.0500	0.2550	0.018(2)

TABLE 1b *Continued*

Atom	x	y	z	Uiso
O(G172)	-0.2040	-0.1230	0.3830	0.018(2)
O(G173)	-0.1340	-0.1230	0.3260	0.018(2)
O(G174)	-0.1630	0.1970	0.3770	0.018(2)
O(G175)	-0.1520	0.0500	0.4130	0.018(2)
O(G176)	-0.1450	-0.1230	0.2850	0.018(2)
O(G177)	-0.2160	-0.1230	0.3420	0.018(2)
O(G178)	-0.1870	0.1970	0.2910	0.018(2)
O(U184)	-0.1920	0.0000	-0.0820	0.018(2)
O(U185)	-0.1200	0.0000	-0.1400	0.018(2)
O(U186)	-0.1830	0.1890	-0.2040	0.018(2)
O(G181)	-0.1920	0.0500	-0.2370	0.018(2)
O(G182)	-0:1990	-0.1230	-0.1080	0.018(2)
O(G183)	-0.1280	-0.1230	-0.1650	0.018(2)
O(G184)	-0.1580	0.2100	-0.1250	0.018(2)

orientations. In order to effectively pursue this hypothesis, it will be necessary to impose chemical constraints on the tetrahedra occupancy values-a feature not currently implemented in GSAS. In addition, to obtain meaningful results, it will be necessary to follow the trend of tetrahedra orientations as a function of the impurity concentration-an investigation that is outside the scope of the current work.

For completeness, the atom positions, occupancies and thermal parameters for monoclinic C_3S are listed in the Table 1 (10). The position of the oxygen and silicon atoms reflect the assignments given by Ref. 9. The positions of the calcium ions are averages of the split coordinates assigned by the X-ray solution.

3.2 Triclinic C_3S. According to Taylor, (1) the presence of triclinic C_3S in production clinkers is rare. Nevertheless, we have analyzed a specimen of the triclinic polymorph (CTL Lot #TJC02). A complete structural solution suitable for use in Rietveld refinement exists only for the T1 polytype, the work of Golovastikov et al., (11) and this was adopted as the refinement starting point.

Triclinic C_3S is again a large unit cell structure, 11.6 × 14 × 13.7 $Å^3$ with Z = 18, requiring 82 atom sites for a complete description. Using the X-ray atom coordinates and setting all of the thermal parameters to Uiso = 0.025, $\chi^2 = 1.44$ was obtained. When the profile parameters (U, V, and W) were added to the fit, χ^2 declined to 1.39. With all of the thermal parameters on all of the atoms constrained to be the same, we obtained Uiso = 0.013 and $\chi^2 = 1.27$. When the thermal parameters for each chemical species was allowed to be different, the χ^2 declined to 1.266 with $wR_p = 0.0811$. In comparison, the minimum wR_p for this data is 0.075.

Although more tractable than is the case with the monoclinic polymorph, we chose to proceed no further than the refinement of the thermal parameters as described above. The neutron diffraction data and refinement results are shown in Fig. 3 and the table of atom

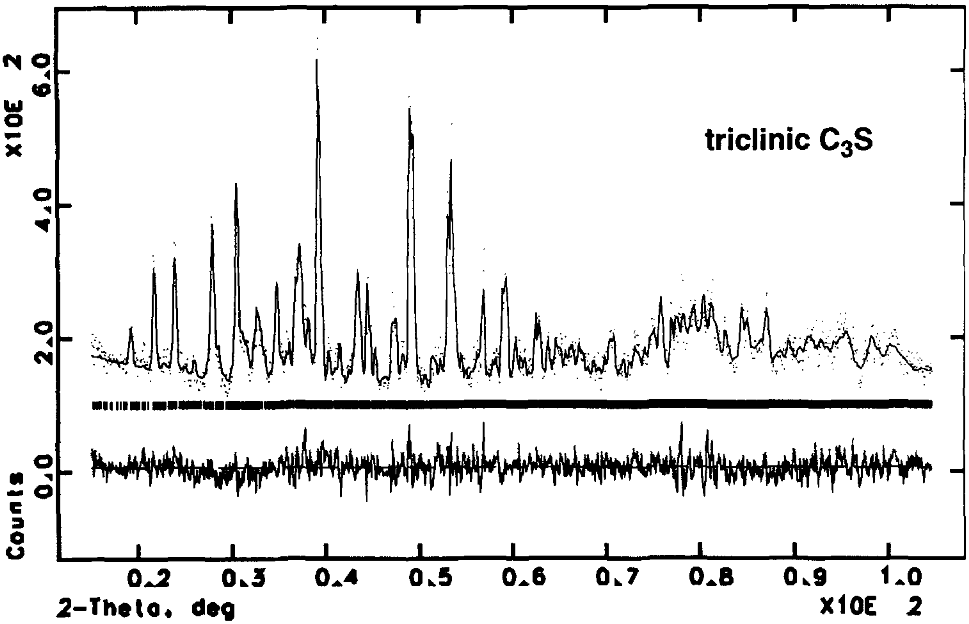

FIG. 3.

Neutron powder diffraction data and refinement results for triclinic C_3S. This refinement, including only the isotropic thermal parameters constrained to be the same for each atom species, obtained a $\chi^2 = 1.27$ with a $wR_p = 0.081$.

coordinates (obtained from Ref. 11) and isotropic thermal factors (from refinement of the neutron data) are listed in Table 2.

Beta Dicalcium Silicate

In typical portland cements, dicalcium silicate, $2(CaO).SiO_2$, or C_2S, in cement notation, can be as much as 57% by weight of a portland cement. It is known in five polymorphic forms although β-C_2S is by far the most common. As is the case with C_3S, the polymorphs differ mainly in the orientation of the SiO_4 tetrahedra that form the fundamental building blocks of the structure. Taylor's book provides a pictorial structural comparison of the polymorphs (1).

Neutron powder diffraction data were obtained with a boron stabilized single phase specimen (CTL Lot #B410). Attempts to refine the atomic positions in β-C_2S using the X-ray structural parameters refined by Cruikshank (12) from data by Midgley (13) produced very poor fits. Refinement of the atomic coordinates yielded atom shifts of 200 times the estimated uncertainty in the positions given by the Rietveld results. We subsequently discovered a more modern X-ray analysis of this structure that confirms our refinements (14). The final results for β-C_2S obtained a $\chi^2 = 1.079$ with a weighted residual, $wR_p = 0.0642$. The minimum possible residual for this data would be 0.0625. Figure 4 shows the data and refinement results for β-C_2S with the crystal data and atom coordinates listed in Table 3.

TABLE 2a

Structure Data for Triclinic Ca_3SiO_5

Formula	Ca_2SiO_4
Space Group	$P2_1/n$ (#14)
Lattice Parameter	a =11.655(16)Å b=14.2390(18)Å c=13.7154(20)Å α = 105.27(1) β =94.57(1) γ = 89.87(1)
Formula Units/Cell	18

TABLE 2b

Atom Coordinates and Isotropic Thermal Parameters Used in the Refinement of Triclinic C_3S.*

Atom	x	y	z	Uiso
CA(1)	0.7102	0.0039	0.9750	0.0139(15)
CA(2)	0.3541	0.1525	0.6527	0.0139(15)
CA(3)	0.6751	0.3207	0.3351	0.0139(15)
CA(4)	0.8454	0.1667	0.1697	0.0139(15)
CA(5)	0.1908	0.3284	0.8152	0.0139(15)
CA(6)	0.3328	0.4107	0.6483	0.0139(15)
CA(7)	0.6476	0.0817	0.3340	0.0139(15)
CA(8)	0.0536	0.1663	0.6176	0.0139(15)
CA(9)	0.6438	0.1808	0.7226	0.0139(15)
CA(10)	0.3830	0.3474	0.3033	0.0139(15)
CA(11)	0.9650	0.3339	0.3678	0.0139(15)
CA(12)	0.0498	0.3977	0.6244	0.0139(15)
CA(13)	0.3604	0.0547	0.2888	0.0139(15)
CA(14)	0.6220	0.4145	0.7117	0.0139(15)
CA(15)	0.9682	0.1048	0.3762	0.0139(15)
CA(16)	0.4651	0.0913	0.8506	0.0139(15)
CA(17)	0.2141	0.2419	0.4658	0.0139(15)
CA(18)	0.8040	0.2472	0.5175	0.0139(15)
CA(19)	0.5363	0.4148	0.1508	0.0139(15)
CA(20)	0.7012	0.4880	0.9589	0.0139(15)
CA(21)	0.7241	0.2378	0.9700	0.0139(15)
CA(22)	0.3039	0.2766	0.0251	0.0139(15)
CA(23)	0.8729	0.0824	0.8173	0.0139(15)
CA(24)	0.1371	0.4262	0.1848	0.0139(15)
CA(25)	0.0205	0.2604	0.9897	0.0139(15)

*The atom coordinates have been taken from the work of Golovastikov et al. (11). The occupancy of all sites has been taken as 1.

TABLE 2b *Continued*

Atom	x	y	z	Uiso
CA(26)	0.0000	0.0000	0.0000	0.0139(15)
CA(27)	0.0000	0.5000	0.0000	0.0139(15)
CA(28)	0.5000	0.0000	0.5000	0.0139(15)
CA(29)	0.5000	0.5000	0.5000	0.0139(15)
SI(1)	0.8322	0.4165	0.1646	0.0067(28)
SI(2)	0.4748	0.3440	0.8710	0.0067(28)
SI(3)	0.1616	0.0800	0.8192	0.0067(28)
SI(4)	0.8002	0.0183	0.5467	0.0067(28)
SI(5)	0.1922	0.4972	0.4486	0.0067(28)
SI(6)	0.5221	0.1553	0.1222	0.0067(28)
SI(7)	0.1492	0.1806	0.2057	0.0067(28)
SI(8)	0.8709	0.3207	0.7842	0.0067(28)
SI(9)	0.4977	0.2486	0.5043	0.0067(28)
O(1)	0.0339	0.1943	0.2619	0.0143(16)
O(2)	0.5127	0.2655	0.1925	0.0143(16)
O(3)	0.6528	0.1486	0.0807	0.0143(16)
O(4)	0.1548	0.0685	0.1427	0.0143(16)
O(5)	0.2204	0.2685	0.6425	0.0143(16)
O(6)	0.5037	0.0541	0.6743	0.0143(16)
O(7)	0.4211	0.1297	0.0254	0.0143(16)
O(8)	0.2625	0.2060	0.2903	0.0143(16)
O(9)	0.6673	0.0923	0.8532	0.0143(16)
O(10)	0.0105	0.2584	0.4944	0.0143(16)
O(11)	0.5133	0.0806	0.1910	0.0143(16)
O(12)	0.1592	0.2553	0.1291	0.0143(16)
O(13)	0.8279	0.3950	0.4729	0.0143(16)
O(14)	0.3124	0.4978	0.4018	0.0143(16)
O(15)	0.1825	0.4137	0.5105	0.0143(16)
O(16)	0.3379	0.4353	0.1771	0.0143(16)
O(17)	0.1610	0.3931	0.9860	0.0143(16)
O(18)	0.0880	0.4729	0.3560	0.0143(16)
O(19)	0.2778	0.0582	0.7617	0.0143(16)
O(20)	0.9492	0.4028	0.1070	0.0143(16)
O(21)	0.1610	0.1919	0.8857	0.0143(16)
O(22)	0.1468	0.0064	0.8928	0.0143(16)
O(23)	0.8031	0.1819	0.3337	0.0143(16)

TABLE 2b *Continued*

Atom	x	y	z	Uiso
O(24)	0.8955	0.1402	0.9995	0.0143(16)
O(25)	0.5583	0.4518	0.3380	0.0143(16)
O(26)	0.0487	0.0587	0.7321	0.0143(16)
O(27)	0.6123	0.2397	0.4460	0.0143(16)
O(28)	0.7683	0.0509	0.6645	0.0143(16)
O(29)	0.4446	0.3903	0.9879	0.0143(16)
O(30)	0.6109	0.3254	0.8630	0.0143(16)
O(31)	0.9981	0.3075	0.7361	0.0143(16)
O(32)	0.6869	0.0169	0.4682	0.0143(16)
O(33)	0.8604	0.2449	0.8521	0.0143(16)
O(34)	0.7189	0.3952	0.0806	0.0143(16)
O(35)	0.7741	0.3028	0.6875	0.0143(16)
O(36)	0.8915	0.0963	0.5267	0.0143(16)
O(37)	0.8639	0.4292	0.8575	0.0143(16)
O(38)	0.4144	0.1476	0.4653	0.0143(16)
O(39)	0.1459	0.0887	0.4737	0.0143(16)
O(40)	0.8270	0.3351	0.2302	0.0143(16)
O(41)	0.3964	0.2440	0.8327	0.0143(16)
O(42)	0.5193	0.2654	0.6264	0.0143(16)
O(43)	0.4178	0.3379	0.4840	0.0143(16)
O(44)	0.1820	0.4733	0.7596	0.0143(16)
O(45)	0.4400	0.4192	0.8047	0.0143(16)

Tricalcium Aluminate

Tricalcium aluminate, C_3A ($3CaO.Al_2O_3$), is present in varying amounts from approximately 1% in a Type V portland cement to as much as 17% in some Type III cements. The aluminate fraction can be responsible for the phenomena of "flash set" and is the main reason that gypsum (which suppresses its rapid hydration) is often interground with clinker in the manufacture of portland cements. Although at least four forms of C_3A are known, only two are found in quantity in normal cements: a cubic and an orthorhombic phase and both of these are available as single phase specimens.

5.1 Cubic C_3A. Mondal and Jeffery (15) determined the structure of C_3A from a refinement of single crystal X-ray data. They describe the structure as cubic, space group Pa3, with lattice parameter a = 15.263 Å and 24 molecules per unit cell. The structure is composed of rings of six AlO_4 units centered on the three-fold axes and composed of two types of distorted AlO_4 tetrahedra. They note that the holes between the rings contain the calcium atoms. Of the 80 sites for calcium available in this structure, 72 are filled leaving 8 sites vacant.

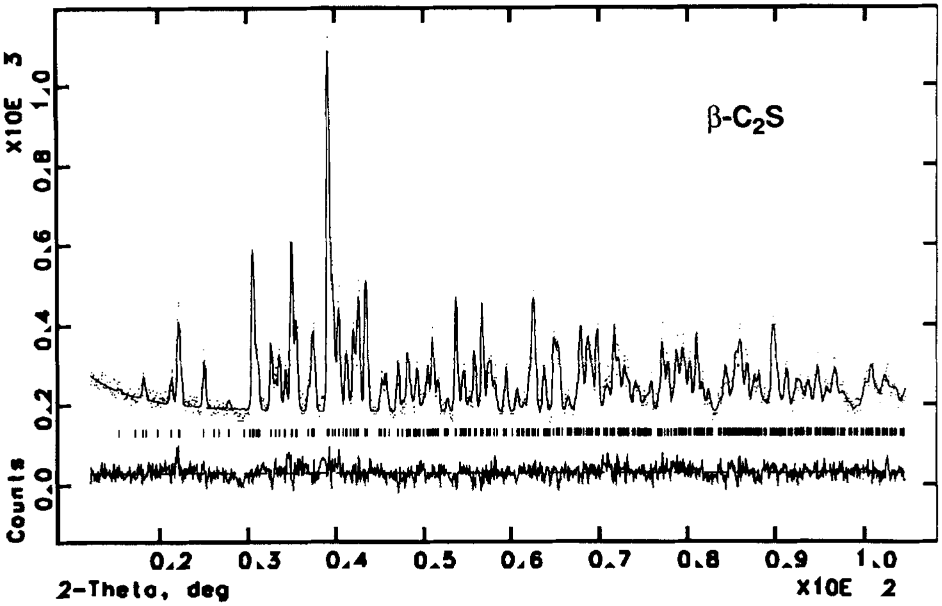

FIG. 4.
Neutron powder diffraction data and refinement results for β-C$_2$S. In this refinement, atom coordinates and isotropic thermal factors have been allowed to vary. The refinement obtains $\chi^2 = 1.08$ and $wR_p = 0.064$.

These vacant sites play a role in the rapid hydration of the C$_3$A and can accommodate impurity ions such as sodium or potassium.

The neutron diffraction data and Rietveld refinement results for cubic-C$_3$A (CTL Lot #AJC31) are shown in Fig. 6. Starting values for the atomic positions were taken from Ref. 15. In the end, the profile scale factor, lattice parameters, isotropic thermal parameters, atomic positions, background parameters (4) and peak profile parameters (3) were refined, providing $\chi^2 = 2.2$ with a weighted residual $wR_p = 0.093$. The minimum possible weighted residual for this data is 0.064. In this fit, the isotropic temperature factor was constrained to be the same for all atoms of a particular species. The atomic positions and thermal factors obtained from the fit are listed in Table 4, below. The results may be summarized by noting

TABLE 3a
Structure Data for β-C$_2$S

Formula	Ca_2SiO_4
Space Group	$P2_1/n$ (#14)
Lattice Parameter	a =5.5172(41)Å b=6.76996(55)Å c=9.32298(80)Å β =94.336(5)
Formula Units/Cell	4

TABLE 3b

Fractional Atomic Coordinates and Isotropic Thermal Factors for β-C_2S Obtained from Refinement of Neutron Powder Diffraction Data

Atom	x	y	z	Uiso
CA(1)	0.2712(12)	0.3442(9)	0.5698(8)	0.0175(18)
CA(2)	0.2729(14)	0.9979(12)	0.3001(7)	0.0165(22)
SI(3)	0.2338(15)	0.7811(9)	0.5825(8)	0.0107(21)
O(4)	0.2802(10)	0.0117(7)	0.5602(6)	0.0109(18)
O(5)	0.0242(11)	0.7454(9)	0.6902(6)	0.0116(14)
O(6)	0.4855(10)	0.6737(9)	0.6403(6)	0.0105(15)
O(7)	0.1592(9)	0.6711(11)	0.4293(5)	0.0126(16)

that the atomic positions for most of the atoms obtained from the neutron data differ only slightly from those obtained by Mondal and Jeffery (15). The largest deviation is 0.2 Å which was obtained for Ca(4). The position deviations for all of the other atoms are less than 0.1 Å. The lattice parameter obtained from the neutron data was 15.3043 Å with an estimated standard deviation 0.0007 Å which is slightly larger than obtained by X-ray methods (15.263 Å).

5.2 Orthorhombic C_3A. Studies of the effect of Na_2O (N) and K_2O (K) impurities on the formation of C_3A confirm that over a restricted range of concentration, they can enter into the C_3A crystal structure. The C_3A-N solid solution series has been the subject of study by a number of workers (16, 17, 20) and is summarized by Taylor (1). Two cubic forms, an orthorhombic form and a monoclinic structure are reported as the Na_2O content increases from 0% to 7.59%, where the compound NC_8A_3 would be formed. These crystal structures are all based on modifications of the same crystal motif-an arrangement of six-membered AlO_4 rings. Sodium atoms occupy the centers of the rings and also preferentially occupy some of the Ca sites.

A specimen of orthorhombic aluminate designated NC_8A_3 (CTL Lot #AJC34) was analyzed by powder neutron diffraction. The oxide composition for this specimen, obtained by X-ray fluorescence spectrometry, is listed in Table 5, below. The chemical formula for this compound, derived from the oxide analysis, is $Ca_{7.95}Na_{1.74}Al_6O_{17.82}$ (here we have ignored the presence of the minor constituents listed in Table 5). With an Na_2O content of 6.70%, this material is at the high end of Na solubility reported for the C_3A-N system. In this range, most workers report a monoclinic structure which is a distortion of the orthorhombic form that appears at lower Na_2O content. Given the X-ray identification of the material as orthorhombic, we have chosen to analyze this specimen using the orthorhombic model as an approximant. Starting values for the atomic coordinates and lattice parameters were obtained from Ref. 20. A comparison of the data and Rietveld refinement results for this specimen are shown in Fig. 6.

The initial attempt to refine the structure produced an occupancy for the Na(6) site of 1.15 ± 0.095. This was taken as an indication that the Na(6) site was fully occupied and for subsequent refinements, the occupation of that site was fixed at one. In the refinement, of the other atom sites, only the occupancy of the Ca(5) site was considered to be variable. In

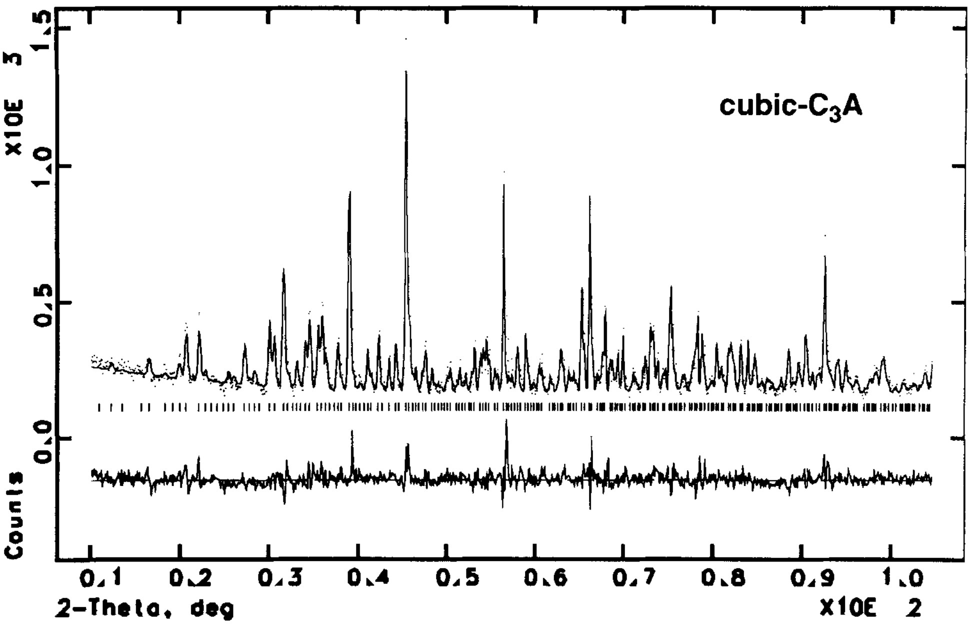

FIG. 5.

Neutron powder diffraction data and refinement results for cubic-C_3A (Fig. 5). In this refinement, the lattice parameter, atom positions and isotropic thermal factors have been allowed to vary. Uiso has been constrained to be the same for all atoms of a particular chemical species. A value of $\chi^2 = 2.2$ with $wR_p = 0.093$ was obtained.

addition, the atom positions, lattice parameters, spectrometer zero, scale factor, isotropic thermal factors, 4-term Chebyshev background and U, V, W peak profile parameters were refined. This result is shown in Table 6. This refinement yielded $\chi^2 = 1.75$ with a weighted residual, $wR_p = 0.0856$.

The occupancy of the Ca(5) site was found to be 0.655(39). In the Rietveld refinement process, however, the quantity that actually enters into the profile calculation is the product of the occupancy and the atom scattering length. What the above result indicates is that the best fit is obtained when the scattering length on the site is $0.655{*}b_{Ca} = 0.3209 \times 10^{-12}$ cm. If the site is partially occupied by Ca and part by Na, the average scattering length associated with the site can be written as:

$$f b_{Ca} = f'_{Ca} b_{Ca} + f'_{Na} b_{Na} \qquad \text{(EQ 1)}$$

where $f = 0.655$ is the quantity obtained from the refinement, and f'_{Ca} and f'_{Na} are, respectively, the calcium and sodium occupancies for the so-called Ca(5) site. We have fixed the occupancy of the Ca(5) site so that the total Na content agrees with the results from oxide analysis. When that is done, we calculate the Ca(5) site is occupied equally by Ca and Na atoms $f_{Ca} = f_{Na} = 0.37$ (the total site occupancy is 0.75). The resulting formula for the compound, derived from the Rietveld analysis is $Ca_{8.73}Na_{1.74}Al_6O_{18}$ in reasonable agreement with the result derived from chemical analysis.

The estimated uncertainties in the refined atom positions are generally of the same order the quoted errors in the single crystal X-ray refinement atom positions from Ref. 20. The

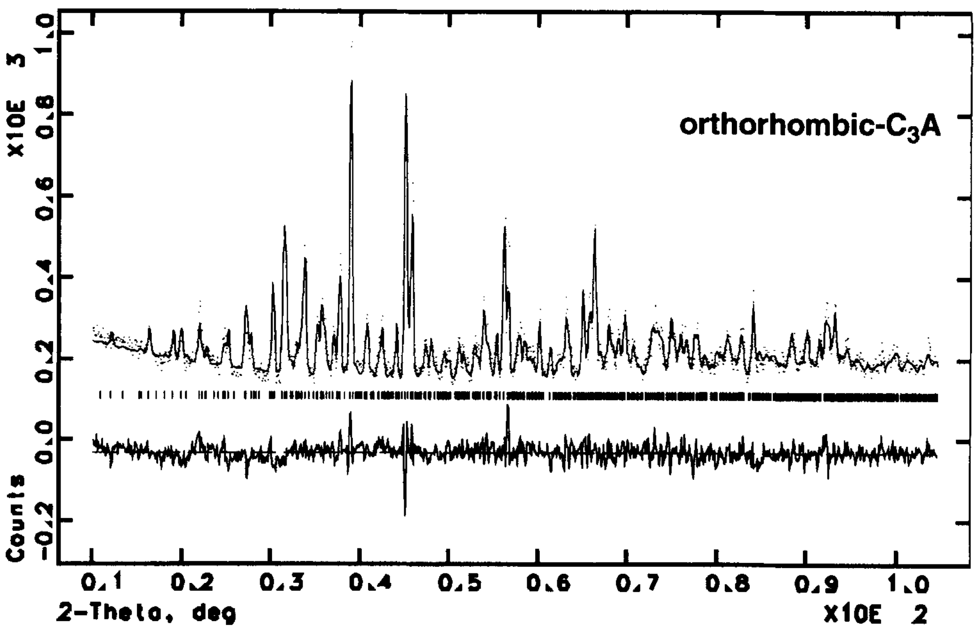

FIG. 6.

Neutron powder diffraction data and refinement results for orthorhombic $Ca_{7.94}Na_{1.74}Al_6O_{17.81}$. In this refinement, the Na site at the ring center has been fixed a full occupancy and the remaining Na atoms are presumed to partially fill the Ca(5) site.

lattice parameters obtained from the neutron data are somewhat larger but they are consistent with the known variation of the lattice parameter with increasing Na content (15).

Calcium Alumino-Ferrite

The presence of iron oxides in the cement kiln feedstock materials leads to the formation of the $Ca_2Fe_{2-x}Al_xO_5$ which is usually designated as C_4AF even though the Al/Fe ratio may differ significantly from one. C_4AF can form as much as 18% of a portland cement and hydrates more slowly but has hydration characteristics that are similar to those of C_3A. Neutron diffraction data was obtained from a C_4AF specimen with an A/F ratio of 1.01 (CTL Lot# FJC43). The diffraction data and refinement results are shown in Fig. 7 and the structural data from the refinement are shown in Table 7. There are a few small peaks in the diffraction diagram which we believe are unrelated to the specimen and are probably the

TABLE 4a

Structure Data for Cubic C_3A

Formula	$Ca_3Al_2O_6$
Space Group	Pa3 (#205)
Lattice Parameter	15.3043 (7) Å
Formula Units/Cell	24

TABLE 4b

Fractional Atomic Coordinates and Isotropic Thermal Factors for Cubic C_3A*

Atom	x	y	z	Uiso
CA(1)	0.0000(0)	0.0000(0)	0.0000(0)	0.0143(14)
CA(2)	0.5000(0)	0.0000(0)	0.0000(0)	0.0143(14)
CA(3)	0.2582(8)	0.2582(8)	0.2582(8)	0.0143(14)
CA(4)	0.3676(10)	0.3676(10)	0.3676(10)	0.0143(14)
CA(5)	0.1376(10)	0.3788(10)	0.1306(11)	0.0143(14)
CA(6)	0.3754(11)	0.3852(8)	0.1208(9)	0.0143(14)
AL(7)	0.2547(11)	0.0137(12)	0.0216(11)	0.0051(25)
AL(8)	0.2430(13)	0.2363(12)	0.0015(11)	0.0051(25)
O(9)	0.2781(7)	0.1244(10)	0.0096(7)	0.0099(11)
O(10)	0.4858(6)	0.1311(10)	0.2524(7)	0.0099(11)
O(11)	0.2669(7)	0.2829(8)	0.1044(8)	0.0099(11)
O(12)	0.2376(7)	0.4041(7)	0.2941(7)	0.0099(11)
O(13)	0.3505(8)	-0.0374(8)	-0.0160(7)	0.0099(11)
O(14)	0.1546(8)	-0.0137(8)	-0.0259(7)	0.0099(11)

*Obtained from refinement of neutron powder diffraction data. The occupation of all the sites has been taken as 1

TABLE 5

Oxide Analysis of Lot #AJC34, Orthorhombic Aluminate

Analyate	Weight % as recd.	Weight % ignited
SiO_2	0.18	0.20
Al_2O_3	36.95	37.90
Fe_2O_3	0.07	0.07
CaO	563.83	55.21
MgO	0.05	0.06
SO_3	0.03	0.03
Na_2O	6.54	6.70
K_2O	0.02	0.02
TiO_2	<0.01	<0.01
P_2O_5	<0.01	<0.01
Na_2O_3	<0.01	<0.01
SrO	0.01	0.01
LOI	2.51	0.00

TABLE 6a

Structure Data for C_3A

Formula	$Ca_{7.95}Na_{1.74}Al_6O_{17.82}$
Space Group	Pbca (#61)
Lattice Parameter	a = 10.8588(15) b = 10.8533(14) c = 15.1181(16)
Formula Units/Cell	4

refinements of C_4AF utilize a 6-term Chebyshev background to accomodate the increase in background level observed at low scattering angles.

Initial attempts to refine the structure used as a starting point the Pcmn space group and atom positions proposed by Bertaut et al. (18). This structure is the same as that of the end member of the solid solution series, $Ca_2Fe_2O_5$, but produced a relatively poor fit with $\chi^2 = 3.6$ and $wR_p = 0.12$.

Colville and Geller (19) show that $Ca_2Fe_{2-x}Al_xO_5$ with $x > 0.28$ assumes the Ibm2 space group. Their X-ray results indicate that the Fe and Al share two sites with the first being Fe-rich (0.76/0.24)and the second Fe poor (0.26/0.76). A refinement using these atom positions and occupancies, refining the isotropic thermal factors for each of the atom species and

TABLE 6b

Atom	x	y	z	frac.	Uiso
Ca(1)	0.0202(24)	0.0173(20)	0.5184(12)	1	0.0123(22)
Ca(2)	-0.0134(28)	0.0263(18)	0.2364(10)	1	0.0123(22)
Ca(3)	0.0006(32)	0.2687(14)	0.1305(11)	1	0.0123(22)
Ca(4)	0.2507(24)	0.2711(18)	0.2530(24)	1	0.0123(22)
Ca(5)	0.2578(390)	0.2493(37)	0.4910(44)	0.655(39)	0.0123(22)
Na(6)	0.0000(0)	0.0000(0)	0.0000(0)	1	0.0302(137)
Al(7)	-0.0109(35)	-0.2186(22)	0.1192(15)	1	0.0002(32)
Al(8)	0.2473(29)	-0.0038(34)	0.1043(24)	1	0.0002(32)
Al(9)	0.2378(30)	0.0059(33)	-0.1125(23)	1	0.0002(32)
O(10)	-0.1513(18)	-0.1320(18)	0.1083(12)	1	0.0122(16)
O(11)	0.1118(18)	-0.1071(19)	0.1211(13)	1	0.0122(16)
O(12)	0.2906(15)	-0.0171(20)	0.0018(18)	1	0.0122(16)
O(13)	-0.0152(19)	-0.2856(16)	0.2202(9)	1	0.0122(16)
O(14)	0.0209(19)	-0.2960(16)	0.0165(10)	1	0.0122(16)
O(15)	0.3538(20)	-0.0720(20)	0.1758(13)	1	0.0122(16)
O(16)	0.1914(17)	0.1432(20)	0.1379(15)	1	0.0122(16)
O(17)	0.1647(15)	-0.1364(20)	-0.1332(14)	1	0.0122(16)
O(18)	0.3673(16)	0.0808(21)	-0.1593(12)	1	0.0122(16)

TABLE 7a

Structure Data for C_4AF

Formula	$Ca2AlFeO_5$
Space Group	Ibm2 (#46)
Lattice Parameter	a =5.56427(25) b =14.53342(65) c =5.34773(24)
Formula Units/Cell	4

with the Al and Fe thermal factors constrained to be the same, obtained $\chi^2 = 1.32$ with $wR_p = 0.75$. Adding refinement of the atom coordinates and Fe and Al site occupancies produced only a small further improvement and small shifts in the atom coordinates. The shifts in atom coordinates were all within the combined errors of the X-ray and neutron refinement results. The Fe/Al occupancy ratios on the two Fe-Al atom sites differ by about 10% from those obtained in Ref. 19 and give an overall Fe/Al ratio of 0.972 ± 0.054.

Summary and Conclusions

We have obtained neutron powder diffraction data for 6 synthetic phase-pure compounds often found in portland cements. The resulting diffraction patterns have been analyzed with full profile (Rietveld) refinements with single crystal X-ray structural solutions as the starting point of the analyses. In the case of tricalcium silicate, we have found that it is necessary to use the more accurate monoclinic or triclinic crystal structure in the analysis-the simpler rhombohedral psuedo-structure cannot provide a reasonable fit to the neutron data. The analysis of β-dicalcium silicate was gratifying in the sense that the neutron refinement starting with an incorrect X-ray structure quite independently produced atom coordinates that were later discovered to be in agreement with the correct X-ray structural analysis. The results for cubic and orthorhombic tricalcium aluminate are in general agreement with the X-

TABLE 7b

Fractional Atomic Coordinates and Isotropic Thermal Factors for C_4AF Obtained from Refinement of Neutron Powder Diffraction Data

Atom	**x**	**y**	**z**	**frac**	**Uiso**
CA(1)	0.0268(7)	0.1084(2)	0.4928(15)	1.000	0.0107(11)
FE(2)	0.0000	0.0000	0.0024(13)	0.691(16)	0.054(10)
AL(3)	0.0000	0.0000	0.0024(13)	0.309(16)	0.054(10)
FE(4)	0.9292(10)	0.2500	0.9551(13)	0.295(12)	0.054(10)
AL(5)	0.9292(10)	0.2500	0.9551(13)	0.705(12)	0.054(10)
O(6)	0.2510(13)	0.9863(2)	0.2548(19)	1.000	0.0098(11)
O(7)	0.0672(5)	0.1442(2)	0.0236	1.000	0.0121(11)
O(8)	0.8578(11)	0.2500	0.6200(14)	1.000	0.0112(16)

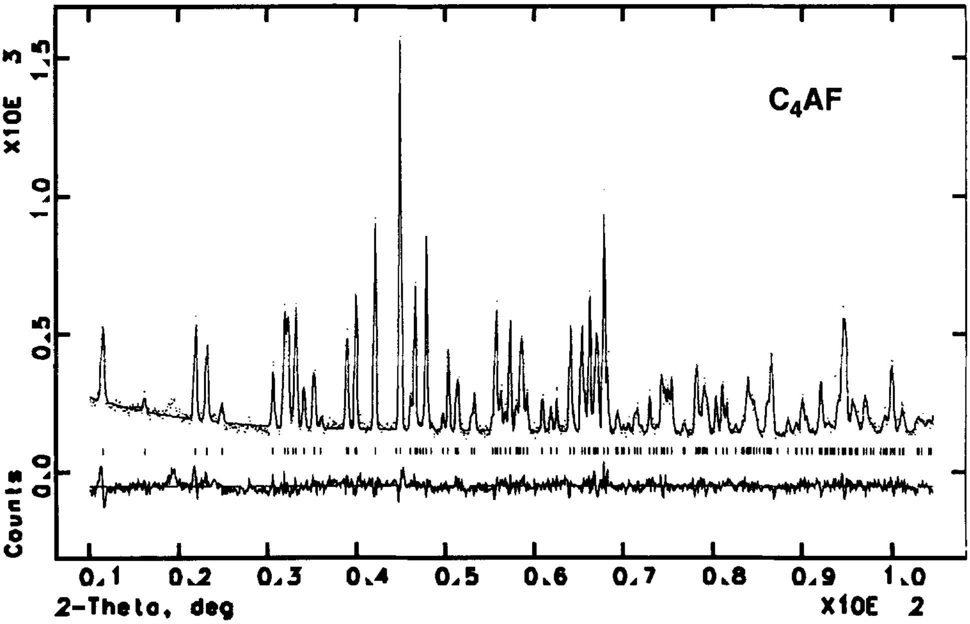

FIG. 7.

Neutron powder diffraction data and Rietveld refinement results for Ca_4AlFeO_5. The occupation of the metal ion sites, which contain both Al and Fe, have been allowed to vary subject only to the constraint that the sites be fully occupied. In addition to these site occupancies, the scale factor, lattice parameter, diffractometer zero, atom coordinates, thermal factors, background parameters (6) and profile parameters (3) have been refined.

ray results. The refinement result for the calcium alumino-ferrite indicates that the neutron diffraction data can be used to obtain quite reasonable results for the A/F ratio when producing the structural refinement.

The structural models developed here have been used in the analysis of standard cement clinkers and provide results that compare well with other methods for the determination of cement phase compositions (21). The greatest utility of this work, however, is that it provides the data and a starting point for the investigation of the hydration kinetics of cement compounds using neutron powder diffraction (22).

References

1. H.F.W. Taylor, Cement Chemistry, Academic Press, London, 1990.
2. L.P. Aldridge, Cement and Concrete Research 12, 381-398 (1982).
3. L.J. Struble, Cement, Concrete and Aggregrates, CCAGDP, 13, (2), 97–102, 1991.
4. H.M. Rietveld, J. Appl. Cryst. 2, 65, (1969).
5. A.C. Larson & R.B. Von Dreele. "GSAS-General Structure Analysis System", Los Alamos National Laboratory Report LAUR 86-748 (1994).
6. The quantities U, V and W refer to the standard description of the resolution for a two axis diffractometer, G. Caglioti, A. Paoletti, and F.P. Ricci, Nucl. Instrum and Meth. 3, 223 (1958).
7. In cement chemist's notation: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, N = Na_2O, and K = K_2O.

8. J.W. Jeffrey, Acta. Cryst. 5. 26 (1952).
9. F. Nishi and Y. Takeuchi, Zeitschrift fur Krystallographie, 172, 297-314 (1985).
10. The tables list the atom coordinates as fractions of the lattice parameters. The thermal parameter Uiso is defined by writing the thermal correction to the structure factor as exp $(-(8\pi^2 U_{iso}/\lambda^2) \sin^2\Theta)$.
11. N.I. Golovastikov, R.G. Matveeva, and N.V. Belov, Sov. Phys. Crystallogr. 20, 441 (1975).
12. D.W.J. Cruikshank, Acta. Cryst. 17, 685-686 (1963).
13. C.M. Midgley, Acta. Cryst. 5, 307 (1952).
14. K.H. Jost, B. Ziemer and R. Seydel, Acta. Cryst. B33, 1696-1700 (1977).
15. P. Mondal and J.W. Jeffery, Acta Cryst. B31. 689, (1975).
16. K.E. Fletcher, H.G. Midgley and A.E. Moore, Concrete Research, 17, 171 (1965).
17. Y. Takeuchi and F. Nishi, Zeitschrift fur Krystallographie, 152, 259-307 (1980).
18. E.F. Bertaut, P. Blum and A. Sagnieres, Acta. Cryst. 12, 149-159 (1959).
19. A.A. Colville and S. Geller, Acta. Cryst , B27, 2311-2315 (1971).
20. Fumito Nishi and Y. Takeuchi, Acta. Cryst., B31, 1169 (1974).
21. R. Berliner, C. Ball and Presbury B. West, in Neutron Scattering in Materials Science, edited by D.A. Neumann, T.P. Russell and B.J. Wuensch (Mater. Res. Soc. Symp. Proc., Pittsburgh, PA, 1994, p. 487.
22. R. Berliner, F. Trouw and H. Jennings, Bull. Am. Phys. Soc. 40, 665 (1995).