based on works[13,14] involving the calculation of the change in the ionic polarizability of the tetravalent cation. Kralnik[12] indicates that it follows from these works that the relative stability of a parallel and antiparallel distribution of dipole moments in a lattice of the CsCl type is determined by the relative magnitude of the dipole moments of the ions of the different translatory lattices. When the difference in these dipole moments is sufficiently large, the antiparallel distribution is favored and conversely, if the difference is insufficiently large, the parallel distribution is favored.

A qualitative application of this influence seems applicable to the systems $(Pb,Ba)HfO_3$ and $PbZrO_3$-$PbTiO_3$. In $PbHfO_3$, there is a large dipole moment attributed to the lead ions and a relatively small dipole moment due to the *Hf* ion. The difference between the dipole moments is apparently large enough to lead to the antiparallel arrangement of dipole moments and therefore the antiferroelectric character is observed in $PbHfO_3$. Replacement of Pb ions by the less polarizable Ba ions apparently reduces the difference between the dipole moments of the tetra- and bivalent cations sufficiently to favor the parallel arrangement of dipole moments, leading to the ferroelectric phase observed in the system $(Pb,Ba)HfO_3$.

The same reasoning leads to a rough explanation of the results observed by replacing the Zr ion in $PbZrO_3$ by the
.. In this system, the smaller Ti ion has a larger ionic
zability than does the larger *Zr* ion. Therefore, in-
ng amounts of *Ti* ions would reduce the difference
:en the dipole moments of the tetra- and bivalent ions
ıereby favor the parallel arrangement of dipoles.
:ursory examination of the analogous systems (Pb,Ba)-
and $(Pb,Ba)ZrO_3$ shows that, for a given temperature,
:es more Ba ions to induce a ferroelectric phase in the
O_3 system than in the $PbZrO_3$ system. Applying the
ning used in the previous paragraphs, this is interpreted
:aning that it takes more Ba ions in the $PbHfO_3$ system
in the $PbZrO_3$ system to reduce the difference between
:etra- and bivalent cations to a level which favors the
llel arrangement of dipoles. This can be explained by
ming that the Hf^{4+} ion has a lower polarizability than the Zr^{4+} ion. The *Hf* ion and *Zr* ion are very nearly equal in size so the ionic polarizabilities would be essentially the same. Therefore, the lower polarizability of the Hf ion would have to be attributed to its lower electronic polarizability. Thus, it seems reasonable to assume that differences which are observed between the analogous hafnate and zirconate systems are due to the lower electronic polarizability of the hafnium ion.

V. Summary of Results

(1) The intermediate antiferroelectric phase observed in $PbHfO_3$ was observed in both the systems $(Pb,Ba)HfO_3$ and $(Pb,Sr)HfO_3$.

(2) A rhombohedral ferroelectric phase was observed in the system $(Pb,Ba)HfO_3$. The angle α between the rhombohedral axes for ferroelectric $Pb_{0.70}Ba_{0.30}HfO_3$ was less than 90° by 6 minutes at 25°C.

(3) A phase transition, in addition to the transition in $PbHfO_3$, was observed in the system $(Pb,Sr)HfO_3$. The transition occurs at a temperature which is above the upper antiferroelectric phase transition of lead hafnate.

(4) The explanation of the appearance of the ferroelectric phase in the system $(Pb,Ba)HfO_3$ was based on a qualitative discussion of the influence of the electrostatic energy on the relative stability of the ferroelectric and antiferroelectric states. The less polarizable Ba ion reduces the difference between the dipole moments of the tetra- and bivalent ions and this reduction favors the parallel arrangement of dipoles.

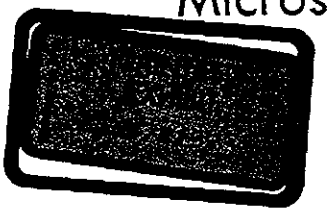
(5) The differences between the analogous hafnate and zirconate systems appear to be due to the smaller electronic polarizability of the hafnium ion.

Acknowledgment

The writers wish to acknowledge the fellowship grant of the Lead Industries Association which made this research possible.

[13] J. A. Sauer, "Magnetic Energy Constants of Dipolar Lattices," *Phys. Rev.*, 57, 142–46 (1940).

[14] Yutaka Takagi, "Ferroelectricity and Antiferroelectricity of a Crystal Containing Rotatable Polar Molecules," *Phys. Rev.*, 85 [2] 315–24 (1952).



Microscopy of Steam-Cured Asbestos Portland Cement Products

by DONALD BAILEY

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A method is presented for the microscopic examination of asbestos-cement products. The use of petrographic thin sections and polished sections in determining composition, texture, grain size, and cement-silica reaction is described. The preparation of thin sections and polished sections, using epoxy resin as an impregnant, is outlined.

I. Introduction

ALTHOUGH the gel matrix of hydrated portland cement pastes consists of poorly crystalline or amorphous material too fine in structure to be resolved by the light microscope, much of significant interest remains in these otherwise fine-grained products which can be observed with the light microscope when properly applied.[1] Pozzolanic materials, fillers, asbestos fibers, and grains of unhydrated portland cement (present even in well-cured products) are among those features which may be brought to light at magnifications of ×100 to ×500.

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[1] L. S. Brown, "Petrography of Cement and Concrete," *J. Res. Develop. Lab., Portland Cement Assoc.*, 1 [3] 23–34 (September 1959).

II. Specimen Preparation

The petrographic thin section frequently affords a comprehensive means of evaluating hydrated portland cement products.[2] Specimens which do not require impregnation before sawing may be sectioned as follows: A wafer cut from the material is surfaced on a glass lap or plate with 600 or 800 silicon carbide in ethylene glycol. After washing and overnight drying, the wafer is impregnated under vacuum in Epon 820 (Shell Chemical Company) plus two drops of *n*-benzyl dimethylamine and two drops of dibutyl phthalate per milliliter of resin. The wafer is then mounted on a glass slide and left in the oven at 65° to 70°C without vacuum for several hours or preferably overnight. When fully cured, the resin forms a hard, transparent solid, possessing excellent mechanical strength and adhesiveness. The refractive index, 1.585, is sufficient to give quartz moderate relief and permits better resolution of portland cement than is possible with Canada balsam. Epoxy resins develop strain birefringence from the impact of abrasive particles, but this is evident only in holes or around edges. The mounted wafer may be reduced to the proper thickness by grinding on a cast-iron lap with 100 silicon carbide, followed by 600 silicon carbide. 320 silicon carbide Wet-or-Dry paper mounted on a rotating wheel affords a rapid alternative method for the final grinding of thin sections and greatly reduces the incidence of strain birefringence in epoxy mounting media. A metal block machined to accommodate the hand and with a flat undersurface into which has been cut a flat trough to take the glass slide will serve as a simple holding device. The same resin formulation used to mount the wafer also serves as a cover glass cement.

The examination of polished sections of hydrated portland cement by reflected vertical illumination will frequently supply specific information not readily obtained through a study of thin sections alone. The two methods in fact supplement each other. Impregnation of the specimen before polishing is necessary, and for this purpose various resins, including methyl methacrylate, have been found to be satisfactory. The section shown later in Fig. 3 was impregnated with the following mixture: methyl methacrylate monomer, 5 ml; Laminac 4116, 2 drops; methyl ethyl ketone peroxide, 2 drops. This mixture cures in from 12 to 24 hours at 65° to 70°C. Equally good results have been obtained with epoxy resins as outlined in the foregoing for thin sections, except that the impregnated wafer is placed on a sheet of aluminum foil instead of a glass slide while curing. After curing of the resin, the aluminum foil is peeled away, and the impregnated wafer is mounted face down in a block of plastic. This mount may be formed of Laminac 4116, plus 1 to 3% methyl ethyl ketone peroxide.[3] The combination sets within a few hours at room temperature and requires only two L-shaped metal blocks as embedding equipment. After the Laminac has cured, excess epoxy resin is removed from the face of the specimen by buffing on a wheel armored with 320 silicon carbide Wet-or-Dry paper. Since only shallow penetration by the epoxy resin will have taken place, care must be used to remove only the excess resin. The specimen is then polished on a canvas lap with Linde A powder in ethylene glycol, washed in alcohol, and etched for 3 seconds in 1% nital.

III. Results

Texture, grain size, shape characteristics, and size distribution are among the factors which may be deduced from microscopic study of thin sections. By means of cross-polarization, mineral analysis is also achieved. Owing to overlapping of grains, only semiquantitative results are possible. However, the method supplies information not obtainable by other means.

Fig. 1. *Autoclaved-cured asbestos cement. Arrows indicate unhydrated cement; Q quartz grains; C chrysotile. Note also the crocidolite asbestos. Light-colored mottling shows carbonation within the gel. (Transmitted light; crossed Nicols with analyzer rotated 16° from crossed position. ×500.)*

In sections impregnated with epoxy resin, quartz is readily seen even without cross-polarization, since both indices of the mineral are sensibly lower than the medium. Quartz grains in steam-cured portland cement products frequently show thin rims of reaction. These show distinctly in epoxy resin, since the reaction product is lower in refractive index than quartz. The rims usually are not strongly birefringent, except in regions of considerable carbonation. A few of these rims may be seen in Fig. 1, where they appear as thin double lines along the edges of quartz grains. Otherwise, quartz may be recognized in the usual manner by its low birefringence, uniaxial character, and absence of cleavage.

Chrysotile asbestos is easily recognized by its fibrous structure, its low refringence and birefringence, and its positive elongation. A small fiber bundle of chrysotile is indicated in Fig. 1. The dark-colored fibers in the photomicrograph are crocidolite. This mineral is easily recognized by its blue color, high relief, and strong pleochroism.

Unhydrated portland cement is almost always present in hydrated portland cement products, whether cured at room temperature or in the autoclave. It occurs as oversized grains which apparently have been walled in by gel and thus protected from further action. The presence of a moderate amount of unhydrated cement is not in any way detrimental, but is in fact a good indication that the product is sound and not excessively porous. It is easily recognized in thin section by its high relief and low to moderate birefringence and by the fact that a single grain usually is comprised of many smaller crystals. Since $3CaO \cdot SiO_2$ has a birefringence

[2] Herbert Insley and V. D. Fréchette, *Microscopy of Ceramics and Cements* Including Glasses, Slags, and Foundry Sands. Academic Press, Inc., New York, 1955. 286 pp.; *Ceram. Abstr.*, 1956, May, p. 108*a*.

[3] E. P. Cadwell, "Color Microscopy for the Mill Man," *Eng. Mining J.*, 160 [1] 81–90 (1959).

Fig. 2. Portland cement clinker. Gray oblong crystals are $3CaO \cdot SiO_2$, twinning structure is $2CaO \cdot SiO_2$, and the white interstitial material is $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in a matrix of darker glass. (Reflected light; ×800.)

of 0.005 and $2CaO \cdot SiO_2$ a birefringence of 0.018, it is sometimes possible to differentiate the two in a thin section. Because, however, of overlapping and small size of the individual crystals, this is not usually practical.

Quantitative determinations usually are possible with properly etched polished sections. Since in this method only

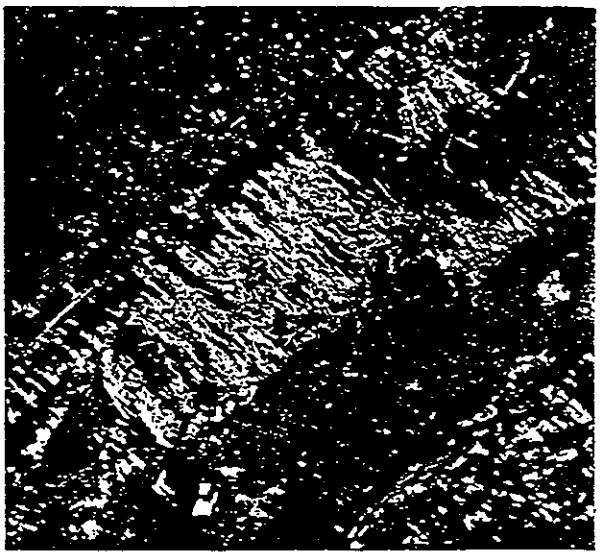

Fig. 4. Crystals of aragonite ($CaCO_3$) filling a crack in autoclave-cured asbestos cement kept 12 years in a corrosive solution in the presence of CO_2. (Transmitted light, crossed Nicols, analyzer rotated 4° from crossed position. ×100.)

those grains exposed at the surface are viewed, the problem of overlapping is eliminated. Moreover, the polysynthetic twinning in $2CaO \cdot SiO_2$ serves to distinguish it from $3CaO \cdot SiO_2$, whereas $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, also present in portland cement, is recognized by its high reflectance. Glass and $3CaO \cdot Al_2O_3$, present as interstitial components, are recognized by their intermediate reflectance. These features are reproduced in Fig. 2, showing a polished section of portland cement clinker. A comparison with Fig. 3, showing a polished section of steam-cured asbestos cement, will illustrate the superiority of the polished section over the thin section for the identification of portland cement. On the other hand, substances of comparable hardness and similar shape characteristics, such as quartz and glass, cannot be differenti-

Fig. 3. Autoclave-cured asbestos cement showing several grains of unhydrated cement. Each of these grains is comprised of individual crystals of $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$, and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in glass. The light-colored grains surrounded by dark borders are quartz. A bundle of chrysotile asbestos may be faintly discerned at the lower left. (Reflected light; ×500.)

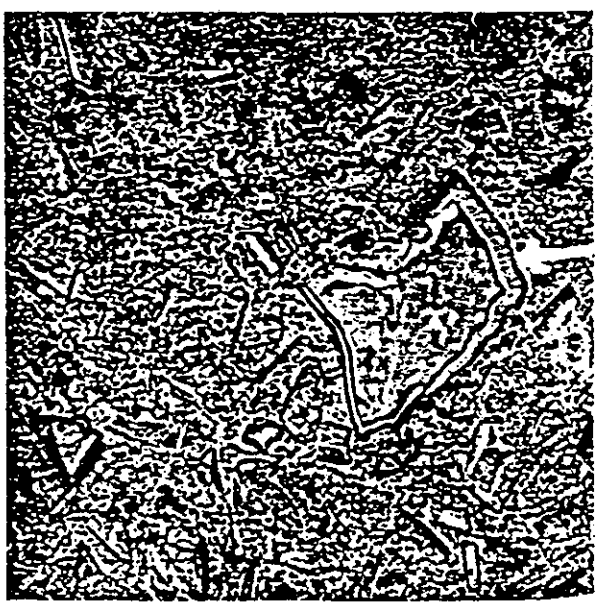

Fig. 5. Thin section of an experimental mixture containing perlite, lime, portland cement, and quartz. Note reaction rim (arrow) about a perlite grain. (Transmitted light; ×500.)

ated in a polished section. For the distinction of such materials, a polished thin section offers definite advantages, provided a means of changing from one type of illumination to the other has been built into the optical system. Thin sections impregnated and mounted in Epon 820, as outlined in the foregoing, have been polished enough to be viewed by either type of illumination. The polishing operation requires care and patience, since a thin section will not tolerate the pressures commonly applied in polishing specimens mounted in plastic blocks. Once the correct pressure has been determined, the task is not unduly time-consuming, provided a proper holding device is used.

Evidence of chemical attack in a portland cement product may be seen in the appearance of secondary crystals which have grown at the expense of the host material. For example, well-preserved microcrystals of aragonite ($CaCO_3$) were found filling a crack within a specimen of steam-cured asbestos cement which had been kept 12 years in a corrosive solution in the presence of CO_2 in the laboratory. These are shown in Fig. 4 and are a good example of the use of epoxy resin as an impregnant for friable specimens.

The occurrence of reaction rims about quartz in steam-cured portland cement products has been noted. An even more striking example of zonal reaction about a pozzolanic substance is indicated in Fig. 5, showing a thin section of a steam-cured mixture containing portland cement, lime, quartz, and perlite. The reaction rim, surrounding a grain of perlite, appears to consist of minute fibers growing perpendicular to the edge of the grain.

Acknowledgment

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Discussions and Notes

Single-Crystal Elastic Constants of BeO from Polycrystalline Measurements

by L. H. SJODAHL and B. A. CHANDLER

THE lack of BeO single crystals of sufficient size has made the direct measurement of single-crystal elastic constants difficult. Young's modulus for single crystals can be deduced, however, from measurements of Young's modulus and orientation distribution functions of three polycrystalline BeO specimens having different degrees of preferred grain orientation. From such measurements an equation has been derived which relates Young's modulus for single-crystal BeO to the angle of measurement from the crystallographic c axis.

The polycrystalline specimens used were rods extruded from a grade of BeO that contains needlelike particles (crystallographic c axis in the direction of the long dimension of the needles) which tend to become aligned in the direction of extrusion and whose growth in sintering enhances the preferred grain orientation of the rods. Orientation of the crystallographic c axes in the direction of extrusion as high as 80% has been measured for rods formed by extrusion and sintered to grain sizes of about 100μ.

Young's modulus measurements used in the calculations were made by dynamic methods, corrected for size, shape, Poisson ratio effect, and corrected to zero porosity by established Young's modulus-porosity correlations.

The degree of preferred orientation was calculated from measurement of reflected intensities from six crystallographic planes by X-ray diffraction on a transverse section, normal to the axis of extrusion. The intensities I for the six planes of the transverse section were compared with the corresponding reflections I_0 from randomly disposed material (I_0 values were normalized so that $I_{0(101)} = 1.00$). The ratios I/I_0 represent the amount relative to random of BeO oriented with c axes at the angles θ between the reflecting plane and the basal plane, which are equivalent to the angles between the c axis and the extrusion direction. A plot of I/I_0 versus θ produces a smooth curve from which the I/I_0 ratio can be interpolated for ten angles corresponding to the midpoints of ten arbitrarily selected zones about

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