Mapping the Phases in Portland Cement Exposed to Sulfate Using EDXRD

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Introduction

Sulfate ions present in soil, groundwater, seawater, decaying organic matter, acid rain, and industrial effluent adversely affect the long-term durability of concrete. Sulfate-containing soils extend across large regions in North America. Concrete structures that will be exposed to sulfate-containing water while in service must be designed for sulfate resistance.

Deficiencies exist in the current understanding of sulfate attack reaction kinetics and damage mechanisms.[1] In order to better understand this process, we are examining a matrix of cement paste samples that have been exposed to sulfate under a range of conditions. By correlating microstructural changes with spatially resolved information on the chemical changes that are occurring, we will be able to build up a more complete picture of the sulfate attack process than is available from conventional destructive evaluation techniques. We will obtain this information from microtomography and energy-dispersive x-ray diffraction (EDXRD).

This report covers our first EDXRD measurements. They were designed to evaluate the ability of the technique to provide a map of the crystalline phases that are present in cement paste samples that have undergone sulfate attack. Only one measurement is reported here. A more complete account of the work is being published elsewhere.

Methods and Materials

The white beam was collimated to 50 μm horizontally by 100 μm vertically. Scattering measurements were made in a horizontal plane. Specimens were mounted so that they could be moved through the sampling lozenge defined by the slit system. The diffracted beam was defined using a pair of slits set to accept ~100 μm horizontally and ~ 1.0 μm vertically. An intrinsic germanium solid-state detector was employed for the data collection. Appropriate undulator settings were established by recording scattering from both glass and cement samples.

A 1.0-cm-diameter type I Portland cement paste (water / cement = 0.4) rod that had been exposed to 1000 ppm Na_2SO_4 solution for seven days and dried prior to the EDXRD measurements was examined. All the data were acquired while rocking the samples through ±15 degrees around a vertical line passing through the middle of the sample. The sample was moved in 50 μm steps over a total distance of 3.0 mm. At each point a diffraction pattern was acquired for 600 s.

Results

During the experiment set up, data was taken from the center of a cement paste rod using Bragg angles of 4° and 6° (see Fig. 1a). While the large d-spacing peaks that are most useful for phase identification are hard to measure by EDXRD, due to the attenuation of lower energy photons by the cement, adequate data could be obtained at both Bragg angles. A Bragg angle of 6° was used for the subsequent measurements. The data obtained by making measurements as a function of depth into the cement paste rod are shown in Fig. 1b. The pattern is complex as there are many different phases in the cement paste, but it is sufficiently well resolved to provide information on the distribution of phases in the sample.

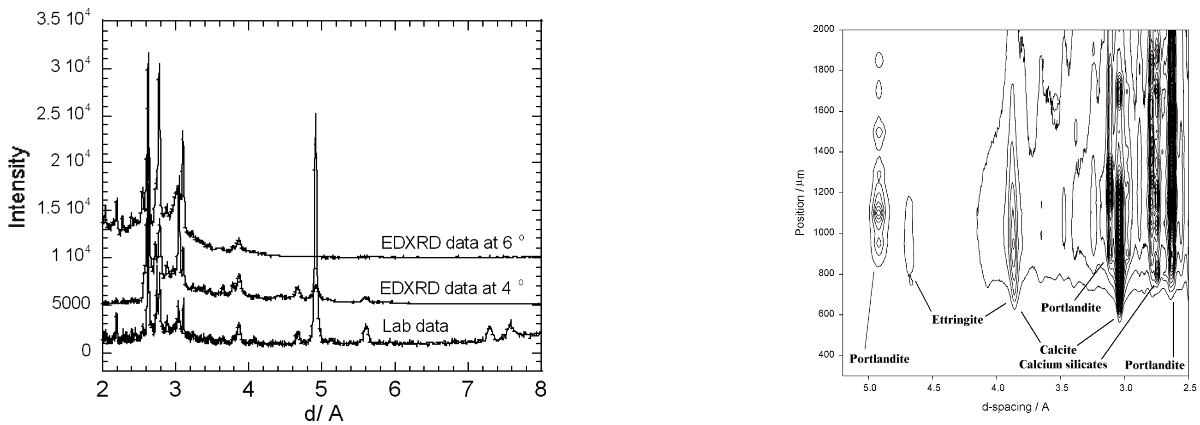

FIG. 1. (a) Energy- and angle-dispersive diffraction measurements on cement paste. The large d-spacing peaks that are most important for phase identification are hard to measure by EDXRD, as the needed low-energy photons are heavily attenuated. (b) EDXRD data obtained as a function of depth on going into a rod of type I portland cement paste. Note the large contribution to the diffraction pattern from calcite in the near-surface region

Discussion

In Fig. 1b, it is notable that there is a large contribution to the diffraction data from calcite in the near-surface region of the sample and that this region seems to be depleted in portlandite. This indicates that the $Ca(OH)_2$ (portlandite) in the surface layer of the sample has reacted with atmospheric CO_2 to form calcite. After seven days exposure to the 1000 ppm Na_2SO_4, there is little evidence for the build up of sulfate containing phases in the near-surface region.

These initial data indicate that EDXRD is a powerful tool for mapping out the phase distribution inside low-Z objects, such as the cement paste rod discussed in this report.

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Reference

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