

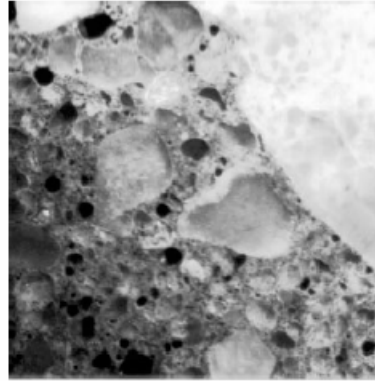
The early evolution of the surface of hydrating portland cement

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Portland cement concrete is the most consumed product on earth, with almost one ton of it being used for each human each year. Within the concrete, the component of greatest interest is the portland cement. Cement is to the concrete as flour is to fruit cake. It is the principal strength-giving and property-controlling component of concrete as well as being by far the most costly. The sand and aggregate that are present usually serve merely as cheap dilutents that limit shrinkage.

Portland cement is a hydraulic cement that gains strength as it reacts with water. Once this reaction has begun, it is initially fairly rapid and slows with the passage of time. Perhaps 40% has reacted after 1 day, 65% after 10 days, 75% after 100 days, etc. The hydration reaction products form as a finely divided, fairly porous solid between the aggregate particles.

The specific surface area of any porous material is a critical descriptive parameter of its microstructure. It is inversely related to the degree of subdivision of a material, and is most sensitive to changes in the smallest details of the microstructure. If these details become smaller, or more plentiful, the surface area increases dramatically. Thus, the surface area is an important window providing insight concerning the state of, and changes to, finely divided microstructures.

Unfortunately, most techniques for measuring surface area require that the material be dried prior to the measurement. For many materials, this presents little or no difficulty. But in the case of hydrated portland cement, it is now well established that drying causes dramatic alterations to the microstructure and its surface area. Thus, many techniques can provide information on only an artificially altered structure. There is one measurement technique, small-angle radiation scattering, that stands virtually alone in not requiring the prior drying of

the sample. The technique can use any radiation, although x-ray radiation has been the most common sort. Results from this technique reflect the unaltered microstructure of hydrated cement paste.

Small-angle scattering has been applied to cement paste on several occasions in the past [1-4]. One finding of this earlier work was that unaltered hydrated cement has an extremely large surface area, 500-700 m²/g, corresponding to an exceedingly high degree of subdivision. Further, it was shown that this area decreased by about a factor of 4 upon drying. All of this earlier work concerned itself with comparatively well hydrated cement. The reason scattering has not been applied previously to the earliest stages of hydration is tied to the nature of the experimental technique.

In this experiment we analyzed the intensity of radiation scattered by the internal surfaces of a material. The intensities are exceedingly low, i.e. only 10⁻⁶ to 10⁻⁹ of the incident beam. With traditional sources of X-radiation, a measuring a single sample could require as much as 24 hours to obtain an accurate result. This long time would seem to eliminate completely the possibility of obtaining data from hydrating cement paste during the early stages of reaction. The solution is to use the intense beam of X-radiation

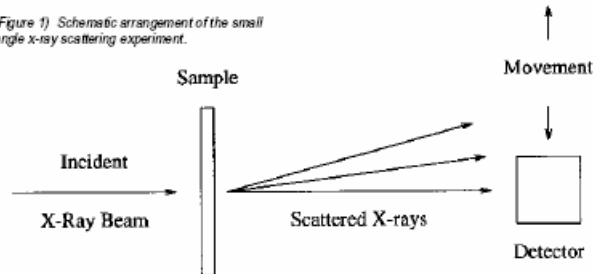
from a synchrotron such as CHESS.

Experimental matters. The experimental arrangement for small-angle scattering is straightforward, are shown schematically in Figure 1. The radiation first passes through the C2 monochromator. For this study, a wave length of 0.71 Å was used because this permits the sample to be of reasonable thickness. The monochromatic radiation then passes through a series of slits that define a beam with a rectangular cross section of 1 mm × 20 mm.

The beam then passed through the sample which was positioned at a right angle to the radiation. The scattered X-rays were detected by an ionization counter, with its own defining slits, located 500 mm downstream from the sample.

The detector is sequentially stepped along a path at right angles to the X-ray beam, and the intensities at various angles are recorded. The angular resolution of the setup used here could be as good as 0.0001°. Intensities were recorded over an angular range from 0° to

(Figure 1) Schematic arrangement of the small angle x-ray scattering experiment.



about 3°. The intensities were recorded with a maximum error of 2% at about 75 angular positions within the experimental range. In addition, the scatter from the experimental apparatus itself, the so-called parasitic scatter, was determined during each experiment and used to correct the data.

The samples were all made from normal portland cement mixed at a water/cement weight ratio of 0.4 under ambient conditions with a small, hand-held, electric food mixer. This mixing technique was used because it provided sufficiently rapid preparation at CHESSE for samples that were to be tested within minutes of mixing. The samples were cast in holders that could be placed directly in the X-ray beam. The sample dimensions normal to the beam were about 10 mm × 30 mm. The sample thickness, parallel to the beam, was about 1 mm. Mylar windows held the cement pastes in place, maintained saturation, and allowed easy transmission of the x-rays.

The scattering data were analyzed to obtain a specific surface area value using the theory of Porod [5]. This involves fitting a straight line through a suitable plot of the scattering in the largest-angle portion of the small-angle scattering region, i.e. the "tail", of the scattering curve. The results also need to be normalized by the area under the entire scattering curve. The details of the analysis have been described previously [2].

Results. Surface areas were determined after periods of hydration ranging from 10 minutes to 1 year. Particular emphasis was placed on samples with reaction times of less than 24 hours. Figure 2 shows the results of the measurements. All of the values in Figure 2 for hydration times of 1 hour or more are the average of 2-4 determinations made on separate samples. Those for times of less than 1 hour are results obtained on single samples.

A single experiment required about 10 minutes, and during this time the sample continued to hydrate. Therefore, any individual result represents a composite surface area of the cement paste as it reacted during an approximately 10 minute period. The effect of this is more important for results with exceedingly short hydration times. However, the data indicate that there is comparatively little change in area at these times so 'blurring' is not significant.

In more recent work, the CHESSE linear position sensitive detector has been used to great advantage. This detector eliminates the need for step scanning, and provides more accurate data in less time.

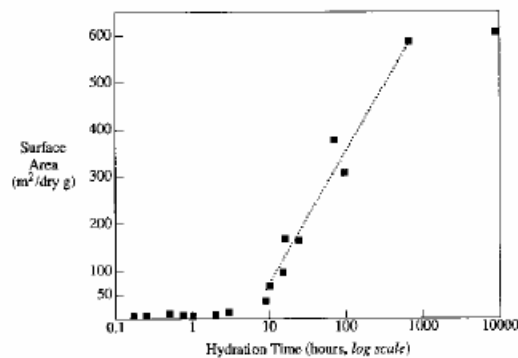
Discussion. It must be kept in mind that the scattering technique is probing size scales that are exceedingly small (of the order of the wavelength of the radiation). Further, this probing is being done on material that has been unaltered by drying. Finally, the surface area of any material is heavily influenced by its most finely divided portion. Thus, the results presented here are a strong reflection of microstructural aspects of cement paste that are not observable by most other experimental techniques.

The surface areas at the earliest stages of reaction show a very modest increase

material that is responsible for the large surface area of well reacted cement. Apparently the earliest aspects of the reaction, while leading to the material's solidification, are significantly different from the subsequent reaction.

The second time regime covers approximately the next 6 weeks. It is during this time frame that concrete gains most of its final strength. And, it is during this time that the vast majority of the finely divided reaction product is formed. Thus, the surface area increases most during this period.

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(Figure 2) Surface area as a function of hydration time as measured with x-rays.

over about the first 10 hours of reaction. After the first 10 hours, the surface area rises much more steeply for the next 1000 hours. By this time the hydration reaction is well advanced, and the increase in surface is much more modest with the continued passage of time beyond this point. The ultimate surface areas of well reacted cement pastes are similar to those reported previously for comparable samples and X-ray wavelength [2].

The first time regime, 0 - 10 hours, spans roughly the time prior to what is called "final set". During this time, concrete made from this cement transforms from a stiff fluid to a weak solid. Although the mechanical nature of the cement has changed during this period, these data make clear that there has been little generation of the finely divided ma-

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