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X-RAY MICROANALYSIS OF HYDRATED CEMENT: IS THE ANALYSIS TOTAL RELATED TO POROSITY?

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ABSTRACT

The significance of the analysis total of X-ray microanalysis of many microporous materials, such as hydrated cement, appears not to be well understood. Taylor (1) has proposed that the analysis total of hydrated cement can be affected by local porosity. The results of the present paper support this idea. Preliminary quantitative results indicate correlation between local porosity and the analysis total. © *1998 Elsevier Science Ltd*

Introduction

X-ray microanalysis, by the electron probe or scanning electron microscope (SEM), of C-S-H resulting from the hydration of Portland cement, generally yield analysis totals that are considerably lower than would be expected from the content of bound water in the C-S-H (2,3). The apparent deficiency in the analysis total of C-S-H can be due to the presence of porosity in the gel. Harrison et al. (2) suggested that internal charging may take place on the surface of the pores, thus creating an internal field that retards the incident electrons. Parts of the organic liquids commonly used for specimen preparation may remain in the material during analyses and may reduce the analysis total as well (2,3). It is also likely that radiation damage caused by the electron beam may be an influential factor. Indication of this was found by Taylor and Newbury (4), as the analysis total decreased on prolonged exposure to the electron beam.

Despite the uncertainties, and several possible influential factors, indications have been obtained showing the analysis total to be influenced by the local porosity (2,5). Further indications are provided in the present paper.

Experimental

Specimens were made of Portland cement, condensed silica fume (CSF), deionized water, and a superplasticizer. The cement used was a Swedish low-alkali sulfate-resistant cement.

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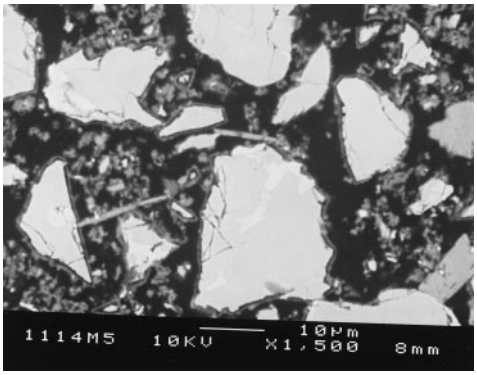

FIG. 1.
Backscattered electron image of the 0.55 w/c ratio paste hydrated for 14 h. The bar denotes 10 microns.

The water/binder ratio (w/b) ranged from 0.25 to 0.55. The binder contained either 100% cement or 90% cement plus 10% CSF by weight. Curing took place in a sealed container at 20°C. The hydration was stopped at desired ages by freeze-drying. Characteristics of the materials and details of mixing and curing is given by Kjellsen et al. (6).

SEM backscattered electron images were obtained. Microanalysis (SEM-EDX) was performed at an accelerating voltage of 10 kV, the working distance was 25 mm, and the beam current was held at 5 nA providing a count rate of about 1500 cps measured on a cobalt standard. The counting time was 100 s. Matrix corrections were made by the ZAF procedure. Pure elemental or mineral standards of the elements to be analyzed were recorded before the first analysis was performed. The cobalt standard was periodically used for control between analysis of any gain change that may occur in the spectrometer and the beam current was frequently measured in a Faraday cup. Analyses were made for Na, Mg, Al, Si, S, K, Ca, Fe, Ti, and Mn. Oxygen was stoichiometrically calculated to provide the analysis total. Each presented result is the average of at least eight analyses. It is our experience that the analysis total is sensitive to even quite small fluctuations in the beam current. Partly for this reason we measured the beam current frequently and those analyses showing a drift in beam current were discarded.

Epoxy impregnated and flat polished specimens were used. The procedure for their preparation is as described by Kjellsen and Monsøy (7).

Results and Discussion

Well performed analyses of anhydrous cement phases typically give analysis totals close to the theoretical 100%. Analyses of large CH particles mostly give totals around or somewhat above the theoretical 76%, water accounting for the difference between 100% and the total. Analyses of hardened epoxy resin give values close to zero. Our experience from analyzing a number of epoxy impregnated and polished specimens is that the analysis total of what is considered to be C-S-H outer product phases increases with increasing age and with decreasing w/b ratio. The changes appear consistent with changes in local porosity.

For example, consider Figure 1, which shows a backscattered electron image of an

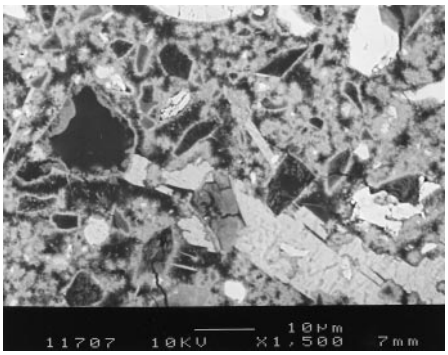

FIG. 2.
Backscattered electron image of the 0.55 w/c ratio paste hydrated for 7 days. The bar denotes 10 microns.

14-h-old paste specimen of 0.55 w/b ratio without silica fume. As the electron beam is focused on the small clusters of reaction products at this stage, analysis totals typically yield values around 45%. The x-ray interaction volume may be up to several cubic micrometers, and is thus generally larger than the clusters of reaction products. Consequently, an analysis will comprise reaction products as well as a considerable volume of epoxy saturated capillary porosity. At Day 1, the continued hydration implies a refinement of the capillary pore system by increased deposition of reaction products, the densification being clearly observable from backscattered electron images. The analysis totals of similar features now give typical values around 55%. After 7 days of hydration (Fig. 2), outer products show totals typically somewhat above 60%, whereas relatively dense C-S-H inner product phases show totals typically between 70 and 80%. The microanalysis indicated that the product phases analyzed in all three specimens were essentially of C-S-H and had similar compositions. The average Ca/Si atomic ratios were 2.3, 2.1, and 2.0 at 14 h, 1 day, and 7 days, respectively. The (Al + Fe)/Ca ratio was approximately 0.05 at all three ages. The changes in analysis total are almost certainly too large to be explained by any possible differences in the chemistry or in the bound water content of the C-S-H phases, but appear to be consistent with the development of local porosity. The analysis of the relatively thin hydration shells (Figs. 1 and 2), demarcating the many hollow-shell pores (6), shows totals around 25% after 14 h and about 40% at 1 and 7 days. These numbers appear to be consistent with the small thickness of the hydration shells, the thickness being considerably less than one micron at 14 h, implying that porosity on both sides of the shell will be included in the analysis yielding the low totals.

Measures of the capillary porosity of the 0.40 and 0.25 w/b ratio specimens, with and without silica fume, after 3 months of hydration have been obtained by Kjellsen and Helsing Atlassi (8). The capillary porosity was obtained from water vapor desorption isotherms, aided by image analysis, and is reproduced in Table 1.

The term capillary pore is used here in accordance with the definition of Verbeck (9). He explained that the part of the original water-filled space that has not become filled with hydration products at a certain time constitutes the “capillary” pore system. The capillary porosity in Table 1 is calculated as the volume of capillary pores relative to the original paste volume. However, this is not a directly relevant measure for the contribution of capillary pores to the local porosity in question. It can only be meaningful to compare the analysis total

TABLE 1
Capillary porosity of the 3-month-old 0.25-0.40 w/b ratio systems, with and without silica fume.

	water/binder-ratio/silica fume (%)			
	0.25/0	0.25/10	0.40/0	0.40/10
Capillary porosity (%)	11.0	2.1	16.3	9.8

with the local porosity of the material exposed to the electron beam. The studied systems were of relatively low w/b ratios and high maturity, implying that the capillary pores were essentially sub-micrometer sized and thus considerably smaller than the x-ray interaction volume. We consider it reasonable to assume, under these conditions and on the scale of the x-ray interaction volume, that the capillary pores are relatively homogeneously distributed throughout the outer product phase. A measure of the local capillary porosity (i.e., the capillary porosity of the outer product phase) was taken as the volume of capillary pores (based on Fig. 3) relative to the volume of the original water-filled space. The analysis total will presumably be affected by the gel porosity and the bound water content, as well as the local capillary porosity. However, because the nature of C-S-H presumably does not change much due to moderate changes in w/b ratios or due to the presence of moderate amounts of silica fume, we consider that the gel/interlayer porosity and the bound water content of a microvolume of outer C-S-H will be similar for all four systems. On these premises the obtained local capillary porosity is compared with the analysis total in Figure 3. As is observed, the four data points do indicate correlation between the "local" capillary porosity and the analysis total.

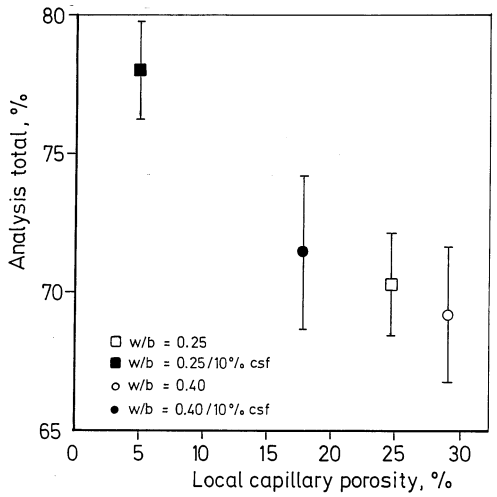

FIG. 3.
Analysis total vs. local capillary porosity. Mean values, standard deviation of the analysis total is indicated.

Conclusions

Results indicate correlation between the analysis total obtained by SEM x-ray microanalysis of C-S-H and local porosity. The analysis total decreases as the local porosity observed from backscattered electron images increases. Quantitative measures of changes in local porosities are in good agreement with the changes in analysis total. The quantitative results are based on only a few data points, and thus need to be confirmed by further experiments. If the analysis total is strongly affected by porosity, as it appears, x-ray microanalysis may be applied to evaluate local differences in fine porosities in the microstructure of cement-based materials.

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