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Quantitative characterization of the transition zone in high strength concretes

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The Paper by Scrivener *et al.* helps tie together several loose ends in terms of a general understanding of how silica fume helps enhance concrete strength. The backscattered electron (BSE) imaging technique applied to sawn and polished surfaces clearly has great advantages over secondary electron imaging of fracture surfaces used in most of the previous literature, because it at last makes possible some form of quantitative phase analysis of cement pastes and concretes on the micron scale.

However, a point which was missed in an earlier paper,[10] and which deserves to be mentioned in this context, is the question of how to represent the phase distribution as a function of distance from the aggregate interface. In the earlier paper,[10] specimens consisting of aggregates embedded in cement paste were analysed by the BSE technique, and were found to show a large increase in porosity, a significant decrease in anhydrous clinker content and no significant change in portlandite (calcium hydroxide) content upon approaching the aggregate interface from the paste side. In the paper, the data were represented in terms of percentages based on areal analysis of two-dimensional images, which are, of course, equivalent on average to percentages by volume if it is assumed, as seems reasonable, that the phases are randomly dispersed and randomly oriented. However, much of the previous work on the distribution of portlandite with distance from the paste-aggregate interface had been done using mass-weighted analytical techniques, such as X-ray diffractometry, often applied to successive planar layers generated by repeated polishing of a flat interfacial zone, prepared by casting a paste against a polished aggregate surface. These techniques have generally led to the conclusion that there is a significant increase in the concentration of portlandite in the paste upon approaching the interface, especially in the absence of silica fume. The apparent discrepancy could probably be removed if the conversion from a volume-weighted to a mass-weighted analysis were made, since the dried hydrated cement paste has, on average, a significantly lower density than portlandite.

In reality, this conversion is not easy to do with great accuracy because the effective water/cement ratio, which dictates the mean paste density, is also clearly a function of distance from the aggregate interface, based on the observed distribution of unhydrated clinker. However, if it is assumed that the anhydrous clinker has a density similar to that of the average ordinary Portland cement and that all the material other than portlandite, anhydrous clinker and the observable capillary pores ($> 0{\cdot}5\,\mu m$) is a dry gel with a density which cannot be ascertained exactly (owing to a lack of knowledge of its true porosity), but which is probably about $2\,g/cm^3$, then the conversion is not terribly sensitive to the exact value of the gel density. Using the volume distribution data for silica-fume-free paste and concrete from reference 10 and from the Paper, respectively, mass fractions on a dry basis can be obtained using the assumed dry densities, as shown in Tables 3 and 4.

It is notable that the portlandite concentration effect is far greater in the plain paste specimens than in the concrete. One possible explanation for this is the higher water/cement ratio used in the paste (0·5) as opposed to the concrete (0·33). Better mixing of the paste in concrete (as evidenced by the tendency of silica fume agglomerates to be well dispersed by mixing in concrete but not in paste) may also contribute to its greater uniformity in terms of portlandite distribution. However, in comparing the absolute portlandite concentrations in the two sets of data, it is apparent that the concrete contains only about half as

*Table 3. Plain paste data from reference 10**

Phase	Assumed dry density: g/cm³	Percentage as a function of distance from interface			
		3 μm		Bulk	
		By volume	By mass	By volume	By mass
Portlandite	2·23	13	20	13	15
Anhydrous	3·15	1	2	8	13
Porosity	0	30	0	8	0
Gel	2·00	56	78	71	73

*Fig. 6, averaged data, 0% silica fume.

much portlandite per unit of cement hydrates (gel) as does the plain paste. The reason for this discrepancy is not clear; it seems unlikely that the small amount of slag in the cement could have reduced the portlandite concentration by such a large factor. Typically, a completely hydrated ordinary Portland cement paste should contain at least 20% portlandite by mass on a dry basis. Do the Authors have any explanation for these observations?

Authors' reply

We would like to thank Dr Gartner for his discussion of our Paper. The conversion of the data from volume fraction to weight fraction is most interesting. Work is now in progress to compare the distribution of calcium hydroxide (CH) relative to the interface by X-ray diffraction and by BSE image analysis on the same specimen.

The difference in the amount of calcium hydroxide measured in the concrete examined in the Paper and in the paste cast against a single piece of aggregate examined in the paper by Scrivener and Gartner[10] illustrates one of the limitations of the measurement of this phase from BSE images. There is only a small difference in grey level between CH and CSH gel. Indeed, because of the variation in the porosity contained within CSH gel the peaks from the two phases usually overlap in the grey level histogram from a typical BSE image. This means that only masses of CH above a certain size (of the order of 2 μm at the magnification used in this work) can be distinguished and measured in BSE images. Smaller regions of CH dispersed within the CSH gel are therefore not included in the analysis.

Studies of a large range of cements and concretes indicate that the morphology and distribution of CH is very sensitive to a number of factors, including

(*a*) water/cement ratio—at low water/cement ratios the space between the cement grains is more tortuous, which results in smaller, more dispersed regions of CH
(*b*) rate of shear during mixing—pastes mixed at high shear rates have fewer large areas of CH and the paste component of concrete will be subjected to higher shear by the aggregate particles
(*c*) presence of chemical admixtures—in this case the use of superplasticizer in the concrete may have had an effect on the formation and distribution of CH.

All these factors may have contributed to the detection of less CH in the concrete.

Despite the problems in measuring the CH, the relative changes in the amount of CH detected with distance from the aggregate surface do reflect real changes in the microstructure of the paste. The considerably greater increase in the amount of CH at the aggregate/cement paste interface in the specimen where paste was cast against a single piece of aggregate indicates that this specimen configuration does not model the situation which exists in concrete where the aggregate particles are present during the mixing process. In the former case it will be more difficult

*Table 4. Concrete paste data from Scrivener et al.**

Phase	Assumed dry density: g/cm³	Percentage as a function of distance from interface			
		4 μm		35 μm	
		By volume	By mass	By volume	By mass
Portlandite	2·23	8	10	8	9
Anhydrous	3·15	1	2	4	7
Porosity	0	14	0	6	0
Gel	2·00	77	88	82	84

*Fig. 3, 0% silica fume, 180 days.

for the anhydrous particles to rearrange, and so the packing at the interface will be poor, resulting in a locally higher water/cement ratio and more open spaces for CH to form in. In addition, the separation between aggregate particles in concrete is too small for long-range perturbations to the paste structure to be possible.

Reference

10. SCRIVENER K. L. and GARTNER E. M. Microstructural gradients in cement paste around aggregate particles. In *Bonding in cementitious composites*, edited by S. Mindess and S. P. Shah, Materials Research Society, Pittsburgh, 1988, Symposium proceedings, vol. 114, 77–85.