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CEMENT AND CONCRETE RESEARCH

Discussion

Reply to the discussion by S. Chatterji of the paper “A neutron diffraction study of ice and water within a hardened cement paste during freeze–thaw” by I.P. Swainson and E.M. Schulson 2001. Cement and Concrete Research 31, 1821–1830

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1. Introduction

In a response to our paper [1], “A neutron diffraction study of ice and water within a hardened cement paste during freeze–thaw,” Dr. Chatterji makes three points:

(i) he questions that negligible change occurs to pore size distribution and geometry during two freeze–thaw cycles;
(ii) he argues that damage occurred during the loss of water before ice formed during the first cooling due to drying; and
(iii) he implies that something is amiss with the data we used for Fig. 5.

We wish to reply to each of these points.

1.1. Point (i)

In Ref. [1], we describe for the first time an experiment performed under well-described and controlled conditions, in which we observe a direct measure of the relative changes in liquid water and solid ice inside the pores of a deuterated, hardened cement paste (hcp). The most novel aspect of Ref. [1] was the ability to measure the relative changes in ice and water inside the pores, and the shape of the hysteresis loop during two freeze–thaw cycles. It is clear that the only changes to which our technique is sensitive would be the potential damage to pores during freezing and thawing in the limits of slow cooling. Our inference of “no damage” was only gleaned by comparing the two hysteresis loops. We therefore do not rule out the possibility of damage to our specimen prior to freezing, as Chatterji suggests [2].

On a related point of “frost damage,” which Dr. Chatterji brings up, we did not generate generalized conclusions about $w/c = 0.4$ cements and their potential immunity under field conditions. In fact, we did not use the terms “frost damage” and “frost resistance” in our paper. Rather, we simply described the behavior of one sample of a deuterated paste within the environment of a neutron diffractometer.

1.2. Point (ii)

We appreciate that “drying” occurs in the pore system. As Dr. Chatterji [2] points out, we reported it as an “expulsion” and “permanent loss.” We attempted to put this observation into historical context by citing Litvan [3]. One thing to notice is that this “drying” does not happen continuously; rather the water content appears to be constant within error until near 250 K, which is close (perhaps coincidentally) to the onset of freezing. At this point, the permanent loss appears to occur fairly suddenly. It is because of this suddenness in the loss of water content that we termed it an “expulsion.” If one compares the microscopic water content of the pores as presented in Fig. 4 of Ref. [1] to that of the thermogravimetric mass loss of Fig. 4 of Ref. [3], then one can see that the overall shape is broadly similar, although only one cycle is reported in Ref. [3]. This is despite the fact that Litvin’s measure was purely water mass loss from the sample, whereas our measure incorpo-

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rates that loss *and* water "lost" upon crystallizing to ice. Furthermore, our measure of the hysteresis in the microscopic ice content of the pores is also broadly mirrored in the extensometer measurements presented in Fig. 1A of Ref. [3] for low *w*/*c* hcps in the limit of slow cooling. While the inherent contraction of the paste must be superimposed, it appears as if the extensometer measurements on these hcps may broadly reflect ice content in the limits of slow cooling. Further measurements would be required to demonstrate this point, but the new information available in measurements such as those presented in Ref. [1] may ultimately allow a link to be made between the microscopic and macroscopic length scales.

In summary, we agree that water is expelled from the pore system, but cannot comment on the effects it may have had on the pore network in this case.

1.3. Point (iii)

There is nothing "amiss" with the data presented in Fig. 5 of Swainson and Schulson [1]. The volume of liquid water was presented in order to make a rather small point and we should restate the strong caveat expressed in Ref. [1] that here we talk of supercooled, bulk light water. The problem appears to lie in confusion over the effects that changing scale have on a graph and also perhaps in an impression that the expansion of water about the 4 °C point of greatest density of light water is symmetrical about that temperature. Dr. Chatterji has exaggerated the specific volume scale by a factor of 30-fold compared to Fig. 5 [1]. The 4 °C maximum density point is present in Fig. 5 of Ref. [1], although it appears as a shallow minimum in specific volume over the temperature range and scale presented there. The change in scale in Fig. A of Ref. [2] amplifies this into a sharp "V" (Fig. A of Ref. [2]). Our choice of scale was made in order to put the volume changes of water in perspective with that of ice (Fig. 5). True, perhaps we should have extended our temperature axis out to + 20 °C. However, this has little effect on the discussion centered around this figure. Fig. A [2] and the data in Ref. [4] show that the specific volume of water at + 20 °C is 1.00015 ml/g. By − 10 °C, this volume has been exceeded on cooling [4]. The expansion of water about the 4 °C minimum is not symmetric; e.g., the specific volume of water at − 30 °C is not reached on heating until + 60 °C [4]. Therefore, a small amount of water may be expected to be ejected from the pore network, even in the absence of freezing or desorption, solely due to volume change in the liquid. The amount ejected depends on the temperature at which the pores were saturated. Our other point in this regard was that one may expect less than 9% change, if one were to use these data, due to the expansion of supercooled water and the simultaneous contraction of ice (Fig. 5 of Ref. [1]).

We appreciate Dr. Chatterji's interest and we hope this reply to his comment clarifies the aims and results of our work.

References

[1] I.P. Swainson, E.M. Schulson, A neutron diffraction study of ice and water within a hardened cement paste during freeze–thaw, Cem. Concr. Res. 31 (2001) 1821–1830.

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