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## Discussion

A discussion 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.

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### 1. Introduction

From their extensive neutron diffraction study on freezing Portland cement paste rods (w/c=0.4) made with, and stored under, heavy water, the authors inferred that "negligible changes to the pore size distribution and geometry" occurred during two cycles of freeze—thaw cycles. One can only wish that it were so. In that case, all the freeze—thaw related problems of concrete could be solved by a mandatory w/c ratio of 0.4 or lower for all concrete mixes. Unfortunately, field experience does not allow for such optimism. The main reason why the authors could not detect any change in the pore structure of their samples is that it had occurred even before any detectable ice has formed in their samples. This can be seen from the following alternative interpretation of their results.

# 2. The state of saturation of the samples during first freezing

The authors cooled their samples from 297 K (24 °C) to 227 K (-46 °C). Figs. 1 and 2 of the paper show that first detectable ice formed at about 250 K (-23 °C). The samples were saturated at the beginning that means at 24 °C. It is of interest to ascertain the state of saturation of the samples during the first freezing. The authors noted that approximately  $23\pm8.5\%$  of total (free?) water was irreversibly lost during the experiment. "The permanent (*irreversible*) expulsion of water takes place above 250 K during the first freezing." This means that the samples

1.0035

-20

Temperature in C

20

40

were drying even before ice formed in the first freezing. During first thawing and the second freeze—thaw cycling, the samples remained partially dried all the time. This large water loss is equivalent to a drying to a relative humidity of 70–80%. This is well known that this degree of drying causes extensive and permanent changes in the pore structure even microcracking [1–4]. The first drying also causes an irreversible drying shrinkage. This irreversible shrinkage is by itself an indication of structural change in the paste. It is also known from laboratory and field observations that such dried samples do not suffer from frost damage. In 1954, Powers [5] has already commented on the beneficial effect of drying on frost resistance of concrete. However, many workers have missed this and the consequent lack of proper precaution

## Sp. volume of water vs temperature plot

has caused some confusion in the field. An outdoor

None 1.000 1.002 1.002 1.001 1.0005 1.0005

Fig. 1. Specific volume of light water at different temperatures.

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concrete structure, of any w/c ratio, does not suffer from frost damage if protected from water ingress from an outside source. These structures naturally dry nearly to the observed extent. It is of no wonder that the authors could not detect any change between the first and second freeze—thaw cycle.

## 3. A comment on Fig. 5 of the paper

In this figure, the authors have plotted the specific volume of light water from about 8 to -30 °C and that of ice in between 0 and -40 °C. The authors should have noticed that something was amiss with the light water data. The curve should have a deep at about 4 °C. In Fig. 1, I have plotted the specific volume data for light water from the same source as that used by the authors. It looks quite different from that of Fig. 5. Fig. 1 shows that a paste sample saturated with light water at 24 °C (297 K) remains

unsaturated (even without any drying) until about -14 °C. This invalidates much of the authors' discussion on Fig. 5.

### References

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