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A Discussion of the Paper "THE MECHANISM OF HARDENING AND HYDRATION OF WHITE PORTLAND CEMENT ADMIXED WITH SALICYLALDEHYDE"

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The work described by the above authors(1) in a study of the effects of salicylaldehyde on WIC, differs in some respects from that carried out by Ball and Tomkins.(2) When normal air-dry WPC is mixed with the aldehyde, an immediate setting reaction occurs, with some yellowing of the mixture. The setting is much slower when OPC is used. This yellow phase can be extracted with 96% alcohol.

a) Studies on the alcohol extract

Ultra-violet spectroscopy showed three peaks (at 325, 255 and 215 nm) which are virtually identical with those shown by salicylaldehyde itself (330, 255 amd 215 nm). We found no evidence for the formation of appreciable amounts of calcium salts in the absence of water. Infra-red spectroscopy showed changes when compared with the free aldehyde: the carbonyl group intensity had virtually disappeared but the aromatic rings were still present and the pattern of substitution in these rings was still the same.

b) Changes on hydration

A strong material is produced on mixing the aldehyde with cement, in the absence of water. When this set material is placed in water, the yellow colour is removed relatively slowly, and the sample appears to harden normally. However, the resultant set cement has a very different morphology from that of material hydrated in the absence of salicylaldehyde (see Figures 1 and 2).

It is likely that the initial dry setting is caused by the polymerisation of the aldehyde. Such polymerisation is well known(3) and could be through:

a) hemi-acetal formation (condensation and loss of water between an alcohol and an aldehyde) producing -CH(OH)- groups which link aromatic rings, or

b) aromatic electrophilic substitution between hydroxyl groups and the ortho- or para-hydrogen atoms on the aromatic ring. Such condensation would produce ether links between the aromatic rings but would leave the aldehyde groups free. The ortho-position in the

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FIG. 1
Normal hydration, x5000

FIG. 2
Hydrated aldehyde-treated cement, x5000

aromatic ring is hindered sterically, so the linear form (para-substituted form) of the polymer is the most likely.

Infra-red spectroscopy indicates that the most likely mechanism is hemi-acetal formation (a), since the carbonyl absorption at 1680cm^{-1} is removed. There is no evidence for oxidation to salicylic acid or more complex changes to the aromatic ring. Hemi-acetal formation is catalysed by acids but not alkali; in this case the acidic species are probably -Si-OH groupings. Different condensation reactions probably take place in the presence of water, and therefore of free lime.

A major problem with further studies is the difficulty of separating the polymer from excess aldehyde, because of the relatively high boiling point of the latter (470K) and its high polarity. Studies on the reaction of WPC with acetaldehyde, which is much more volatile, show that polymerisation occurs in this case also.(4)

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