

Discussion

on papers published in the
Magazine of Concrete Research

Volume 36, Number 127 : June 1984

The permeability of concrete in a marine environment*

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Contribution by Dr Emil Koelliker

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Dr Buenfeld and Dr Newman have found a fall in permeability of various mixes on exposure to sea-water and they have concluded that this is due to the formation of a surface layer. They see important connotations of such a permeability-reducing mechanism with respect to the performance of concrete in the tidal and splash zones.

These results can be considered in a more general way and they agree well with investigations described in reference 1. It appears that in corrosion studies on concrete the fundamental question is usually: 'Why is concrete destroyed?', which directs our interest in the processes of destruction by implying that concrete in general should not be destroyed. However, a different point of view is possible if we ask: 'Why is concrete not destroyed?' and this leads to the study of pro-

TECTIVE mechanisms. This question implies that the destruction of concrete is a natural occurrence. In fact, there are good reasons to believe in this latter working hypothesis, for hydrolytic decomposition of concrete has been known for a long time and the equations of equilibrium are known also⁽²⁾. These show that natural water is not in equilibrium with cement paste and hence the tendency is that the latter will be decomposed.

In reference 1, two different protective layers have been described and in the paper by Buenfeld and Newman another type has been investigated. It is expected that, by studying the conditions of formation and the properties of surface layers, a fruitful new picture of corrosive mechanisms on concrete can be developed.

Contribution by B. K. Nyame PhD

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Dr Buenfeld and Dr Newman provide evidence for the formation of a permeability-reducing layer on the surface of submerged marine concrete which they call 'aragonite-brucite'.

They determined the flow of sea-water into concrete at low pressures. In principle, the mineralogical transformations of hardened concrete resulting at low pressure flows have a major influence upon the durability of marine concrete in the splash and tidal zones, where hydrostatic pressures are low.

*Pages 67 to 76 of *MCR* 127.

At low pressures, surface and capillary forces have more influence than hydraulic gradients as flow potentials⁽³⁻⁵⁾. As the depth of immersion increases, however, hydraulic gradients have a greater influence.

In good-quality mature cement pastes, a unit hydraulic gradient drives bulk water at rates slower than about 30 molecular diameters/day, in pore spaces which are no wider than 260 molecular diameters.⁽⁶⁾ Hence more sea-water ions penetrate and combine with cement minerals and hydroxides to form the aragonite-brucite described by Dr Buenfeld and Dr Newman. In effect, the thickness of the layer increases with depth of immersion in sea-water, as a result of greater permeation.

In this connection, some selected properties of the aragonite-brucite layer reported in the paper may be used to obtain a preliminary picture of the stiffness of the layer with respect to the hardened concrete from which it was formed. The stiffness of the layer will have an important bearing upon its cavitation and erosion resistance, and therefore establish the long-term stability of the layer as a protective surface for the durability of concrete.

Dr Buenfeld and Dr Newman have noted that these layers:

- (a) are about 0.3% diameter thick in 2 months;
- (b) are spherulitic, rather porous and underlined with brucite which grows at early stages by rapid nucleation.
- (c) form simultaneously with constriction of the cement pore system.
- (d) may precipitate or dissolve with change in sea-water condition.

It can be estimated from (a) and (d) above that a critical formation or erosion rate for the layer is in the

order of 0.15% diameter per month of immersion, so that a concrete cover of 12% diameter may be either effectively doubled or flaked-off and eroded in 80 months, depending on the relative cavitation resistance of the layer to its rate of formation. That the layers are spherulitic and rather porous (b) suggests that they are less stiff than the hardened concrete they cover. In addition, the evidence from (c) would seem to indicate that attempts to form the layers in situ, as a development process, may be impeded by the very mechanism considered to result in enhanced durability. That is, the rate at which the layer develops is impeded by pore blocking. These considerations leave the issue of the stability of the aragonite-brucite layer very much an open question. In addition, the lack of such a layer on real offshore structures, as indicated by the authors, with explanations, tends to indicate that the potential estimated rate of erosion may be close to reality, and structurally unsafe.

As the search for oil spreads increasingly to deeper seas, and concrete continues to offer an alternative material for platform design, evidence of durability of the type reported in the paper must be established confidently and carefully. Clearly, the nucleation of a material with permeability-reducing property, as shown by Dr Buenfeld and Dr Newman, must also be assessed for cavitation and erosion damage durability.

To sum up, the important question that arises is:

What is the potential resistance of the aragonite-brucite layer to cavitation, spalling, abrasion and erosion damage?

The authors could, for example, enlighten us on this issue by referring to the details of their observations on the ease of grinding-off the aragonite-brucite layers during their experiments.

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Reply by the authors

We thank Dr Koelliker and Dr Nyame for their interest in our paper.

Dr Koelliker's contribution was particularly wel-

come, since it reinforced our belief in the importance of protective mechanisms in controlling concrete durability. We are currently investigating crack-blocking

phenomena and the role of protective mechanisms associated with carbonation, sulphate attack and chloride ion ingress.

Before addressing the issues raised by Dr Nyame relating to the stability of aragonite and brucite surface layers, we feel that we should first comment on Dr Nyame's interpretation of our paper.

- (1) In our synopsis we are not *naming* the surface layer 'aragonite-brucite', we are simply describing its composition.
- (2) The aragonite and brucite layers are formed on the *surface* of the concrete and it is therefore most unlikely that greater sea-water ion permeation into the bulk of the concrete, as a result of increased depth of immersion, would affect layer thickness. However, the more widespread pore closing or blocking which we discussed in our paper is likely to be enhanced at greater depths.
- (3) Dr Nyame considers layer thickness in terms of specimen diameter. However, there is no reason to believe that layer thickness is in any way related to the specimen dimensions and particularly not to the diameter.
- (4) Surface layers were examined after 18 weeks, not 2 months, of immersion in sea-water.
- (5) We only described *very large* aragonite spherulites as being rather porous, this porosity probably being due to their particularly rapid early growth.
- (6) Dr Nyame considers the additional thickness provided by the developing surface layer in relation to a hypothetical concrete cover. He chooses a cover of '12% diameter', i.e. 12 mm. This is an exceptionally low value in comparison with the minimum cover recommended by appropriate codes of practice. For submerged concrete, ACI⁽¹⁾ and DNV⁽²⁾ recommend a minimum value of 50 mm, whilst FIP⁽³⁾ and BS 6235⁽⁴⁾ suggest 60 mm.

(7) Dr Nyame assumes that, in the absence of 'cavitation and erosion', the surface layers thicken at a constant rate. Tests in which layer development was visually monitored have shown that layer development reduces with time; typically, after 4 days, the layer had reached around 25% of the thickness developed over 18 weeks.

Dr Nyame's concern over the stability of surface layers in an actual marine environment is quite justified. Whilst it is unlikely that water velocities high enough to produce cavitation would be encountered in the vicinity of a conventional offshore structure⁽⁵⁾, the swirling action of the sea creates an environment in which nucleation, growth and erosion of surface layers are very difficult to predict. Laboratory simulation of such an environment is also difficult, the only truly reliable source of quantitative data therefore being specimens taken from naturally exposed concrete.

In response to Dr Nyame's question regarding the mechanical properties of the surface layers, the following observations may be of interest.

- (a) A scalpel was used to take scrapings from specimens in order to produce samples for X-ray diffraction analysis. Samples from the surface layers were more easily removed than hydrated cement paste and the brucite layer was generally harder than the overlying aragonite.
- (b) Surface grinding sometimes caused the layers to shear away from the mortar.
- (c) Water jetting (which is often used to remove marine growth prior to the inspection of offshore concrete) caused the disruption or total removal of the surface layer.

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