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Discussion

# Reply to the discussion by T.U. Mohammed and H. Hamada of the paper "Chloride threshold values to depassivate reinforcing bars embedded in a standardized OPC mortar"☆

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The main concern of Mohammed and Hamada (M & H) is on the heterogeneity introduced by the voids created by bleeding when the reinforcements are cast horizontally. They emphasize the need to specifically mention this particularity more than the $Cl^-/OH^-$ value. However, we think that if bleeding voids induce corrosion it is precisely because the $Cl^-/OH^-$ value in them is exceeding the threshold.

That is, following the M & H argument on the role of bleeding voids below the reinforcement, it might be deduced that only reinforcements cast horizontally would corrode. However, this is not the evidence because reinforcements cast vertically also corrode.

When corrosion develops in bleeding voids, it should be due to the lower $OH^-$ concentration or the higher $Cl^-$ one to reach a $Cl^-/OH^-$ value higher than the threshold needed for depassivation. Another additional reason could be that the oxygen content is higher, so that the corrosion potential is more anodic than the pitting potential [2,3].

In any case, in our opinion, the fundamental factors are oxygen (corrosion potential value) and $Cl^-/OH^-$ ratio [1,2] and not the existence of voids due to bleeding.

We have tried to explain in the introduction of our paper that many factors related to concrete, pore solution composition and steel nature have been related to chloride threshold. We have tried to study one of the most fundamental among the technological ones, that which encounter all the others. We think that the $Cl^-/OH^-$ ratio and corrosion potential are the most basic among those considered by previous authors working in concrete. The voids below reinforcements produced by the bleeding is a phenomenon that cannot be quantified in fundamental terms (how large do they have to be to become aggressive?), unless it is expressed by the changes the voids induce in the $Cl^-/OH^-$ at the steel surface and in the corrosion potential values [2].

M & H add at this respect "that steel–concrete interface have a major influence to predict the onset of corrosion" and "the nature of the steel–concrete interface was emphasized with regard to chloride ion induced corrosion." Obviously, we agree in that statement, because corrosion always happens at the steel–concrete interface. The $Cl^-/OH^-$ value, which is relevant, is that existing in the interface. The main difficulty is how to measure the $Cl^-/OH^-$ a few micrometers around the reinforcement. It has to be accepted that it has to be measured in the concrete or paste bulk. When large bleeding or air voids are produced, the difficulty lies on the measurement of the $Cl^-/OH^-$ value in them [3].

Another aspect mentioned by M & H is that "the chloride threshold value cannot be considered as a sufficient and single criterion to forecast the corrosion development." Therefore, they are thinking in another parameter complementing the $Cl^-$ concentration. Thus later in their comment (4) they insist by saying "will be more meaningful if defines as *Chloride threshold value is a level of chloride ion concentration that causes the initiation of active corrosion of steel bars in concrete, provided that, there are voids damage at the steel–concrete interface*." It seems then that when M & H are referring to another parameter which complements the $Cl^-$ concentration, they neither have in mind the $OH^-$ nor the corrosion potential but only the existence of voids/damages. We cannot agree with that due to many reasons, being one of the main, the ambiguity of the parameter "voids/damages" (how to quantify it?), and the other, we have before expressed that these voids will present a different $Cl^-/OH^-$ and oxygen concentration

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than the paste. For us, in any case, reinforcement corrosion will be induced when the $Cl^-/OH^-$ threshold for each reinforcement potential is exceeded.

M & H noticed that we have not discussed in detail the influence of this parameter in our paper. We simply mention the results recorded because in order to fully characterize the influence of steel nature many more tests than those in our paper are needed. In addition to the difference in the roughness between the ribbed and smooth (machined) rebars, it has to be realized that when machining the rods the internal metallurgical composition is slightly different than the external one. That is, the elimination of the steel skin by polishing introduces not only a change in roughness but also in metallurgical composition.

As we did not study in detail the effect of this double change, we preferred only to record the result but not to discuss it in detail until appropriate studies are made.

Thus, the superficial inclusions and remaining stresses due to the quicker cooling of the skin rod in addition to the phosphatizing treatments are likely to play a role in the nucleation of pits, which has to be studied rigorously.

M & H consider 0.1 $\mu A/cm^2$ as very conservative but they do not justify why. In fact their argument is supported by one of our own references (Ref. [7] in their paper). It is clear that we cannot contradict ourselves.

We proposed 0.1 $\mu A/cm^2$ a long time ago, with the occasion of the thesis of C. Andrade [4] and further papers [5,6]. The identification of that threshold value came from two reasons: (a) the empirical observation that when rust developed in reinforcements in alkaline solutions or in mortar the corrosion current values were never below that value of 0.1 $\mu A/cm^2$ and (2) that 1.16 μm/year of corrosion (generation of rust) may lead into cracking in between 5 and 10 years (depending upon cover/rebar diameter ratio, corrosion attack penetration of 10 μm is enough to induce cover cracking).

After the referred first papers, this limit is now generally accepted and common worldwide: a corrosion current above 0.1 $\mu A/cm^2$ with generation of visible rust means that depassivation has occurred [7].

This concept of depassivation, however, should not be mistaken with the concept of "end of service life" or critical corrosion penetration from a technological point of view.

M & H say that our paper does not consider the macrocell corrosion. There are two reasons for that: (1) we have extensively studied macrocell corrosion in other papers [8,9] and (2) it is not a crucial parameter regarding depassivation.

Before depassivation, no significant macrocell activity exists because the corrosion potential is more or less uniform all along the steel surface. Macrocell activity influences the progression of corrosion after generation of the first corroding spots, but this is another different subject related to the rate of corrosion, enlargement of the corroding pits and generation of further ones.

In summary, macrocell activity does not exist before depassivation and after, macrocell activity is important to increase the rate of corroding areas, but either it protects the neighboring potential-influenced areas (cathodic protection) or it does not influence those sufficiently far away. That is, macrocell activity is not a crucial parameter when studying depassivation.

We thank again M & H for their discussion and the chance to extend our arguments further. Depassivation of reinforcements is still a subject of controversy, which needs numerous fundamental studies. We have tried in our paper to contribute to a better understanding of the phenomena but many aspects remain to be studied.

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