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THE INFLUENCE OF SURFACE FINISH OF REINFORCING STEEL AND pH OF THE TEST SOLUTION ON THE CHLORIDE THRESHOLD CONCENTRATION FOR CORROSION INITIATION IN SYNTHETIC PORE SOLUTIONS

L.T. Mammoliti, L.C. Brown, C.M. Hansson and B.B. Hope
Queen's University, Kingston, Ontario, Canada, K7L 3N6

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ABSTRACT

Electrochemical tests of reinforcing steel in the laboratory are often conducted on metallographically polished specimens in alkaline solutions to simulate the behaviour of steel in concrete. The present project illustrates two of the drawbacks associated with this procedure but suggests that the results may provide a guide to improving rebar corrosion resistance.

Introduction

With the increasing use of chlorides as de-icing salts and the increasing construction in coastal zones, degradation of reinforced concrete structures due to chloride induced corrosion of the reinforcing steel has become the major cause of the infrastructure deterioration in many parts of the world. Various methods have been used to delay the initiation of corrosion of the steel the most effective of which are the use of coated steel, the use of inhibitor admixtures in the concrete and the application of cathodic protection. All of these techniques are expensive and involve careful control of the system. While there has been some discussion about whether or not the mill scale should be left on the steel, very little effort has been addressed simply at the effect of the surface finish of the steel itself on the corrosion initiation [1] although this is generally known to influence corrosion pitting and subsequent rates of attack [2, 3].

In a study of the effectiveness of chemical inhibitor admixtures on the threshold value of chloride concentration for corrosion initiation [4], it was observed that corrosion could not be initiated in highly polished samples of rebar steel tested in synthetic pore solution despite very high chloride concentrations. It was decided, therefore, that an investigation should be made of the influence of surface finish (and of pH of the test solution) on the concentration of chlorides necessary to initiate corrosion. The first-qualitative-phase, involved reinforcing steel with three different surface conditions, namely (i) as-received and degreased deformed rebar; (ii) ground, smooth rebar steel and (iii) a polished cross section of deformed rebar. The second phase involved a repeat of the measurements using mounted cross-sectional samples of deformed rebar which were ground and polished to different roughnesses.

Experimental Procedure

Specimen Preparation. The specimens studied in Phase I are shown schematically in Fig. 1. One consisted of a 20 mm length of deformed rebar which was degreased in acetone. The second specimen was a 20 mm length of smooth mild steel bar, the cylindrical surface of which was ground using 600 grit SiC paper and degreased in acetone. The third specimen was a section of deformed rebar, mounted in epoxy resin and metallographically polished to an $0.05\mu\text{m}$ alumina finish. The specimens were drilled and tapped and attached to mounting rods, as illustrated in Fig.1, and the rods and ends of the cylindrical specimens were coated in rubber. The compositions of the steels are given in Table I.

The specimens used in the Phase II study were all of the same composition as that of the polished specimen in Phase I. They were mounted in epoxy resin and ground and/or polished to different finishes: (i) to 240 grit, (ii) to 600 grit and (iii) to 6 μm diamond. The surface profiles, determined using a *Hommel Tester T500* roughness tester, are given in Figure 2.

Electrochemical Measurements

The specimens were tested in two different electrolytes, a saturated $\text{Ca}(\text{OH})_2$ solution of pH 12.5 and a simulated cement pore solution of pH 13.3 containing NaOH and KOH and an excess of $\text{Ca}(\text{OH})_2$. For the Phase I tests, the $\text{Ca}(\text{OH})_2$ solution was filtered and both the solutions also contained 0.1 wt. % $\text{Ca}(\text{NO}_2)$ as a corrosion inhibitor. For the Phase II tests, the $\text{Ca}(\text{OH})_2$ solution contained excess $\text{Ca}(\text{OH})_2$ and was, thus, effectively buffered to a pH of 12.5.

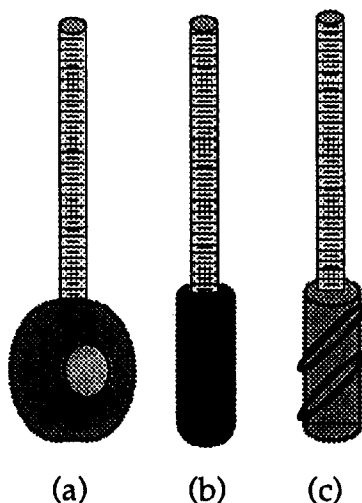


FIG. 1.

Schematic representation of samples: (a) mounted, polished rebar; (b) smooth, ground rod and (c) degreased, deformed rebar.

TABLE 1
Composition of Steels

Element	Polished Rebar	Ground Smooth Bar	Degreased Deformed Rebar
C	0.22	0.17	0.47
Si	0.25	0.18	0.19
S	0.026	0.006	0.022
P	0.018	0.011	0.019
Mn	1.24	0.69	1.5
Ni	0.07	0.10	0.01
Cr	0.10	0.04	0.11
Mo	0.02	0.02	<0.01
Fe	bal.	bal.	bal.

The specimens were immersed in the electrolyte in an electrochemical cell with a saturated calomel reference electrode (SCE) and a stainless steel counter electrode. A cyclic potentiodynamic polarization curve was obtained on each specimen by scanning the potential, from the corrosion potential, at a rate of 1 mV/s in the anodic direction to +500 mV SCE, reversing the scan to a cathodic potential of -1000 mV SCE and reversing it again back to the start point. An addition of 0.5 wt.% Cl⁻ as NaCl was then made to the solution and the system was allowed to equilibrate over a period of 1-7 days after which the polarization curve was again determined. The process was repeated with 0.5% or 1% additions of chlorides until all specimens were actively corroding. The pH was monitored after each chloride addition.

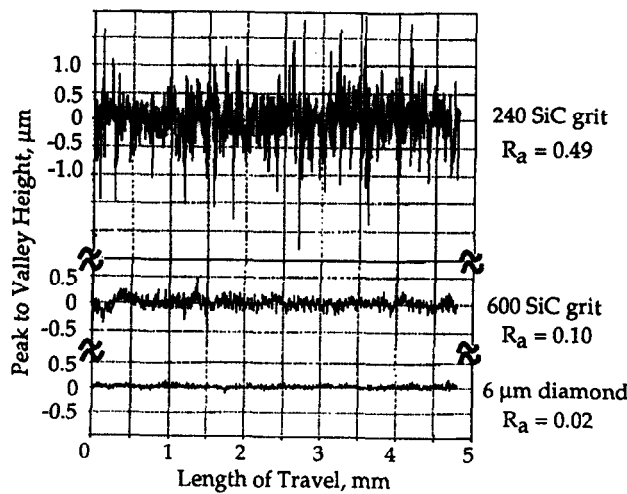


FIG. 2.
Surface roughness profiles of specimens ground to 240 grit, 600 grit and 6µm diamond finishes.

Results and Discussion

For both sets of specimens, none exhibited any consistent corrosion in the high pH electrolyte (the simulated pore solution) even at chloride concentrations as high as 10 wt.%, although several specimens gave some indication of pit initiation but then repassivated. This effect is illustrated in Fig. 3 for the Phase I specimens and similar results were obtained for the Phase II specimens in the high pH solution.

In the filtered $\text{Ca}(\text{OH})_2$ solution, on the other hand, severe corrosion was detected at concentrations dependent on the surface finish of the steel. Fig. 4 shows the corrosion current densities of the Phase I specimens: pitting was initiated at 0.5% Cl^- in the specimen ground on 600 grit and at 1% Cl^- in the as-received rebar and the corrosion rate increased consistently in these specimens with increasing chloride content. For the polished specimen, however, while pitting was initiated at 1.5% Cl^- , the rate of corrosion increased only slightly as the Cl^- content was increased. The pH of the filtered solution decreased with increasing Cl^- additions to below 10.

The anodic portions of the dynamic polarizations curves of the Phase II specimens tested in the saturated, buffered $\text{Ca}(\text{OH})_2$ solution containing 3% Cl^- are given in Fig. 5. It is clear from these curves that the highly polished specimen is still completely passivated; the specimen ground to 600 grit is initially passive but cannot maintain the passivity at high potentials and the specimen ground to 240 grit exhibits an initial high leakage current and pitting is initiated at a potential of ~ 250 mV SCE. The pitting potentials of the two latter specimens are given as a function of Cl^- content in Fig. 6.

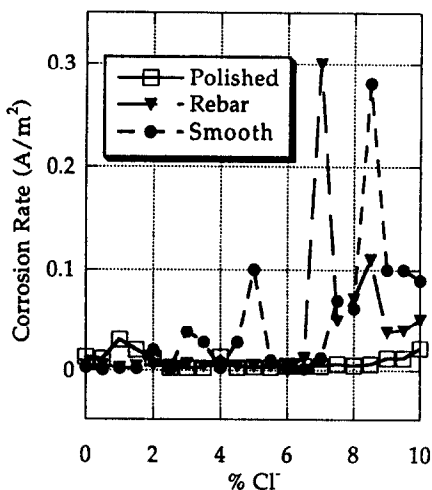


FIG. 3.

Corrosion currents of polished deformed, and ground specimens in pore solution of pH 13.3.

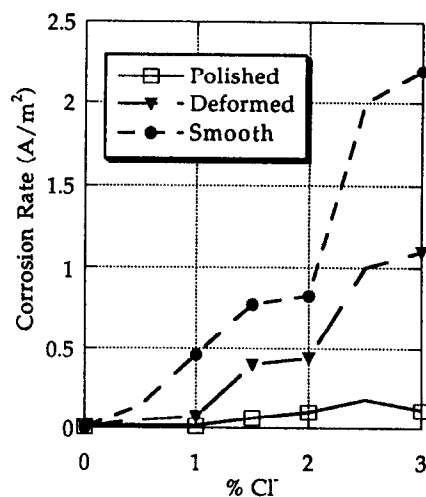


FIG. 4.

Corrosion currents of polished, deformed and ground specimens in filtered $\text{Ca}(\text{OH})_2$ solution in which the pH decreased with increasing Cl^- .

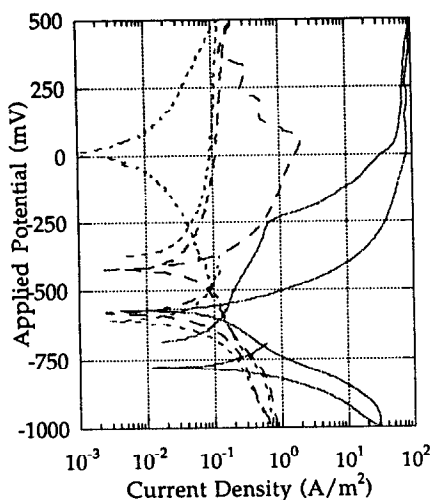


FIG. 5.
Anodic polarization curves of specimens and tested in buffered Ca(OH)_2 solution containing 3 wt.% Cl^- .
— 240 grit, -- 600 grit, --- 6 μm

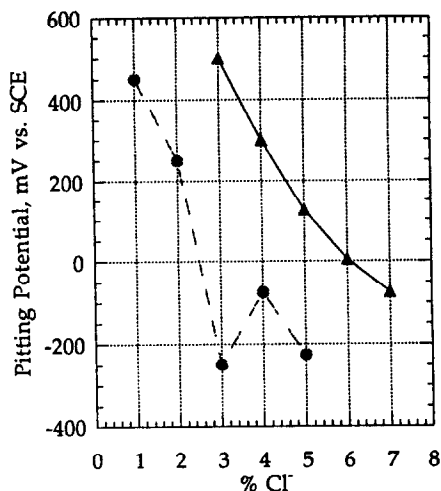


FIG. 6.
Pitting potentials of specimens as a function of Cl^- content in buffered Ca(OH)_2 solution.
— 240 grit, -- 600 grit

Conclusions

The pH of the testing solution (or of the concrete) plays a major role in determining the initiation of corrosion due to chlorides: the simulated pore solution with pH 13.3 provided sufficient protection to all the specimens that continued pitting was not induced even at chloride ion concentrations as high as 10%, although some pit initiation and repassivation was observed in the rougher specimens at $\text{Cl}^- \geq 5\%$. For the Ca(OH)_2 solutions, that containing excess Ca(OH)_2 provided greater protection than the filtered solution, again presumably because of the lower pH in the latter. These results suggest that testing of reinforcing steel in lime-water, particularly in a filtered solution, is not realistic. Even when using a synthetic pore solution of high pH, there is an additional disadvantage in trying to simulate the corrosion conditions of steel in concrete: since concrete is such an inhomogeneous material, it is highly likely that the pH of concrete varies locally allowing the easy development of concentration cells leading to macrocell corrosion. Solutions tend to be very homogeneous and the development of macrocells would be determined only by the inhomogeneity of the steel surface.

As the present data indicate, the surface condition of the steel has a major influence on the "chloride threshold value" for corrosion. In the laboratory, corrosion tests are usually conducted on highly polished surfaces to allow for repeatability of the tests. It is clear from these data, however, that such a procedure is inappropriate for reinforcing steel investigations. Moreover, the surface condition of the steel is often not adequately reported in the literature which could account for apparent inconsistencies in results of different investigators.

On the practical side, while the rebar obviously cannot be highly polished prior to embedment in concrete, the surface finish could be better controlled than at present thereby, potentially, providing better resistance to chloride attack. Lack of such control may be one of the factors responsible for the fact that rebars in some concretes containing very high chloride levels do not exhibit corrosion whereas those in other structures with much less chloride are corroding very rapidly. Furthermore, it has been speculated [5] that the superior corrosion resistance of cold drawn prestressing steel strands may be due to adsorption of the zinc phosphate, calcium stearate and other lubricants used in the drawing process, but the present study suggests that the highly polished drawn surface itself may provide the observed corrosion resistance.

Acknowledgments

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References

1. Hansson, C.M. and Sørensen, B. *The Threshold Concentration of Chloride in Concrete for the Initiation of Reinforcement Corrosion*. in *Corrosion Rates of Steel in Concrete*. 1990. Baltimore, U.S.A.: ASTM STP 1065.
2. Fontana, N.D., *Corrosion Engineering*, Series in Materials Science and Engineering, 1978, New York: McGraw Hill.
3. Jones, D.A., *Principles and Prevention of Corrosion*. 1992, Toronto: Maxwell McMillan.
4. Mammoliti, L., "*Evaluation of Corrosion Inhibitors in Synthetic Concrete Pore Solutions*", M.Sc. thesis, 1995, Queen's University, Kingston, Ontario, Canada.
5. Pfeifer, D.W., J.L. Langren, and A. Zoob, *Protection System for New Prestressed and Substructure Concrete*. 1987, Federal Highway Administration Report #FHWA/RD-86/193, 121pp.