3.1.1 <u>Wire Coating</u>

Cross-sections of the welded wires as illustrated schematically in Figure 3-1, were cut from the samples provided for both the initial corrosion testing and the longer-term, accelerated corrosion testing and observed in the SEM, and analyzed by EDS. It should be noted that the chromated layer is too thin to be resolved in the SEM. The zinc layer in the first set of wires was found to be approximately $5[\mu m]$ (0.20[mils]) in thickness as shown in Figure 3-2 (a). Close to the weld, Figure 3-2 (b), the zinc appears oxidized but not removed by evaporation. A few isolated contamination particles of lead were observed embedded in the zinc.

In contrast, the thickness of the coating in the welded corner sections from the longer term tests, shown in Figure 3-3, was more variable, ranging from below 1 μ m to approximately 10[μ m] (0.39[mils]) as illustrated in Figure 3-3 (b) and (c). Moreover, some of the welds exhibited weld expulsion with complete absence of zinc, Figure 3-3 (d).



Figure 3-1 Schematic of analyzed cross section



Figure 3-2 initial corrosion testing SEM of wire cross-section (a) away from the weld, (b) near the weld

Corrosion of Welded and Chromated Galvanized Lath Reinforcement



Figure 3-3 Accelerated corrosion testing SEM of wire cross-section (a) overview, (b) thin zinc coating (<5μm), (c) Thicker coating (~10 μm) and (d) weld expulsion. The numbers given in (a) and (b) refer to the areas for EDS analysis.

3.1.2 <u>Cement Constituents</u>

The elemental compositions of the three stucco powders, without lime, were determined using the EDS system on an environmental scanning electron microscope. The major constituents are listed in Table 3-3 and indicated that the Stucco B is calcium silicate based, but with more calcium and less silicon than the OPC, suggesting it may contain some calcium carbonate. The composition of the Stucco A indicates it is a calcium aluminate based.

	Mg	Al	Si	S	Ca	Fe
OPC	1.4	3.8	14.6	4.0	73.2	2.9
Stucco B	0.8	3.2	5.6	1.4	87.9	1.11
Stucco A	1.3	24.3	6.0	3.4	63.7	1.3

Table 3-3 Elemental Composition of Cementitious Powder (Without Lime)

3.2 Initial Corrosion Testing

Figure 3-4, Figure 3-5, and Figure 3-6 below show the results of the initial corrosion rates for the first set of cylindrical stucco samples in chloride-free lime water. The conversion of $1.0[\mu A/cm^2]$ ($6.5[\mu A/in^2]$) is equivalent to $15[\mu m]$ (0.59[mils]) zinc loss per year. The half-cell potential of the non-chromated specimens in both stuccos was initially ~-1600[mV_{SCE}], representative of bare zinc at high pH. The potentials then became more positive as the protective calcium hydroxyzincate formed and the corrosion rate decreased. Thereafter, it remained in the region of $-800[mV_{SCE}]$. For the chromated specimens, there was no initial low potential or high corrosion rate illustrating the efficacy of the chromate in protecting the zinc during the setting stage of the stucco.



Figure 3-4 Initial corrosion current density vs. time: straight galvanized wire in OPC and Stucco B



Figure 3-5 Initial corrosion current density vs. time: welded galvanized wire in OPC and Stucco B



Figure 3-6 Initial corrosion current density vs. time: welded galvanized chromated wire in OPC and Stucco B

3.3 Accelerated Corrosion Testing

Figure 3-7 below shows the average corrosion current density vs. time of all specimens for comparative purposes. Figure 3-8 through to Figure 3-11 below show the corroding current densities vs. time for the individual stucco mixtures.



Figure 3-7 Average corrosion current density vs. time



Figure 3-8 Average OPC stucco corrosion current density vs. time

Hunt et al.



Figure 3-9Average Stucco A corrosion current density vs. time



Figure 3-10Average Stucco A + lime corrosion current density vs. time



Figure 3-11Average Stucco A + set-retarder corrosion current density vs. time

4.0 DISCUSSION

4.1 <u>Theory</u>

The pore solution in cured concrete typically maintains a pH between 12.6 and 13.7 due to the presence of excess hydroxides. In this pH and at potentials more anodic than $-1.2[V_{SHE}]$ zinc is not thermodynamically stable and will actively corrode as shown in Figure 4-1b.

In concrete, the zinc corrosion products can react with the calcium ions found in the pore solution to produce calcium hydroxyzincate, $Ca(Zn(OH)_3)_2$. This compound has been shown to form a protective coating over the zinc, thus slowing the corrosion [3]. However, it takes up to two days to develop the protection and, until it does, the active corrosion rate of the zinc is very high. The use of chromating treatments after galvanizing have been found to eliminate the high rate of corrosion and the accompanying hydrogen evolution, prior to the formation of CHZ in ordinary Portland cement concrete [3].

The corrosion potentials for zinc and iron in the pH range of 13 are around $-1.2[V_{SHE}]$ and $-0.8V[_{SHE}]$ respectively. When these two metals are coupled and form a galvanic cell, the mixed corrosion potential lies between these two values.



Figure 4-1 Potential (SHE) vs. pH, diagram of iron (left) and zinc (right) [7]

When the zinc coating is non-continuous (such as the case for welded sections where the zinc is oxidized or vaporized) the zinc can still offer galvanic protection. The ability for zinc to offer this protection is directly related to the size of the exposed region as well as the surrounding solution (more specifically the conductivity of the solution).

4.2 Initial Corrosion

The areas at the spot welds were mostly devoid of metallic zinc. Although the temperature required for welding steel \sim 1500[°C] (\sim 2700[°F]) is significantly higher than the vaporization temperature \sim 900°C (\sim 1700[°F])of zinc the coating oxidized rather than evaporating.

The chromated wire from the initial testing showed much better resistance to the high pH at the initial stages than the straight non-chromated wire. The effects of welding on the joint were also negligible: it appears that the zinc

oxide in the local region of the weld together with the remaining zinc provided sufficient cathodic protection to the specimen.

Once submerged in the wet concrete the zinc and zinc oxide layer will be converted to $Zn(OH)_2^{-4}$. These zinc products then begin to react with the available calcium in the pore solution resulting in the formation of CHZ. This is observed between the second and eleventh day for the straight bars and the second and eight day for the welded bar.

The chromated bar did not exhibit the early rapid corrosion and showed lower corrosion rates comparable to the steady state corrosion rates of the non-chromated bars. It is known that stainless steels in concrete are corrosion resistant, and it is possible that the chromate layer provides similar protection of the wire.

4.3 Accelerated Corrosion

Despite the high measured corrosion rates, no red rust stains have been observed on any of the specimens, as were observed in the field over a similar period. This indicates that the zinc coating is preferentially corroding compared to the steel wire.

The general trends observed for all specimens are the high initial corrosion rates upon immersion into the NaCl solution, both for the initial exposure to the solution and after every drying period. This is attributed to the high oxygen content provided during the drying period and, as this abundant oxygen is depleted in the subsequent wet period by the cathodic half-cell reaction accompanying the corrosion of the zinc, the corrosion rate decreases.

In all stucco mixtures, the wire with no post weld chromating treatment performed the worst within the first 10 to 15 days. The longest lasting effects were seen in the Stucco A mix with set-retarder. HGC and EGC wires in Stucco A exhibited a similar trend of poor performance within the first 10 to 15 days; however, the corrosion rates were lower than the Stucco A samples with set-retarder.

In OPC stucco all wire types behaved similarly with corrosion rates below $1.0[\mu A/cm^2]$ (6.5[$\mu A/in^2$]). The initial corrosion of this test showed that the OPC outperforms all permutations of Stucco A used. This is likely a result of the OPC stucco providing an ample supply of calcium and the appropriate pH to produce CHZ. However, within 15 days, Stucco A with lime and, within 30 days, Stucco A with set-retarder exhibited corrosion rates comparable to the OPC stucco.

In Stucco A without lime or retarder, the corrosion rate of all wires varies from above $0.50[\mu A/cm^2]$ ($3.2[\mu A/in^2]$) to below $2.0[\mu A/cm^2]$ ($13[\mu A/in^2]$) which is higher than the other stuccos by about a factor of 2. The HGC performed the worst followed by EGC and HG. HGC was also most affected by the cyclic exposure as described above.

The addition of lime to Stucco A improved the corrosion resistance of all wires, showing current densities at about $0.50[\mu A/cm^2]$ ($3.2[\mu A/in^2]$) and lower. This is likely due to the change in pH which allows the formation of protective CHZ. The HGC consistently outperforms the other wire types in Stucco A having current densities of about $0.25[\mu A/cm^2]$ ($1.6[\mu A/in^2]$). Corrosion current density of EGC seems to be steadily increasing with time at negligible rate.

With the protective zinc coating on the laboratory specimens of the order of $5[\mu m]$ (0.20[mils]), the corrosion rates measured indicate a life of the coating to be ~ 2 to 4 months. Thus, despite the considerably more aggressive conditions in these experiments, this predicted life expectancy matches the current observations in the field.

Red rust was not visible on the surface of the laboratory specimens although the wires were found to be corroding when autopsied. This is in contrast to the observations in the field, where surface rust was observed after a few months. The difference may be attributed to two factors. First, the corrosion in the laboratory specimens had not destroyed the zinc layer completely. The second factor is the better quality stucco produced under laboratory conditions, where the stucco was placed horizontally and wet cured. In the field, where the stucco is applied to a vertical surface, with limited curing, it is probable that it will be more porous, allowing more rapid diffusion. Therefore, it is concluded that the lower concentration of salts in field exposure is compensated by the higher rate of ingress of chlorides through the more porous stucco coating.

Corrosion of Welded and Chromated Galvanized Lath Reinforcement

5.0 CONCLUSIONS

The chromate layer reduces the amount of corrosion and is a viable method for protecting the zinc coating from depletion within the first 12 hours of curing. This equates to saving approximately $0.20-0.30[\mu m]$ (0.0079-0.012[mils]) of cover thickness. This is about 4% of the total cover of the bars. After the first 12 – 24 hour period, the chromate does not provide any additional protection.

In the absence of any rust stains on the specimens, it must be concluded that the galvanized lath in the field has not been treated carefully and that some of the zinc may have been removed during transport and handling. Moreover, the stucco observed in samples from the field were imperfectly compacted, an additional factor to be considered in the limited service life.

Nevertheless, the corrosion rates observed in the present study suggest that the zinc is likely to be consumed within a few months. A considerably thicker hot dip galvanized layer would add significantly to the service life.

With regards to the stucco, there appeared to be little difference in the performance of OPC stucco and Stucco B. The lath in calcium aluminate based Stucco A, however, exhibited corrosion rates 2 to 3 times higher than that in the OPC stucco. The presence of a set-retarding agent increases the initial corrosion rate for about the first 4 weeks of the products life.

Although not recommended by the manufacturer, additions of lime to Stucco A, resulted in corrosion rates comparable with those in the OPC stucco.

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Preliminary Studies of High-Strength Stainless Prestressing Steels

Robert D. Moser, Lawrence F. Kahn, Preet M. Singh, and Kimberly E. Kurtis

Synopsis:

This paper presents the preliminary results of a study examining the stress vs. strain behavior, stress relaxation, and corrosion resistance of six candidate high-strength stainless steels (HSSSs) for potential use as corrosion-resistant prestressing reinforcement in concrete structures. Austentic grades 304 and 316; duplex grades 2101, 2205, and 2304; and a precipitation hardened martensitic grade 17-7 were selected for the investigation and cold drawn to diameters of approximately 4 mm (0.16 in). Tensile strengths of 1290 to 1550 MPa (185 to 225 ksi) were achieved in the cold-drawn HSSS wires. 1000-hr stress relaxation of all candidate HSSSs was predicted to be between 6 and 8 % based on the results of short-term relaxation tests conducted at 70% ultimate tensile capacity. Cyclic polarization testing for chloride-induced corrosion resistance determined that in alkaline pore solutions, 2205 and 2304 exhibited low corrosion susceptibility and 304 exhibited moderate corrosion susceptibility at 0.5 M chloride, grades 2205 and 2304 exhibited low and moderate corrosion susceptibility, respectively. Duplex grade 2205 exhibited superior corrosion resistance in all cases. Based on these results, optimal HSSSs were identified as duplex grades 2205 and 2304.

Keywords: Stainless Steel, Prestressed, Concrete, Corrosion, Chloride, High-Strength, Stress Relaxation