

Volume 6 Paper 005**PASSIVATING SYSTEMS TO PROTECT GALVANISED STEEL DURING
INITIAL INTERACTION WITH CONCRETE**

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mcalonso@ietcc.csic.es**Abstract**

Galvanised steel reinforcements will passivate in concrete assuming that a microscopic film of calcium hydroxizincate crystals can be formed on the surface of the metal. The formation of this passive film is strongly dependent on the pH of the pore solution. However during the first few hours of interaction of galvanised rebar and concrete (before the passive layer develops), strong electrochemical reactions take place that partially dissolve galvanised layer and induce the evolution of hydrogen. The evolution of hydrogen gas initially results in formation of a more porous interfacial zone between rebar and concrete thus leading to initial reduction of bond. This phenomenon disappears after the passivation takes place.

In present paper several protected methods to reduce this reactive interaction process during passivation of galvanised steel are being investigated based in changes in galvanised layer composition (addition of Ni and V to the hot deep bath) or covering the surface with a non reactive film.

Results indicate that the initial reactivity of galvanised steel is significantly reduced if an organic passive film is used. Also the addition of 1% of Ni with or without V reduces the hydrogen evolution risk and forms a more passivating film of calcium hydroxizincate crystals with small size and compactness.

1. Introduction

The high alkaline nature of concrete allows the passivation of reinforcement by the developing of a passive film. Nevertheless, many cases have been reported where corrosion of reinforcement has led to destruction of this passive state and the initiation of corrosion process. In most usual environments an adequate design and a correct execution of the concrete are enough to guaranty long term durability of structures. However, for very aggressive environmental conditions, other complementary protection methods are needed, as for instance the galvanization of reinforcements.

Zinc is an amphoteric metal that remains stable in wide ranges of pH, from approximately 6 to 12.5, but below and above these values the corrosion rate increases exponentially [1,2].

During the first hours of contact, after mixing cement with water, the solution filling the pores is over saturated in Ca(OH)_2 . Later equilibriums with other species are reached, such as NaOH and KOH. The pH value of these aqueous solutions vary from 12 to 14 as a function of the alkaline content of the cement and the degree of hydration [3]. One

particular feature of these alkaline solutions, which is relevant for the behaviour of Zinc, is that the concentration of Ca^{2+} decreases when the pH increases [4]. At lower pHs typical of early stages in cement hydration, up to 12.5, the $[\text{Ca}^{2+}]$ lies above the line of equilibrium which indicates over saturation of this ion in the solution. This is important because the presence of Calcium ions is needed for passivation of the Zn [5] in such alkaline conditions.

Soon after the first contact between the zinc and the alkaline media, the generation of hydrogen occurs. But it steadily decreases with time due to the continued formation of the layer of corrosion products which eventually becomes continuous. The reason for passivation of Zn in calcium alkaline media is the formation calcium hydroxizincate crystals (CaHZn) [6,7]. The morphology, size and distribution of the crystals, over the galvanised surface varies in function of the pH of the media [8]. A pH threshold of 12.8 has been found for the onset of hydrogen evolution [9]. Total duration of hydrogen evolution periods depends mainly on the alkalis content in the cement [10]. The main consequence of hydrogen evolution is the formation of gaps at the rebar-concrete interface due to the trapped bubbles formed during cement setting. The initial bond between reinforcements and concrete is affected due to this fact.

Different procedures can be applied to protect the galvanised layer during this initial period, including changes in concrete composition to control the pH (type and amount of cement), use of protected agents (such as additives or polymer coatings [11-14] or change the structure of galvanised coating.

Present paper deals with these last two aspects: 1) Study of the effectiveness of several polymer-type protective films and 2) modification of the structure of the galvanised layer by adding Nickel and Vanadium to the hot deep bath.

2. Experimental

2.1. Materials.

Steel reinforcements with strengths of 400 and 500 MPa were galvanized in a hot-dip bath of Zn during 90 seconds and 450 °C. The bath contained variable percentages of Nickel: 0.00, 0.08, 0.12, 0.16 and 0.20. A fix concentration of Vanadium together with Ni was added to the bath in some cases, using a percentage of 0.04 %V. The reinforcements used for galvanizing have a ribbed surface showing 6 mm nominal diameter and 80 mm in length. The chemical composition of the bars was given elsewhere [15].

The thickness of the galvanized layer, for total galvanised layer and external η layer of pure zinc are given in table I. The alloyed layer is very uneven, but the addition of Ni to the bath induces a thinner size. The thickness of this layer is practically unaltered due to the addition of Vanadium.

The galvanised reinforcement of 500MPa was protected with three different organic polymers, two of them, GM-3W and GM7 having chromium in their composition and a third, 661 W/2, without chromium. Through immersion, in a solution having the polymer, an homogeneous film covering the surface of about 2 μm was obtained.

| Hot Deep Galvanised Bath Composition | Type of Steel | Total Galvanized Layer (μm) | η -Layer Size (μm) |
|--------------------------------------|---------------|--|--------------------------------------|
| 450°C 90s 0.00%V+0.00%Ni | 400 | 104.8 ± 20.8 | 43.4 ± 22.0 |
| 450°C 90s 0.00%V+0.08%Ni | 400 | 85.5 ± 20.26 | 44.6 ± 23.5 |
| 450°C 90s 0.00%V+0.12%Ni | 400 | 62.6 ± 9.2 | |
| 450°C 90s 0.04%V+0.08%Ni | 400 | 57.6 ± 6.0 | 14.2 ± 9.4 |
| 450°C 90s 0.04%V+0.12%Ni | 400 | 87.4 ± 33.9 | 3 4.1 ± 29.8 |
| 450°C 90s 0.04%V+0.16%Ni | 400 | - | - |
| 450°C 90s 0.04%V+0.20%Ni | 400 | 67.0 ± 16.0 | 17.4 ± 13.1 |
| 450°C 90s | 500 | 135.8 ± 35.7 | 60.14 ± 35.4 |

Table 1. Thickness of galvanized layer, from optic microscopy.

2.2. Corrosion cell and tests

Corrosion tests of galvanized reinforcement were performed in media simulating the alkaline aqueous phase in the pores of the concretes. The composition of the dissolutions were:

- $\text{Ca}(\text{OH})_2$ saturated, pH = 12.5
- $\text{Ca}(\text{OH})_2$ saturated + 0.2 M KOH, pH = 13.2

The corrosion cell was a polyethylene flask in which the electrolyte is located, covered with a paraffin oil layer to prevent the alkaline solution from carbonation. A carbon bar of 5 mm diameter and 50 mm length was employed as counter electrode, for corrosion measurement. Two identical galvanized rebar were immersed in the solution in order to obtain mean values of corrosion parameters. The testing area was of 5.87 cm^2 . The cells were maintained during one month at 25°C in a thermostatic bath. The testing was divided into two periods:

- 1) The initial Hydrogen Evolution Period
- 2) The Passivation Period.

Corrosion potential, E_{corr} , and corrosion rate, I_{corr} , measurements were performed along the experiment duration. For E_{corr} measurement, a calomel electrode was

employed. The I_{corr} was estimated from polarisation resistance measurement, following the procedure described in [15].

The formation of the passive layer in the different conditions tested was followed using scanning electron microscopy. The consumption of galvanized layer during passivation process was determined by observation of the transversal cut of the galvanised rebar with optic microscopy.

3. Results

Passivation in presence of organic films.

In the reference galvanised steels (no protected) after the immersion in the solution of pH 13.2 evolve to follow a sharp decrease of the E_{corr} to very negative values, below -1000 mV (SCE). This situation lasts 25 days. Such low potential values on the galvanised steel surface are reduced after three days when the rebar surface is covered with the organic film 661 W/2 and it is completely inhibited with the films having chromium (GM-3W and GM7). Figure 1 shows these results. The I_{corr} measurements show similar behaviour, high values of I_{corr} are registered if no film is used ($75 \mu\text{A}/\text{cm}^2$) even after 15 days of testing. With the organic films (GM-3W and GM 7) the I_{corr} is reduced, and in case of 661 W/2 is more than ten times lower than the I_{corr} of the reference, the initial high I_{corr} are less dramatic, figure 2.

The pH 12.5 is less aggressive and does not show differences with the presence or not of the organic films and with the type of polymer film, either in the E_{corr} and the I_{corr} measurements, figure 1 and 2.

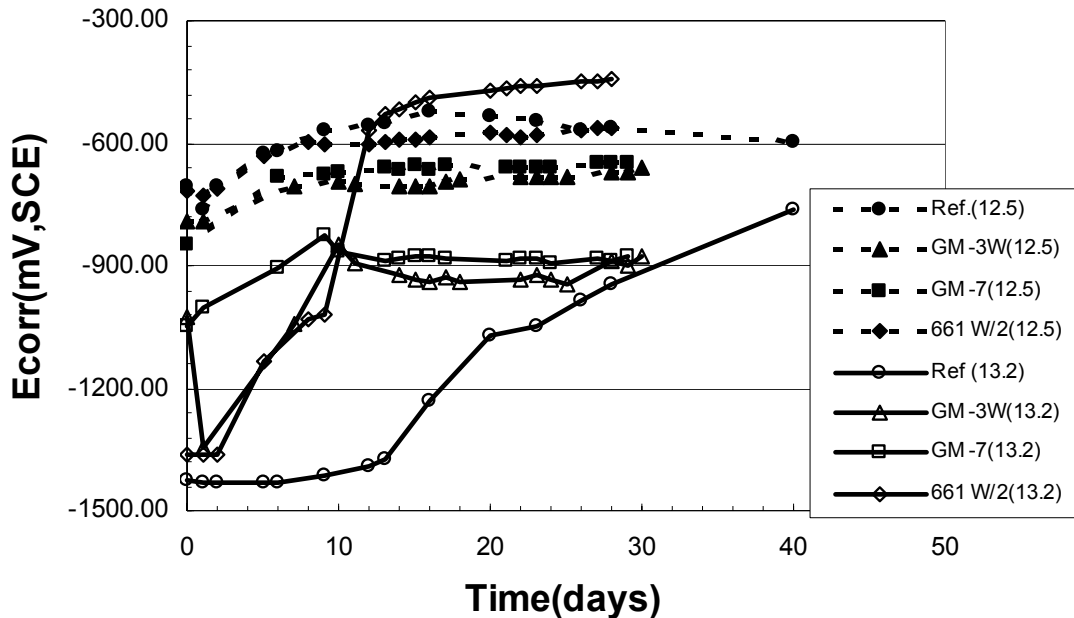


Fig. 1. E_{corr} evolution of galvanised reinforcement interaction with alkaline simulated pore media, in presence of organic coatings.

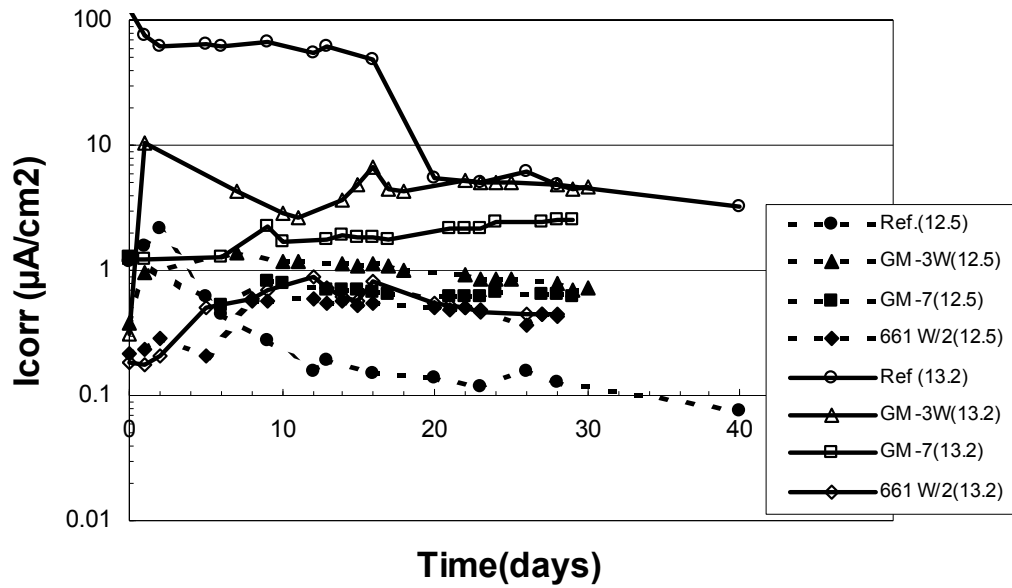


Fig. 2. Icorr evolution of galvanised reinforcement interaction with alkaline simulated media in presence of organic coatings.

Electrochemical weight losses were calculated from the Icorr measurements, after application of the Faraday law. This procedure allows to estimate the galvanised layer loss during the steps involved in passivation process in the pHs 13.2 and 12.5.

The weight loss during the hydrogen period, at the pH 13.2, is reduced in one or two orders of magnitude if an organic film is used, and the underneath galvanised layer is practically not affected during this period. In passivation step, identified by a decrease of the corrosion activity to non dangerous values $I_{corr} < 0.2 \mu A/cm^2$, is also reduced due to the presence of the film covering the surface of the galvanised steel.

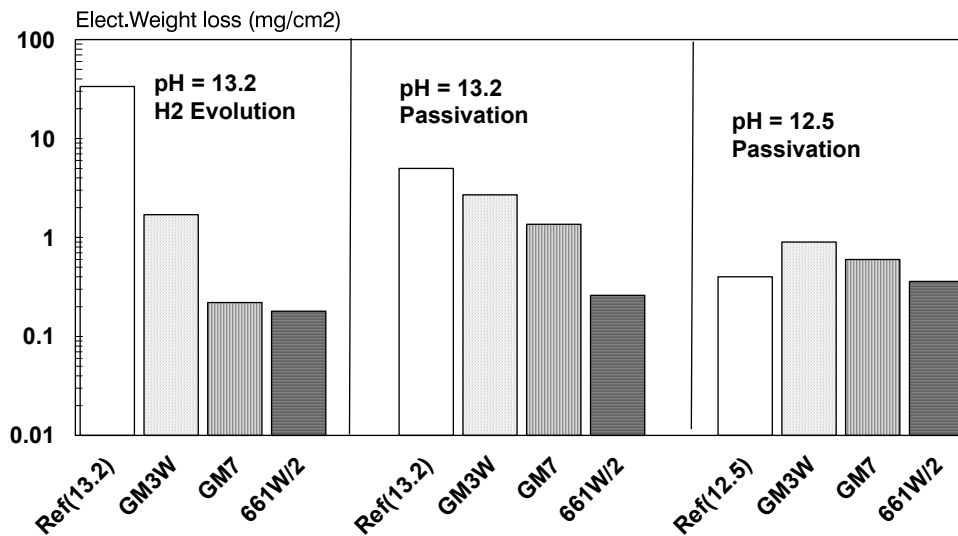


Fig. 3.- Weight loss of galvanised layer during passivation obtained from Icorr measurements.

At the pH 12.5, the effect on weight loss is not significant with or without the use of organic coating and the hydrogen period completely disappears.

Influence of the addition of Ni and V in the passivation process.

The stability of the galvanized rebar has been studied in calcium containing alkaline media. The effect of the pH in the corrosion of galvanized is different for pH 13.2 to 12.5. The initial corrosion potential exhibited by the reinforcements is very negative, as may be noticed in figures 4 and 5, for Ecorr and Icorr measurements. An important feature to be considered here is the length of the period with hydrogen evolution.

The microstructure of the galvanized coating influences on the length of the hydrogen period. In present case the addition of Nickel and/or Vanadium to the hot dip bath has reduced the length of this period, from 10 days in case of for 0 %Ni respect to 2 days for 0.2 %Ni + 0.04 %V.

The further evolution of Ecorr to more positive potentials indicate that the passivation is possible in both pHs and with Ni and/or V. This process seems to occur faster in pH = 12.5 solution. Icorr values are always lower for the lower pH solutions. The reason for this is the different calcium content in the solution, that is used to form the passive layer of Calcium hydroxizincate.

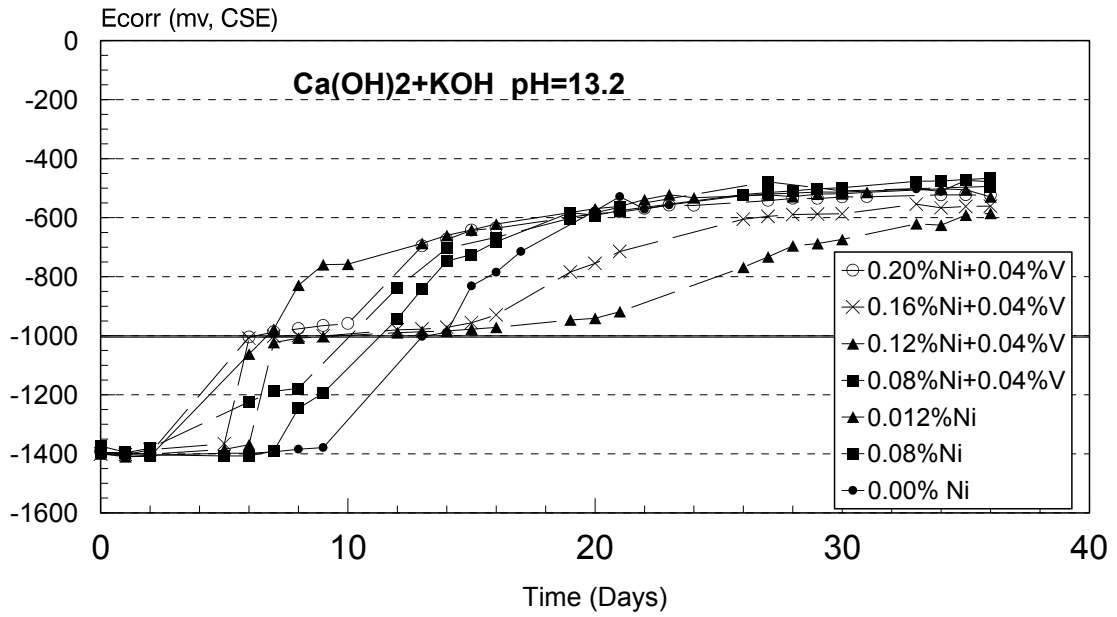


Fig. 4. Ecorr evolution of galvanised reinforcement interaction with alkaline simulated pore media, if Ni and V is added to the hot deep bath.

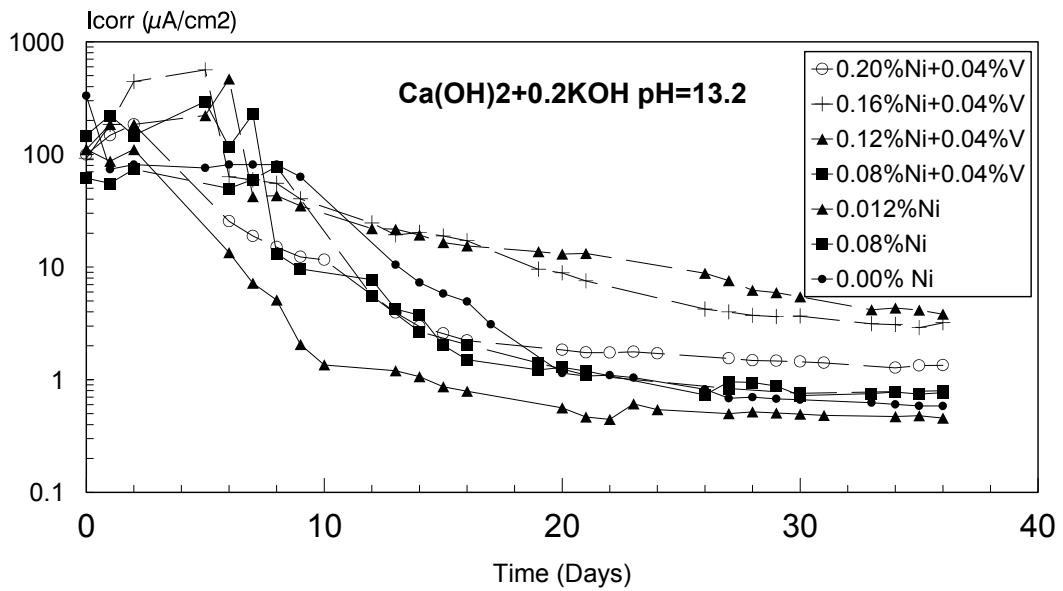


Fig. 5. Icorr evolution of galvanised reinforcement interaction with alkaline simulated pore media, if Ni and V is added to the hot deep bath.

The weight loss estimated from the Icorr results is represented in figure 6. Although the effect of Ni and V addition is less important than if an organic coating is used, also is noticed a reduction in weight loss, nearly one order of magnitude less during hydrogen period with vanadium and Nickel. In passivation period is less relevant but more effective in galvanised reinforcements with only Ni addition in the hot deep bath.

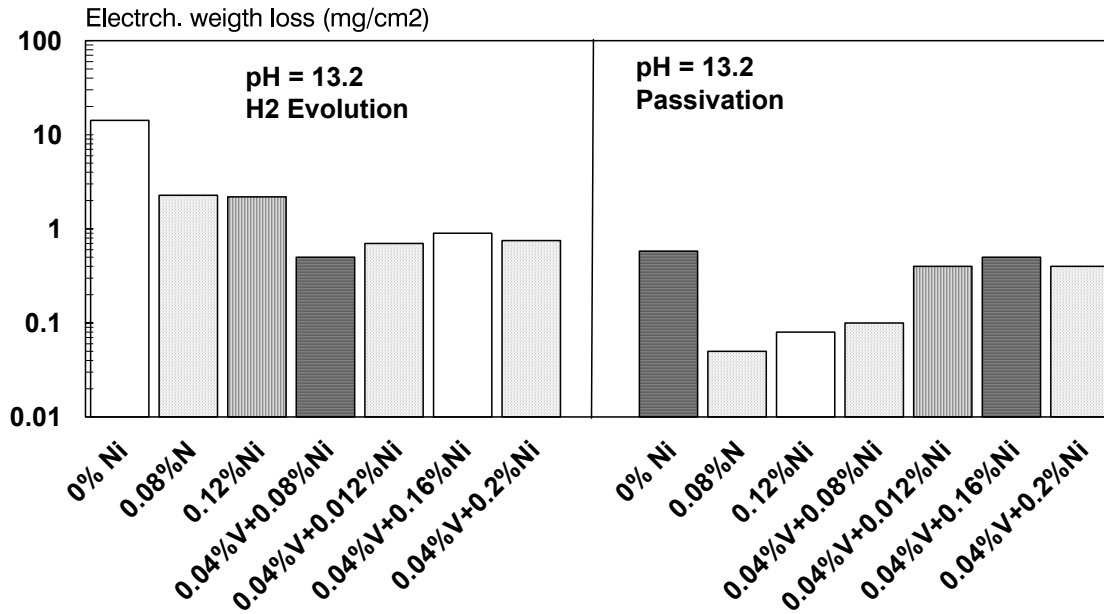


Fig. 6. Weight losses of galvanised layer during passivation. Effect of Ni and V addition in the hot deep bath.

4. Discussion

One important feature of the alkaline media containing calcium, as those present in the pores of the concrete, is that the increase of the pH from 12.5 to 13.2, induces a decrease of the Ca^{+2} in the solution, while the formation of the specie CaOH^+ , is more favoured [4]. To this reason is attributed the delay in the passivation process with the pH increasing.

Passivation protection process of galvanised reinforcement in alkaline media containing calcium:

The passivation of galvanised rebar in alkaline media of the concrete is possible due to the presence of calcium ions that reacts to the formation of the passive layer of crystals identified as Calciumhydroxyzincate (CaHZn). The morphology of the CaHZn crystals is different depending on the pH formation. During passivation process of galvanised if the pH in the pore solution allows the presence of calcium ions a passive layer on the surface of the galvanised is developed that protect the underneath metal from further dissolution in the alkaline media. The passivation process occurs as follow:

1. At pH =12.5 the typical hexagonal crystals of CaHZn perfectly overlap forming like stars that grow until the entire surface is covered. and a comparison with traditional galvanised is made.
2. At pH 13.2 the passive layer of CaHZn is developed more slowly due to the lack of Calcium ions in the solution and so isolated crystals grow on the surface of the galvanised. The surface not covered with the CaHZn crystals continue corroding and hydrogen evolution is possible.

Figures 7 show the morphology and distribution of CaHZn crystals on the surface of the rebar.

Passivation protection process of galvanised reinforcement formed in presence of Ni and V in alkaline media containing calcium.

If Ni and/or V is added to the bath besides to reduced the size of the alloyed layers (Zn and Fe) the new type of galvanised layer modifies the passivation process in the next aspects:

1. At high pH (12.5) the initial high reactivity of the galvanised steel with the alkaline media is maintained, the difference is that in presence of Ni and V the CaHZn crystals forming the passive layer have smaller size that lay to lower corrosion rates. Figure 8, left micrograph show the type of crystals, for the aim of comparison they have the same magnification than figure 7.
2. In very alkaline conditions, the new galvanised steel with Ni and V react forming more crystals of CaHZn although the distribution is different than at lower pHs, the hydroxizincate crystals are more irregular, imperfect and overlap in a less order way. Again the difference of this passive layer in galvanized with Ni-V is the size of the crystal, lower also with Ni-V addition, respect to the case with 0% Ni and /or V addition to the hot dip bath.

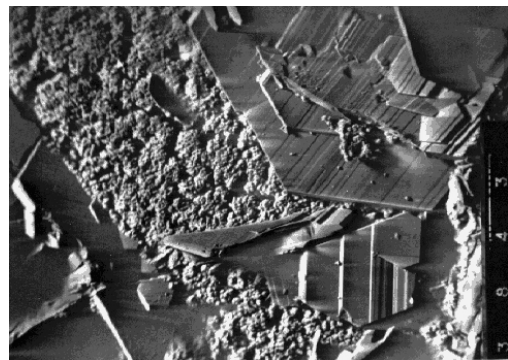
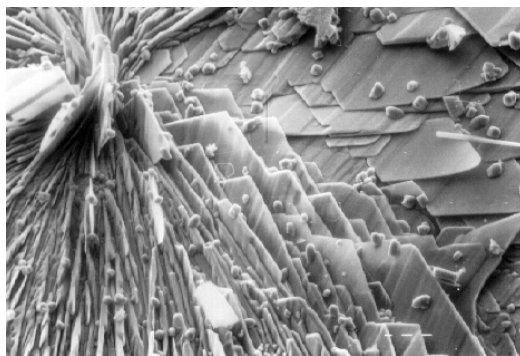


Fig. 7. Galvanized steel produced 450°C, 90s. passivated in calcium containing solution of pH= 12.5, left and 13.2, right. Same magnification.

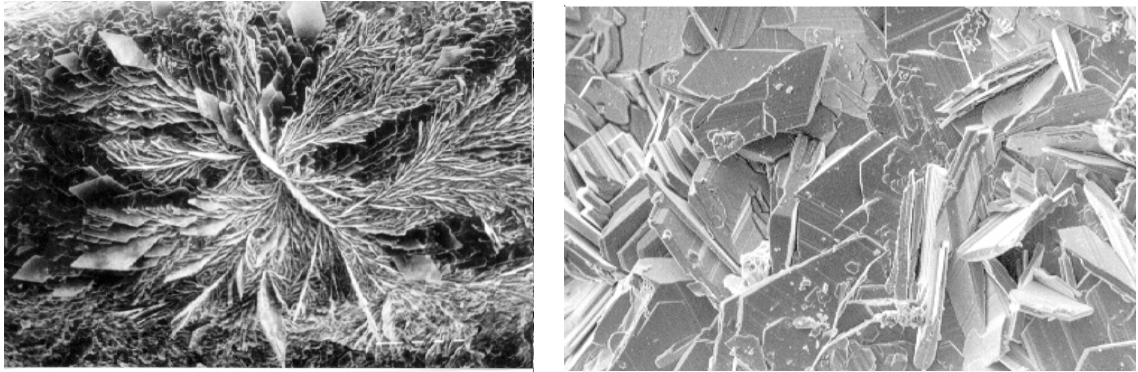


Fig. 8. Galvanized steel produced 450°C, 90s. 0.04%V+ 0.2% Ni, passivated in calcium containing solution of pH=12.5, left, and 13.2, right. Same magnification

Passivation protection process of galvanised reinforcement formed cover with polymeric organic film in alkaline media containing calcium.

When an organic film is covering the surface of the galvanised, the initial very reactive process of the galvanised with the alkaline media does not occur, the film actuates as a barrier isolating the surface of the galvanised from the environment. However as soon as the polymer film has pores or damage areas, the galvanised is exposed to the alkaline environment and calcium hydroxizincate crystals are developed, to contribute to the passivation of the galvanised. The micrograph of figure 9 shows this effect.

However the porosity of the coating could result beneficial in time. The reason is that one doubt that emerges from the protection of galvanised rebar with an organic coating is that the smoothness of the surface is increased. This could affect the bonding of the galvanised reinforcement with the concrete. The grow of CaHZn crystals in the pores will contribute to reduce such undesirable effect. In fact the growing of CaHZn is attributed the delay in bonding forces when galvanised reinforcement is used, but the bond increases with time improving that of uncoated steel and precisely to the developing of the passive layer of crystals is considered [16].

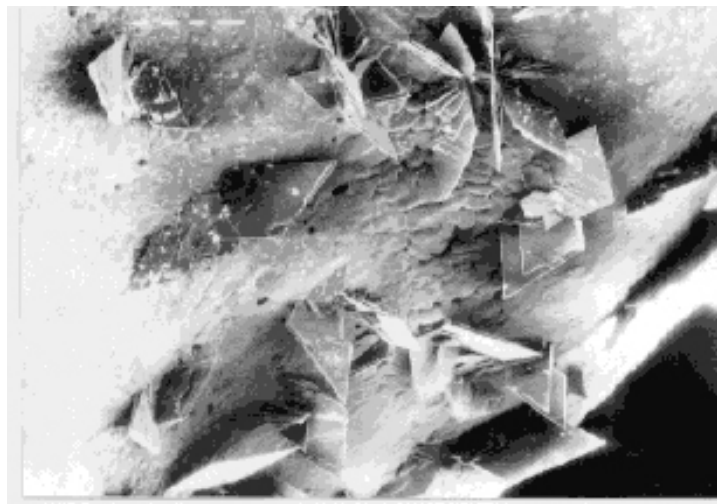


Fig. 9. Aspect of the surface of the galvanised steel covered with a film, after immersion in pH 13.2. Growing of crystals of CaHZn in pores.

4. Conclusions

1. In the first hours the galvanized steel is very reactive, and precisely is during this time when the higher amount of galvanized layer is lost.
2. The addition of Ni to the hot dip bath reduces the period of hydrogen evolution. This fact is also affected by the addition of Vanadium.
3. The best corrosion behaviour has been detected for the galvanized layer developed in 0.08% and 0.2% of Ni and 0.04% V.
4. The size of the crystals of the passive layer is lower in those galvanized with Ni and/or V addition in the hot dip bath. The passive layer results more protective.
5. The use of organic films to protect the galvanised reinforcement reduces or completely avoid the hydrogen evolution period. CaHZn crystals can grow in pores to contribute to the complete passivation of the galvanised steel in the alkaline media..

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