The Effect of Fly Ash on the Corrosion Behaviour of Galvanised Steel Rebars in Concrete

Francesca Tittarelli, Alessandra Mobili, Tiziano Bellezze
Department of Materials and Environment Engineering and Physics (SIMAU)
Università Politecnica delle Marche (UNIVPM), UdR INSTM, Via Brecce Bianche, 60131 Ancona, Italy

Abstract: The effect of fly ash on the corrosion behaviour of galvanised steel rebars in cracked concrete specimens exposed to wet-dry cycles in a chloride solution has been investigated. The obtained results show that the use of fly ash, replacing either cement or aggregate, always improves the corrosion behaviour of galvanised steel reinforcements. In particular, the addition of fly ash, even in the presence of concrete cracks, decreases the corrosion rate monitored in very porous concretes, as those with w/c = 0.80, to values comparable with those obtained in good quality concretes, as those with w/c = 0.45. Therefore, fly ash cancels the negative effect, at least from the corrosion point of view, of a great porosity of the cement matrix.

Keywords: Concrete, Corrosion, Galvanized Reinforcements, Fly Ash.

1. INTRODUCTION

Cracks induced by loading, shrinkage, creep, thermal and flexural stress and mechanical shocks greatly increase the concrete surface permeability, since they represent preferential paths for penetration of aggressive ions, such as sulphates and chloride ions in polluted area and coastal zone [1]-[2]-[3], promoting concrete deterioration and corrosion of embedded reinforcements.

In these cases hydrophobic coatings/admixtures, due to their ability to make concrete less susceptible to water saturation [4]-[5], or galvanised steel reinforcement due to the formation of a passive layer resistant to chloride attack at higher concentration levels than in bare steel, can be used as a preventive method to slow down steel corrosion and prolong the service life of structures [6]-[7]-[8]-[9]-[10]. The formation of a dense protective passive layer on galvanised steel reinforcement seems to be favoured by less alkaline conditions in the concrete pore solution [11] and this occurrence can be achieved by fly ash addition to concrete, because of its pozzolanic activity. In addition, concrete containing fly ash is an example of a sustainable construction material since fly ash is a by-product of thermal power generation and if not used has to be disposed of in landfills at a certain cost. This pozzolanic addition can be used partially...
replacing either fine natural aggregate or cement; in the first case it leads to saving natural resources which are rapidly depleting; in the second case, the reduction of carbon dioxide emission, strictly related to Portland cement production, is obtained.

In this work, the effect of introducing fly ash in the concrete mixture at a dosage of 30% by cement weight, replacing either cement or fine aggregate, on the corrosion behaviour of galvanised steel reinforcements in cracked structures has been investigated. In particular, this work wants to verify if the simultaneous use of galvanised steel reinforcements and fly ash in concrete could assure not only the concurrence of the environmental and technical benefits derived from the use of both steel galvanisation and fly ash concrete, but it could further provide a useful synergic effect, as it could be really foreseen.

2. EXPERIMENTAL

2.1 Specimens

Prismatic concrete specimens (28 cm × 7 cm × 7 cm) were manufactured with a nominal water/cement (w/c) equal to 0.45 or 0.80, with and without fly ash. This mineral admixture was added at a dosage of 30% by cement weight, replacing either cement or fine aggregate, thus changing the water to cementitious material (w/cm) ratio. The different concrete mixture proportions are reported in Table 1, where the compressive strength achieved after 1 month of air curing is also indicated.

| Mixture         | w/c | Water kg/m³ | Cement kg/m³ | Sand kg/m³ | Crushed Aggregate kg/m³ | Fly Ash kg/m³ | w/cm | Compressive Strength at 30dd (MPa) |
|-----------------|-----|--------------|--------------|------------|-------------------------|---------------|------|----------------------------------|
|                 |     | w/cm         |              |            |                         |               |      |                                   |
| no Fly Ash      | 0.45| 240          | 533          | 639        | 847                     | -             | 0.45 | 58.3                             |
| Fly Ash for cement | 0.64| 240          | 300          | 1043       | 639                     | -             | 0.80 | 22.1                             |
| Fly Ash for aggregate | 1.14| 240          | 210          | 1022       | 627                     | 160           | 0.45 | 50.0                             |
|                 |     | 240          | 373          | 650        | 862                     | 160           | 0.80 | 19.0                             |
|                 | 0.45| 240          | 533          | 449        | 847                     | 160           | 0.35 | 66.8                             |
|                 | 0.80| 240          | 300          | 938        | 639                     | 90            | 0.60 | 33.0                             |

Each prismatic specimen was reinforced with a galvanised steel plate (7 cm × 4 cm × 0.1 cm) embedded with concrete cover of 4 cm. The zinc coating was 100 µm thick, obtained by molten zinc immersion, with an outer pure zinc layer about 20 µm thick. The galvanised reinforcements, just before their embedment in the fresh concrete, were submerged for 5 s in 15% NaOH solution to dissolve the ZnCO₃ layer eventually formed during atmospheric storage. The electric contacts among the reinforcing plates and the measuring equipment were arranged according to a previously reported methodology [12]. After 1 month of air curing the specimens were cracked by flexural stress so that a crack width of 1 mm was produced in a pre-formed notch area with the apex of the crack reaching the reinforcement. Then the specimens were exposed to weekly wet-dry cycles (2 days dry followed by 5 days wet) in a 10% NaCl solution.
2.2 Evaluation of the corrosion behaviour

The corrosion probability of the reinforced concrete specimens exposed to the aggressive environment was evaluated by free corrosion potential measurements with a saturated calomel electrode (SCE) as reference. The kinetic of the corrosion process was followed by polarisation measurements. The polarisation resistance was measured through the galvano-dynamic method, using an external graphite bar as counter-electrode, by calculating its average value between the anodic and cathodic ones. The corrosion rate was calculated through the Stearn and Geary law adopting the value of 26 mV/decade as B constant. The electrochemical values reported in the graphs are the averaged data obtained by measuring three specimens of each type during the immersion period.

In order to validate the electrochemical measurements, after 12 wet-dry cycles in the chloride solution, the concrete specimens were examined to evaluate the corrosion development by visual observation. After splitting the concrete specimens, the galvanised plates were removed and metallographic analyses were carried out on the cross section to evaluate the decrease in coating thickness due to the corrosive attack. The free chloride concentration on the galvanised steel plate was also measured at the end of the test by water extraction.

3. Discussion of Test Results

Fig. 1 shows the free corrosion potential of the galvanised steel plates embedded in concrete specimens with w/c = 0.80 as a function of the number of wet-dry cycles. Just after the exposure to the chloride environment, all the galvanised steel plates are assumed to have activation values of about −1100 mV/SCE regardless of the type of the cement matrix, reflecting a general great corrosion risk. However, only the reference concrete without the pozzolanic additions remained at these activation values for all the test time, while, in the presence of fly ash, the free corrosion potentials moved towards more passive values after a few wet-dry cycles.

Fig. 1. Free corrosion potential (Ecorr) of the galvanised steel plates embedded in cracked concrete specimens with w/c = 0.80 as a function of the number of wet-dry cycles.
At the same time, the corrosion rate (Fig. 2) assumes initial values of about 30 µm/year, but while in the reference specimens it further increases with the test time, in the presence of fly ash the corrosion rate is kept constant at values significantly lower with respect to those detected in the reference matrix without the mineral admixture.

The better corrosion behaviour monitored in the presence of fly ash, regardless of the substitution type, cannot be attributed to the lower chloride concentration at the galvanised steel surface due to densification and chloride adsorption of the cement matrix with the pozzolanic additions. In fact, in this case, cracks represent preferential paths for chloride penetration through the concrete cover and, at the end of the test, the chloride concentration on the surface of the reinforcements is almost the same regardless of the presence of fly ash (Table 2) and, however, greatly overcoming the concentration threshold (1.2% by cement weight) generally reported as the critical value able to induce the corrosion process in galvanised reinforcements [6]. Therefore, in the presence of concrete cracks, the better corrosion behaviour observed in the presence of the mineral admixture could be attributed foremost to the lower alkalinity of the cement matrix due to the pozzolanic reaction, that seems to effectively improve the corrosion resistance of the galvanised reinforcement, as it was already suggested in the literature, even in the presence of concrete cracks [11]-[13].

Table 2. Chloride concentration on the galvanised steel plate embedded in cracked specimens with w/c = 0.80.

| SPECIMEN TYPE          | % CHLORIDE (by cement weight) |
|------------------------|-------------------------------|
| no fly ash             | 7.96                          |
| fly ash for cement     | 7.46                          |
| fly ash for fine aggregate | 7.33                          |

On the other hand, a good quality concrete matrix with a w/c ratio as low as 0.45 seems to mask the beneficial effect of the pozzolanic additions. The corrosion risk described by the free corrosion potential measurements (Fig. 3) is the same regardless of the cement matrix while the corrosion rates (Fig. 4) remain a little bit higher in the reference matrix without the mineral admixture.
admixture but the difference is not as evident as that observed in the more porous cement matrix.

![Fig. 3](image-url)  
**Fig. 3.** Free corrosion potential (Ecorr) of the galvanised steel plates embedded in cracked concrete specimens with w/c = 0.45 as a function of the number of wet-dry cycles.

![Fig. 4](image-url)  
**Fig. 4.** Corrosion rates of the galvanised steel plates embedded in cracked concrete specimens with w/c = 0.45 as a function of the number of wet-dry cycles.

The post exposure evaluation confirmed the electrochemical measurements. As a matter of fact, in the reference high quality concrete (w/c = 0.45 without FA), the corrosive attack really appeared much localized at the crack apex and also very deep, even showing well recognizable iron corrosion products (Fig. 5a). Moreover, far from the crack apex, Fe-Zn alloy appeared on the plate surface meaning that total consumption of the pure zinc layer due to the corrosive attack occurred, as later confirmed by metallographic analysis (Fig. 5b).

On the other hand, the galvanised steel plates extracted from high volume fly ash concrete showed a surface coating made of white zinc corrosion products (Fig. 6a), later identified as calcium hydroxyzincate by X-ray diffraction. Calcium hydroxyzincate is a well passivating zinc corrosion product whose formation seems to be effectively favoured by low alkalinity of
the concrete pore solution [13] as achieved when high volume fly ash is added because of its pozzolanic activity. Once formed, calcium hydroxyzincate protects the underlying pure zinc layer from further corrosion as metallographic analysis well put into evidence (Fig. 6b).

Fig. 5. Visual observation (a) and metallographic cross section (b) of the galvanised steel plates embedded in concrete with w/c = 0.45 without fly ash.

Fig. 6. Visual observation (a) and metallographic cross section (b) of galvanised steel plates embedded in concrete with w/c = 0.80 with fly ash concrete.

4. CONCLUSIONS

The use of fly ash, as partial replacement of either cement or aggregate, always improves the corrosion resistance of galvanised steel reinforcements in cracked concrete specimens exposed to wet-dry cycles in a chloride solution. In particular, the pozzolanic addition of fly ash, even in the presence of concrete cracks, decreases the corrosion rate monitored in very porous concretes, as those manufactured with w/c = 0.80, to values comparable with those obtained in good quality concretes, as those manufactured with w/c = 0.45. In other words, fly ash cancels the detrimental effect, at least from the corrosion point of view, of a great porosity of the cement matrix.

As a matter of fact, the use of galvanised steel reinforcement in fly ash concrete, not only assures the concurrence of the technical and environmental benefits derived from the use of both steel galvanisation and fly ash addition to concrete, but it can further provide a useful synergic effect because the pozzolanic activity favours the formation of a dense protective passive layer on galvanised reinforcement, which remains stable even in the presence of concrete cracks.
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Francesca Tittarelli graduated in Chemistry with honour, PhD in Materials Engineering, Associate Professor at UNIVPM in the field Materials Science and Technology. She teaches Material Science and Technology for Civil and Environmental Engineering. Since 2012 is associated to the Institute of Atmospheric Sciences and Climate of the National Research Council of Italy (CNR-ISAC). She published more than 150 papers on durability and sustainability of materials for Engineering. She is referent of COSMOMET "Concrete Structures Monitoring Network" developed after the patent "Monitoring system for preventative maintenance of reinforced
concrete structures." AN2005A000045 ". For UNIVPM, she is member of the Academic Board of the PhD Program in Industrial Engineering, the Scientific Council of the Center for Research and Service in Nanostructures Microscopy (CISMIN), the Scientific Council of the Center for Research and Service Engineering Apparatus Motor (CIAM), the Joint Commission. She is founder professor of the Center for Research and Service SMALL (SMArt Living Lab) of UNIVPM and member of the relative board. She is UNIVPM representative in the INSTM board and in the EIP on Raw Material “C&D-WRAM”. She is member of AIMAT, INSTM, ACI, RILEM. She is invited member of ATINER. She is member of the Italian SC5 Consultation Board, she is member of the HDB RILEM Technical Committee. She is referee for several international scientific journals and Evaluator of Projects for Italian MIUR and Romanian National Council.

**Alessandra Mobili** has a Master Degree in Building Engineer - Architecture at Polytechnic University of Marche (UNIVPM) of Ancona, Italy. She is a civil engineer and has a PhD in “Materials, Environmental and Territorial Engineering”. From April 2015 to July 2015 she was visiting PhD student at VrijeUniversiteit Brussel (VUB) of Brussels, Belgium. Actually she is working in the area of innovative building materials and their sustainability. She is concrete technologist. The actual research is about the study and the development of innovative and environmentally friendly materials for building applications prepared also by re-cycling industrial by-products. Furthermore, her research work is focused on the field of geo-polymeric materials for rehabilitation and restoration of ancient and modern buildings.

**Tiziano Bellezze** was graduated with honours in Chemistry at the University of Parma (Italy) in 1995, discussing a thesis in the field of theoretical chemistry. He took the PhD in Materials Engineering at the University of Bologna (Italy) in 2000, discussing a thesis in the fields of Corrosion Science. The PhD thesis won the prize ‘Fondazione Oronzio De Nora 2001’ given by the Electrochemical Division of the Italian Society of Chemistry. Since 2007, Tiziano Bellezze is Researcher at the Polytechnic University of Marche (Italy). He is member of Italian Corrosion Technical Committee within the Italian Metallurgical Association (AIM). Furthermore, he is member of European Federation of Corrosion (EFC) though AIM, member of Italian Association of Materials Engineering (AIMAT) and member of National Interuniversity Consortium of Materials Science and Technology (INSTM). He is author of more than 100 papers in the field of Corrosion Science.
Corrigendum:
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The published references are not correct.

Please replace with:

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