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The effect of pH and fly ash on the electrochemical performance of stainless steel concrete reinforcement in harsh environments

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Abstract

The investigation of the effect of pH and fly ash (FA) as a corrosion inhibitor on the electrochemical behavior of 316L and 304L concrete reinforcements in a simulating concrete pore solution exposed to acid rain is the main objective of the present study. The corrosion performance of 316L and 304L stainless steel is examined by means of cyclic potentiodynamic polarization. Two types of electrolyte were used. The first electrolyte is a highly alkaline solution simulating fresh concrete exposed to acid rain (pH ≈ 12), while the second electrolyte is a mildly alkaline solution simulating corroded concrete cover that has exposed the reinforcement to direct acid rain attack (pH ≈ 8). Both solutions contained saturated $Ca(OH)_2$, an acid rain simulating solution and FA (0 wt.% - 25 wt.% of the dry mixture) as corrosion inhibitor. In both electrolytes the beneficial effect of FA up to 20 wt.% content on the corrosion resistance of both steel rebars was manifested. However, this trend was reversed at 25 wt.% FA. The above finding was also confirmed by SEM/EDX examination of cross-sections of rebars embedded in concrete after 4 m of salt spraying. An important conclusion of this study is the feasibility of replacing 316L stainless steel with 304L in critical applications, such as the restoration of ancient monuments, provided that FA is included in the concrete mixture, even at low contents (15 wt.%).

Introduction

The employment of modern materials in the framework of restoration works of ancient and modern monuments, such as AISI 316L stainless steel in the ancient theater of Dodona, Epirus, Greece, has been a common practice in the last decades. The replacement of an expensive steel reinforcement (316L steel) with a less expensive steel (304L) combined with low-cost and environmentally friendly corrosion inhibitors could become a profitable alternative, provided that it is an equally safe solution.

Corrosion of steel reinforcement is the most significant factor responsible for the premature deterioration of the durability and seismic resistance of reinforced concrete structures [1-4]. The two commonest types of atmospheric attack to the concrete are (a) chloride ion penetration in marine environments and (b) concrete carbonation, as a result of the reaction between the atmospheric CO_2 (mostly in urban areas) and $Ca(OH)_2$ of concrete [1-4]. Besides these two factors, concrete is also subjected to acid rain (AR) attack as a consequence of the intensive urban and industrial activity during the last decades. The deterioration of concrete under acid rain attack is attributed to the combined effect of H^+ and SO_4^{2-} [5].

Amongst the various methods utilized in order to protect reinforced concrete against corrosion, the partial replacement of Ordinary Portland Cement (OPC) with fly ash (FA) is a relatively inexpensive and ecological method. The addition of FA leads to a refinement of the concrete pore structure and therefore reduces its permeability, whilst at the same time the produced insoluble hydration products (C-S-H) of the pozzolanic reaction of FA with C-H ($Ca(OH)_2$) fill the capillary voids of concrete [2-4]. Preliminary studies conducted by the authors have shown the beneficial effect of FA up to 20 wt.% on the corrosion and mechanical properties of stainless steel rebars embedded in concrete or immersed in concrete pore mimicking solutions during exposure in saline and acid rain environments [3,4].

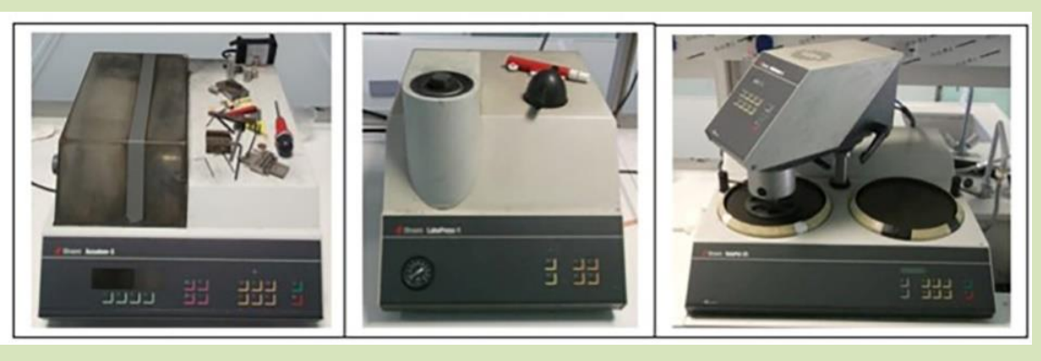
Experimental procedure

ACM Instruments Gill AC 1044

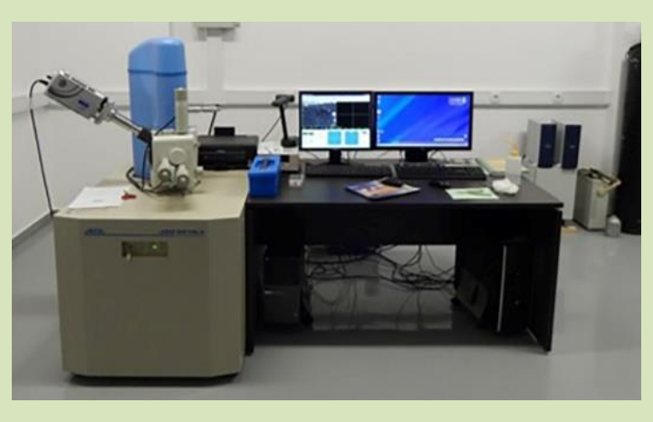
- ✓s. $Ca(OH)_2$ + AR + FA (pH = 7.5 - 7.9 & pH = 12.3 - 12.7)
- ✓ FA: (0 wt.% - 25 wt.%) of the dry mixture ($Ca(OH)_2$ + FA)
- ✓2 h of immersion under open circuit, R.T.
- ✓Scan rate: 10 mV/mm

Reference electrode:
Ag/AgCl (3.5 M sat. KCl)

Auxiliary electrode:
Platinum gauge (Pt)



Metallographic preparation (Struers Accutom-5, Struers Labopress-2, Struers Rotopoll-25)

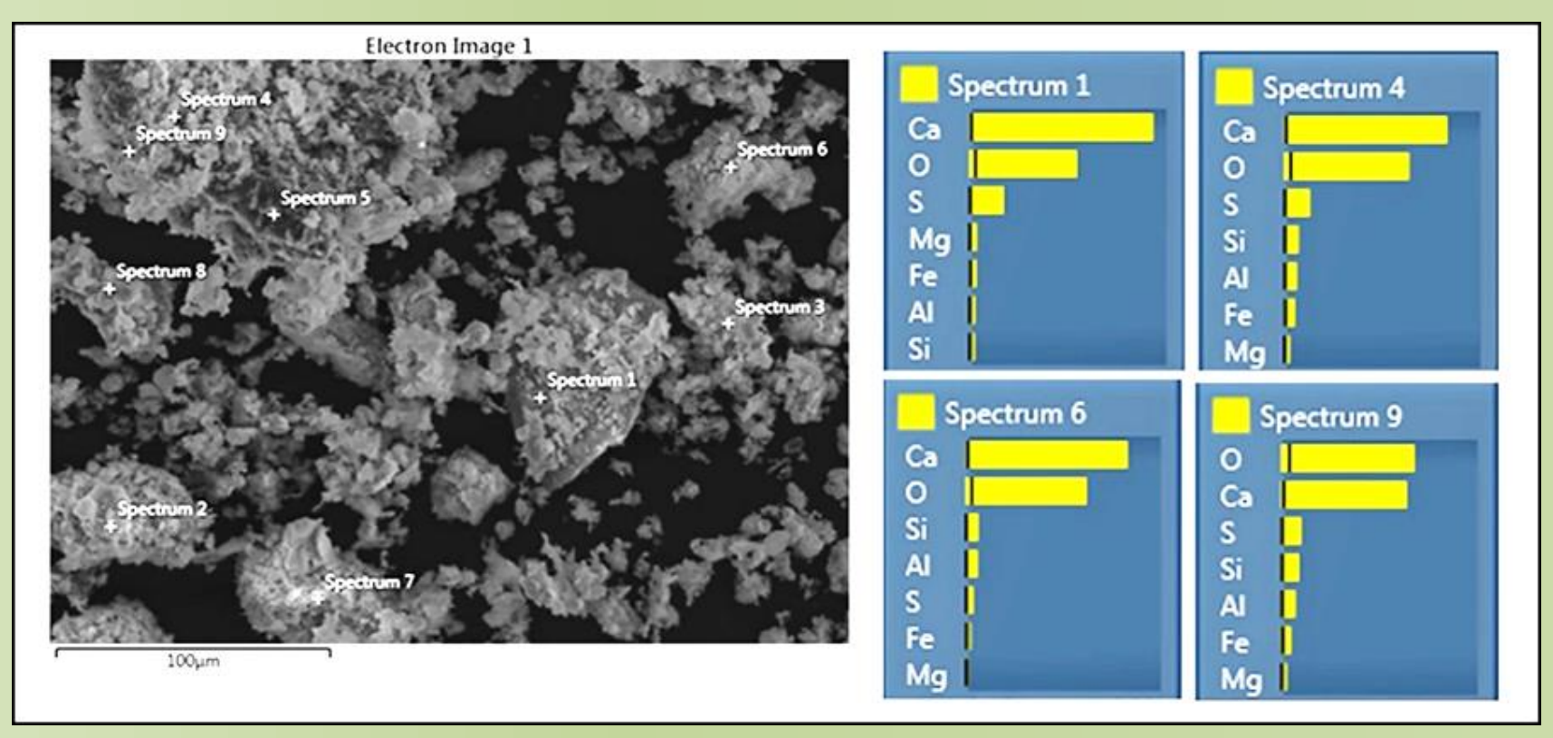


SEM / EDX (JeoL JSM 6510 LV SEM / Oxford Instruments X- Act EDX)

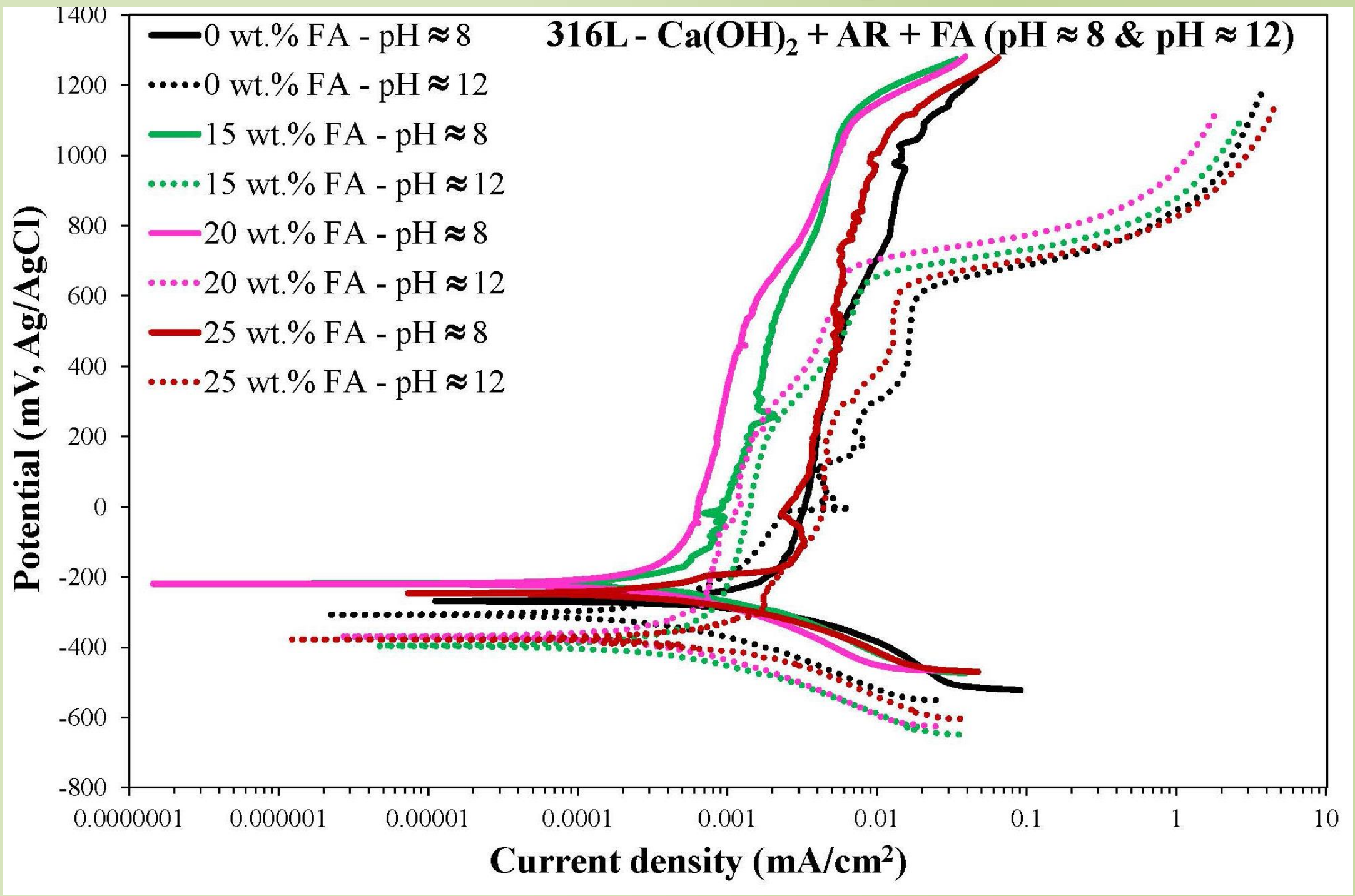
Chemical analysis of acid rain simulating solution (pH = 3.1) [6]

Chemical compound	g/l water
H_2SO_4	0.032
HNO_3	0.015
Na_2SO_4	0.032
$NaNO_3$	0.021
NaCl	0.084
$(NH_4)_2SO_4$	0.046

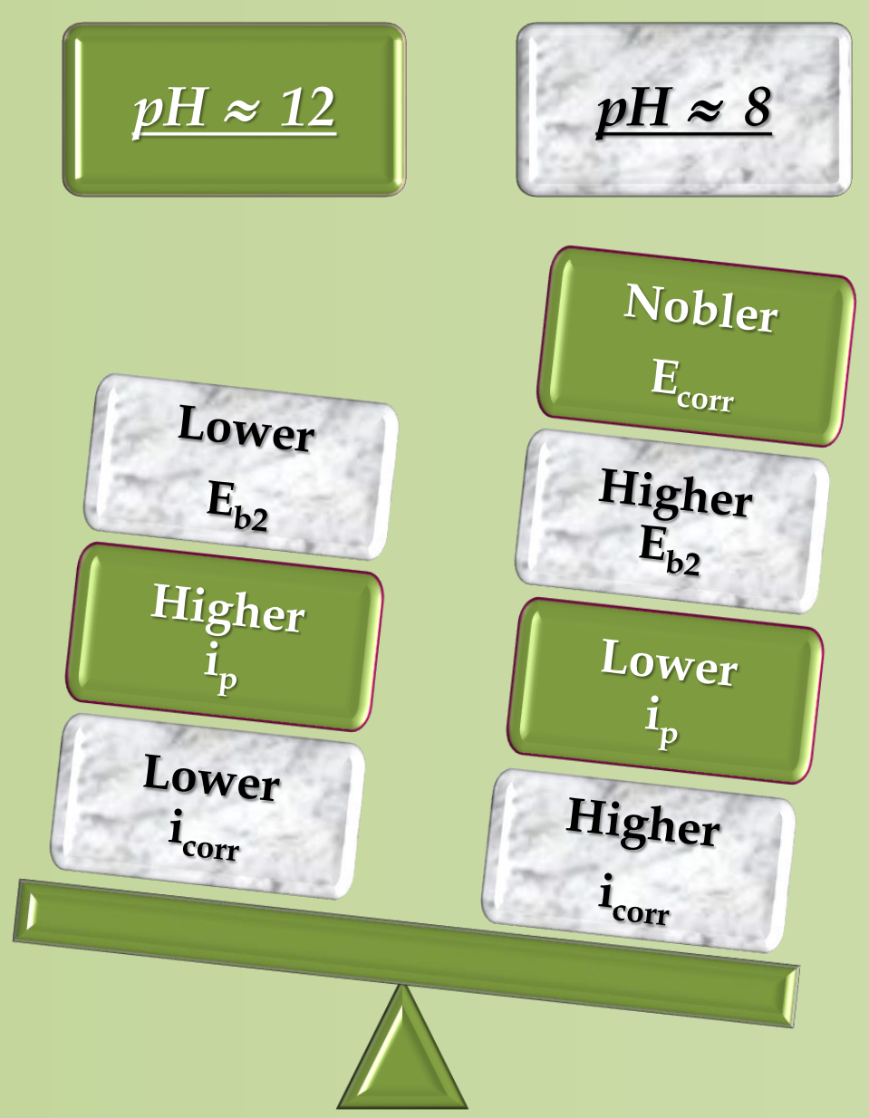
✓Fly ash from the Hellenic Public Power Corporation lignite mines, Western Macedonia, Greece was utilized as corrosion inhibitor.



2. Effect of pH



- ✓ The increased corrosion current density (i_{corr}) at pH ≈ 8 is due to the faster Fe^{2+} dissolution [7].
- ✓ The decreased passive current (i_p) at pH ≈ 8 is due to the increased concentration of Cr^{3+} oxides in the inner layer of the passive film [8].
- ✓ Breakdown of passivity is due to oxygen evolution and Cr_2O_3 transpassive dissolution.

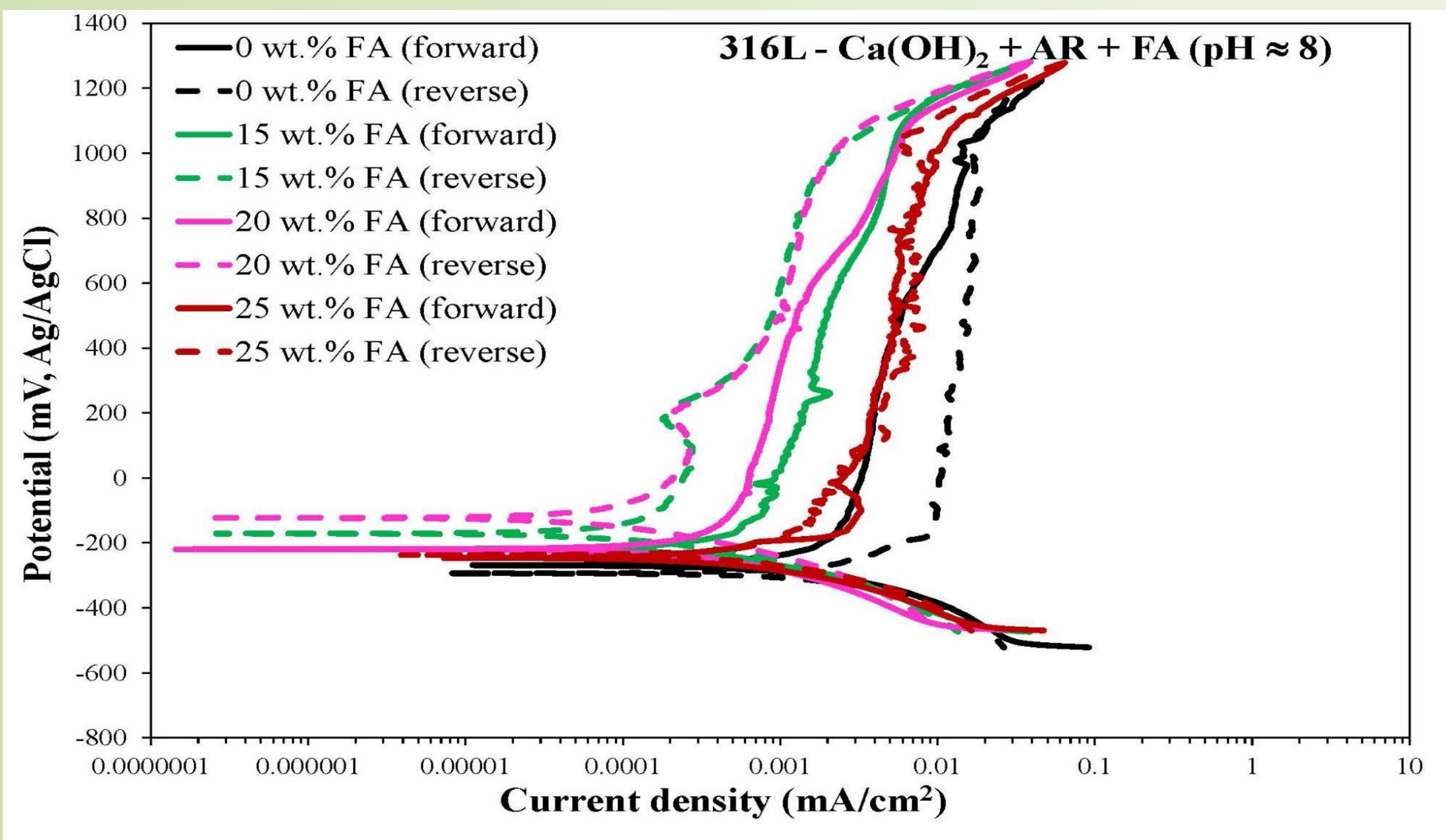


Conclusions

- ✓ Potentiodynamic polarization of 316L and 304L stainless steel rebars in a slightly alkaline electrolyte (pH ≈ 8) and a strongly alkaline electrolyte (pH ≈12) containing $Ca(OH)_2$, an acid rain simulating solution and fly ash at different contents revealed very low corrosion current densities and true passivity.
- ✓ The corrosion resistance increased with FA increasing (up to 20 wt.%). However, this trend was reversed at 25 wt.% FA content.
- ✓ 316L presented a superior passivity in the slightly alkaline electrolyte (pH ≈ 8) as compared to the strongly alkaline electrolyte (pH ≈ 12), but higher corrosion rate.
- ✓ 316L in the slightly alkaline electrolyte (at pH ≈ 8) manifested less thermodynamic tendency for corrosion and superior passivity compared to 304L. However, this trend was reversed in the strongly alkaline electrolyte (at pH ≈ 12).
- ✓ 304L stainless steel can replace 316L in critical applications, such as the restoration of ancient and modern monuments and historical buildings, when the pH of the environment is strongly alkaline (mild attack by acid rain, small presence of Cl^-) and when the pH of the environment is mildly alkaline (severe attack by acid rain, small presence of Cl^-), provided that fly ash is included in the concrete mixture even at low contents (15 wt.%).

Results

1. Cyclic potentiodynamic polarization of 316L



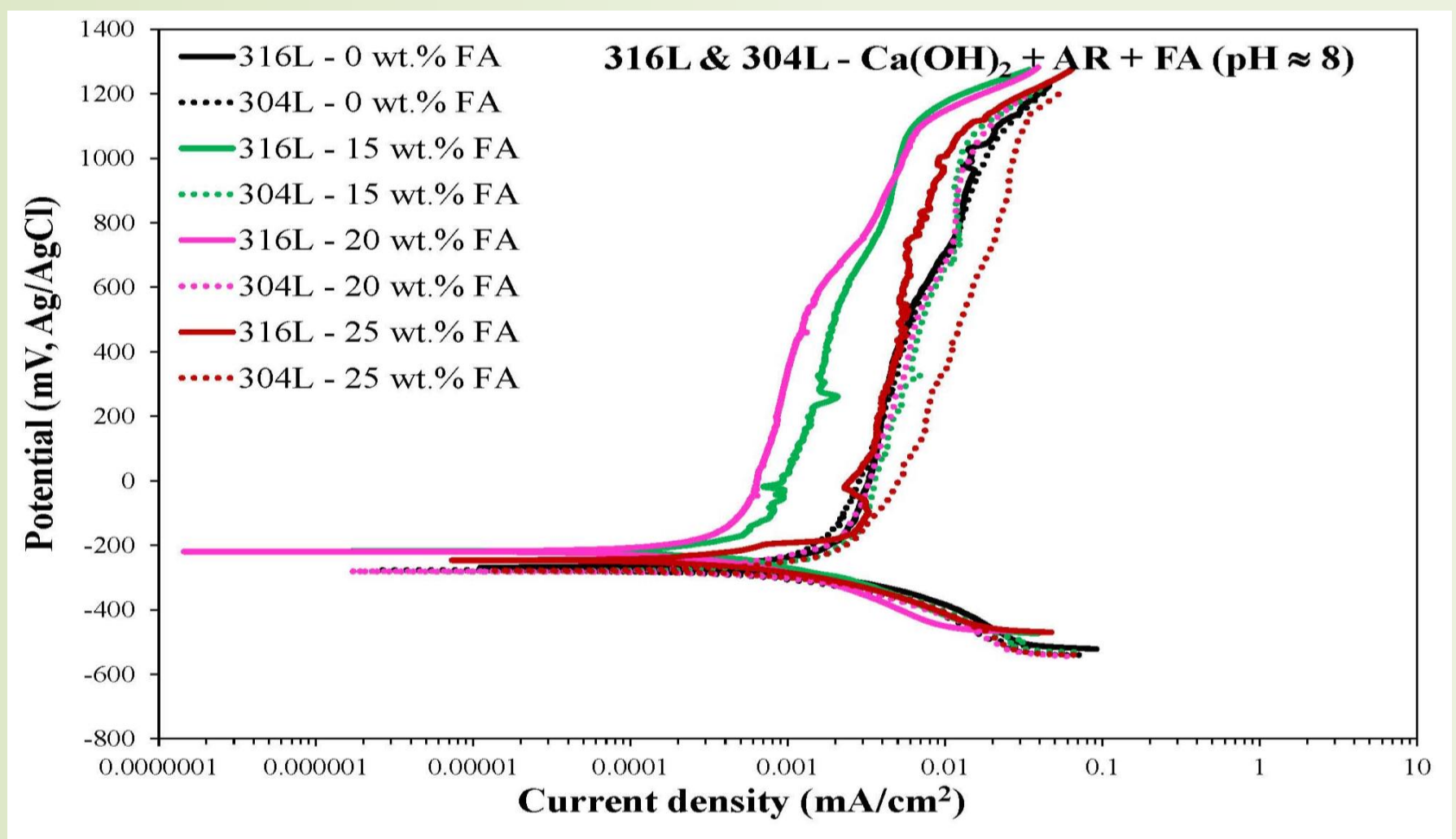
- ✓ Positive hysteresis loops of the anodic polarization curves for all FA contents.
- ✓ All anodic polarization curves exhibit passive regions of high potential range and very low current density values indicating true passivity.
- ✓ The addition of fly ash up to 20 wt.% FA has led to a shift of the forward polarization curves to lower i_{corr} and nobler E_{corr}. However, this trend is reversed at 25 wt.% FA.

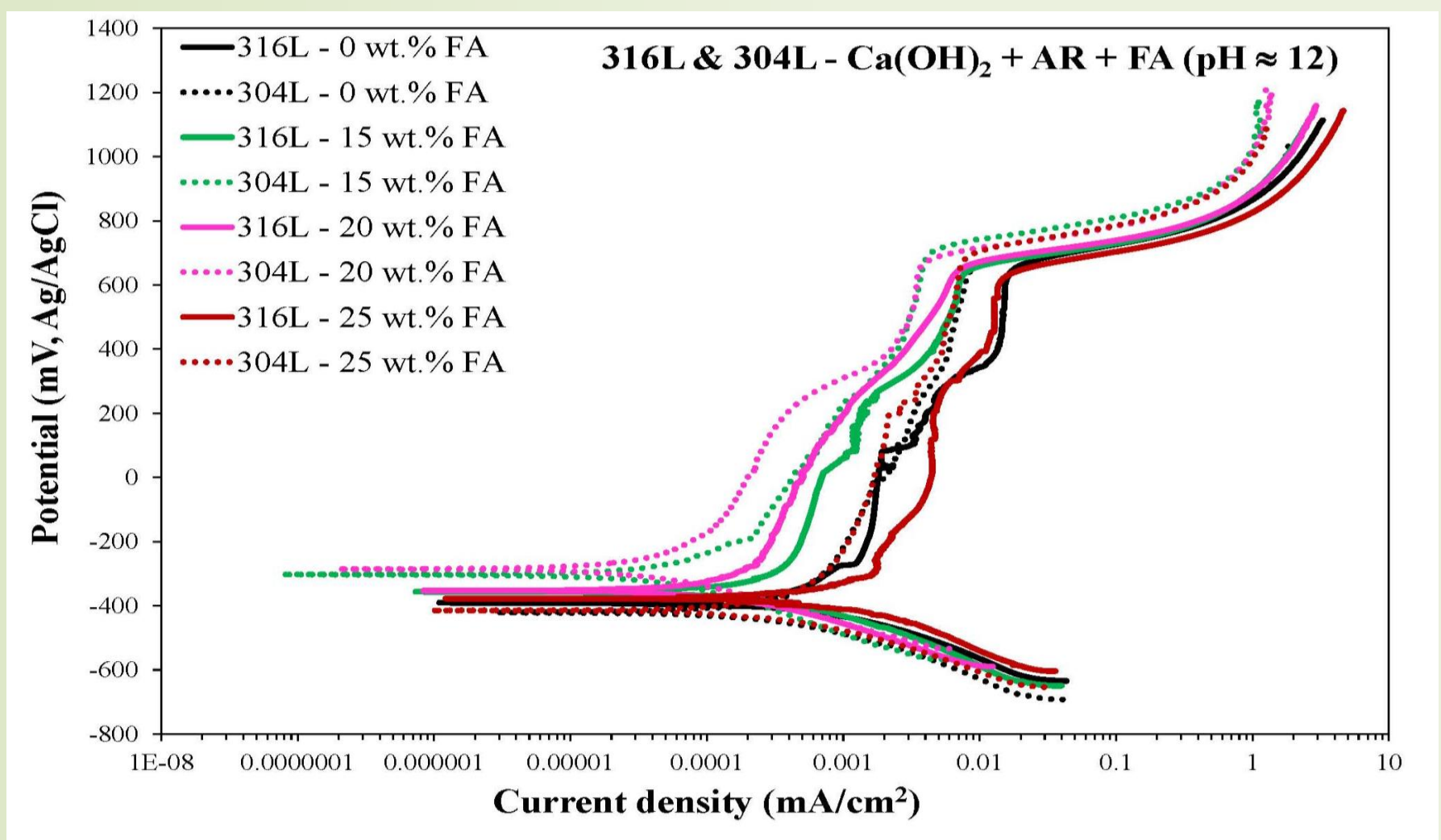
3. Comparison of 316L & 304L

- ✓ **pH ≈ 8:** 316L manifested higher corrosion resistance than 304L in terms of:
  - ➢ more stable passive film (lower i_p) and
  - ➢ nobler E_{corr}

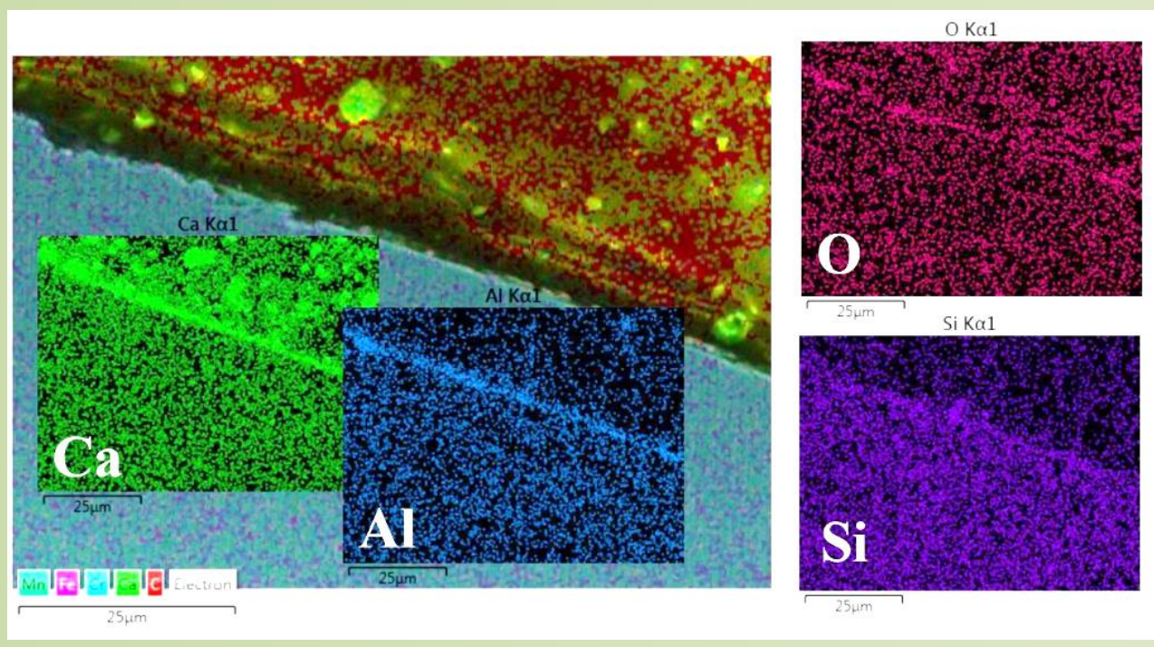
  due to the beneficial role of Mo.
- ✓ **pH ≈ 12:** 316L manifested lower corrosion resistance than 304L in terms of:
  - ➢ less stable passive film (higher i_p) and
  - ➢ less noble E_{corr}

  due to the poor performance of Mo in strongly alkaline environments [9].

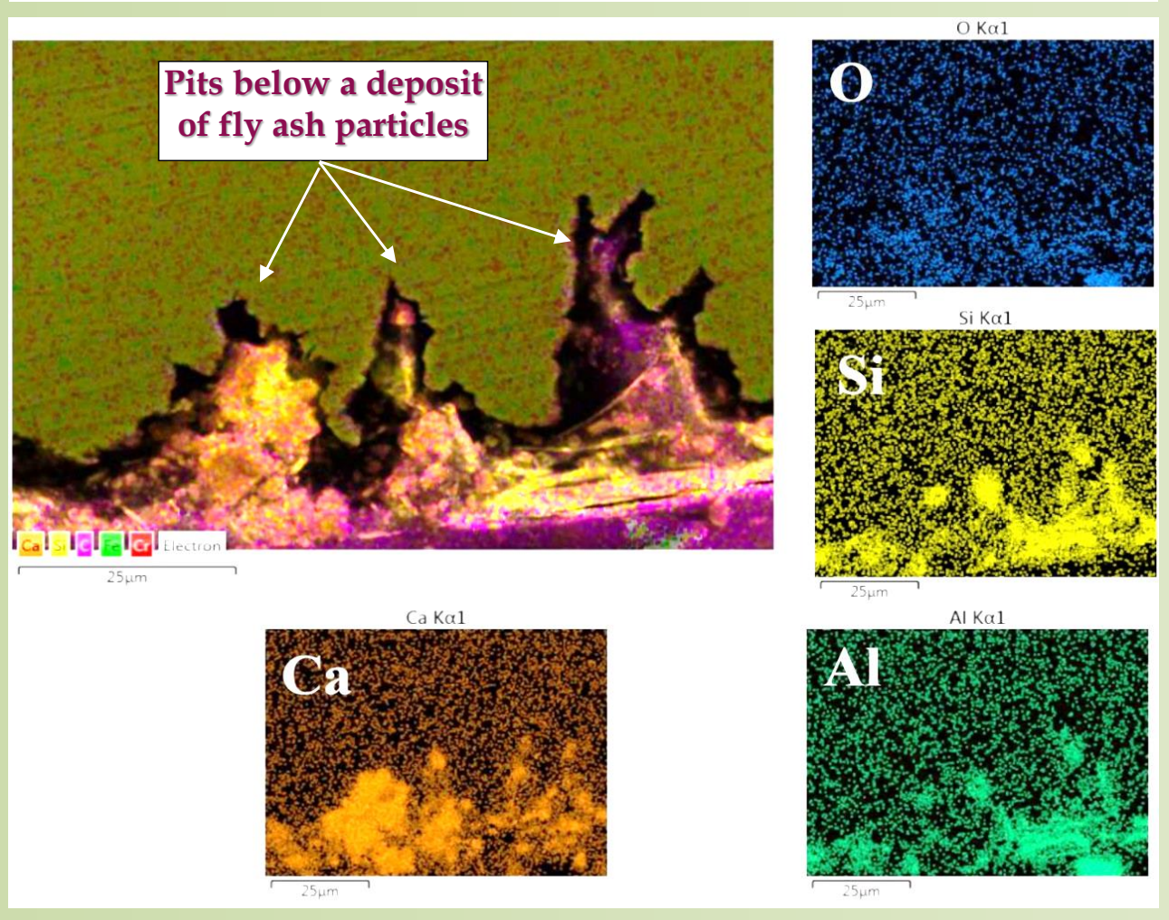




4. SEM / EDX



SEM cross-sectional micrographs of 316L rebars embedded in concrete (20 wt.% FA) after 4 m of salt spraying.



SEM cross-sectional micrographs of 316L rebars embedded in concrete (25 wt.% FA) after 4 m of salt spraying.

- ✓ **20 wt.% FA:** A compact surface film is formed on steel. The increased Si on the steel surface manifests the positive role of the FA on the formation of a uniform protective film.
- ✓ **25 wt.% FA:** Agglomerates of FA form differential aeration cells in pre-existing defects of the steel surface.

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