



A Raman spectroscopy study of steel corrosion products in activated fly ash mortar containing chlorides



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HIGHLIGHTS

- The corrosion products were iron oxyhydroxides, goethite and lepidocrocite.
- Raman spectra were obtained with 532 nm and a power from 0.025 to 0.25 mW.
- Raman spectra were obtained with 633 nm and a power greater than 2.5 mW.
- For 532 nm line the phases formed were transformed into hematite at above 0.5 mW.
- For the line of 532 nm with 5 mW showed fluorescence.

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ABSTRACT

Raman spectroscopy was used to characterise the corrosion products of reinforcing steel embedded in activated fly ash mortars in the presence of 0.4% and 2% chlorides. Two alkaline solutions with different soluble silica contents were utilised to activate the fly ash. Raman spectra were obtained using two excitation wavelengths (532 and 633 nm) and making power scans to select the suitable conditions of register for each wavelength. The main steel corrosion products identified were iron oxyhydroxides with low crystallinity, goethite (α -FeOOH) and lepidocrocite (γ -FeOOH). These products need to be studied using a spectrometer with the laser line of 532 nm at low powers from 0.025 to 0.25 mW or a spectrometer with the laser line of 633 nm at high power between 2.5 and 25 mW.

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1. Introduction

The degradation of reinforcing steel due to corrosion is of great concern for the durability of concrete structures and can lead to serious economic implications [1–3]. The most important causes of reinforcing steel corrosion initiation are the ingress of chloride ions and carbon dioxide to the steel surface. The depassivation of steel rebars can lead to the localised formation of porous oxide layers at the steel/concrete interface. The volume of iron oxide layers is two to four times larger than that of iron, and the high tensile stresses generated by the expansive volume of the corrosion products [4–6] can result in internal microcracking and spalling of the concrete cover. The rate of corrosion is a limiting factor of the remaining service life of a corroding reinforced concrete structure (RCS).

Therefore, the study and characterization of corrosion products in reinforced concrete is an important issue with a view to assessing the corrosion state within RCS and predicting their remaining service life. Several techniques like Raman spectroscopy [7], X-ray photoelectron spectroscopy (XPS) [8], Mössbauer spectroscopy [9], ellipsometry [10], secondary ion mass spectrometry (SIMS) [11], and atomic force microscopy [12] have been employed to study the passive film on the steel surface.

Micro-Raman spectroscopy is a preferred method because it is a non-destructive technique that is well suited for the in situ characterization of various oxides and oxyhydroxides involved in the corrosion of iron. Moreover this spectroscopy presents two important advantages: the lack of any need for sample preparation and the quick and easy obtainment of water/metal interface spectra [13–16].

Iron oxides and oxyhydroxides are known to be sensitive to thermal transformations even at low laser power because they are opaque to visible light and heat up. Indeed, a temperature rise

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induces a transformation to the most stable phase, i.e. hematite ($\alpha\text{-Fe}_2\text{O}_3$) [15]. As some iron oxides are highly sensitive to laser irradiation, several authors have used a set of density filters to modulate the laser power and avoid any thermal effect on iron (III) compounds [15,17–19].

De Faria et al. [20] employed Raman microscopy to investigate the laser power dependence of the Raman spectra of oxides and oxyhydroxides like hematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), wüstite (FeO), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$) and feroxyhyte ($\delta\text{-FeOOH}$). The results obtained showed that increasing the laser power causes the characteristic bands of hematite to show up in the spectra of most of the studied compounds, with the consequent band broadening and shifts of the hematite spectrum. Under high laser power all the investigated oxyhydroxides showed the characteristic peaks of hematite, with the power threshold being dependent on the surface morphology.

Nieuwoudt et al. [21] demonstrated that significant enhancements of the Raman spectra for iron oxides and oxyhydroxides can be achieved using an optimised excitation wavelength of 636.4 nm, providing further improvement over those attained with the 632.8 nm excitation wavelength under similar conditions. When compared, the Raman spectra for standard iron compounds in the low wave number region ($<1000\text{ cm}^{-1}$) obtained using a tuneable dye laser with the 636.4 nm line are more intense and well-defined than those obtained using an excitation wavelength of 514.5 nm.

Taking into account all these premises, the main aim of this paper was to study the corrosion products formed on steel embedded in alkali activated fly ash (AAFA) mortars in the presence of chloride ions using a Micro-Raman spectrometer with two excitation wavelengths (532 and 633 nm) and making power scans to select the suitable conditions of register for each laser line. Since several oxyhydroxides can be formed as corrosion product it is important to discern if they become from laser irradiation transformation or as corrosion products.

The choice of AAFA as cementitious matrix is due to the fact that this is being used in concrete for reasons related with environmental impact, economic sustainability and social responsibility [22]. The alkali activation of type F fly ash consists of mixing the fly ash with highly alkaline solutions ($\text{pH} > 13$) and subsequently curing the resulting paste at a certain temperature to produce a solid material. Considering that RCS safety and durability are two of the most important requirements for building protection, the capacity of an AAFA mortar to passivate steel rebars is a necessary property to guarantee both aspects of RCS constructed using these new materials.

2. Experimental

Concrete reinforcement electrodes were cut from carbon steel plates with a chemical composition of 0.45% C, 0.22% Si, 0.72% Mn, $<0.010\%$ P, 0.022% S, 0.13% Cr, 0.13% Ni, 0.18% Cu, and balance Fe. The specimen surfaces were polished with emery paper from 120 to 600, washed with double distilled water and degreased with acetone.

The cementitious material used was a type F fly ash (FA) from a coal-fired power plant at Aboño, Asturias, Spain. The chemical composition of the FA is shown in Table 1. The percentage of

reactive silica (SiO_2) in the FA, determined according to UNE 80-225-93 standard [23], is 41.23% and the vitreous phase content is 65.60%. The procedure used to determine the vitreous phase content was similar to that described elsewhere [24]. Briefly, 1 g of FA was added to 100 ml of 1% hydrofluoric acid (HF) in a plastic beaker and stirred for 6 h at room temperature. The granulometry distribution, determined by laser ray diffraction, showed only one mode in which approximately 85% of particles were smaller than $45\ \mu\text{m}$ and 50% smaller than $13\ \mu\text{m}$.

The FA was activated using two different highly alkaline solutions with roughly the same sodium oxide (Na_2O) content ($\sim 20\%$) and varying proportions of soluble SiO_2 . The products used to prepare the solutions were laboratory grade reagents: sodium hydroxide (NaOH) pellets and waterglass (Na_2SiO_3) containing 27% SiO_2 , 8.2% NaOH, and 64.8% H_2O . One activating solution was prepared with 8 M NaOH, and the other with 85% 10 M NaOH and 15% waterglass.

Accordingly, two types of AAFA mortars were manufactured: one using the NaOH solution (FAA mortar) and the other using the 85% NaOH and 15% waterglass mixture (FAB mortar) with a “liquid/solid” ratio of 0.45. The mortars were prepared with sand/AAFA ratio of 2:1. The moulds containing the fresh AAFA mortars were cured in an oven at $85\ ^\circ\text{C}$ in a saturated water vapour atmosphere for 20 h. Different amounts of sodium chloride (NaCl) (99% pure Panreac PRS-CODEX): 0.4 and 2% chloride (in relation to binder weight) were added to the FA. Two prismatic mortar specimens of each type, with dimensions $8\text{ cm} \times 5.5\text{ cm} \times 2\text{ cm}$, were prepared for comparative purposes [25]. All the specimens were stored at room temperature in an atmosphere of high relative humidity (RH), $\sim 95\%$, for up to 720 days.

The steel was extracted from the FAA and FAB mortars and Raman spectra were obtained directly from the steel plate surface and analysed. Dispersive Raman spectra at 633 and 532 nm were recorded in a RM 1000 Renishaw Raman Microscope System. The Raman spectrometer is equipped with a Leica microscope and an electrically refrigerated CCD camera. The spectra were obtained with $\times 50$ magnification objective lenses. The final spectra were the result of 10 accumulations to improve the signal-to-noise ratio and the integration time was 10 s. The software employed for data acquisition and analysis was Wire for Windows and Galactic Industries GRAMS/32TM. Five scans were recorded to improve the signal-to-noise ratio. The Raman shift was calibrated before the measurements according to the silicon peak at 520 cm^{-1} . The 633 nm line had a laser power from 0.25 to 25 mW and finally, the 532 nm line had a laser power from 0.0005 to 5 mW. The measurements were done directly in the sample (in situ), the sample preparation is not necessary.

3. Results and discussion

Fig. 1 shows the steel specimens after extraction from the FA mortars in the presence and absence of chlorides for 720 days of experimentation. The steel specimens embedded in the mortars without chlorides present tiny amounts of corrosion products on a practically smooth surface, indicating that the steel was in the passive state in this new cementitious system. The steel specimens extracted from the chloride-polluted mortars present small

Table 1
Chemical composition of the tested fly ash (% mass).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	MnO	P_2O_5	TiO_2	LOI	Others	Total
51.78	27.80	6.18	4.59	1.52	0.71	0.59	2.51	0.06	0.62	1.35	2.23	0.06	100

LOI, loss on ignition.

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