Is the Weathering Steel Resistant to all Environments? Study of Some Weathering Steel Facades Exposed to Bilbao Urban Atmosphere

/ JULENE ARAMENDIA (*), LETICIA GÓMEZ-NUBLA, OLIVIA GÓMEZ-LASERNA, KEPA CASTRO, JUAN-MANUEL MADARIAGA

(1) Department of Analytical Chemistry, University of the Basque Country (UPV/EHU), P.O. Box 644, E-48080 Bilbao, Spain

INTRODUCTION

Weathering steel is a very common material used, mainly, for structures and facades exposed outdoors. The useful life of facades (and in less extent of structures) is conditioned by the environment where they are located. Some materials need the application of protective coatings or paints that increases the cost. In contrast, this kind of steel does not need to be coated nor especially maintained regularly. The economic aspect was predominant for the development of weathering steel.

This material has among its alloy elements low concentrations of Ni, Zn, Cu, Mn and Co which helps in the development of a protective rust layer that avoids the corrosion of the metal. Besides, that coating brings a characteristic texture and color which make this steel very attractive for some constructions.

Even though this material was designed for resisting different environmental factors, some stressors could damage the surface of the weathering steel. It is demonstrated that wet-dry cycles together with the presence of acid gases (SO_2, CO_2 and NO_x) damage the steel surface (Wang et al 2010). Rain reacts with these gases giving rise to their respective acids (H_2SO_4, H_2CO_3 and HNO_3) and forming their respective salts on the surface of the steel. (Damian et al 2000) Sulphates, carbonates and nitrates are very reactive species and attack the different iron species present in the surface. Consequently, these new products are dissolved giving rise to a process of material loss and to the acceleration of the corrosion process. (Wang et al 1997) This fact produces a reduction of the useful life of this steel and an increase of the maintenance costs.

In this work, four weathering steel facades exposed to the urban atmosphere of Bilbao were studied. These constructions are located in different places and affected by several pollution sources. Two of these facades are in a good conservation state. The others, in contrast, have their surface detached in steel chips. They are involved in a decay process, promoting a serious damage of the protective layer. This study allowed us to identify which is the fact that causes the decaying process of steel structures and helped us to relate pollution sources with decay processes.

MATERIALS AND METHODS

A combined research of *in-situ* and laboratory works and a combination of qualitative and quantitative techniques were used in order to diagnose the conservation state of these steel structures.

For the *in-situ* analysis an InnoRam ultramobile B&WTEK_{inc} Raman spectrometer provided with a 785 nm excitation laser and a microprobe was used. The spectra were collected with less than 20% of the laser power avoiding the thermodecomposition of the samples.

Laboratory Raman analyses were performed with a Renishaw RA100 spectrometer, operating with a 785 nm excitation laser, coupled to a CCD detector and lens objectives of 20x and 50x. Collection conditions in both cases were between 5-15 seconds and 5-15 accumulations.

Quantitative analyses were done with a soluble extract of steel samples obtained through boiling point extraction method. This method consists on introducing 0.1 g of steel in 5 ml of deoinized water, heating then until the boiling point. Water has to be boiling for 45 minutes. This method is said to have around 100% efficiency. (SSPC 2005) Then this extract was analyzed by two different equipments.

On the one hand, a Dionex ICS 2500 ionic chromatograph with a suppressed conductivity detector ED50 was used to quantify anions and cations such as: sulphate, nitrate, nitrite, ammonia, calcium, sodium, magnesium, etc. On the other hand, metals were determined and quantified by means of an Elan 9000 ICP-MS (PerkinElmer) provided with a Ryton cross-flow nebulizer, a Scott-type double pass spray chamber and standard nickel cones.

RESULTS AND DISCUSSION

The protective layers of the studied steels are composed of various iron oxyhydroxides, mainly lepidocrocite (γ-FeOOH) and goethite (α-FeOOH). However, attached to their surface, appeared a substantial quantity of atmospheric particles such as silicates, amorphous carbon and carbonates. These compounds cause a negative effect in the rust layer. For example, silicates delay the development of the rust layer, producing a persistent active state of the surface.

Besides, the particles, together with the iron compounds, act as target phases for the acid gases. By means of Raman spectroscopy, it was possible to identify different sulphates and nitrates produced by reaction between SO_x and
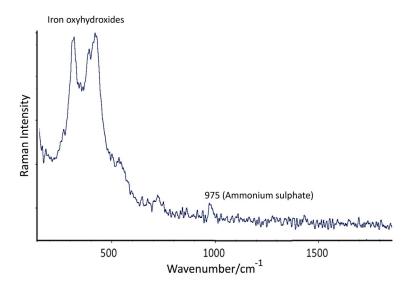
fig 1. *Raman spectra of ammonia sulphate in a steel surface.*

NO_x and the mineral phases present on the surface.

This fact explains the presence of gypsum ($CaSO_4 \cdot 2H_2O$, main Raman band at 1008 cm^{-1}). This compound is formed due to a reaction between the calcite present on the surface of the steel (also detected by its Raman main peak at 1085 cm^{-1}) with the H_2SO_4 aerosol (produced by oxidation of the SO_x gases). Calcite arrives at the steel surface as particulate matter during dry deposition from the atmosphere (Inza, 2010). The presence of calcite and gypsum produce white crusts over the steel surface.

Other sulphates were detected by Raman spectroscopy. For example, a magnesium sulphate epsomite ($MgSO_4 \cdot 7H_2O$, main Raman at 985 cm^{1}), as well as ammonium sulphate (the dominant sulphate in the atmosphere, Fig 1, main Raman band at 975 cm^{-1}), formed as a consequence of the ammonia sulphation by the atmospheric H_2SO_4 aerosol.

As it was mentioned previously, acid gases also react directly with iron and steel alloy elements. This fact would explain the presence on the surface of nickel sulphate (retgersite $NiSO_4 \cdot 6H_2O$, main Raman band at 987 cm^{-1}) and rozenite ($FeSO_4 \cdot 4H_2O$, main Raman peak at 991 cm^{-1}).

NO_x gases also react with the steel surface-forming nitrates. The nitrates identified by Raman spectroscopy in this study are products of the interaction between sea spray and atmospheric anthropogenic pollutants. Moreover, they were detected in the surfaces exposed to the Bilbao estuary. Among others, nitratine ($NaNO_3$, 1065 cm^{-1} main Raman band) and nitromagnesite ($Mg(NO_3)_2 \cdot 6H_2O$, main Raman band at 1059 cm^{-1}) were identified. These compounds are the result of the reaction of NaCl (marine) with HNO3 (anthropogenic), yielding the formation of NaNO3 (particle) and HCl (gas). The same applies to $Mg((NO_3)$.

Correlation analyses were done with quantitative data, supporting the Raman results. According to these analyses, it could be seen a strong correlation between sulphate and calcium in all cases. Sulphate concentration was higher in those structures which were in worse conservation state. Besides, sulphate was usually related to the traffic input, because in those facades not affected by road traffic this anion was under the quantification limit. Nitrate anion had a high correlation with sodium and magnesium, supporting the results obtained by Raman spectroscopy. In the facades where the ammonium sulphate was detected by Raman spectroscopy, an elevated concentration of dissolved ammonium cation was quantified by ion chromatography.

In spite of being iron the main metal present in the steel composition, by using ICP-MS it was seen that the concentration of dissolved nickel was higher than dissolved iron.

CONCLUSIONS

Weathering steel in spite of being very suitable material for outdoors facades and structures, it is affected by the urban environment where it is exposed. In the case of hard contaminated atmospheres, this material could need conservation or restoration maintenance. In this work, sulphates and nitrates have been detected in facades and structures; both are mainly affected by SO_x and NO_x, which attack principally the atmospheric particles deposited on its surfaces giving rise to the detected mineral phases.

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