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Structural and chemical analyzer system for the analysis of deposited airborne particles and degradation compounds present on the surface of outdoor weathering steel objects

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ABSTRACT

The weathering steel is a high strength low alloy special kind of steel theoretically resistant to the atmospheric corrosion. In the present work, several weathering steel structures exposed to the urban atmosphere were analyzed by means of structural and chemical analyzer, a spectroscopic system that combines micro-Raman and SEM/EDS microscopy measurements in the same spot, in order to detect the deposited atmospheric material and to characterize it. Several kinds of silicates and aluminosilicates containing particles were identified on the steel surface of the analyzed works. In addition, other atmospheric particles such as calcite, charcoal and chromium rich particles were detected together with several compounds coming from the reaction of the steel and the deposited particles with the acid gases of the atmosphere. These particles have negative effects in the conservation of the weathering steel changing the visual appearance of the surface and decreasing the atmospheric resistance of the material.

1. Introduction

Even though weathering steel was developed for its use in architecture and sculpture, sometimes, due to the exposure of this material to certain atmospheric conditions, it is possible to observe uncontrolled corrosion. This corrosion can be probably originated due to an unusual development of the protective patina. The so-called patina or protective rust layer is composed by a mixture of iron oxides and its composition changes from the most reactive lepidocrocite to the most stable goethite with the exposure time. One of the most famous weathering steel washouts is the former Omni Coliseum (Atlanta, Georgia, USA). It never stopped rusting, and eventually large holes appeared in the structure. This was the major factor in the decision to demolish it just 25 years after its construction [1]. Besides, the use of weathering steel outdoors presents further problems. During the initial weathering process, considerable quantities of dissolved Fe (II) are washed off, which can cause staining of adjacent surfaces, especially in porous materials such as concrete and masonry because the colorless Fe^{2+} cation is oxidized to the yellow-orange Fe(III) oxy-hydroxides. An example of this fact is the US Steel Tower in Pittsburgh, Pennsylvania (USA). The initial weathering of the material resulted in a coloration of the surrounding city sidewalks as well as other nearby buildings [2].

The main factor that could induce these problems is the damage caused by pollutants and atmospheric particles affecting to the durability of the material. The chemical composition of the atmosphere is of special significance for the thermodynamics and kinetics of the corrosion process. For instance, it is known that certain high concentrations of acid gases such as SO_2 together with a high humidity modify the natural or normal weathering process of steel, while high concentration of these acid gases could lead to serious problems in the development of the protective rust layer [3]. Actually, SO_2 is considered the worst factor affecting to the corrosion process. Together with SO_2, other gaseous pollutants such as NO_x, CO_2 and O_3 are reportedly the most significant species involved in atmospheric corrosion [4,5].

Moreover, there are more atmospheric particles and airborne that can affect also to the weathering steel conservation. For instance, an important factor that accelerates the corrosion process in weathering steel is the marine airborne (mainly composed by sodium chloride). The influence of chloride ions may be severe, especially in environments near to the coast. It has been noticed that weathering steel does not form a well protective patina in the presence of chlorides [6,7]. This is due in part to the hygroscopic characteristics of the salt that keeps the steel moist for longer periods of time, preventing the occurrence of dry conditions necessary for the patina formation. The other factor is that the presence of chloride ions accelerates the rate of corrosion of the metal by changing redox potentials of Fe. Besides, Cl^- favors the formation of relatively large amounts of akaganeite (β-FeOOH) [8–11]. This oxide does not convert into goethite (α-FeOOH). This mineral phase is one of the main components of the protective oxide layer of weathering steel and, besides, the one that exerts the protection [12]. In addition, Mg salts are also concentrated in marine environments. It

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has been checked that a high concentration of Mg in the rust layer (around 3.8 wt.%) [13] has a great influence on the corrosion behavior of weathering steel, especially on the later stage of the corrosion process, giving rise to the formation of β-FeOOH, magnetite (Fe_3O_4) and lepidocrocite (γ-FeOOH). These mineral phases are the most active phases of the protective layer of weathering steel and did not give any protection to the metal [14–16]. Moreover, complex corrosion phases can also be formed such as magnesioferrite ($MgFe_2O_4$) and iowaite ($Mg_4Fe(OH)_8OCl \cdot 4H_2O$) [13].

Finally, silicate particles are sometimes highly concentrated in most of the atmospheres. The presence of any kind of silicate matter has a huge effect in the evolution of the protective rust layer of weathering steel since they inhibit and retard the transformation of lepidocrocite into goethite and in consequence, the passivation of the rust layer. Therefore, the protective ability is reduced [13–15].

Taking into account the effects that the presence of some particles can have in the development and the conservation of weathering steel structures, it is crucial the study of the conservation state of artworks or other structures (facades or urban furniture) made of this material and the assessment of the impacts that the deposition of particles could be having in the material. The more suitable analytical techniques that can be used for the characterization of deposited particles are the so-called non-destructive ones, since sampling a great amount of material in artworks or buildings can affect to the surface homogeneity and therefore, to the visual appearance. Among these kinds of techniques there are several that can be used for the off-line study of particles, no matter if they are sampled by passive methods of if they are deposited on a surface. For instance, infrared spectroscopy [17,18] or Raman spectroscopy [18] but most of the articles published in this field have employed SEM (scanning electron microscopy) or TEM (transmission electron microscopy) sometimes coupled to EDS (energy dispersive spectroscopy) or EDX (energy dispersive X-ray spectroscopy) analyzers due to their high resolution [19–21]. However, from the characterization point of view, using TEM or SEM coupled to EDS only elemental information can be extracted. In addition, in those cases where atmospheric particles deposited on a surface need to be analyzed with molecular techniques (Raman or infrared spectroscopy) there are some drawbacks related to the particle size and the background, i.e. the studied surface. Even though the analysis of the particles is performed using microscopy, if the particle size is too small and taking into account that the background gives, normally, a huge signal, Raman or infrared signals belonging to the particles cannot be detected. To avoid these problems, the use of the so-called Raman SCA emerging technique (structural and chemical analyzer) that couples Raman micro-spectroscopy and SEM–EDS measurements in the same spot area, seems to be an adequate alternative. By this technique, really specific elemental and molecular analysis of particles can be performed, such as those performed on metallic dust particles from abandoned mine areas [22] or from black slag materials [23].

In this work different weathering steel structures exposed in an urban–industrial atmosphere are studied. These structures present some flaking processes and some discoloration areas in their surfaces, being a worrying problem. Through some previous works it was supposed that some of these problems could be generated by deposited particles [5,24,25]. In this way and in order to deepen in this problem, in the present paper a deep study of the characterization of different atmospheric particles and an assessment of their possible consequences in the steel surface has been carried out.

2. Materials and methods

2.1. Structures and location

In this study five steel structures were analyzed. All of them were made of weathering steel with little variations in the elemental composition or in the manufacture used in the fabrication. The main characteristics are summarized in Table 1. They are exposed to the same urban–industrial atmosphere of Bilbao city, Northern Spain, subjected to several pollution or/and particle sources such as traffic, urban works, marine airborne, etc. Bilbao is the largest city of the Basque Country and it is located around 14 km south of the Golf of Biscay, where the estuary of Bilbao is formed. The entire city is crossed by the Nerbioi–Ibaizabal estuary, thus, subjected to tidal effects. Its main urban core is surrounded by two small mountain ranges and the surrounding is mainly formed by limestone and sandstones [24].

The estuary is the most industrialized area in the Northern Spain since the 19th century. For more than 100 years a very important economic and industrial activity has been developing in the estuary banks. In the last decades, the environmental problems started to be a social worry and therefore some human activities were stop. Nowadays, in Bilbao Metropolitan area the industrial pressure is still present, with steel industry, harbor activities and chemical plants. However, the high traffic has become the main pollution source [26,27]. Actually, in 2007 the average values in air for CO_3^{2-}, SO_4^{2-}, NO_3^-, Ca and SiO_2 were 8.5, 2.5, 2.5, 5.6, and 6.2 μg/m^3 respectively [28]. In addition, the atmosphere of Bilbao is of an acid nature and the microclimate of Bilbao is characterized by a high number of rainy days and a high annual rainfall rate. In fact, the annual precipitation is 1170 mm and they are 3000 h per year of wetness [28]. Due to these humidity conditions, together with the high concentration of industrial acid gases, Bilbao city is considered as a highly corrosive ambience, inside the C4 corrosion category by the ISO 9223 [29]. All these factors make the particle deposition and the material degradation considerable.

In this kind of studies it is crucial to know the direction of the winds. In this case, the predominant winds in Bilbao city have west component due to topographic conditions covering its influence from March to August, having a maximum in June. During autumn and winter the frequencies of the eastern components are predominant [30].

2.2. Equipment and methods

For this work the combination of SEM–EDS and Raman SCA device was used. This Raman SCA interface allows the user to perform Raman spectroscopy simultaneously with secondary electron (SE) imaging inside the SEM, on the spot areas selected previously because the laser light and Raman signal are both transmitted between the Raman spectrometer and the SCA via 2 m fiber optic cables up to the SEM vacuum chamber (Supplementary material 1).

In this way, first, it is possible to perform a scanning chemical image of a micro area of the sample surface using SEM. Then it is possible to analyze that area identifying the present/absent elements using EDS, and finally, by Raman SCA device it is possible to focus the laser beam on the point of interest to get Raman spectra. Therefore, this SEM–EDS/SCA device allows to get elemental and molecular information of the same point. This approach resulted very useful for the identification of deposited particles and degradation compounds because the surface of the steel is very homogeneous from the elemental point of view and all the exogenous compounds were easily discerned from the background. Besides, by using SEM–EDS, the deposition rate of the detected compounds could be ascertained by the observation of EDS distribution maps, where it can be seen in a SEM image how many microns of the steel surface are covered by exogenous particles.

Weathering steel micro-samples were deposited on the surface of a special aluminum pin and glued to the surface by using a carbon adhesive tape. As the samples were well electrical conductors, they were not necessary to cover by graphite or gold since the emission of electrons was enough for having good quality SEM images. By this way, the samples were not covered allowing further analysis with other techniques. The experimental platform has three units. On the one hand, an EVO 40 EDS (Carl Zeiss NTS GmbH, Germany) coupled to an X-Max Energy-Dispersive X-Ray spectroscopy equipment (Oxford Instruments, UK) was used for electron image acquisitions and elemental composition