THE CONSERVATION OF WEATHERING STEEL SCULPTURES, A COMPARATIVE STUDY OF CHILLIDA’S SCULPTURES EXPOSED IN BILBAO.

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Abstract  

Weathering steel (high strength low alloy steel also known as Cor-Ten® or U.S. Steel) has been widely used in architecture and engineering for its unique characteristics and resistance against atmospheric corrosion. This self-protecting material has the quality of gradually forming a stable corrosion resistant oxide patina through outdoor weathering. However, specific problems from its use in art have not been so deeply investigated; there is still an insufficiently explored field for conservator-restorers dealing with this type of works. Investigations carried out in this work involved identification and characterization analysis of corrosion products from four public sculptures (pieces by E.Chillida, exposed to outdoor urban seacoast environment in Bilbao). Analytical diagnosis combined non-destructive techniques such as Raman and X-Ray fluorescence. The main compound identified was lepidocrocite (γ-FeOOH), instead of goethite (α-FeOOH) the compound claimed as that corresponding to a stable passivation layer. As all of the sculptures have already been exhibited to outdoor environment over 10 years, theoretically enough time for the stable polymorph of FeOOH to form, we must conclude the negative effect of the urban environment on the long-term stability of some of these artworks.

Key words: sculptures, weathering steel, urban seacoast environment, corrosion, Raman, XRF.

Introduction  

CorTen steel differs from other steel because it develops a protective layer composed of iron oxides that increases the resistance against atmospheric corrosion. The rust layer is produced by the particular distribution and concentration of alloying elements such as Cu, Co, Ni and Zn. The presence of these elements and the exposition of the steel to the weather (wet-dry cycles) accelerates the development of this protective patina.  

This layer makes the CorTen steel a very adequate material for works exposed outdoor. Besides, it does not need any kind of protective painting, thus, it suppose an important save of money. From an artistic point of view, its color-changing surface and its chemical characteristics make this material the preferred steel material by artists for artworks exposed outdoor.

It is generally accepted that the protective layer of weathering is composed of goethite (α-FeO(OH)), lepidocrocite (γ-FeO(OH)), and another non-crystalline compounds. The fraction of these compounds present in the rust layer depends on the exposition time. At initial time of exposure the main mineral phase present in the layer is the lepidocrocite, and after decades of exposure this lepidocrocite will transform onto goethite (γ-FeO(OH)), the stable iron oxyhydroxide [1]. Thus, the ratio α/γ increases proportionally to the exposure time. Furthermore, as this mineral phase change occurs, the corrosion rate decreases. Nowadays, this index is used as an evaluator of the protection provided by the rust layer.

However, the composition of the layer can change due to some environmental aspects, such as the presence of salt airborne, acid gases, etc. Moreover, sometimes, these kinds of steels are subjected to some processes like sanding, that could affect to the development of the rust layer.
It is very interesting to research on the protective layer and to study the factors that affect the formation of the rust layer because the durability of this material exposed outdoors is going to depend on it.

The aim of this study was to compare CorTen steel sculptures in good state of conservation with ones in bad state in order to discover the differences among them. This information would define the factors that affect the durability of this material.

**Experimental**

**Samples**

There were studied four Eduardo Chillida’s sculptures made of CorTen steel. They have different origin, manufacture and they have been exposed in diverse locations along their history. Therefore, the conditions of each one are very different in spite of being nowadays exposed in the same urban seacoast environment of Bilbao (North Spain). The sculptures were selected for the analysis because each one is exposed to different environmental factors such as traffic pollution, salt airborne, atmospherical particles, etc. The studied collection is the following: Besarkada XI (1996) exhibited in Guggenheim Museum of Bilbao, near the Nervión-Ibaizabal estuary but a little bit protected. Buscando la Luz IV (1998), beside the estuary. Elogio del Hierro III (1991) affected by dense road traffic and made in Reco steel, a CorTen steel but with a high concentration of Cu, Mo, Cr and Ni. Begirari IV (2000), is exhibited in front of the estuary and near a low traffic road. All the sculptures were analysed in-situ with portable Raman and XRF instruments. However, microsamples were also taken and sent to the laboratory for deeper analysis.

**Equipment**

For the in-situ characterization it was used an handheld InnoRaman spectrometer (BWTEK INC., Newark, EEUU) provided with a 785 nm excitation laser and a microprobe. The spectra were acquired with the BWSpec™ software version 3.26 (BWTEK INC., Newark, EEUU).

The equipment implements a controller of the laser power (a scale from 0% to 100%). Considering that the laser power of the instrument is 330 mW± 15% at the source and 255 mW ± 15% at the surface of the analyzed sample, the protocol to measure the samples consisted of acquiring first a spectrum at lower laser power and then increase the applied power until a good signal to noise ratio was obtained. After each measurement, the spectrum and the analyzed area were checked in order to see if thermodecomposition had occurred. Generally a 20% of laser power was enough for obtaining a good spectrum without damage the sample.

When it was possible, the InnoRaman spectrometer was helped by an automatic tripod, motorized in X,Y and Z axis with a spatial resolution of 10 microns per electrical pulse, that has 4x, 20x or 50x objectives and it allows to focus the laser on a 10-200 µm diameter spot, depending on the used lend. The focusing of in-situ analysis of Buscando la Luz IV, was carried out with the help of the tripod.

For analysis carried out in the laboratory a Renishaw RA 100 system (Oxford,UK), equipped with 785 nm diode laser and a CCD detector (Peltier cooled) was used. The laser beam was focused on the samples by 20x or 50x microscope objective. The nominal power of the excitation source is 150 mW. The power was modulated to avoid the burning of the sample. The spectrometer was calibrated with the 520 cm⁻¹ silicon band. The data were acquired with WIRE 2.0 software (Renishaw, UK).

For spectral analysis it was used the Omnic software of Nicolet (Madison, Wis., USA). The spectrum interpretation was done by comparison with pure standard compounds contained in the e-VISARCH, e-VISART, e-VISNIC spectral database and with rruff on-line database. The e-VISNIC library is an on-
line Raman Spectra Database of Natural, Industrial and Cultural Heritage compounds (available at http://158.227.5.164/RamanDB/).

Samples were analyzed with portable ArtTax μ-EDXRF equipment by Rontec (nowadays Brucker AXS; Berlin, Germany) that incorporates a molybdenum anode working at a maximum voltage of 50 kV and a maximum current of 700 μA. All spectra processing and manipulation were carried out by using ArtTAX 4.9.13.2 program by BrukerAXS.

**Results**

The elemental characterization of the samples was carried out by EDXRF. The collected data shown that the main elements were the alloy elements: Fe, Ni, Mn, Cr, Cu and Zn. With this technique it was possible to identify elements associated to urban and coastal atmospheres. For example in those sculptures exhibited near the estuary it was found Cl. Besides, in most of the cases Ca and S were identified. These elements could come from gypsum particles present on the surface of the sculpture (see Figure 1). Another elements coming from atmospherical particles were Si and K that surely come from potassium silicates. Finally, Pb and Sr were identified, which probably have their origin in road traffic.

![Figure 1. EDXRF spectra of a Besarkada XI sample. It can be seen a gypsum (S+Ca) deposition and also other elements coming from different environmental impacts.](image)

Several iron(III) oxides were identified with Raman spectroscopy. These mineral compounds change depending on the conditions of exposure. In Besarkada XI the main mineral phase present in the rust layer was lepidocrocite (γ-FeOOH). The lepidocrocite is the active polymorph and it changes to goethite (α-FeOOH) with the exposure time. In this sculpture in spite of being constructed in 1996, the α/γ ratio is still very low because the presence of lepidocrocite is higher than the presence of goethite. Some authors [2] used this ratio as a protective ability index, and using here this index, it could be said that the rust layer in this artwork is still in an active state.

This sculpture has the most external part of the corrosion layer detached in chips. They are composed only by pure lepidocrocite (Figure 2) and no goethite appears in the external part of the rust. Other parts of the artwork still present the original black patina formed during the cooling process of the steel in the
foundry, because it was not taken away by a sanding process. This patina is composed by magnetite (Fe$_3$O$_4$, with his characteristic main Raman band at 664 cm$^{-1}$). Under this patina it was checked that lepidocrocite is growing. Magnetite was also identified in areas without black patina. In this sculpture haematite was also present all over the surface. This black patina could be delaying the normal development of the rust layer.

![Figure 2. Raman spectra of lepidocrocite found on the surfaces of Besarkada XI.](image)

In *Buscando la Luz IV* and in *Elogio del Hierro* the development of the protective layer is normal. *Elogio al Hierro* is the oldest one and it is the sculpture with the highest amount of goethite. Here, the lepidocrocite presence in the rust layer is minimal. This propitious state of the protective layer can be seen in the homogeneous appearance of the sculpture surface. In the case of *Buscando la Luz*, the presence of lepidocrocite was lower than in *Besarkada XI* and the presence of goethite higher, although the goethite was not the main phase. This means that this sculpture is more stable than *Besarkada XI*. This artwork is having a good evolution, if we take into account of its visual appearance and its chemical development too.

It must be pointed out the elevated presence of haematite (Figure 3) on the surface of *Begirari IV*. The visual appearance of this sculpture is very similar to the *Besarkada XI*, but with Raman spectrometry it could be seen that the molecular composition was rather different. In fact, in this artwork the main mineral compound was the haematite ($\alpha$-Fe$_2$O$_3$). In addition, *Begirari IV* still preserves the original black patina, but instead of magnetite as in the case of *Besarkada XI*, its external layer was composed of haematite.

In sculptures exhibited beside the estuary, on the face of the sculpture oriented to the Nerbioi-Ibaizabal estuary it appeared sporadically a kind of iron oxide rather uncommon in a weathering steel rust layer: akaganeite (β-FeO(OH), Figure 4, Raman bands at 312 and 391 cm$^{-1}$). This iron oxide appears in seaside environments with high amount of NaCl air-borne [3]. Thus, akaganeite is often observed as a corrosion product of iron in marine environment. This phase was detected especially in *Buscando la Luz IV*. 
Conclusions

With this work it has been checked that the composition of the rust layer present on the surface of the CorTen steel depends not only on the exposure time, but also on the effect of some environmental factors such as salt airborne or atmospheric depositions. The composition of the steel used to built the public sculptures could affect the normal development of the rust layer.
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