



Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Weathering steel as a potential source for metal contamination: Metal dissolution during 3-year of field exposure in a urban coastal site[☆]



Simona Raffo^a, Ivano Vassura^{a, b}, Cristina Chiavari^{c, 1}, Carla Martini^d, Maria C. Bignozzi^e, Fabrizio Passarini^{a, b}, Elena Bernardi^{a, b, *}

^a Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy

^b Interdepartmental Center for Industrial Research (CIRI) Energy and Environment, University of Bologna, Via Angherà 22, 47900 Rimini, Italy

^c Interdepartmental Center for Industrial Research (CIRI) Advanced Applications in Mechanical Engineering and Materials Technology, University of Bologna, Viale del Risorgimento 2, 40136 Bologna, Italy

^d Department of Industrial Engineering, University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy

^e Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Via Terracini 28, 40131 Bologna, Italy

ARTICLE INFO

Article history:

Received 1 January 2016

Received in revised form

20 February 2016

Accepted 1 March 2016

Keywords:

Urban runoff

Atmospheric corrosion

Cor-Ten

Marine environment

Chloride deposition

PCA

ABSTRACT

Surface and building runoff can significantly contribute to the total metal loading in urban runoff waters, with potential adverse effects on the receiving ecosystems. The present paper analyses the corrosion-induced metal dissolution (Fe, Mn, Cr, Ni, Cu) from weathering steel (Cor-Ten A) with or without artificial patinas, exposed for 3 years in unsheltered conditions at a marine urban site (Rimini, Italy). The influence of environmental parameters, atmospheric pollutants and surface finish on the release of dissolved metals in rain was evaluated, also by means of multivariate analysis (two-way and three-way Principal Component Analysis). In addition, surface and cross-section investigations were performed so as to monitor the patina evolution. The contribution provided by weathering steel runoff to the dissolved Fe, Mn and Ni loading at local level is not negligible and pre-patination treatments seem to worsen the performance of weathering steel in term of metal release. Metal dissolution is strongly affected by extreme events and shows seasonal variations, with different influence of seasonal parameters on the behaviour of bare or artificially patinated steel, suggesting that climate changes could significantly influence metal release from this alloy. Therefore, it is essential to perform a long-term monitoring of the performance, the durability and the environmental impact of weathering steel.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Weathering steel is a low-alloyed steel, containing small amount of Cr, Cu, Ni and P. Due to the technological and aesthetical characteristics, during last decades, weathering steel (WS) has been increasingly used for a wide range of outdoor infrastructures and architectural or artistic applications.

After exposure in low-moderate aggressive environments, WS forms a patina more solid and adherent than that developed on plain carbon steel, showing higher resistance to atmospheric corrosion (Choi and Kim, 2003; Zhang et al., 2002). The natural protective patina growing on WS shows a 'double-layer' structure, with an outer and porous layer of lepidocrocite (γ -FeOOH) and an inner and compact layer of goethite (α -FeOOH); lepidocrocite forms during the first period of exposure (several months/a few years) and slowly turns (some years) to goethite (Asami and Kikuchi, 2003; Kimura et al., 2002; Yamashita et al., 1994). Goethite structure consists of double chains of $\text{Fe}(\text{O},\text{OH})_6$ octahedral units

Abbreviations: 3W-PCA, Three Way – Principal Component Analysis; AAS, Atomic Absorption Spectroscopy; ANOVA, ANalysis Of VAriance; ARPA E-R, Agenzia Regionale per la Prevenzione e l'Ambiente dell'Emilia-Romagna; BA, Bare; EDS, Dispersive Energy Spectroscopy; EDXRF, Dispersive Energy X-ray Fluorescence; HDPE, High-density polyethylene; IC, Ion Chromatography; ISO, International Organization for Standardization; LoD, Limit of Detection; LoQ, Limit of Quantification; MV, Mass Variation; E, East; S, South; SW, South-West; PA, Pre-patinated; PC, Principal Component; PCA, Principal Component Analysis; PCC, Pearson's Correlation Coefficient; PWA, Pre-patinated and Waxed; RH, Relative Humidity; SEM, Scanning Electron Microscopy; T, Temperature; WHO, World Health Organization; WS, Weathering Steel; Wt%, Weight percent.

[☆] This paper has been recommended for acceptance by Wen-Xiong Wan.

* Corresponding author. Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy.

E-mail address: elena.bernardi@unibo.it (E. Bernardi).

¹ Present address: Department of Cultural Heritage, University of Bologna, Via degli Ariani 1, 48121 Ravenna, Italy.

alternating double chains of vacant sites (Kimura and Kihira, 2005; Kimura et al., 2002) and is stabilized by the presence of alloying elements. Specifically, Cr is supposed to give greater compactness and to increase the cationic selectivity of the inner layer, thanks to the formation of ultrafine crystals of Cr-goethite (Cook et al., 1999; Yamashita et al., 2004); Ni is supposed to act similarly to Cr, thus reducing penetration of corrosive species (e.g. Cl^-) toward the metal surface (Kimura et al., 2005; Yamashita et al., 2004); moreover, Cu and P tend to form insoluble products, which accumulate in the inner layer, enhancing its densification and protectiveness (Chen et al., 2005; Dillmann et al., 2002; Guedes et al., 2006; Yamashita et al., 1994).

The proper formation of the patina is strongly affected by the environment of exposure; specifically, regular and continuous cycles of wet/dry, low time of wetness (TOW), no water stagnation on the surface, photo-catalytic action of sunlight and low amounts of corrosive agents (atmospheric pollutants and air-borne salt particles) are necessary to develop protective layers (Morcillo et al., 2013). As regards gaseous pollutants, SO_2 effect has been the most investigated and, while low amounts of SO_2 seems to promote the patina stabilization, levels higher than $20 \text{ mg}_{\text{SO}_2} \text{ m}^{-2} \text{ d}^{-1}$ are reported to accelerate WS corrosion (Díaz et al., 2012; Morcillo et al., 2013). Nowadays the reduction of SO_2 levels in many parts of the world increased the relative importance of further pollutants such as NO_x , O_3 and particulate matter and shifted the attention on their action (Aramendia et al., 2015; Leuenberger-Minger et al., 2002; Oesch, 1996).

However, chlorides still represent the most corrosive agents for WS: so, coastal areas and zone where deicing salts are extensively used, are really critical exposure environments (Morcillo et al., 2013; Z. Wang et al., 2013) and recent provisional studies predict that, in general, future atmospheric corrosion will be dominated by the effects of chloride deposition, especially in coastal areas of southern Europe (Tidblad, 2012). In Cl^- rich environments, one of the main corrosion products growing on WS is akaganeite ($\beta\text{-FeOOH}$), that inhibits the formation of more stable compounds. Akaganeite shows anion-selectivity properties and may act as chloride reserve or chloride channel, causing a ionic flow toward the inner part of the patina and accelerating corrosion (Asami and Kikuchi, 2003; Kamimura et al., 2006; Ma et al., 2009; J. Wang et al., 2013).

Precipitations (rain or snow) can modify the chemical and physical properties of the electrolyte film on metals, accelerating the corrosion rate, and the characteristics of the events (e.g. rain amount, intensity, frequency) may have a great influence on corrosion (Corvo et al., 2005); on the other hand, rainfall may also contribute to remove corrosive species deposited on the surfaces (Pedefferri, 2007).

During precipitation events, alloying metals can be released in environment through runoff processes and the reduction of the protective properties of the patina can increase this phenomenon (Hedberg et al., 2015). Although they can be influenced by the same parameters, corrosion and runoff processes generally proceeds independently and with different rate; therefore, an estimation of metal release over time cannot be performed only by considering the corrosion rate trend (Faller and Reiss, 2005; Hedberg et al., 2014). Moreover, metal release from alloys cannot be predicted on the basis of the behaviour of their pure metals or considering the bulk composition (Bernardi et al., 2008; Herting et al., 2008; Wallinder et al., 2006).

Metals washed out from the alloy may disperse and accumulate and, depending on the amount, chemical form, mobility and bioavailability, they can represent a hazard to health and environment. In fact, although some metals, e.g. Cr, Cu or Mn, are essential to organism metabolism, excessive amounts may influence

biological processes, altering ecosystems (IARC, 1990; Kabata-Pendias, 2011; Manahan, 2003; Nagajyoti et al., 2010). The estimation and identification of significant diffuse and point sources of metal pollution from urban installations and activities is recommended by the EU Water Framework Directive 2000/60/EC (2000/60/EC, 2000). In this context, surface and building runoff can significantly contribute to the total urban runoff loading (e.g. Ni due to urban runoff represent till the 20% of Ni in EU urban waste waters), releasing metal species usually in a freely dissolved, so mobile and readily bioavailable form (EC - European Communities, 2001; Joshi and Balasubramanian, 2010). Solid surfaces in the near vicinity of buildings can change metal bioavailability and act as sinks for released metals, with different efficiency depending on the metal form (e.g. free, complexed, particulate) and on the nature of the surfaces (e.g. permeable/impermeable, asphalt, concrete, limestone, PVC, cast iron ...) (Hedberg et al., 2014; Lindström and Wallinder, 2011; Murphy et al., 2015).

Until now, field studies on metal release from alloys mainly focus on copper and zinc alloys, galvanized or stainless steel (Belghazi et al., 2002; Faller and Reiss, 2005; Herting et al., 2008; Robert-Sainte et al., 2009; Sandberg et al., 2007; Wallinder et al., 2006). Several works discuss the behaviour of WS in different environments in terms of rust composition and corrosion rate (Asami and Kikuchi, 2003; Chen et al., 2005; Cook et al., 1999; Diaz et al., 2013; Guedes et al., 2006; Kamimura and Nasu, 2000; Kamimura et al., 2006; Kimura and Kihira, 2005; Kimura et al., 2002, 2005; Leuenberger-Minger et al., 2002; McCuen et al., 2005; Melchers, 2008; Morcillo et al., 2013; J. Wang et al., 2013; Z. Wang et al., 2013; Yamashita et al., 2004); however, despite its large use for outdoor applications, very few studies, in laboratory conditions, have been conducted on metal release from this material (Chiavari et al., 2012).

Moreover, although general guidelines for application in non-critical outdoor conditions suggest to use bare WS, during the last decades time-saving and/or aesthetical reasons led several artists and architects to patinate (Gallagher, 2001) or to use commercial WS with an artificially-rusted surface finish, even for exposure in corrosive environments. An evaluation of the behaviour of both bare and patinated WS is therefore needed.

The present work is based on 3-year field exposure of WS, with and without artificial patinas, in unsheltered conditions, at an urban-coastal site. The focus is set on the early years of exposure, during which rust layer is not well stabilized yet (Morcillo et al., 2013) and the environmental impact could be greater. The aims of this paper are (i) to quantify corrosion-induced metal release from WS in the freely dissolved fraction, in relation to potential environmental risks; (ii) to analyse the possible influence of environmental parameters and surface finish on metal dissolution, also through multivariate analysis of experimental data.

Moreover, surface analyses were performed, so as to provide a general description of patinas developed during the period of exposure and involved in the dissolution process.

In this work, the “dissolution process” is intended as the whole of the electrochemical, chemical and physical processes that lead to the release of dissolved metals in rainwater (fraction of metals that pass through a $0.45 \mu\text{m}$ membrane filter assembly prior to sample acidification (US-EPA, 1994)).

2. Materials and methods

2.1. Materials

Commercial flat specimens ($50 \times 50 \times 2 \text{ mm}$) of WS (Cor-Ten A) with three different surface finishes, bare (BA), pre-patinated (PA) and pre-patinated with a beeswax covering (PWA), were tested.

Download English Version:

<https://daneshyari.com/en/article/6314949>

Download Persian Version:

<https://daneshyari.com/article/6314949>

[Daneshyari.com](https://daneshyari.com)