NaCl and Na$_2$SO$_4$ solution effect on weathering steel visual appearance when the ambient temperature changes cyclically

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Mindaugas Daukšys$^{1, *}$, Evelina Bitautaitė$^1$, Jūratė Mockienė$^1$ and Dalia Nizevičienė$^2$

Abstract: Visual appearance—colour and texture variation—of weathering steel was compared by testing weathering steel samples in aggressive and non-aggressive conditions, and cyclical changes of ambient temperature. This paper introduces a new method for determining visual appearance of weather-resistant steel in different environmental conditions. Weathering steel samples were tested in H$_2$O, 3% NaCl and 3% Na$_2$SO$_4$ solutions under ambient temperature changing from +20°C to −20°C per day. The structure of steel surface viewed under optical microscope revealed corrosion products in all steel samples. X-ray diffraction analysis of corrosion products revealed the presence of oxy-hydroxides, such as lepidocrocite (γ-FeO(OH)), goethite (α-FeO(OH)) and magnetite (Fe$_3$O$_4$) in different environment. Optical microscopy images of corroded surfaces had different visual appearance and orange, yellow, sandy, black or anthracite colours, which indicate that the corrosion products primarily contain lepidocrocite (γ-FeO(OH)), goethite (α-FeO(OH)) and magnetite (Fe$_3$O$_4$). EDS analysis revealed that the rust of samples kept in 3% NaCl solution had the highest amount of iron ions.

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PUBLIC INTEREST STATEMENT

Visual appearance of weather-resistant steel was compared by testing weathering steel samples in aggressive and non-aggressive conditions and cyclical changes of ambient temperature. The new method proposed allows to determine the visual appearance of weather-resistant steel in such environmental conditions. In Lithuania, the average annual total frequencies of freeze-thaw events with the daily maximum +20°C and minimum −20°C temperatures ranges from 9 to 17 cycles. The facades finished with Cor-Ten steel cladding may be located close to the road treated with de-icing 3% NaCl solutions salts or close to sea, the water of which contains some amount of Na$_2$SO$_4$ salts. By applying the method proposed, we can determine the visual appearance of weather-resistant steel surface, when it is exposed to different environmental conditions and is affected by cyclical changes of ambient temperature. Under laboratory conditions, we can simulate the influence of different numbers of cold seasons on weather-resistant steel’s visual appearance.
1. Introduction

Weather-resistant steel is widely used in architecture for its aesthetic and technological features. Cor-Ten steel is used for applications such as bridges and other load-bearing structures, transmission towers, building frontages and roofs. It is one of the most popular materials for outdoor sculptures (Angelini, Grassini, Parvis, & Zucchi, 2012; Chiavari, Bernardi, Motori, & Bignozzi, 2012; Decker, Bruggerhoff, & Eggert, 2008; Gallagher, 2000). Weathering steels, due to their chemical composition, exhibit increased resistance to atmospheric corrosion compared to unalloyed steels. The corrosion retarding effect of the protective layer is produced by the nature of its components in the steel structure and the particular distribution and concentration of alloying elements in it. The anticorrosive properties of weather-resistant steel are based on the protective oxide layer, which forms on the surface of the steel.

When weather-resistant steel is exposed to different environmental conditions in which the steel is wetted and dried alternately, it becomes covered with a film of rust. The mechanism of atmospheric corrosion is divided into three different stages: wetting of the dry surface (1 stage), wet surface (2 stage) and drying out of the surface (3 stage). In the first stage, anodic dissolution of iron is balanced by cathodic reduction of lepidocrocite (c-FeO(OH)) in the rust layer; in the second stage, oxygen is reduced inside the oxide scale; the third stage results in a very high corrosion rate in which O$_2$ reduction is the cathodic reaction (Stratmann, Bohnenkamp, & Engell, 1983). The corrosion rate is the highest in the third stage and this stage results in goethite formation and lepidocrocite generation. The atmospheric corrosion products of iron and its alloys comprise numerous oxides, hydrated oxides, oxyhydroxides and miscellaneous crystalline and amorphous substances that develop as a result of the reaction between iron and its environment. The proportion of each type of component depends on the composition of the iron material and the environment where it is exposed (Morcillo, Díaz, Cano, Chico, & De la Fuente, 2019). The principal component in the rust layers developed on weather-resistant steel evolved from lepidocrocite (less than a few years), via an amorphous substance (several years) to goethite (decades), and as a consequence the rust layer’s protective ability materializes only after several years of exposure (Yamashita, Miyuki, Matsuda, & Nagano, 1994).

The colour of the rust depends on the corrosivity of the atmosphere, on the steel type, exposure time, etc. According to standard EN ISO 9223 (2012), rust presents a darker colour at the higher corrosivity index of the atmosphere. The causes of irregularities and discolorations on the surface of parts of a weathering steel sculpture, which had been in contact with wood pallets, depended on the presence of iron oxalates and calcium oxalates (Aramendia, Gómez-Nubla, Arana, & Madariaga, 2015a). When weather-resistant steel is used in marine atmospheres rust presents a considerably lighter colour and the higher the atmospheric salinity is, the darker the tone is.

Grain size of corrosion products is closely related to the texture of the rust layer’s outer surface. Texture is determined by sense of touch in terms of smoothness, unevenness and roughness. The morphology of the outer surface of rust formed on weathering steel in atmospheric exposure can take the form of grains or particles, agglomerates of grains, flakes, and layers or laminates (Alcántara et al., 2017; Calero et al., 2017).

The protection ability inherent in weathering steel can be affected by the environment in different kind of atmospheric particles rich urban atmospheres (Aramendia, Gómez-Nubla, Castro, & Madariaga, 2014). The presence of atmospheric particles of calcium carbonate does not have a significant negative role in the metal decay process. However, the presence of high
magnesium calcite plays an important role in the formation of magnesioferrite, another deleterious product present in the surface of the weathering steel. As all these sulphates are soluble, rainwater can dissolve them leading into a continuous decaying and material loss process. Other atmospheric particles such as calcite, charcoal, and chromium rich particles were detected together with several compounds produced in the reaction of steel and deposited particles with acid gases of the atmosphere (Aramendia, Gomez-Nubla, Castro, & Madariaga, 2015b; Nishimura et al., 2000). These particles have a negative effect on the conservation of weathering steel because the change the visual appearance of steel surface and decrease its resistance to atmospheric agents. Chiavari et al. (2012) concluded that pre-patination had no beneficial effects on corrosion of Cor-Ten with different surface finish. Corrosion rate of weathering steel is considerably lower than that of the standard carbon steel. Nevertheless, the possible effect of corrosion on reliable service of the structure throughout the designed service life should be considered when designing the structures (Křivý, 2012; Křivý & Konečný, 2013; Urban, Křivy, & Kreislova, 2015).

In practice, there are different corrosion tests and methods used, which evaluate corrosion losses, corrosivity rate, texture and morphology of the outer surface of rust formed on weathering steel, discolorations on the surface. The new method developed by the author, Křivý (2012), takes into account actual environmental conditions in the location of the structure, exposure conditions, position and location of the surface in the structure, influence of neglected maintenance and compliance with recommended structural principles. The HSV colour model is used for the assessment of steel substrate conditions (Momber, 2012). HSV—the hue (H), the saturation (S) and the value (V)—is defined in a way to reflect the subjective brightness perception of a colour for humans along a lightness–darkness axis. Based on the adjustment of two parameters of the model, different rust grades, or different stages of severity of rusting, can be distinguished.

The aim of this paper is by applying the new test method to determine the influence of $\text{H}_2\text{O}$, 3% NaCl solution and 3% Na$_2$SO$_4$ solution on weather-resistant steel surface colour and texture variation, when the ambient temperature changes cyclically.

2. Materials and methods
Cor-Ten steel B group samples were used for the test. This weather-resistant steel corresponds to steel types S355J2G1W and S355J2G1W according to standard EN 10,155. Dimensions of the samples: length about 190 mm, width about 150 mm and thickness about 2 mm; the average density was 7735 kg/m$^3$.

Wet and dry cycles are necessary during the tests for the formation of the protective rust layer—patina. Cor-Ten steel samples were formed to this end and placed in plastic containers on special supports: two containers were filled with tap water (control samples), two containers were filled with 3% Na$_2$SO$_4$ solution, and the remaining two containers were filled with 3% NaCl solution (Figure 1).

The tested specimen was placed above the level of water or salt solution. The container with the specimen was tightly covered with a polyethylene film. Containers with test samples were placed
in the climatic chamber so that the tested surface was subjected to temperature fluctuation from +20°C to −20°C during 24 h. Vapour of the salt solution built up in the tightly sealed container at higher temperatures. At lower temperatures, the vapour deposited on the surface of the tested specimen and dampened it. The temperature at the centre of the tested surface was continuously taken in the climatic chamber. Time measuring was started in the first cycle after 0 ± 30 min, since the specimen was placed in the climatic chamber. Good air circulation in the climatic chamber is required in order to ensure that temperature cycles are exactly the same for all samples. After 100 cycles, each specimen was treated as follows: a) Cor-Ten steel samples were taken out from sealed containers and left for the surface to dry. Photos of wet and dry samples were taken; and b) the surface of Cor-Ten steel samples was cleaned with a brush until no traces of oxidation products were left on the sample surface. Afterwards, X-ray diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDS) analyses of oxidation products and microscopy analysis of the structure of Cor-Ten sample surface were done.

After cyclical temperature variations from +20°C to −20°C in 24 h in different environment, the resulting compounds precipitated on the surface of the Cor-Ten steel samples were tested using an XRD analysis method. XRD measurements were done with diffractometer Bruker D8 Advance, which uses an X-ray tube with a Cu anode as the primary X-ray beam source. CuKα radiation and Ni filter were used. The power XRD patterns were identified with references available in PDF-2 date base (PDF-2 International Centre for Diffraction Data, 12 Campus Boulevard Newtown Square, PA19073-3273 USA).

X-rite, Incorporated (Sweden), Colour measurement tool NCS Colour Scan 2.0 and fan deck NCS Index 1950 Original with 1950 NCS colours were used to define the colour of Cor-Ten steel samples.

Olympus BX51TF microscope with 10x, 20x, 40x objectives, spot insight 4.2 camera, QCapture Pro image analysis and capture tool was used for Cor-Ten steel visual appearance testing.

Bruker AXS Microanalysis GmbH (Germany) was used for elemental analysis (EDS). Energy resolution of 133 eV (Mn Kα) guaranteed at 100,000 cps, stable over the whole throughput range at a given shaping time. Maximum pulse load 1,000,000 cps, active area of 30 mm², detection from Boron (5) to Americium (95), Peltier cooling.

SEM images were done with the scanning electron microscope FEI Quanta 200 FEG with high resolution low-vacuum FEG SEM and with extended low-vacuum capabilities. The microscope can be operated under high, low or even environmental (ESEM™) vacuum. The accelerating voltage can be changed from 200 V to 30 kV, with the probe current up to 100 nA. The maximum achievable resolution under high vacuum at 30 kV using secondary electrons is 1.2 nm.

3. Results and discussion

According to the climate conditions, Lithuania falls into climate zones 5 and 6 where ice storms, blizzards, drifting snow, snowing and sleet occur. The average annual total frequencies of freeze-thaw events with the daily maximum +20°C and minimum −20°C temperatures ranges from 9 to 17 cycles. Roads, highways and sidewalks can be covered by snow or ice during the wintertime. De-icing of roads has traditionally been performed using salt, often mixed with sand and gravel, spread by snowplough or dump trucks designed to spread it, on slippery roads. De-icing can be accomplished by use of dry or liquid chemicals designed to lower the freezing point of water (e.g. various salts). The most common de-icing chemical is sodium chloride (NaCl). It has a strong tendency to cause corrosion, rusting the steel used in most constructions. The most popular chemicals used for de-icing purposes in Lithuania are 3% NaCl solution and other mixes of salts. Sodium sulphate (Na₂SO₄) is relatively common in alkali lakes, ground water and sea water. The facades finished with Cor-Ten steel cladding may be located close to the road treated with de-icing 3% NaCl solutions salts or close to sea, the water of which has some amount of Na₂SO₄ salts. In
the cold season, the facade may be exposed to cyclical temperature fluctuations in water or different salt environment. In this way to imitate winter conditions, which appear in Lithuania, 3% NaCl and 3% Na₂SO₄ solutions were chosen. The solutions concerning other salts and different ambient temperature were not taken into account in this manuscript. In this case, these factors can have a different effect on the forming of patina layer (e.g. visual appearance and colour) on the surface of Cor-Ten steel plates.

Based on these factors—aggressive and non-aggressive conditions and cyclical changes of ambient temperature—the method of standard LST L 1428.17 (Concrete. Test methods. Part 17: Determination of frost resistance to volumetric freezing and thawing) was adapted to create necessary conditions for testing Cor-Ten steel samples. During the test, concrete specimens are also exposed to different environmental conditions: H₂O, 3% NaCl and 3% Na₂SO₄ solutions. By applying the proposed practical method, the visual appearance of weather-resistant steel surface, when it is exposed to different environmental conditions (H₂O, 3% NaCl and 3% Na₂SO₄ solutions) and is affected by cyclical changes of ambient temperature can be determined.

Artificial laboratory conditions were created for the forming of patina layer on the surface of Cor-Ten steel samples. Temperature fluctuation from +20°C to −20°C in 24 h was modelled in climatic chamber for Cor-Ten steel samples in H₂O, 3% NaCl and 3% Na₂SO₄ salt solutions. When Cor-Ten steel samples are exposed to different environment conditions (H₂O, 3% NaCl and 3% Na₂SO₄ solutions) in which the steel is alternately wetted and dried, it becomes covered with a film of rust. As illustrated in Figure 2, rust films were formed on weathering steel. One hundred cycles’ simulate the influence of five cold seasons on visual appearance of Cor-Ten steel samples. After 100 cycles test, the visual appearance of weathering steel samples shows that the biggest amount of oxidation products were formed on the surface of steel samples that were exposed to 3% NaCl solution environment (Figure 2(b)). Sodium chloride is usually used as de-icing salt in Lithuania. Less oxidation products were found on the surface steel samples exposed to 3% Na₂SO₄ solution environment (Figure 2(c)). Sodium sulphate is relatively common in alkali lakes, ground water and sea water. The smallest amount of oxidation products were formed on the surface of steel samples exposed to water (Figure 2(a)). After the tests in different environment conditions, the rust film on weathering steel samples changes from a matte grey colour typical of newly non-rusted steel to matte red-orange colour (Figure 3). This and other aspects show that the appearance of weathering steel is affected by environmental conditions, in which the weathering steel is used.

S 6500-N code was determined by a digital colour reader before measuring the influence of different environments on the surface structure and colour change of Cor-Ten steel samples subjected to cyclic temperature fluctuation from +20°C to −20°C in 24 h. The colour selected from the range is presented in Figure 3. The codes and corresponding colours of Cor-Ten steel samples kept in H₂O environment (Figure 3(a)) and 3% NaCl (Figure 3(b)) and 3% Na₂SO₄ salt solution (Figure 3(c)) environments. The colour of the rust layer is not only related to the environmental conditions but also to the time of corrosion reaction. In this case, the time factor is not taken into account in this manuscript. There are many publications on colour change of rust of weathering steel.

Different colours seen in Figure 3 illustrate the change of Cor-Ten steel colour in H₂O environment (non-aggressive), 3% NaCl and 3% Na₂SO₄ salt solution environment (aggressive). The facade with Cor-Ten steel cladding situated close to the road may have a different colour due to exposure to cyclical temperature fluctuations and 3% Na₂SO₄ or 3% NaCl salt solutions compared to the facade not exposed to de-icing salts. Architects should have in mind that the colour of Cor-Ten steel cladding can be influenced by the environment where the building or structure will be located. In this case, engineers and designers should work together to consider changes of the Cor-Ten steel visual appearance due to environmental conditions.
Presumably, in cyclical temperature fluctuation conditions and in the presence of 3% Na$_2$SO$_4$ or 3% NaCl salts, the Cor-Ten steel facade cladding may be covered by a layer of oxidation products, which subsequently may be washed by rain. In cases where Cor-Ten steel cladding is combined with concrete or brick facade, brown stains can appear on the façade. The stains may also appear.
Rust is a complex system consisting of several iron corrosion products and other salt deposits, natural and industrial salts. The composition of a rust layer depends on the complexity of the atmosphere. Compounds formed on the surface of Cor-Ten steel samples due to cyclical temperature fluctuation conditions and the presence of 3% Na$_2$SO$_4$ or 3% NaCl salts were tested by means of XRD analysis method to determine the mineral composition of corrosion products. Figure 4 reveals that FeO(OH) is the main product of steel corrosion. It crystallizes as modifications of goethite $\alpha$-FeO(OH) and lepidocrocite $\gamma$-FeO(OH). These minerals are mixed with magnetite Fe$_3$O$_4$ in aggressive atmosphere conditions. The biggest amount of magnetite was found on samples kept in Na$_2$SO$_4$ environment. As goethite $\alpha$-FeO(OH) and lepidocrocite $\gamma$-FeO(OH) are good sorbents, thin films with high concentration of Cl$^{-}$ and SO$_4^{2-}$ ions are formed on the surface of the metal when dew droplets condense in cyclical temperature fluctuation conditions. These films intensify the destruction of steel even more. The least damage caused by corrosion was observed in samples kept in water environment.

The EDS analysis confirms the same. Figure 5(c) illustrates that the highest amount of iron ions was found in corrosion products of samples kept in 3% NaCl solution. Cl anions are corrosion activators. According to Pedeferri (2018), they accelerate the corrosion of corrosion-resistant steels with Cr-Ni. The NaCl solution produces local corrosion, and the latter causes corrosive spots on concrete or other type of paving next to the building. Oxidation product drainage ducts must be installed to avoid the staining of facades or paving.
Chloride anions activate corrosion more than sulphate anions. This is related to higher NaCl solubility in water than Na$_2$SO$_4$. The solubility of NaCl in water is 35.7 kg/100 kg of water, while the solubility of Na$_2$SO$_4$ is 4.76 kg/100 kg of water.

XRD patterns (Figure 4) of the oxidation products show that the same phases are contained in different environment: Lepidocrocite $\gamma$-FeO(OH), Magnetite Fe$_3$O$_4$, and Goethite $\alpha$-FeO(OH).

EDS analysis of oxidation products on the surface of weather-resistant steel samples is given in Figure 5. EDS analysis revealed the presence of Cr, the concentration of which on the metal surface increased.

In the next stage, the samples were analysed by means of scanning optical microscopy methods. Images of Cor-Ten steel sample surface structure before the test are presented in Figure 6. The surface structure of Cor-Ten steel samples resembles randomly scattered scums. Some places reveal oxide formations, which are not possible to see by the naked eye.

Images of Cor-Ten steel sample surface structure before the test is given in Figure 7. During the traditional “life cycle” of rust formation, the following conversion products can be produced.

$$\text{Fe(OH)}_x \rightarrow \text{FeOOH} \rightarrow \gamma\text{-FeO(OH)} \rightarrow \alpha\text{-FeO(OH)} \rightarrow \text{Fe}_3\text{O}_4$$

This process of rust shifting can be compared to crystallization. Figures 7 and 8 illustrate the products of this conversion. The final product of corrosion depends on the age of the rust layer and the environment where the samples were kept (Momber, 2012). Lepidocrocite is the first product to crystallize in the progress of atmospheric corrosion. The colour of this mineral is orange. Goethite may be yellow, sandy or brown. Magnetite is of black or anthracite colour (Gerke, Maynard, Schock, & Lytle, 2008; Momber, 2012).

The SEM images of oxidation products on the surface of weather-resistant steel samples are given in Figure 8. The SEM analysis revealed the crystal structure specific of goethite and lepidocrocite. Goethite crystals have a cotton ball structure, and lepidocrocite crystals have a flowery plate structure (Momber, 2012).
Future plans: The results of XRD and EDS tests were not done every few hours to reveal the evolution of rust layer. These tests authors are planning to do in the future experiments, such as testing the composition of rust layer every few hours.

When weather-resistant steel is exposed to aggressive and non-aggressive conditions and cyclical changes of ambient temperature, we can predict the visual appearance of it. Under
laboratory conditions, we can simulate the influence of different numbers of cold seasons on weather-resistant steel's visual appearance, it means that we only need to choose the necessary number of cycles and environmental conditions. After that, we can describe changes in visual appearance of Cor-Ten steel.

4. Conclusions

(1) The new method proposed allows to determine the visual appearance of weather-resistant steel when it is exposed to different environmental conditions (H\textsubscript{2}O, 3% NaCl and 3% Na\textsubscript{2}SO\textsubscript{4} solutions) and is affected by cyclical changes of ambient temperature. When the weather-resistant steel is used in such environmental conditions, we can predict the visual appearance of it under laboratory conditions.

(2) Testing in different environmental conditions showed that the rust film on weathering steel samples changes from a matte grey colour, typical of newly non-rusted steel, to matte red-orange colour. The optical microscope images of corroded surfaces have different visual appearance and have orange, yellow, sandy, black or anthracite colours, which indicate that the corrosion products primarily contain Lepidocrocite (γ-FeO(OH)), Goethite (α-FeO(OH)) and Magnetite (Fe\textsubscript{3}O\textsubscript{4}).

(3) The XRD analysis of corrosion products shows the presence of Oxy-hydroxide like Lepidocrocite (γ-FeO(OH)), Goethite (α-FeO(OH)) and Magnetite (Fe\textsubscript{3}O\textsubscript{4}) in different environment. As Goethite and Lepidocrocite are good sorbents, thin films with high concentration of Cl\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} ions are formed on the surface of metal when dew droplets condense in cyclical temperature fluctuation conditions. These films intensify the destruction of steel even more. The least damage caused by corrosion was observed in samples kept in water environment.

(4) EDS analysis results lead to the conclusion that the highest amount of iron ions was found in corrosion products of samples kept in 3% NaCl solution. The NaCl solution produces local...
corrosion, and this corrosion causes corrosive spots (pitting). Chloride anions activate corrosion more than sulphate anions and this is related to higher NaCl solubility in water than Na$_2$SO$_4$.

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Correction
This article has been republished with minor changes. These changes do not impact the academic content of the article.

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