



## Review

## Weathering steels: From empirical development to scientific design. A review



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## ABSTRACT

The design of the first weathering steels was purely empirical and focused on a small number of conventional alloying elements such as manganese, silicon, chromium, nickel, copper and phosphorus, mainly. The environmental conditions that promote the formation of protective rust layers: existence of wet/dry cycling, absence of very long wetness times, atmospheres without a marine component, etc., were identified by trial and error. This paper makes a bibliographic review of the abundant literature that has been published on the atmospheric corrosion of weathering steels, setting out in chronological order the advances made in the scientific knowledge of important matters such as: atmospheric corrosion mechanisms of weathering steel, formation of protective rust layers, and the role played by alloying elements. The work ends with an overview of the scientific design of new weathering steels, placing special emphasis on the new compositions developed for application in marine atmospheres.

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## 1. Introduction

Weathering steels (WS), also known as low-alloy steels, are mild steels with a carbon content of less than 0.2 wt%, to which mainly Cu, Cr, Ni, P, Si, and Mn are added as alloying elements totalling a few percent maximum [1]. The development of the first WS in the early 20th Century was essentially empirical, based on results obtained in wide-scale research programmes undertaken by ASTM [2] and the steelmaker US Steel Corporation [3].

The enhanced corrosion resistance of WS is due to the formation of a dense and well-adhering corrosion product layer known as the patina. Besides possessing greater mechanical strength and corrosion resistance than mild steel or plain carbon steel (CS), the patina is also valued for its attractive appearance and self-healing abilities. The main applications for WS include civil structures such as bridges and other load-bearing structures, road installations, electricity posts, utility towers, guide rails, ornamental sculptures and façades and roofing.

The environmental conditions which promote the formation of protective rust layers: existence of wet/dry cycling, absence of very long wetness times, absence of a marine component in the atmosphere, etc., were also initially identified by means of trial and error. Extensive research work has subsequently thrown full light on the requisites for a protective rust layer to form, and it is now well

accepted that wet/dry cycling is essential to form a dense and adherent rust layer, with rainwater washing the steel surface well, accumulated moisture draining easily, and a fast drying action (low time of wetness) [4]. Surfaces protected from the sun and rain (sheltered) tend to form loose and poorly compacted rust, while surfaces freely exposed to the sun and rain produce more compact and protective rust layers. Structures should be free of interstices, crevices, cavities, and other places where water can collect, which are vulnerable to corrosion due to the absence of a protective patina. It is also inadvisable to use bare WS in continuously moist exposure conditions due to the lack of alternate wetting and drying cycles which are necessary to physically consolidate the rust film, or in marine atmospheres where the protective patina does not form [5,6].

Matsushima et al. [7] studied the effect of a large number of variables on WS behaviour in architectural applications and verified the decisive influence on the formation of the protective patina of whether or not the surface was wetted by rainwater, and whether or not the points where moisture tended to collect were well drained. These effects are most pronounced in atmospheres with high pollution levels, where the protective patina may never get to form. An exhaustive bibliographic review on the effect of exposure conditions on atmospheric corrosion of conventional WS (Cor-Ten) has been published in a previous paper [8].

Since the first studies by Copson [2] and Larrabee and Coburn [3], great advances have been made in scientific knowledge of the mechanisms that govern WS behaviour.

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This paper presents a bibliographic review of the abundant literature that has been published on the atmospheric corrosion of WS, setting out in chronological order the advances made in the scientific knowledge on important matters such as the atmospheric corrosion mechanisms of WS, the formation of protective rust layers, and the role played by alloying elements.

It ends with an overview of the scientific design of new WS, placing special emphasis on the new compositions developed for application in marine atmospheres, one of the main limitations of conventional WS.

## 2. Empirical development of WS

### 2.1. Brief historical development

Albrecht and Hall [9] made an exhaustive study of the historical development of WS. By way of summary, the following milestones represent the most important advances in the empirical development of WS.

#### 2.1.1. 1910 (Buck [10])

Buck, of US Steel Corporation, conducted a large-scale atmospheric exposure test of copper steel in the industrial coke regions (sulphurous fumes) of Pennsylvania, Atlantic City (marine) and Kittanning (rural). This research showed the beneficial effect of copper in steels for atmospheric exposure. Most of the effect due to the presence of copper was achieved with the first 0.03 wt% or so added.

#### 2.1.2. 1916 (Committee A-5 ASTM [11])

The first major exposure study was conducted on large 260 corrugated sheets, with copper contents varying between 0.01 and 0.25 wt%, at three USA locations: Fort Pitt in Pittsburgh, Fort Sheridan and Annapolis. The findings indicated that with 0.04 wt% copper the atmospheric corrosion rate slowed down considerably, and that a copper level of 0.15 wt% was ample.

#### 2.1.3. 1926 (Committee A-5 ASTM [12])

The second major exposure study was conducted in four USA locations: Altoona, State College, Sandy Hook and Key West. Larrabee [12] summarised the results of these two major studies and concluded on behalf of Committee A-5 that the ratios of time to perforation varied depending upon the type of steel and location. The average life of all sheets with 0.20 wt% minimum copper was about twice that of sheets with residual copper. The more copper the steel contained, the longer its life. A higher phosphorus content contributed to corrosion resistance.

#### 2.1.4. 1929 (V.V. Kendall and E.S. Taylerson [13])

In the sulphurous industrial atmosphere of Pittsburgh, copper and especially a combination of copper and phosphorus had a strongly beneficial effect on corrosion resistance. This influence was greater in steels than in irons. In the rural atmosphere of Fort Sheridan the attack was much less severe, but in general the indications from Pittsburgh were valid here as well.

#### 2.1.5. 1933 (US Steel Corporation)

US Steel launched the first commercial WS under the name of USS Cor-Ten steel.

#### 2.1.6. 1941 (Committee A-5 ASTM [2,14])

71 low-alloy steels were exposed to an industrial atmosphere at Bayonne and to marine atmospheres at Block Island and Kure Beach (250 m). It was found that rust coatings in the industrial

atmosphere were more protective, with the corrosion rate dropping to lower values than in the marine atmospheres.

#### 2.1.7. 1942 (United States Steel Co. [3])

Different steels were exposed in the following atmospheres: Kearny (industrial), South Bend (semi-rural) and Kure Beach, 250 m (marine). It was found that the rust film developed during the first 4 years of exposure in the industrial atmosphere was more protective than the film developed in the marine atmosphere. The corrosion rates for all three materials (mild steel, copper steel and Cor-Ten steel) in the industrial atmosphere decreased markedly after one to 2 years of exposure, as was shown by the flatness of their corrosion/time curves indicating more and more protective rust, whereas the rust had a lesser effect on the corrosion rates of mild steel and even copper steel in the marine atmosphere.

### 2.2. Effect of alloying elements

The development of the first WS compositions was initially an empirical task based on steel mass loss results in atmospheric exposure, and not on scientific knowledge of the influence of alloying elements. The early studies of Copson [2] and Larrabee and Coburn [3], the former beginning in 1941 by ASTM Committee A-5 and the latter in 1942 by US Steel Corporation, represented an important step forward in the empirical development of WS based on a knowledge of the effect of different alloying elements. There follows a short summary of the effect of the main alloying elements in atmospheric corrosion of WS.

#### 2.2.1. Phosphorus

Phosphorus is not essential for protective patina formation, but its addition to a copper-bearing steel leads to a marked improvement in corrosion resistance. As an alloying element, phosphorus has a notable effect on the mechanical properties of steel, and may be beneficial or harmful depending on its content in the alloy and on the processing method. It is one of the most powerful solid solution ferrite hardeners, raising the yield strength and tensile strength by approximately 62 MPa with just a 0.17 wt% phosphorus addition [15]. However, it presents high solubility and low diffusion in steel at the thermal treatment temperatures, and as a result tends to segregate at austenite grain boundaries, severely reducing both fracture toughness and ductility, and thus embrittling the steel. A common example is the embrittlement experienced by low-alloy steels for tempering when they are thermally treated during processing.

It is estimated that a proportion of more than 0.1 wt% phosphorus can promote brittle fracture in steel when subjected to vibratory forces or blows, as a result of either solid dissolution of the phosphorus in ferrite, which reduces ductility, or the formation of Fe<sub>3</sub>P. The latter, along with austenite and cementite, forms a ternary eutectic known as steadite, which is highly fragile, hard, and has a relatively low melting point (960 °C), appearing at the grain boundaries and causing embrittlement of the steel [16].

From the viewpoint of atmospheric corrosion, phosphorus notably improves the resistance of WS, reducing the average mass loss or thickness loss as the phosphorus content in the steel composition rises. However, as has been seen above, its upper limit is controlled by its adverse effect on the mechanical properties of steel, and so phosphorus should not exceed 0.1 wt% in the composition of structural steels intended for atmospheric exposure.

Fig. 1 shows the results obtained by Copson [2] and Larrabee and Coburn [3] in the industrial atmospheres of Bayonne and Kearny respectively, for steels with different P contents as a function of the copper content. It can be seen that corrosion decreased as the phosphorus and copper contents increased.

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