

CORROSION BEHAVIOUR OF STEEL AND COPPER AS INFLUENCED BY LOCAL ATMOSPHERIC CONDITIONS

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Abstract. Corrosion of steel (0147, JUS) and copper (99.99%) was studied during past 18 years in a network of 8 testing sites situated in locations of R. Macedonia with typical microclimate. Climate conditions were registered simultaneously, in order to establish their effect on the observed phenomena. Weight loss, as well as increase of electrical resistance and time of wetness were periodically registered. Testing in a climate chamber was also performed in order to elucidate the individual effect of the most significant parameters. It was found that the corrosion rate depends strongly on the: atmospheric pollution, humidity and temperature, as well as on the time of wetness of metallic surface; thickness and compactness of accumulated corrosion products; composition and morphology of primary corrosion products; orientation of the corroding metal surface, etc. A model based on the sequential nature of the corrosion of metals in atmosphere was developed, based on the measured pattern of time-of-wetness and precise insight in the discrete progress of the corrosion process.

Keywords: atmospheric corrosion, steel, copper, pollution, humidity, temperature, climate chamber, time of wetness, model.

AIMS AND BACKGROUND

The process of atmospheric corrosion of metals (ACM) is a phenomenon known from the beginning of human civilisation. No matter that a major progress in this field was achieved many years ago by Vernon^{1,2}, Castle³, Sereda⁴, Rozenfeld⁵, etc., the interest for ACM, both theoretical and practical, remains permanent. The understanding of the mechanism of ACM and, more important, of the remedies preventing or diminishing the damage become crucial in recent years.

The increased environmental concern is only one of the related aspects. So, e.g., the annual rate of steel production remained almost constant in past 30 years, while the global human population doubled itself. The decreased demand in primary production is attributed to lower metal's consumption in developed countries due to saturation of their needs and neglectible buying power in the developing countries. Improved corrosion protection is one of the main technical reasons for the decreased demand in primary metal's production. Contemporary

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steels are tailored for every specific application and this is the reason why it is difficult to find a steel brand older than, typically, 5 years⁶. One of the principal contributions to the recent metal's economy belongs to good understanding of the effect of polluted environment to the stability of metallic materials. The aim of this paper is to present some of the results of our extensive corrosion study.

EXPERIMENTAL

Steel (0147, JUS) and copper (99.99% Cu) specimens were exposed to atmosphere in a network of 8 testing sites situated throughout of Republic of Macedonia, as shown in Table 1.

Table 1. Scope of testing sites and their characteristics

Test site	Altitude (m)	Climate type	Relative humidity (%)	Estimated aggressiveness*
Skopje	301	urban-industrial	67	4
Veles	175	industrial	70	5
Bitola	586	urban	67	3
Ohrid	760	urban-rural	66	2
Lazaro Pole	1332	rural	74	0
Demir Kapija	123	rural	65	1
Berovo	824	rural	74	1
Miladinovci	335	industrial	—	3

* Aggressiveness ratings: 5 – the most aggressive, 0 – virgin nature.

Simultaneously, weather parameters were monitored by the State Meteorological Service. The rest of the parameters significant for ACM, as e.g. time of wetness of corroding metal surface, were measured as part of this testing.

Specimens weight loss was measured and corresponding corrosion rate was calculated after given periods of exposure. The pre- and afterexposure treatment of specimens is described elsewhere⁷. In order to determine the effect of only one of the relevant parameters, accelerated testing was done in a climate chamber under controlled temperature, humidity and pollution conditions. Increase of electrical resistance of a corroding steel wire was measured in both real and modelled conditions, in order to get insight in the discrete progress of the ACM.

The effect of the initial exposure's climate conditions was studied by exposing a set of 72 steel plates to a 2³ different combinations of pollution, relative humidity (RH) and temperature values in a climate chamber for 48 to 120 h. 2 extreme values were given to each parameter, e.g. clean or polluted air (0.01% H₂S), dry (30-50% RH) or wet (100% RH) air and cold (20±2°C) or warm (65±3°C) air. After initial corrosion products were formed, the specimens were moved from the

climate chamber and transferred to a nearby testing site where they were exposed for 3, 6 or 12 months to a real atmosphere.

RESULTS AND DISCUSSION

Weight loss versus time of exposure. The general feature of weight loss versus time patterns, recorded in the past 15 to 18 years of exposure, is similar to the ones referred elsewhere (see Ref. 8). The clean bare metal surface corrodes without any obstruction in the presence of air and covers itself with corrosion products growing from thin films up to the thick phase oxides. Generally, the presence of moisture and, especially, pollutants affects the rate of ACM as discussed in Refs 1 and 4. The accumulation of corrosion products on top of the metal surface is also an important factor that hinders the progress of ACM by preventing free access of oxygen to the metal-air interface and/or of the corrosion product in the opposite direction. More details about the composition of Fe and Cu corrosion products are given in Refs 9 and 10.

Some of the specific features, characterising the effect of meteorological conditions in Republic of Macedonia, are as follows:

(i) Differences up to 2.7 and 3 times were measured for steel and copper corrosion rate respectively, no matter that the testing sites cover only a tiny region of 100×200 km, and that the industrial activity (and pollution) in this region is a rather symbolic. Normally, for both tested metals the highest aggressiveness values were measured in locations with industrial and/or urban activities. The absolute values of corrosion rates are given in Table 2.

Table 2. Corrosion rate during the tested period

Location's aggressiveness	Low		Intermediate		High	
	Fe	Cu	Fe	Cu	Fe	Cu
Year of exposure						
1	2.7	0.11	4.2	0.20	11	0.27
3	1.8	0.07	3.1	0.15	7	0.21
10	1.2	0.06	1.9	0.12	4.2	0.17
16	0.88	0.05	1.5	0.10	2.4	0.15
Location(s)	L. Pole, D. Kapija		Res 4		Veles	Skopje

(ii) The atmosphere in test sites enables formation of thick and compact corrosion products that cause steep decrease of corrosion rate with time during the initial exposure (3-5 years) and a moderate one after 10-16 years. So, e.g. steel corroded at 2.7 MDD in the first year and only 0.88 MDD in the 16th year (see Table 2).

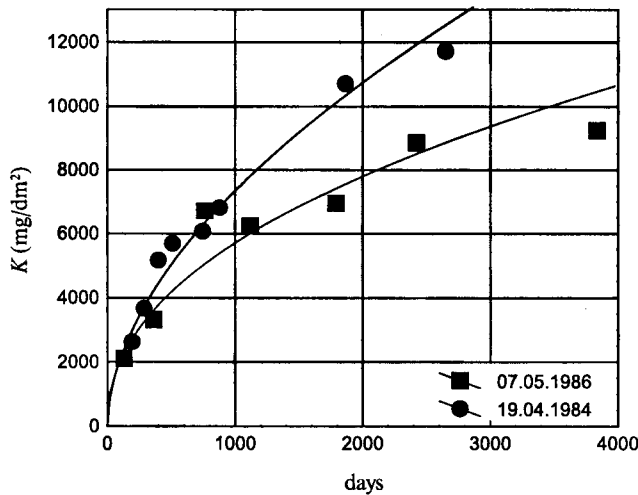


Fig. 1. Effect of weather conditions during initial exposure to the corrosion reaction rate

(iii) Weather conditions existing during the primary exposure affect the nature of corrosion products, so that differences in corrosion rates higher up to 35% were measured with series initiated at different weather periods (2 years later, as in Fig. 1). In order to get inside this phenomenon a combined exposure experiment (formation of primary corrosion products in modelled conditions and later exposure to a real atmosphere) was performed, as described above. After such combined exposure it was found that the steel specimens initialised in a climate chamber in polluted and wet conditions, regardless of the temperature, corrode in real atmosphere much faster than the specimens under the rest six (less aggressive) initialising conditions. So, after 12 months, the weight loss of the former specimens corrosion loss was 1.83 g/dm² and 2.06 g/dm² for wet-polluted-cold and wet-polluted-warm conditions, respectively, as compared with only 1.36±0.02 g/dm² for the latter (see Table 3).

(iv) The specimen's surface facing downwards corroded up to 30% faster than the sky looking ones (Fig. 2). This phenomenon was explained in terms of easier formation of a moisture film on a downwards plate side and troubles in its evaporation, leading to longer wetting of this side.

Table 3. Effect of the conditions during primary exposure (climate chamber) to the course of further corrosion of steel specimens (real atmosphere)

Conditions during primary product formation		Weight gain in the climate chamber (mg/dm ²)		Weight loss in the test site (g/dm ²)					
		cold	warm	102 days		184 days		365 days	
				cold	warm	cold	warm	cold	warm
Dry	clean	0	0	0.397	0.445	0.3	0.445	1.37	1.35
	polluted	2.5	1.2	0.519	0.509	0.59	0.869	1.36	1.35
Wet	clean	1.2	72	0.521	0.613	0.86	0.747	1.33	1.38
	polluted	389	252	0.905	1.19	1.39	1.21	1.83	2.06

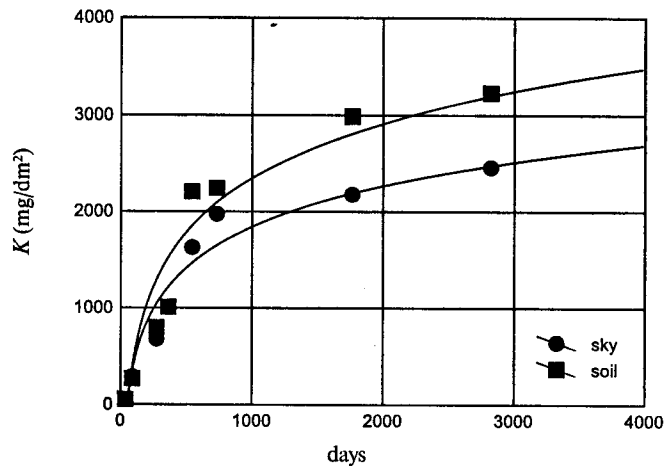


Fig. 2 Specimens orientation towards sky or soil affects the corrosion reaction rate

Model. A model aimed to take into account the uneven course of the ACM was developed, based mainly on two experimental findings. First, parameters defining the corrosion agresiveness of the atmosphere vary in a wide and random changes. Second, the ACM progress is uneven. Accordingly, the existing habit to express this progress as a continuous function of time is applicable only for the description of the general trend of long-term weight loss data. Opposite to this, one should take into consideration that the ACM is not a continuous and smooth process, but rather an intermittent one, composed of sequences of fast progress, as those in wet and polluted conditions and of practical zero rate, as in dry and clean conditions. The model's development was reported in more details elsewhere⁷.

CONCLUSIONS

Corrosion of steel and copper in atmosphere was measured for 15-18 years in a network of test sites in Republic of Macedonia. No matter that the covered region is of limited size, differences in the corrosion rate up to 3 times were measured, caused mainly by differences in air pollution. In industrial and urban locations rates as high as 11 MDD and 0.27 MDD were measured for steel and copper, respectively.

Regularities in the course of corrosion reaction caused by the thickness and compactness of accumulated corrosion products as well as of its composition and morphology were identified.

The intermittent nature of the atmospheric corrosion of metals was elaborated in the suggested model.

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