Relationship between Oxidation of Metal Surface Layer and Air Quality in Wuhan

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Abstract. In order to find out the relationship between the oxidation of surface layer and air quality, the correlation analysis method and elemental analysis is used in this paper. Based on the analysis of the database of RAPIDC Corrosion Project, dose-response functions for the tested metals were derived through non-linear regression method. The established dose-response functions for carbon steel and zinc are applicable to use in Wuhan and the results show that the proposed method can thus improve overall system performance substantially.

1 Introduction

Wuhan City used to be known as a region of heavy air pollution and acid rain in China. Many efforts have been invested in the control of air pollution and acid rain since the 1980s. It is found these two nuisances have negative impact on both ecological environment and structural materials, endangering some cultural heritages in this region. In recent years, the local government has taken many actions such as “Clean Energy”, “Clean Sky Action” and so on, to reduce SO₂ emission and improve the quality of atmospheric environment in Wuhan. As a result, the situation has ameliorated gradually in urban areas. Thus corrosion of materials in this new mitigating environment becomes an interesting subject once again. Our research which was one of the subprograms for corrosion problems of an international project, Regional Air Pollution in Developing Countries (RAPIDC), was targeted at the impacts of air pollution and acid rain on corrosion of three metals—carbon steel, zinc and copper- at an urban site Wuchang and a rural site Qingshan in Wuhan. It was accomplished by cooperation with Swedish Corrosion Institute (SCI) and Swedish Environmental Institute (SEI), in 2002.

Standard specimens of carbon steel, zinc, and copper were exposed at an unsheltered position on racks. At the same time, atmospheric pollution data were gathered bi-monthly with passive samplers for SO₂, NO₂, HNO₃, O₃ and particle matter. Data of precipitation, and precipitation pH, relative humidity and temperature were obtained from nearby automatic air quality monitoring stations. This methodology was established by the cooperation of SCI and SEI, and it had been successfully applied to exposure experiments in Europe and Northern America [1].

2 Result and Discussion

A variety of materials are subject to atmospheric corrosion, such as metals, limestone, paint coatings, etc. In this work, we concentrated only on carbon steel, zinc, and copper, for which the atmospheric corrosion rates of first-year exposure were respectively (782.5, 9.1, 24.2) g m⁻² a⁻¹ at GYQ and (492.0, 11.6, 17.9) g m⁻² a⁻¹ at TSP. Clearly, the more serious air pollution in the urban area gave rise to the higher corrosion rates of carbon steel and copper at GYQ, but for zinc, because of its high sensitivity to humidity and precipitation acidity, its corrosion rate at GYQ was a little lower than that at TSP where the environment was characterized by high humidity and precipitation acidity. This abnormal phenomenon was also observed in Cuba by Mendoza, et al [2].

Compared with corresponding results previously reported [3], it can be seen that the annual corrosion rates for carbon steel, zinc and copper in the year from 1987 to 1988 at GYQ were as much higher as 2.8, 4.0 and 3.2 times those in the year from 2002 to 2003, respectively. The decrease in corrosion rates could be, to a large extent, ascribed to the improved situations of SO₂ and acid rain pollution. However, the reduction trend of corrosion rate of carbon steel in the same period was not as obvious as that of SO₂ concentration, which may partly reflect the combined effects of multi-pollutant situation on atmospheric corrosion of materials.

In the RAPIDC Corrosion Project, exposure tests were carried out at 16 sites in an extended geographical zone that covered 8 countries in Asia (mainly South Asia) and Southern Africa (Fig. 1), which involved rural, urban and

industrial atmospheres. The nearly synchronous tests made the comparison among RAPIDC sites possible and meaningful. The atmospheric environment characteristics of RAPIDC sites were shown in Fig. 1. In general, the pollution situation of SO₂, particle matter and acid rain (H⁺) at both urban and rural site of Wuhan was more serious than that at most other RAPIDC sites. Accordingly, the atmospheric corrosion rates of carbon steel, zinc and copper at the two sites in Wuhan were higher than those at most of other RAPIDC sites. These comparisons confirm us the importance and necessity to further abate air pollution in Wuhan. Grey system theory was first proposed by Deng in 1982 [4], and it has been successfully applied to many fields including atmospheric corrosion. Grey system theory can be applied to any uncertain system in which information does not suffice to support a relational analysis. Therefore, this method is a helpful tool to find out intrinsic regularity existing in atmospheric corrosion process whose mechanism remains relatively unclear due to the complexity of the process itself and the variability of atmospheric environment. We used the grey system theory to analyze the data in this study. Here, the atmospheric corrosion rate of a tested metal was taken as the reference sequence, and the environmental parameters as compared sequences. The grey relational grades between tested metal and environmental parameters were calculated according to the principle of grey relational analysis.

A factor with an order is not larger than 4 was regarded as the main factor that affected the atmospheric corrosion of the tested metal. We derived the following conclusions from grey relational analysis:

- 1) The main factors that affected atmospheric corrosion of carbon steel and copper were almost identical, which included SO₂, Particle and H⁺, and herein SO₂ was especially crucial.
- 2) For atmospheric corrosion of zinc, the primary factors were H⁺, relative humidity, precipitation amount and SO₂ in order, which could well explain the abnormally high corrosion rate of zinc at Qingshan, Wuhan;
- 3) In general, the two important indicators of acid environment, SO₂ and H⁺, were common primary factors that affected atmospheric corrosion of all tested metals, which demonstrated again the strong destructive effect of acid precipitation on metals. Principal component analysis (PCA) is a pattern recognition technique to find out similarities among the observations, and also to ascertain which variables are related to each other. It is noted that all variables are treated simultaneously in an n-dimensional space by PCA, whereas in a simple statistical study only two variables are considered at the same time, usually by means of a two-dimensional diagram [5]. With PCA method, a loading plot can be made for all variables, and shown as an abstract projection in the k-dimensional space. In this work, k=2.

It can be seen that Component 1 had higher loadings on variables such as Zn, H (H⁺), RH, and TOW (time of wetness, which is defined as a period of time when the metal surface is sufficiently wetted for corrosion to occur [6]); whereas Component 2 had higher loadings on variables such as Fe, Cu and S. Therefore, Component 1 was mostly correlated with zinc corrosion rate, and Component 2 with corrosion rates of carbon steel and copper. Also, in a loading plot, variables in close vicinity of each other are usually, but not always, correlated. Accordingly, S is likely related to Fe, and by less extent related to Cu, while H is likely related to Zn. All of above basically agree with the grey relational analysis. In addition, the variables TOW and RH were also closely related which was consistent with the definition of TOW and reflected the reality and reliability of the PCA processing.

1: Wuchang, Wuhan, China 2: Qingshan, Wuhan, China 3: Hong Kong, China; 4: Kitwe, Zambia
5: Magoye, Zambia; 6: Ho Chi Minh, Vietnam 7: Hanoi, Vietnam 8: Mytho, Vietnam
9: Bhubaneswaru, India 10: Bhubaneswarr, India 11: Phrapradaeng, Thailand 12: Bangkok, Thailand
13: Johannesburg, South Africa; 14: Kuala Lumpur, Malaysia 15: Tanah Rata, Malaysia 16: Harare, Zimbabwe

Fig. 1. Comparison of (a) main gaseous pollutants; (b) particles and precipitation pollution; (c) tested metals at sites in RAPIDC corrosion project.

The obtained dose-response functions (DRF) confirmed the dominant effect of dry deposition of SO₂ on atmospheric corrosion of the three metals, which agreed well with the outcomes of grey relational analysis and principal component analysis.

In the case of zinc, the effect of wet deposition of H⁺ was sometimes also as important as that of dry deposition of SO₂, especially in the places with acid rain of high frequency and large amount. This could be clearly demonstrated by comparison of the experimental data of GYQ with that of TSP in Wuhan. So, in the following part, we focused on only the corrosion of carbon steel and zinc. The established dose-response functions except the one for copper had a relatively high R², which means they agreed well with the experimental data. However, there were still some uncertainties on whether they could be applied to areas other than the RAPIDC sites. So, we performed a preliminary verification of the DRF for carbon steel using some publicly available data. The calculated carbon steel corrosion results are shown in Fig. 2, in comparison with the reported data. The DRF prediction turned out to be very accurate, especially at sites such as Wuhan and Shanghai. The unavailability of reliable data about zinc and copper corrosion frustrated our attempt to verify the other two dose-response functions respectively for zinc and copper. However, it can also be deduced by some certainty that they have a comparable prediction power to that for carbon steel, based on the fact that SO₂ and H⁺ were common crucial factors influencing corrosion of these three metals. Thus, we applied the three functions to further research of corresponding metal corrosion in Wuhan.

Fig. 2. The carbon steel corrosion rates calculated by the dose response function for outdoor carbon steel compared with corresponding reported data.

3 Conclusion

The combined results of the grey relational analysis and principal component analysis suggest that the two typical agents of acidic environment, SO₂ and H⁺ were the common factors that contribute most to the atmospheric corrosion of carbon steel, zinc and copper, which demonstrates again the strong destructive effect of acid deposition on metals. Based on the analysis of the database of RAPIDC Corrosion Project, dose-response functions for the tested metals were derived through non-linear regression method. The established dose-response functions for carbon steel and zinc are applicable to use in Wuhan, but the function for copper needs further modifying considering the relatively low R² value.

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