Role of anion interaction on copper atmospheric corrosion.

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Summary

Many factors are involved in atmospheric corrosion process given its complex nature. In the present time, due to the decrease of sulphur dioxide concentrations in the atmosphere and the increase in nitrogen oxides, ozone and particulates, a multipollutant situation is occurring. Diverse pollutants dissolve in the water layer formed in metals and anion interaction could occur in the electrolyte layer formed. Different concentrations of mixed anions (chloride, sulphate and nitrate) were deposited on the surface of copper sensors. Sensors were submitted to two different relative humidity conditions. Electrochemical Noise data series is obtained and Rn and Localization Index were determined. Results about the interaction between chlorides, sulphate and nitrate ions on copper corrosion at different concentrations and RH are presented.

1 Introduction

Air pollutants in combination with climatic parameters accelerate the corrosion of metals [1-2]. The influence of contaminants in metals degradation depends on the deposition characteristics of the different contaminants and the reactions occurring in the humid surface of the metals. The decreasing sulphur dioxide levels in most parts of Europe and many other countries and the increasing car traffic causing elevated levels of nitrogen compounds, ozone and particulates has created a new multipollutant situation [3]. A synergistic corrosive effect of sulphur dioxide and nitrogen dioxide has been reported. With decreasing levels, SO2 is no longer regarded as the only important gaseous corrosion stimulator. Instead, its effect in combination with other gaseous pollutants such as NO2 and their reaction products needs to be considered. A multi-pollutant situation has arisen where also two other pollutants deserve special attention, nitric acid and particles.

The interaction between air pollutants could significantly change their influence on materials degradation. An important air constituent usually not considered in research carried out in Europe is the influence of chloride aerosols.

In the case of copper, some authors have found in laboratory studies a notable synergistic effect of NO2 and SO2. This is attributed to an increase in the sulphite to sulphate oxidation rate in the presence of NO2. However, other authors have not encountered this effect in field studies [4]. A mixture of tenorite (CuO) and NaCl remained unreacted after four weeks of exposure in pure humid air, as well as when NO2 was added to the air [5]. The lack of detectable reaction is suggested to be explained by an initial formation of hydroxy chloride on the tenorite surface. This initial reaction increased pH locally, resulting in that tenorite becomes thermodynamically
stable. Cuprite (Cu$_2$O) pretreated with NaCl and exposed to SO$_2$+NO$_2$, formed only small amounts of sulfate.

Mariaca [4] reported that Zaquipour and Leygraf found an increasing effect with the NO$_2$ concentration, and detected the existence of Cu(NO$_3$)$_2$ among the corrosion products and, conversely, Schuber detected no nitrogen-based corrosion products at a similar NO$_2$ concentration. The last author highlighted the significant influence of the relative humidity: there was no reaction between NO$_2$ and copper at RH 65%, but above this value copper catalysed the reduction of NO$_2$ to NO.

Copper corrosion in laboratory atmospheres polluted with NO$_2$ depends fundamentally on the RH. At 90% RH the attack is similar to that experienced in pure atmospheres, with the transformation of Cu$_2$O into CuO and Cu(OH)$_2$. As the RH decreases, nitrite and nitrate ions are formed at isolated points on the surface and the resulting acidity causes local dissolution of the cuprite layer and the formation of basic copper nitrite (soluble) and nitrate, gerhardtite (Cu$_2$(OH)$_3$NO$_3$), and copper experiences localized attack.

In mixed atmospheres (NO$_2$+SO$_2$), when [NO$_2$]<[SO$_2$] copper corrosion experiences an inhibiting effect, whereas if [NO$_2$]>[SO$_2$] the mixture of the two gases causes a synergistic effect. At high RH, NO$_2$ contributes to the oxidation of SO$_2$, reinforcing the formation of sulphuric acid, which is the species that reacts with copper, while low RH values favors the reaction of NO$_2$ with the adsorbed water, forming nitrous and nitric acids, which are the species that react with copper in this case, giving rise to an outer film of basic copper nitrite (soluble) and nitrate (insoluble) over an intermediate layer formed mainly of copper sulphite and sulphate resulting from the previous interaction of sulphuric acid with cuprite.

Xia Cao et al report the existence of a synergistic effect of chloride and NO$_2$ on the atmospheric corrosion of bronze [6] at 85% relative humidity and temperature 20°C. Corrosion rate was measured by weight loss and EIS. In the same way than other authors, no corrosion products containing Nitrogen were found. A significantly more defective and porous rust layer was found in samples submitted to the mix NaCl + NO$_2$. Thus, the corrosion rate induced by Chloride + NO$_2$ was much higher than that induced by NO$_2$ during the initial corrosion stage and thus a synergistic effect occurs. A proposal that NO$_2$ acts as a catalyst during the corrosion process when the availability of coexistent chloride ions is high was made.

Nowadays there is no clear the influence of pollutants interaction in atmospheric corrosion. Tests carried out under laboratory conditions usually confirm the influence of different contaminants interaction in atmospheric corrosion, but no confirmation in general has been found in field tests. Usually, tests have been carried out in testing chambers and corrosion has been evaluated by weight loss and other methods.

Almost all pollutants show acid character, but also produce different types of anions which could in a different way take part in the corrosion process. It is possible that the influence of anion interaction in atmospheric corrosion could change depending on different factors such as relative humidity, concentration levels of the different pollutants and so on. Synergistic and antagonistic effects could be present.

Copper sensors using circuit printed boards have been developed and used in the present paper in order to measure atmospheric corrosion rate in presence of one or two different anions using Electrochemical Noise. This technique is particularly useful for atmospheric corrosion because it only measures natural current and potential produce by copper in the thin electrolyte layer and it is no depending on electrolyte layer electrical resistance. It is the only electrochemical technique showing this characteristic. Using this electrochemical technique it is possible to obtain data concern-
ing Noise Resistance and Localization Index in a very short time. The influence of anion interaction on copper corrosion can be determined in a relatively short period of time. Actually, direct corrosion rate is not obtained, but Noise Resistance is proportional to the inverse of corrosion rate and a relative value is obtained. To measure in presence of anion mixes of different concentrations allow to compare differences in atmospheric corrosion rate and to determine the influence of anions mixes.

2 Experimental Procedure

2.1 EN and TOW sensors.
Printed circuit copper boards were used to develop copper sensors. Four interdigital copper sensors were obtained using printing screen technique. The following image show the set of sensors developed, three for EN measurements and a fourth one for Time of Wetness (TOW).

Figure 1: Copper sensors developed on a printed circuit board.

Figure 2: Schema of the copper electrodes and circuit for EN and TOW measurement.
2.1 Second-level Heading

The above circuit is based on the use of a Zero Resistance Amp meter for measurement of the electrochemical current (I). Electrochemical potential (V) is measured using an instrumentation amplifier. Small currents can be measured, in the order from nano to micro amperes.

A three electrode system is used for measurement. All electrodes are copper lines presented on the printed circuit board. Current and potential values were determined every 0.5 s during about 3 hours. A set of 2048 values was selected when TOW was constant in order to assure constant conditions of surface humidity. TOW of wetness was constantly measured during all the time of the experiment.

2.2 Salts deposition and Relative Humidity conditions

Chloride deposition rate values representing S1 (15 mg Cl⁻/m²), S2 (150 mg Cl⁻/m²) and S3 (1500 mg Cl⁻/m²) classifications according to ISO 9223 [7] were selected. Surface area of every sensor was measured (0.00159 m²) and a solution allowing to deposited the corresponding amount to obtain the given deposition rate was prepared.

In order to assure a correct distribution of the solution in the sensor surface a filter paper of the same size of the sensor surface was placed on the sensor and the prepared solution was added on the filter paper. It could be considered that the filter paper could represent an inert matrix similar to a corrosion products layer usually presented on the surface of copper.

In this paper, chloride deposition was selected as the higher contribution and low depositions of nitrate were added to the chloride solution to evaluate the possibilities of interaction on corrosion process. Sulphate deposition rates corresponding to P1, P2 and P3 ISO 9223 classifications for SO₂ (supposing only the influence of sulphate anion and not the acid character of SO₂) were added to determine its influence in interaction with chloride ions in atmospheric corrosion of copper. It means that, in this paper, a simulation to a coastal atmosphere has been made with presence of low concentrations of nitrate as possible pollutant in addition to chloride. It has been also simulated a coastal atmosphere with influence of sulphate deposition. In the future, different deposition ratios will be tested. Salt mixes used are presented on Table 1.

A filter paper sheet was also placed in the sensor used for TOW measurement. Chloride solution used corresponded to S1, S2 or S3. The main objective of this measurement is to observed when estabilized conditions of TOW are reached and then select the EN values set to process.
Table 1: Concentrations of chloride, sulphate and nitrate solutions used to obtain contaminant deposition mixes.

<table>
<thead>
<tr>
<th>Chloride deposition + anion deposition (mg/m²)</th>
<th>NaCl conc. (mg/mL)</th>
<th>Vol. used (mL)</th>
<th>Na₂SO₄ conc. (mg/mL)</th>
<th>Vol. used (mL)</th>
<th>NaNO₃ conc. (mg/mL)</th>
<th>Vol. used (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-15 Cl⁻</td>
<td>0.039</td>
<td>1</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>S2-150 Cl⁻</td>
<td>0.393</td>
<td>1</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>S3-1500 Cl⁻</td>
<td>3.93</td>
<td>1</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>S1Cl⁻+0.15 NO₃⁻</td>
<td>0.049</td>
<td>0.8</td>
<td>-</td>
<td>0</td>
<td>0.016</td>
<td>0.2</td>
</tr>
<tr>
<td>S2Cl⁻+1.5 NO₃⁻</td>
<td>0.491</td>
<td>0.8</td>
<td>-</td>
<td>0</td>
<td>0.163</td>
<td>0.2</td>
</tr>
<tr>
<td>S3Cl⁻+15 NO₃⁻</td>
<td>4.91</td>
<td>0.8</td>
<td>-</td>
<td>0</td>
<td>1.63</td>
<td>0.2</td>
</tr>
<tr>
<td>S1Cl⁻+20 SO₄²⁻</td>
<td>0.049</td>
<td>0.8</td>
<td>0.352</td>
<td>0.2</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>S2Cl⁻+40 SO₄²⁻</td>
<td>0.491</td>
<td>0.8</td>
<td>0.704</td>
<td>0.2</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>S3Cl⁻+100 SO₄²⁻</td>
<td>4.91</td>
<td>0.8</td>
<td>1.76</td>
<td>0.2</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

Two levels of RH were established: water saturated atmosphere and about 80% RH. An hermetic plastic box was used to place inside the four sensors. A vessel containing distilled water was placed into the box containing sensors to obtain a water saturated atmosphere at room temperature (25-28°C). The box was closed and measurement of EN signal began 0.5 hours after closing the box. Data for processing was selected after about 7500 s starting measurement according to the information obtained from TOW sensor.

An atmosphere of about 80% relative humidity was obtained by placing a water-glycerine solution containing 40% by weight of glycerine.

Figure 3: Schema of the measurement system used for EN and TOW determination.
3 Results and Discussion

3.1 Role of Relative Humidity and chloride deposition on copper corrosion.
Noise resistance (Rn) determined on copper sensors at different airborne salinity classifications and two RH conditions is presented on figure 4. It can be observed that Corrosion Rate (proportional to 1/Rn) is higher when RH= 80% for S1 and S3 salinity classification and almost equal for S2 classification. It is very well known that Oxygen diffusion is an important factor in atmospheric corrosion and in the case of RH=80% there are better conditions for oxygen diffusion because water layer is thinner. Under this base, it is normal that copper corrosion is higher when RH=80 % respecting water saturated atmosphere. In the case of S2 classification, perhaps the influence of the existing concentration of chloride could compete with oxygen diffusion and a similar corrosion rate is obtained.

![Figure 4: Noise Resistance (Rn) vs Chloride Deposition Rate classification according to ISO 9223 at two different conditions of RH.](image)

Respecting chloride deposition, copper corrosion is higher at S2 classification in a water saturated atmosphere and at S1 classification at RH about 80%. It seems that the influence of chloride ions on corrosion does not show a linear relation with corrosion. Perhaps non linear dynamic studies should be performed. Localization index (IL) vs chloride deposition classification is presented on figure 5. It can be observed as a coincidence, the higher IL corresponds to S2 classification in water saturated atmosphere and at RH=80%. For the higher corrosion a higher localization index is found. It is possible that under S2 classification, conditions for localized corrosion occurrence improve and a higher corrosion rate is obtained.
3.2 Role of sulphate and nitrate additions to chloride solutions on copper corrosion in a water saturated atmosphere.

The behaviour of sulphate and nitrate additions to solutions of chloride corresponding to three deposition classifications established on ISO 9223 is shown on figure 6. It is clearly observed that the presence of sulphate or nitrate ions causes an increase of corrosion rate in a water saturated atmosphere. Nitrate deposition rate is lower in magnitude than sulphate. Perhaps it could be the cause of a higher corrosion in the case of sulphate respecting chloride without addition and chloride added with nitrate ions. Respecting Localization Index (IL) it is interesting to note that under nitrate addition (figure 7) the lowest IL are obtained, that is, corrosion tends to have a more uniform character, but the addition of sulphate increases IL excepting at chloride classification S2. As we have seen above, the behaviour of Rn and IL at S2 deposition rate is different and should require a deeper study, possibly using non linear dynamic.

Figure 5: Localization Index (IL) vs Chloride Deposition Rate classification according to ISO 9223 at two different conditions of RH.
Figure 6: Noise Resistance (Rn) vs chloride deposition classification with and without addition of sulphate and nitrate ions in a water saturated atmosphere.

Figure 7: IL vs chloride deposition classification with and without addition of sulphate and nitrate ions in a water saturated atmosphere.
3.2 Role of sulphate and nitrate additions to chloride solutions on copper corrosion at about 80% of relative humidity.

The behaviour of sulphate and nitrate additions to solutions of chloride corresponding to three deposition classifications established on ISO 9223 is shown on figure 8. It can be observed that corrosion rate decreases with addition of sulphate and nitrate at S1 and S3 chloride classification, but a different behaviour is obtained for S2. For IL, a different behaviour to a saturated atmosphere is obtained, because the addition of nitrate increases IL at S1 and S3 chloride classification, but decrease at S2 classification. A significant difference exists respecting water saturated atmosphere. It shows a significant influence of RH in determining the role of anions in corrosion electrochemical process. The addition of sulphate increases IL at S1 and S3 chloride classification, but decrease at S2 classification. There is no doubt that a different behaviour occurs at S2 chloride classification. A deeper analysis should be made in this sense.

![Figure 8: Noise Resistance (Rn) vs chloride deposition classification with and without addition of sulphate and nitrate ions in an atmosphere of about 80% relative humidity.](image)
4 Conclusions

- A new set of sensors for determining atmospheric corrosion based on Electrochemical Noise has been developed using copper printed circuit boards. This set includes a sensor for Time of Wetness determination.
- A significant interaction of sulphate and nitrate ions on corrosion process in chloride solutions corresponding to S1, S2 and S3 chloride deposition classifications has been found.
- Interaction significantly changes from a water saturated atmosphere to about 80% relative humidity.
- The character of the interaction is different for S2 chloride deposition classification. It could be caused by non linear dynamic processes and should be investigated.
5 References

[1] Vladimir Kucera, S. Fitz, Direct and indirect air pollution effects on materials including cultural monuments, Water, air and soil pollution, 85, 153-165, 1995.