CORROSIVITY OF ATMOSPHERES
IN RELATION TO AMBIENT AIR QUALITY

Andrei Vasile, Elena Bucur, Mihaela Petrescu

National Research and Development Institute for Industrial Ecology – INCD ECOIND, 71-73 Drumul Podu Dambovitei street, sector 6, zip 060652, Bucharest, Romania
poluare.aer@incdecoind.ro

Introduction

Atmospheric corrosion is not a very clearly defined subject. It occupies the territory between immersed corrosion and dry oxidation, since metals may be exposed to damp atmospheres or may be subjected to the full force of the weather. It is usually taken to include packaging and storage, painting and preparation for painting, and the effects of climate and air purity.

Metals exposed to uncontrolled "normal" atmospheres may corrode more rapidly and by different mechanisms than those kept in pure, dry air – even if they are not exposed to rain.

In dry atmospheres, the growing oxide film usually protects the underlying metal, giving rise to a logarithmic or square-root time law. In uncontrolled atmospheres, the rate usually remains constant for a period, but may fall off when the film has grown to an appreciable thickness. If the metal is exposed to

rain, it may corrode while it is wet at the rate appropriate to immersion in impure, well-aerated water, but the rate will fall when it dries. Equations for predicting rates of atmospheric corrosion must therefore contain a term for "time of wetness" as well as for average temperature, average relative humidity, atmospheric purity and so on.

These equations are of limited value because it is almost impossible to specify the local conditions sufficiently precisely. Detailed results are often difficult to rationalise but in general it is clear that persistent wetness, high temperatures and contamination by strong electrolytes are responsible for the highest rates of corrosion.

Rates of rusting in impure controlled atmospheres without the complication of rain are low if the relative humidity is kept low, and remain fairly low even at 100% RH in the absence of strong electrolytes. The rate increases sharply at some RH in the region of 60-80% if the surface is contaminated with particles of sodium chloride, or ammonium sulphate, or if the atmosphere contains sulphur dioxide.

Vernon showed that there was an increase in rate at about 60% relative humidity even in pure air, and a further sharp increase at 80% in the presence of 0.01% of sulphur dioxide. The increase was larger and the corrosion product less protective if the surface was contaminated with particles of charcoal. More recent evidence suggests that the SO_2 content in this work was unrealistically high, and that higher RH is needed to initiate rapid corrosion with 1 ppm SO_2 or less. In general, it seems that the "critical" relative humidity is set by the vapour pressure of some salt hydrate in the corrosion product, and that chlorides and sulphates are the most effective corrosive agents.

The effect of moist atmospheres is to set up droplets of some strong electrolyte with the classical pattern of corrosion with a small anode in the centre of the drop acting as a source of ferrous ion and oxygen-reduction cathodes at the edges producing hydroxyl ion. Such droplets become covered by a transparent skin, presumably of ferrous hydroxide, which darkens and thickens and eventually runs through the range of hydrated ferric oxides up to Goethite and lepidocrocite. According to atmospheric conditions, these droplets may remain as discrete scabs, or may spread, or produce tracks that wander over the surface. When the rust layer is completed, the metal surface may become starved of oxygen, and it is quite common for a layer of Fe3O4 to form under the hydrated rust. The presence of corrosive salts will, however, prevent this layer from becoming very protective.

Vernon showed that a carefully cleaned steel specimen would not rust even in a normal laboratory atmosphere if it was enclosed by muslin stretched over a wire frame. The protective oxide film continued to develop, and if the specimen was removed from the enclosure after, say, a year, it would remain unaffected by dust particles, perhaps for several weeks, before spots of rust appeared.

Factors conducive to rusting of iron and steel are therefore:

- Sensible moisture High RH (above 70-80%)
- Salt mist
- Surface contaminants (dust, sweat residues, soldering fluxes, etc)
- Atmospheric contaminants (SO2, HCl, organic acids)
- High temperature.

Case study

This paper presents the results of a study ordered by the biggest Cogeneration Plant from Romania, started in November 2012 and finished in August 2013. The study involves three stages of air quality and meteorological parameters monitoring. Each stage was 30 days long, and was developed in represented periods of the year (November, April and July). The main objective of the study was to establish the potential influence of the ambient air quality and meteorological parameters, on the corrosion of metals and alloys. Because the Cogeneration Plant is located nearby a very big Refinery Plant, another important objective was to establish the influence of the Refinery Plant on the quality of ambient air from the area. Because the Cogeneration Plant uses natural gas in order to produce electricity so they have a small level of emissions, it was expected that the Refinery Plant to be the main polluter from the area

In addition to running in normal conditions in open environment of any industrial equipment, in the case of cogeneration plant installations, atmospheric air is used in the process of burning natural gas. In these conditions, ambient air quality and the level of chemical air pollution and weather conditions can cause corrosion of the equipment. It is therefore of great interest to know the level of air pollution in the area and determine / estimate the degree of corrosivity of the atmosphere, the overall objective of this study.
In order to assess the ambient air pollution level and to obtain sufficient informations necessary for forecasting the atmospheric corrosivity, have been developed a number of three air quality monitoring campaigns lasting 30 days each, distributed in 2012 to 2013 so as to provide enough data whose average can characterize pollution and weather conditions specific to a calendar year.

Specific indicators of ambient air pollution have been monitored, including: particulate (PM 2.5 , PM10 and sediment particles NO_2, SO_2, CO, metals from dust (lead, cadmium and nickel) ions soluble in water (Na^+, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, NO_3^- from particulate matter and PO_4^{3-}, NO_3^-, Cl^- in particulate sediment). Weather paramters where also monitored: temperature, pressure, humidity, wind speed and direction.

For the specific indicators of ambient air pollution have been used the following methods and equipments, as indicated in *Table no. 1.*

Table no. 1 *Indicators, methods and equipment used for air quality monitoring*

Indicator	Method	Equipment
0	*1*	*2*
PM 2.5, PM10 and sediment particles	Gravimetric	Sven Leckel
NO_2	Chemiluminescence	Environment MMS

0	1	2
SO_2	Fluorescence	Environment AF22
CO	Infrared	Environment MMS
Metals from dust (lead, cadmium and nickel)	Atomic absorption spectroscopy	Varian 280
Ions soluble in water (Na^+, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, NO_3^- from particulate matter	Ion chromatography	Thermo Scientific
PO_4^{3-}, NO_3^-, Cl^- from particulate sediment	Ion chromatography	Thermo Scientific

Both the automated equipments for air quality monitoring and those for metheorological parameters monitoring were installed on a mobile test van designed to provide special environmental conditions necessary for the operation of these equipments.

Data interpretation

Analyzing the results obtained in the three periods of ambient air quality monitoring as compared with the limit imposed by environmental legislation in force, namely:

- Law 104/2012 on ambient air quality for daily average values for SO_2 and PM10 and NO_2 hourly;
- STAS 12574-87 - Air-protected areas. Terms of quality, where the average daily values of cadmium and nickel and monthly average sediment particles.

It can be seen that, in general , concentrations of air pollutants are below the permissible limit values with some exceptions in the case of PM 10 particulates that have exceeded the maximum permitted levels in 12 of the 90 monitored days in October - November 2012, period that can be caracterized by a big number of neighboring demolition and construction activities. In general, the concentrations of dust in this period are higher than in the other two test periods .In these conditions we can say that given the profile of the unit and its location in the vicinity of Rafinery, the level of ambient air pollution at the point where monitoring was conducted , located inside the unit, is situated in the field of a specific industrial areas.

Data interpretation for the corosivity of atmosphere was made based on international standards, leading the SR EN ISO 9223:2012 standardization. This is the standard by which we can achieve corrosiveness estimate by calculating and comparing the measured values for ambient air pollutants and meteorological factors with reference values. Key factors are specified in atmospheric corrosivity of metals and alloys, namely:

- Humidity-temperature system;

- Pollution with sulfur dioxide;
- The degree of salinity of the air, expressed as the concentration of Cl⁻ in dust.

Atmospheric corrosivity around th cogeneration plant was estimated by monitoring the atmospheric pollutants affecting air quality and meteorological factors mainly for the duration of the determinations. According to the standard were established six categories of corrosivity of the atmosphere, as shown in *Table no. 2*.

Tabel no. 2 *– Categories of corrosivity*

Category	Tipe of corrosivity	Rate of corrosivity for steel (µm/a)
C1	Very Low	$r_{corr} \leq 1.3$
C2	Low	$1.3 < r_{corr} \leq 25$
C3	Medium	$25 < r_{corr} \leq 50$
C4	High	$50 < r_{corr} \leq 80$
C5	Very High	$80 < r_{corr} \leq 200$
CX	Extreme	$200 < r_{corr} \leq 700$

Framing in one of the six categories of corrosion is achieved by determining or estimating the corrosiveness, respectively. Both methods represent a generalized approach and are characterized by uncertainties and limitations.Given the specificity of the Air Pollution Control Laboratory of INCD ECOIND and requests of the Power Plant management to execute the measurements in order to characterize air pollution and related environmental factors of the site area, the method chosen to evaluate its corrosiveness is estimation, starting from the most important factors specified in evaluation standards, namely SO_2 concentration, humidity, ambient temperature and the concentration of Cl-in the dust.

According to the standard, the estimation of corrosive attack after the first year of outdoor exposure is achieved depending on the concentration of SO2, particulate chlorine concentration, temperature and humidity. Relationships for calculating exposure based on the results of corrosion worldwide and covers all types of climate and pollution situations.Dose-response equation to calculate the loss of material due to corrosiveness of the first year for steel is defined as:

r_{corr} = 1.77*$P_d^{0.52}$* exp (0,020* RH + f_{St}) + 0.102* $S_d^{0.62}$* (0.033* RH+ 0.040*T);
f_{St} = 0.150* (*T*-10) where *T* ≤ 10 °C; so -0,054 (*T*-10);
r_{corr} = rate of firs year corrosion for a mettal, expressed in µm/an;
T   = anual average temperature, expressed in Celsius degrees (°C);
RH = annual average humidity expressed in percents (%);

P_d = annual amount deposited of SO_2, expressed in milligrams per square meter per day [mg/(m^2*z)];

S_d = annual amount deposited of Cl$^-$, expressed in milligrams per square meter

per day [mg/(m^2*z)].

Methods for determining SO_2 by volumetric method Pc and Pd by deposition method is considered to be equivalent using the formula Pd = 0.8 Pc [Pd in mg / (m^2 * z) and Pc g/m^3];

The data needed to estimate atmospheric corrosiveness in the studied area , ie SO2 concentration , humidity , ambient temperature and the concentration of Cl- in the dust in the three test periods are presented in Table no. 3 .

Table no. 3   Data used to establish air quality and the corrosivity of atmosphere in the first year

No.	November 2012			April 2013			July 2013		
Crt.	SO$_2$	RH,	Temp.	SO$_2$	RH	Temp	SO$_2$	RH	Temp
	µg/Nm^3	%	C	µg/Nm^3	%	C	µg/Nm^3	%	C
1	25.6	71	16	21.3	68	7	32.4	75.4	21.3
2	31.3	69	17	43.8	71	8	28.9	76.7	20.6
3	28.6	74	15	51.7	75	8	29.4	60.9	22.7
4	11.9	67	16	39.6	69	9	31.8	65.4	22.7
5	13.2	71	15	41.3	62	8	35.4	63.2	23.5
6	25.4	68	18	37.6	65	6	34.1	55.7	23.1
7	27.9	66	16	36.8	77	7	35.3	57.1	22.4
8	21.4	73	16	13.5	71	7	41.2	64.3	20.6
9	36.7	71	17	22.7	74	6	30.4	71	19.7
10	44.2	69	16	34.9	75	9	29.6	62.2	21.9
11	27.6	82	15	26.4	81	12	68.7	60.1	22.5
12	29.3	63	13	48.9	80	12	75.4	60.7	23.5
13	19.3	65	14	45.3	72	15	52.9	57.4	24.5
14	18.7	77	16	74.9	64	14	47.6	52.4	21
15	19.7	72	16	94.2	57	12	33.9	57.3	21.7
16	28.4	59	15	65.3	51	13	36.7	55.8	22.9

17	96.4	61	13	31.5	45	12	39.9	51.5	23.7
18	82.1	53	14	29.7	45	12	22.3	46	24.9
19	66.3	54	12	26.1	56	13	75.9	61.1	23.3
20	18.1	67	14	22.4	53	14	76.1	64.4	23.1
21	44.1	74	14	27.4	55	15	42.1	58	25.3
22	31.3	83	13	31.3	56	14	36.8	54.6	27.9
23	45.2	81	6	34.5	58	15	22.5	56.7	27.5
24	59.4	62	9	38.9	53	19	68.3	78.6	21.8
25	76.2	81	6	21.3	45	20	58.4	62.4	24.7
26	61.4	83	12	65.3	46	19	32.5	57.2	24.7
27	53.9	70	12	76.9	49	21	33.8	51.6	26.2
28	69.5	69	13	34.2	50	22	22.3	55.3	24.7
29	34.2	73	11	42.5	49	22	24.9	52.7	24.7
30	30.3	76	13	38.5	50	23	45.9	51.7	25.8
31							35.9	50	26.3
average	39.25	70.1	13.8	40.62	60.7	13.1	41.33	59.6	23.52
median	30.8	70.5	14	37.2	57.5	12.5	35.4	57.4	23.3
Average of averages			**40.4**	**63.5**	**16.8**	**r corr**	**28.3**	**µm/an**
Average of medians			**34.5**	**61.8**	**16.6**	**r corr**	**25.5**	**µm/an**

To estimate the corrosion rate were taken into account soluble chloride concentrations of particulate matter from the three test periods, the average of the three periods: 1082 mg/m2/day.

Corrosion rate in the first year was calculated in two situations: using the average median indicators and indicators on others using three test periods treated as average / median annual after removing conflicting values. Characterization of data series, including the calculation of the mean and the median was performed using statistical data treatment software Analise-it.
In both cases, on the base of corrosion rate, atmospheric corrosivity falls to the lower limit of category C3 – Medium corrosivity.

Conclusions

To assess ambient air pollution level and to obtain information necessary for forecasting the atmospheric corrosivity, three air quality monitoring campaigns lasting 30 days each have been done, distributed in 2012 to 2013 in order to

provide necessary data of the environment to characterize pollution and weather conditions specific to a calendar year.

Specific indicators of ambient air pollution have been monitored, including: particulate (PM 2.5 , PM10 and sediment particles NO_2, SO_2, CO, metals from dust (lead, cadmium and nickel) ions soluble in water (Na^+, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, NO_3^- from particulate matter and PO_4^{3-}, NO_3^-, Cl^- in particulate sediment). Weather paramters where also monitored: temperature, pressure, humidity, wind speed and direction.

Analyzing the results obtained in the three periods of ambient air quality monitoring can be seen that, in general, concentrations of air pollutants are below the permissible limit values with some exceptions in the case of PM 10 particulates that have exceeded the maximum permitted levels in 12 of the 90 monitored days in October - November 2012, the period in which they were conducted a number of the neighboring demolition and construction activities. In general, concentrations of dust in this period are higher than in the other two test periods.

In these conditions we can say that given the profile of the unit and its location in the vicinity of Rafinery, the level of ambient air pollution at the point where monitoring was conducted , located inside the unit , is situated in a field of a specific industrial areas.

To estimate the atmospheric corrosiveness in the area of the Cogeneration Plant, we used mainly the following indicators : SO_2 concentration, humidity and ambient temperature and the concentration of Cl^- in the dust in the three periods. Corrosion rate in the first year was calculated in two situations: using the average median indicators and indicators on others using three test periods treated as average/ median yearly. In both cases, the rate of corrosion , atmospheric corrosivity falls to the lower limit of category C3 – medium corrosivity .

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