Atmospheric Corrosion of Copper, Interpretation and Modeling

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Abstract

Atmospheric corrosion of metals is affected by many factors related to the environment, and the metal as well. Atmospheric corrosion of copper attracts a considerable attention due to the wide application of copper objects in this medium. Copper samples were exposed to the atmospheric attack in 8 testing sites in the R. N. Macedonia over a period of 13 years. The weight loss was measured in increasingly long intervals, as e.g. 3, 6, 12 etc. months. Each specimen served for only one period of exposure. Further treatment of the randomly scattered results followed. The familiar parabolic-like pattern of corrosion rate *vs.* time plots were registered. The corrosion process course is burdened with the impermeable properties of accumulated corrosion products on top of the copper surface. Interpretation of acquired results was not an easy task due to the intermittent course of process affected by the continuous changes of corrosion affecting parameters (wetness, pollution, sun radiation, etc.). Special attention was paid to the effects of the atmospheric conditions during primal exposure, specimen surface orientation (skyward or groundward), number of duplicated specimen, because they could affects the results. A development of model based on the premise that the atmospheric corrosion of metals is not a smooth and continuous process, but is rather sequential was performed. Such approach gives possibility to deal with this multivariable phenomenon that ends in scattered data.

Keywords: long-term exposure; results treatment; buildup of models.

1. Introduction

Atmospheric corrosion of metals was subject of wide scientific and technical interest [1-3]. Corrosion mechanism, kinetics, product properties, etc. were and still are investigated worldwide [4-7]. As result, many important data were acquired. It seems that at present time we know practically everything about this phenomenon. Then, why need for further dealing with it? The answer is: because it is still difficult to tailor the effects of parameters variation or to predict the long term behavior based on short term or accelerated testing [8 - 10].

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Atmospheric corrosion of copper was over a long period subject of study of our group at the Faculty of Technology and Metallurgy, and continues to be of concern. Both experiments with outdoor exposure of copper, experiments in the lab, as well as literature studies were performed since the 1980s. The acquired results were only qualitatively related to the atmospheric conditions recorded over the same period, the records being provided by the official weather reporting services. Unfortunately, more detailed studies were not done due to the lack of more sophisticated equipment. The results of the outdoor exposure are the most valuable do to their duration (up to 13 years), spread location of testing sites and the number of duplicate samples. A brief summary of these results are summarized further in this paper. Next, the effect of the exposure conditions (i.e. the prime corrosion products), the direction of specimen exposure (skyward or groundward), the number of identical samples to the result's statistical exactness were studied as well [11, 12].

2. Experimental

The corrosion rate was studied by measuring the weight loss of copper, 99.99% specimen according to the pretreatment recommended by ASTM-B-117 and G1-81 standards, as described elsewhere [13]. Copper plates of 100x200x2 mm were grinded with fine emery paper, degreased with acetone, immersed in 1:1 de-aerated solution of hydrochloric acid and water, rinsed in distilled water and dried. The same procedure was applied and after the plates exposure. In order to determine the size of duplicate samples, series of 10 samples each were exposed during 3, 6 and 12 months and the results subjected to statistical treatment. It was find that the mean value of three samples differs from the mean value of ten samples for ±12 %. So, the three samples size was chosen as the optimal number [11].

Table 1: Testing sites characteristics.

Test site	Altitude, m	Climate type	RH, average %	Aggressiveness (estimated)
Skopje	301	Urban/Industrial	67	4
Veles	175	Industrial	70	5
Bitola	586	Urban	67	3
Ohrid	760	Urban/Rural	66	2
Lazaropole	1332	Rural	74	0
Demir Kapija	123	Rural	65	1
Berovo	824	Rural	74	1
Miladinovci	335	Industrial	–	3

The plates were exposed mounted at the platforms in 8 testing sites as shown in Table 1. Each withdrawn sample was substituted with a new one, and so the volume of exposure was increased. Doing so, maximal number of specimen were exposed, but with different conditions during the initial exposure. At the end of testing this practice appeared to be useful to gain more complex insight.

3. Results

The copper corrosion rates during the 13 years of exposure did varied from site to site, and within individual sites as well. The problem how to present the results was bypassed by choosing one location to start with. Thus, in Table 2 the complete list of testing events in Veles is given. It contains the history of 18 samples exposed in

5 turns over 3 years, i.e. the time of start and the duration of exposure, the weight loss (individual and mean weight loss value and specific weight loss (mg dm^{-2}), and finally the corrosion rate in MDD (linearized value for the whole exposure period).

Table 2: Results of testing in Veles for exposures started in different seasons of 3 years.

Exposure, start	Exposure, days	ΔM_1 mg	ΔM_2 mg	ΔM_3 mg	ΔM_{mean} mg	K mg·dm^{-2}	Rate, MDD
24.05.1985	111	86.0	/	/	86.0	21.50	0.193
07.05.1986	132	/	210.0	150.0	180.0	45.00	0.292
19.04.1984	196	213.0	/	/	213.0	53.25	0.270
19.04.1984	289	333.3	/	/	333.3	83.25	0.280
07.05.1986	365	330.0	370.0	330.0	343.3	85.83	0.230
19.04.1984	400	439.1	/	/	439.1	109.77	0.274
19.04.1984	511	512.0	/	/	512.0	128.00	0.250
19.04.1984	748	836.3	/	/	836.3	209.07	0.270
07.05.1986	764	/	670.0	840.0	755.0	188.75	0.247
19.04.1984	880	934.0	/	/	934.0	233.50	0.265
12.09.1985	1001	1128.0	/	/	1128.0	282.00	0.281
07.05.1986	1119	/	820.0	750.0	785.0	196.25	0.175
16.09.1986	1400	1000.0	1264.0	1160.0	1141.3	285.33	0.203
19.04.1984	1867	1323.0	/	/	1323.0	330.75	0.177
07.05.1986	1902	/	1380.0	1480.0	1430.0	357.50	0.187
19.04.1984	2650	1704.8	/	/	1704.8	426.20	0.160
19.04.1984	3170	1801.7	2020.5	/	1911.1	477.77	0.150
07.05.1986	3841	1650.0	/	/	1650.0	412.50	0.107

Data in Table 2 are organized according to the duration of exposure from 0.33 up to 10.5 years (i.e. from 111 to 3841 days). The following irregularities were detected in this table:

- The weight loss values ΔM (mean) do not increase regularly with time of exposure. The increase is continual up to the exposure of 1.4 years, and further becomes irregular, i.e. changes are up and down, as e.g.:

… 512, 836.3(?), 755, 934, 1128, 785(?), 1141.3 (?) …

- The irregularity is even more obvious in the changes of corrosion rate, e.g.:

… 0.193, 0.292 (?), 0.270, 0.280, 0.230 (?), 0.274, 0.247 (?), 0.265, 0.281, 0.175(?) …

- The duplicate specimen show variations in weight loss of some 11 %, in the following items:

raw 2 (210, 150); raw 5 (330, 370, 330); raw 9 (670, 840); raw 13 (1000, 1264, 1160)

Due to the above irregularities, no diagram was drawn with all of the data in Table 2. Instead, only tests that did initiate at the same time were used for graphical presentation. In Fig. 1 two plots are shown, one for the series exposed on 19. April 1984 (9 samples) and on the other for the series exposed on 07. May 1986 (6 samples).
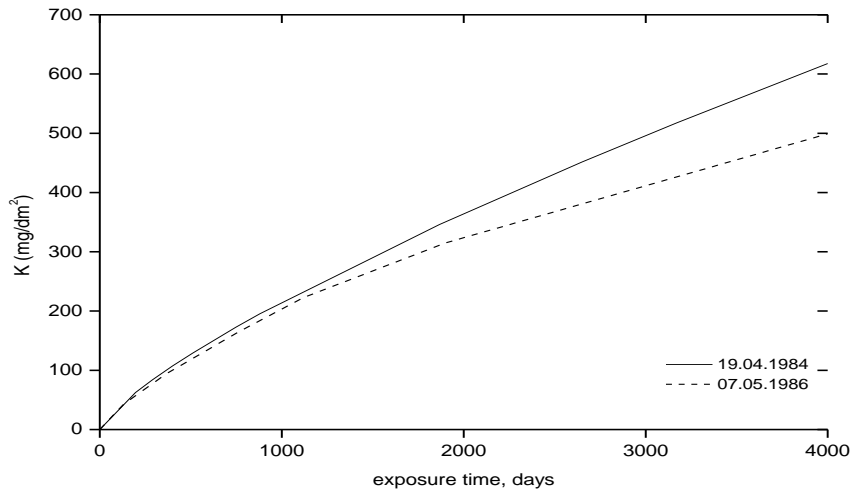
Figure1: Weight loss vs. time of exposure for test site in Veles for different exposure date.

It was found that these experimental series do follow parabolic relation of the type

$$K = a \cdot t^n \quad (1)$$

where $\underline{a}$ and $\underline{n}$ ($n < 1$) are constants influenced by the atmosphere corrosiveness and the properties of formed corrosion product (*patina*). The calculated parabolic relations are:

- For the series exposed at 19.04.1984: $K = 1.13 \cdot t^{0.76}$
- For the series exposed at 07.05.1986: $K = 1.54 \cdot t^{0.697}$

Corresponding correlation factors ($\underline{r}$) are 0.988 for the former and 0.985 for the latter case. Such values confirm that the experimental data considerably fit into parabolic low. This is also visible from the values of the discrepancy ΔK between the measured and calculated weight loss given in the last columns of tables 3 and 4. The discrepancies are up to -17.4% in former, and up to 17.6% in latter series. Having in mind how simple procedure was applied in cleaning the specimen surface, these figures are quite satisfactory.

Table 3: Copper series exposed in Veles on April 19. 1984.

Exposure, days	K measured mg·dm^{-2}	K calculated mg·dm^{-2}	ΔK, %
196	53.25	62.40	17.1
289	83.25	83.82	0.6
400	109.77	107.31	-2.2
511	128.00	129.26	0.9
748	209.07	172.68	-17.4
880	233.50	195.38	-16.3
1869	330.75	346.05	4.6
2650	426.20	451.59	5.9
3170	477.77	517.46	8.3

Table 4: Copper series exposed in Veles on May 07. 1986.

Exposure, days	K measured mg·dm^{-2}	K calculated mg·dm^{-2}	ΔK, %
132	45.00	46.29	2.8
365	85.83	94.06	9.5
764	188.75	157.55	– 16.5
1119	196.25	205.37	4.6
1902	357.50	297.25	– 16.8
3841	412.50	485.15	17.6

Similar treatment of the experimental data for the rest six sites are summarized in Table 5. Data in Table 6 provide indications that the exponent n in the parabolic equation varies between testing sites in a mainly narrow interval of values for all 7 sites. The pre-exponential constant a varies in a wider interval. Correlation factor's r values are mainly close to the maximal value of 1. More data are needed for drawing quantitative conclusions about the effect of exposure condition.

Table 5: Exposure time, specific weight loss and discrepancy between K_m and K_c for copper in 6 locations.

Location	Exposure days	Spec. weight loss mg·dm^{-2}		ΔK %	Location	Exposure days	Spec. weight loss mg·dm^{-2}		ΔK %
		$K_{measured}$	$K_{calculated}$				$K_{measured}$	$K_{calculated}$	
Skopje 1	93	33.30	25.90	– 22.22	Skopje 2	140	42.50	44.86	5.55
	192	42.50	45.26	6.49		365	92.50	88.75	– 4.05
	309	46.75	65.29	39.65		1057	202.50	189.23	– 6.55
	532	103.25	99.21	– 3.91		1189	192.50	205.77	6.89
	672	125.25	118.76	– 5.18		1303	231.25	219.63	– 5.02
	1589	242.25	230.40	– 4.89		1939	310.00	291.48	– 5.97
	2445	338.75	321.07	– 5.22		2435	336.25	342.79	1.94
	2967	429.92	372.65	–13.32		3222	386.25	418.44	8.33
	3754	413.75	446.67	7.95					
Demir Kapija 1	115	27.25	22.44	– 17.65	Demir Kapija 2	360	62.50	63.70	1.92
	178	30.00	29.19	– 2.70		795	98.75	97.31	– 1.45
	289	28.25	38.80	37.34		1115	112.50	121.07	7.61
	531	53.50	55.69	4.09		1897	187.50	163.73	– 12.67
	658	62.50	63.26	1.21		2293	193.75	182.34	– 5.88
	1646	120.00	109.05	– 9.12		3775	217.50	242.03	11.27
	2428	156.70	137.38	– 12.32					
	2824	182.00	150.28	– 17.47					
	4306	182.50	193.08	5.79					
Lazaropole	200	73.75	81.45	10.44	Berovo	143	70.25	77.75	10.67
	363	118.25	110.19	– 6.90		475	220.25	151.74	– 31.10
	694	168.50	153.06	– 9.16		760	160.25	197.15	22.83
	1345	205.00	214.07	4.42		1102	248.75	242.48	– 2.52
	1713	248.75	241.99	– 2.71		1638	272.00	302.39	11.17
	2461	301.50	290.79	– 3.55		2243	418.75	360.25	– 13.98
	4646	399.25	401.33	33.11		2757	384.25	404.12	5.17
Bitola	147	68.33	66.11	– 3.24	Ohrid	371	108.70	108.05	– 0.60
	370	121.66	123.06	1.15		594	153.25	149.02	– 2.76
	798	200.83	206.43	2.78		1382	273.00	265.28	2.82
	1160	252.50	265.52	5.15		2124	398.25	355.79	– 10.66
	1900	389.16	370.10	– 4.89		2608	481.75	409.34	– 15.03
	2384	440.00	431.17	– 2.00					

Table 6: Calculated values of <u>a</u> and <u>n</u> in $K = a \cdot t^n$ for all testing sites.

Testing site	a	n	r
Veles, exposure 1	1.13	0.78	0.988
Veles, exposure 2	1.54	0.697	0.985
Skopje, exposure 1	0.73	0.785	0.985
Skopje, exposure 2	1.2	0.729	0.997
Bitola	2.3	0.673	0.998
Ohrid	1.9	0.683	0.993
Berovo	4.9	0.557	0.946
Demir Kapija, exp. 1	1.0	0.637	0.979
Demir Kapija, exp. 2	1.4	0.631	0.990
Lazaropole	4.8	0.53	0.990

The goal of corrosion testing and research sometimes has been simplified to determination of relative aggressiveness of different atmospheres, over time periods as long as 10 or 15 years or more [14 – 16]. Recently, a broad list of more sophisticated research, reaching highlights in computer aided registration of a complete set of corrosion relevant parameters as, e.g. time of wetness, complete pollution and meteorological data, composition of the corrosion products has been applied and covers wide geographical regions [17, 18]. As a result, the corrosion behavior of many metals and alloys in given atmospheres was determined and regularities of the effect of exposure duration, composition and pollution of both partners in the corrosion reaction were suggested. Despite of it, a general theory that explains the intrinsic nature of atmospheric corrosion of copper and other metals is still missing.

Copper metal and its alloys are highly prized due to the aesthetically pleasing patina that protects them from further corrosion. Patina's composition, structure, appearance and protective properties were subject of number of investigation [19 – 21]. It was confirmed that initially a film of cuprite (Cu_2O) is formed, and latter a layer of hydrated CuO is built on top of it. Protective nature of the cuprite sub-layer is responsible for the decreasing corrosion rate with exposure. The corrosion rates in atmospheric exposures outdoors being two orders of magnitude greater than corrosion rates indoors, indicate that the protective nature of the cuprite film is degraded by the presence of a water layer on its surface. Outer layer of brochantite as individual crystals on the cuprite surface causes the patina's green color. In atmospheres with sulfur containing species copper sulfate precipitates over exposure and gradually transforms in crystalline posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$).

Analytical techniques as microscopic, spectroscopic and electrochemical were employed for in-depth investigations of patina's surface characteristics and bulk properties. Auger electron spectroscopy, X-ray photoelectron spectroscopy, and glow discharge optical emission spectroscopy were employed for surface chemical composition analysis. Atomic absorption spectroscopy, cathodic reduction and electrochemical impedance spectroscopy were used as well for different purposes. Other sophisticated techniques were used to identify the phases of corrosion products.

The presence of compounds such as carbon dioxide (CO_2), ozone (O_3), ammonia (NH_3), nitrogen dioxide (NO_2), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), hydrogen chloride (HCl) and organic acids were identified as dominant corrosive species. Aerosol of chlorides (Cl^-) and sulfates (SO_4^{2-}) are corrosion stimulators [22]. In many outdoor exposures it was found that corrosion process is mainly influenced by chloride ions and/or sulfur

dioxide and climatic factors such as relative humidity and temperature.

4. Discussion

The existing habit to express the progress of the atmospheric corrosion reactions as a function of time, e.g. $\Delta K = a \cdot t^n$, is successful for rough mathematical description only. Analysis given bellow is an attempt to produce deeper insight in this matter.

A proof that the atmospheric corrosion is not a continuous and smooth process could be produced if measurements were taken as frequently as possible. The acquired data will show the periods of steep rate increase in the 'wet' months of the year, as opposite to the behavior in summer months. Each period of constant corrosion rate is to be regarded as a separate sequence, while the integral process is a sum of all sequences.

In Fig. 2 two idealized situations are presented, i.e. (1) individual corrosion damage in each time unit is constant, and (2) individual corrosion damage decreases uniformly with time. The sequences with damage are followed by sequences without any corrosion. Summarizing the individual constant damages, a stepwise but linear cumulative plot is constructed (Fig. 2, plot 1). Doing the same, but with the sequences of decreasing corrosion damage, a parabolic like plot is produced (Fig 2, plot 2) similar to those registered in real atmospheric testing. The zeroth rate sequences produce retardation effect similar to the real one. Thus, if the corrosion reaction takes place in a run of sequences of uniformly decreasing rate, a smooth parabolic curve is constructed and presents a plot of the cumulative corrosion vs. time.
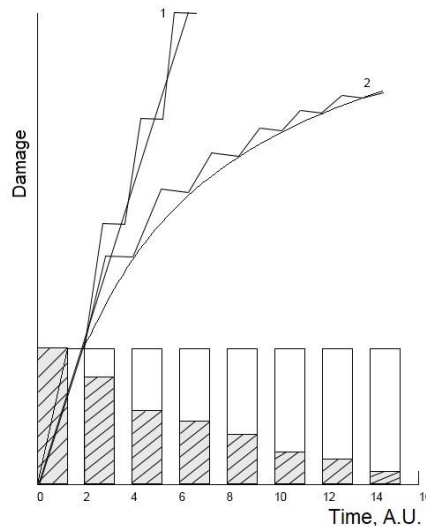

Figure 2: Development of linear, respectively parabolic plot from individual corrosion events of constant, respectively decreasing damage.

4.1. Realistic model approach

According to the results of testing in modeled conditions (climate chamber), the intensity of corrosion process is the most severe in 'wet + polluted' atmospheres, while in 'dry + unpolluted' ones it is negligible. The corrosion practice is situated between these two limiting cases visualized in Fig. 3.
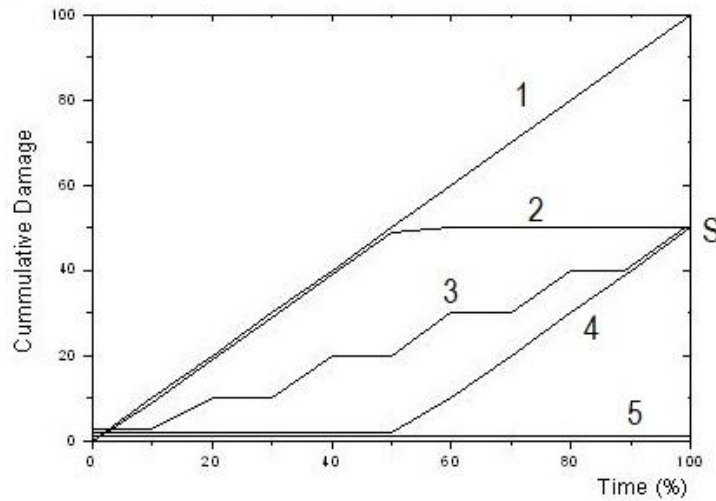

Figure 3: Possible combinations of the exposure conditions between maximum aggressive and maximum non-aggressive and their effect on cumulative damage: Plot 1: continuous exposure to maximum aggressive conditions; Plot 2: first half exposure to maximum aggressive conditions and the second half to maximum non-aggressive; Plot 3: tenfold variation of maximum aggressiveness and maximum non-aggressiveness; Plot 4: opposite to plot 2, non-aggressive followed by aggressive; Plot 5: continuous exposure to maximum non-aggressive ones.

Plot 1 in Fig. 3 corresponds to the case of permanent existence of 'wet + polluted' conditions and its opposite limiting case is the plot 5 for permanent 'dry + unpolluted' conditions. The combined action of these extreme cases is presented with plots 2, 3 and 4. In plot 2 the aggressive conditions were present during the first half of exposure, and the non-aggressive during the second half. Plot 4 is for exposure opposite then in plot 2, non-aggressive conditions are followed by the aggressive ones. Plot 3 further approaches to the reality, with 10 alterations of the 'dry + unpolluted' and 'wet + polluted' exposure conditions. The model supposes that the resulting cumulative damage is the same for plots 2, 3 and 4 and is marked as point S.

Taking in account that regular changes of exposure conditions are feasible only in modeled testing, it is easy to accept that in real cases, when the conditions do randomly change in time and severity, the cumulative damage plot as in Fig. 3 will be presented with irregular plot, situated between plot 1 and plot 5.

Plots weight loss vs. time of exposure in general are of parabolic shape, but when compiled from random start of specimen exposition irregular plots, far from smooth ones are produced. This "failure" is not caused by experimental error, but is rather due to the intrinsic nature of the atmospheric corrosion process. Parameters that define the atmospheric corrosiveness undergo continuous changes in wide span of values. As a result, the progress of corrosion reaction is uneven. The measured corrosion rates vary randomly around the supposed plot.

This is in contrast to the smooth plots, where the rate in every moment is determined by the slope of tangent drawn in that point. In this case copper corrodes with continuous rate decrease that becomes extremely slow as the parabola becomes almost parallel with x-axes. With the real (irregular) experimental plots such rate determination is impossible. Calculation of linearized corrosion rate by dividing the total corrosion damage with the time of exposure does not possess any physical meaning.

To solve this puzzle one has go to fine details. If continuous measuring of corrosion rate is applied, plot like the histogram in Fig. 4 will be registered. Here the individual corrosion damage is shown with vertical lines of variable length. This visualizes how corrosion rate varies with time.

Next is to summarize the individual damages and get the cumulative corrosion damage. Adding the value of individual damage one after-the-another results in curve of irregular shape (bold line in Fig. 4 down). There is no doubt that this curve exactly visualizes the increase of corrosion damage with time. Unfortunately the applied procedure is long (more than 10 or 15 years), time and labor consuming, i.e. out of recent need for quick and exact measurement.

To simplify the procedure, a different approach was applied. Instead of enormous number of extremely short time intervals, let's turn back to a reasonable number of much wider time intervals. The cumulative damage in such a case is shown by points in Fig. 4 down. They are the ones of the practical research. According to the procedure in regular treatment of results, follows the best fitting to determine the geometrical type of plot. In this case it is a parabola, and the constants are in the equation $\Delta K = a \cdot t^n$ (n<1). This result is shown in Fig. 4.
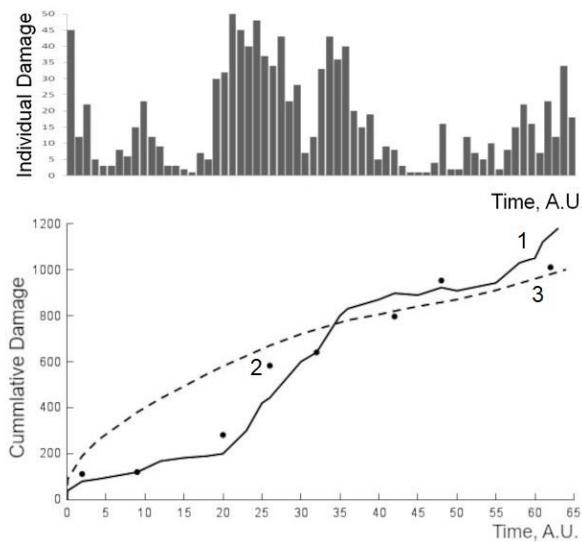

Figure 4: Three possibilities for evaluating the cumulative damage from the same (real) individual damages.

Plot 1: real change (the bold line is constructed by superposition of individual damages shown in the histogram above); Plot 2: experiment with only few exposures (8 points situated around the Plot 1);

Plot 3: parabolic plot fitted through the points produced in Plot 2.

Now follows the crucial moment. The experimental data like the ones in Fig. 4 usually are treated erroneously, trying to get a well-defined geometrical figure and determine its analytical geometry parameters. All this is due to the habit to deal preferentially with well-defined figures, as e.g. straight line, circle, parabola, etc. are. Using irregular patterns is almost strange.

4.2. Modeling

A procedure for conversion of the measured (irregular) plot, difficult for dealing with, into symmetrical and easy for calculating plot is shown in the model, Fig. 5.

It is developed in four steps. In step 1 **measured** result are presented. Transforming the sequential random shape into rectangular one of equivalent surface (step 2), chaotic shapeless plot is converted into well-defined plot composed of many rectangles. This is **linearization** step. In step 3 the multiple rectangles are **normalized** into a rational number of large rectangles, but keeping the total surface area unchanged. In the final step 4 they are transformed in **modeled** shape where calculation of the surface area, i.e. the corrosion rate, is easy to perform. The fine details of transformations in the block scheme Fig. 5 are to be elaborated further.
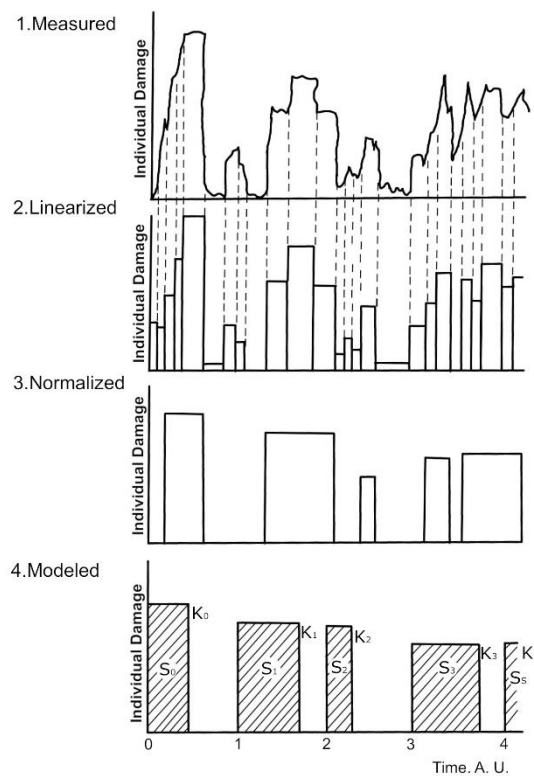

Figure 5: Block scheme of model developing procedure starting with the measured date (irregular sequences), linearizing them (rectangles), then normalizing (summarizing the rectangles in a unique one), and finally the modeled plot that is convenient for determining the process kinetics.

5. Conclusions

Investigations made in this study of the atmospheric corrosion of copper resulted in a number of useful knowledge. Here are some of them.

- Although the weight loss experimental procedure is simple and non-sophisticated, it yet brings results that could improve the existing knowledge for the studied phenomenon and give rise to important conclusions.
- One should be very cautious when planning the experimental procedure. There are many aspects that at first sight seem insignificant, but deserve a full attention if we wish to perform research of proper quality. From this study one should remember not to put together results from identical testing but initiated at different exposure conditions. Shown separately they follow the familiar parabolic patterns, but with different values of the pre-exponential and exponential constants $\underline{a}$ and $\underline{n}$. If the results of the two series were putted together, a very troublesome plot will result, with low chances to resolute it on a satisfactory way.
- Only in the late steps of exposure it was possible to perform ranking of the atmosphere corrosiveness in different locations. The score was 1:3, the lowest rate registered in sites far from urban and/or industrial activities and where dry periods dominate over the year.
- Continuous decrease of the corrosion rate with time is not necessarily uniform and this questions the validity of given reading as meritorious for ranking.
- Facing the experimental cases of complex plots troublesome for interpretation and understanding, a great help was find in building the model of the atmospheric corrosion process, starting with the simplest and going towards more and more complex situation. The excellent results were achieved that could be further improved.

The proposed model of atmospheric corrosion offers a possible explanation of experimental findings is based on a concept that the integral process is a sum of individual corrosion sequences. It helps to understand the mechanism of atmospheric corrosion and produces guidelines how to interpret the experimental data.

Further model improvement is needed for bringing it to a level to explain the corrosion behavior in terms of the corroding system parameters.

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