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DETERMINATION OF THE EFFECT OF ENVIRONMENTAL FACTORS ON THE CORROSION OF WATER DISTRIBUTION SYSTEM BASED ON ANALYSIS OF ON-LINE CORROSION MONITORING RESULTS

Corrosion of water distribution system is a significant issue causing problems with quality, safety and continuity of distribution. The changes of corrosion rates of the water distribution systems in Cracow made of carbon steel were investigated by analysis of online corrosion monitoring system results. Corrosion rates were determined using the linear polarization method. The impact of rain, temperatures, conductivity, dissolved oxygen content on corrosion rate were characterized. The corrosivity of different water sources like mountain water, underground water or river water were indicated. The possible actions for reducing corrosion losses were characterized. Results show that pollution of the environment in the form of acid rain and runoff from agriculture as well as the type of the source water has significant influence on corrosion of water distribution system. Corrosion monitoring system gives possibility of controlling corrosion rate by mixing waters from different sources in the way to obtain less corrosive mixture. (see Fig 8).

Keywords: water distribution system, acid rain, corrosion monitoring, online, linear polarization method

1. Introduction

Drinking water from the water supply network is an electrolyte containing ingredients of natural origin – mineral salts, dissolved gases (oxygen, carbon dioxide, hydrogen sulfide), organic compounds (from vegetables, animal origin, pollution) and ingredients added to the water for its treatment – deprivation bacterial flora (chlorine, ozone), regulation of carbonate balance, pH stabilization, etc. It is an environment with a specific corrosion aggressiveness in relation to metals, depending on its chemical composition, physicochemical (temperature, pressure) and hydrodynamic properties (type and flow rate).

The permissible level of individual mineral and organic components is included in the Regulation of the Minister of Health [1,2] and the European Union directive [3]. According to the EU directive, the quality of water intended for human consumption should be monitored, consumers should be informed about its quality, and the necessary steps should be taken to ensure that any substances or materials used in conditioning or distribution do not deteriorate its quality and do not directly or negatively affect people health.

Most of the water pollution, harmful to health comes from the distribution system, not from the water source. Corrosion and the processes of precipitation of corrosion products have a very large contribution here. Corrosion products stimulate the formation of a biofilm layer inside the pipelines and result in biological contamination of water.

According to the American authors [4], corrosion in water distribution and wastewater treatment systems consumes around US $ 3 billion a year in the US. There are also costs associated with the deterioration of water quality. Deterioration is related with to two phenomena: intrusion (penetration of impurities through perforations of corroded pipes as a result of pressure surges) and leaching of corrosion products (heavy metals, aluminum from cement coatings, etc.). Intrusion can be a cause of contamination of drinking water with groundwater. This often leads to bacterial contamination.

Many theories describing the influence of water quality on its corrosive aggressiveness can be found in the literature. The first of these is the theory of Tillman and others [5] assuming that the corrosion rate is regulated by the stability of the crystalline calcium carbonate layer on the surface of steel or cast-iron

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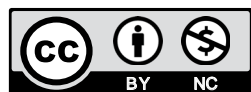
pipes ("carbonate model"). The authors noted that the increase in pH for hard waters causes a reduction in the rate of corrosion by increasing the stability of the calcite protective layer. For soft waters, the corrosivity of water mainly depends on the saturation with carbon dioxide, the content of calcium ions and the pH value. Langlier [6] proposed a Langlier Saturation Index (LSI) that captures thermodynamic conditions for the precipitation of calcium carbonate. In the literature can be find a number of indicators, empirical or based on solubility equilibria, predicting the precipitation of the sediment from water. These are: Ryznar stability index (RSI), Puckorius, Stiff-Davis, Oddo-Tomson precipitation index, momentary excess index and CCPP (Calcium Carbonate Precipitation Potential). The calculation method of these indicators and the conditions of their application are described in Roberge's monograph [7].

Subsequent studies have shown that the mentioned precipitation factors are not a sufficient parameter to predict the precipitation of a protective carbonate film on the surface of steel or cast iron pipes [8-10]. The sediment may precipitate under non-saturation conditions, because the pH on the metal surface is usually higher than at the depth of the solution due to the cathodic reduction of dissolved oxygen in water. In addition, the Solubility Product Constant of siderite solubility (corrosion product) is less than calcite. An important parameter determining the stability of the carbonate film is the buffer capacity of water [11]. The high buffer capacity stimulates the formation of the protective layer of the $FeCO_3$ siderite. The latter oxidizes to magnetite or pseudomorph goethite to form a dense, well-adhering to the metal protective layer. The carbonate model (siderite model), based on solubility equilibria, is unsuitable in very soft waters. Sander et al. [12] proposed a model based on surface acid-base reactions and surface complexation reactions. This model can be used for both soft and hard waters.

Corrosion aggressiveness of water also depends on physicochemical conditions, mainly on temperature, type and flow rate. Temperature fluctuations have a significant impact on several parameters determining corrosion aggressiveness of water (oxygen solubility, diffusion coefficients, activity coefficients, enthalpy of chemical reactions, oxidation-reduction reaction rate, stability of chemical compounds, biological activity) [13].

Integrated corrosion monitoring and management systems are already widely used in the management of pipelines for substances with a high degree of risk in terms of safety and environmental protection (oil, gas). Increasing costs of drinking water distribution and increasing requirements as to its quality result in increased interest in such systems in water supply networks [14,15]. This mainly applies to the United States, where the cost of corrosion of water supply systems is about 8% of the total corrosion-related losses in the country's economy (about $ 22 trillion) [4]. Previous systems for managing risk networks in drinking water distribution systems are based mainly on numerical risk modeling based on the age of pipes and system failure ("repair or replace" management). This modeling mainly considers the pipe working time, water pressure, temperature, material, GIS (geographical identification system) data. Meanwhile, there

is no evidence of management systems based on a network of corrosion monitoring and physicochemical properties of water. Therefore, the developed system in large city of Poland – Krakow is the first such solution of risk management based on the analysis of current data for water distribution systems [16-18].

This introduction draws attention to the very large, almost civilizational, importance of scientific research in the field of corrosion protection and corrosion monitoring systems in drinking water distribution systems.

This research shows results of online corrosion monitoring system installed in water distribution system in Krakow. The changes of corrosion rates during six months of normal work of the system were obtained by online linear polarization measurements. It was possible to characterized impact of rain, temperatures, conductivity, dissolved oxygen content on corrosion rate. The corrosivity of different water sources like mountain water, underground water or river water were also indicated.

2. Experimental

Corrosion monitoring system consists of Linear Polarization Resistance (LPR), dissolved oxygen, pH and temperature sensors. A three-electrode sensor was used for linear polarization measurements, all electrodes were made of carbon steel. The appropriate measurement time (measurement length), sampling density and sensitivity of sensors are of key importance in the monitoring system.

Corrosion rate measured by linear polarization method was done with one point method (in automatic way due to on-line technology). Corrosion rate values were determined empirically on the basis of the relationship:

$$CR\,[\text{mm/year}] = 0,052 + 0,2755 \left(\frac{10^3}{R_p} \right)^{0,9776} \qquad (1)$$

$$R_p = S \frac{\left(10 - 0,5 \cdot I \cdot R_E\right)}{I} \qquad (2)$$

Where:

CR – corrosion rate [mm/year],
R_p – polarization resistance [Ω],
S – working area of the sensor [cm],
I – value of direct current from one point measurement for polarization equal to 10mV [A],
R_E – electrolyte resistance [Ω].

The location of monitoring points was also carefully selected to ensure the registration of relevant data. There are three locations named as a "Hallera", "Kopiec Kościuszki" and "Huta" showed on the Fig. 1. There are also mentioned types of source water operated in the each of selected location. Description of each water source can be found in the Result and discussion part.

For relatively low corrosion rates, the LPR polarization resistance technique is appropriate. LPR is the sum of Rs (electrolyte resistance) and Rp (polarization resistance). The latter
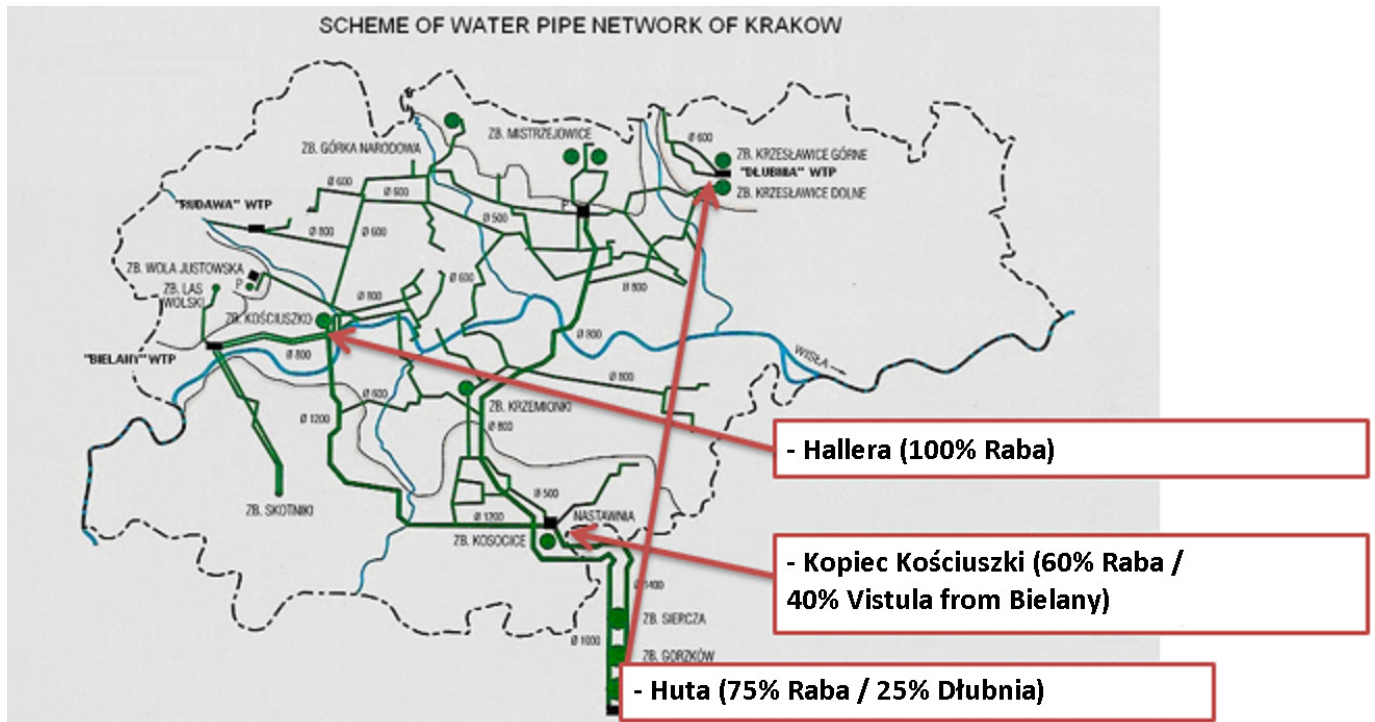
Fig. 1. Localization of the sensors on the Scheme of water pipe network of Kraków [19]

is used to determine the corrosion rate. For low corrosion rates, usually $Rp \gg Rs$. The small water conductivity and the high Rs value is not problematic to the use of LPR in drinking water.

Corrosion monitoring system features:

- Measurements of the corrosion rate of unalloyed steel in a water environment;
- Measurement performed inside the pipeline using a corrosion sensor;
- Measurement performed by linear polarization resistance method;
- Measurement of the instantaneous corrosion rate;

- Measurement made every 2 hours;
- The purpose – explain changes in the rate of corrosion. Implementation of measurements:
- water temperature,
- water conductivity,
- oxygen content in water,
- each monitoring point allows the same range of measurements,
- The measurement is carried out by the SC1000 computer module, allowing display of the measured parameters online.

Assembly of sensors is presented in the Fig. 2

Fig. 2. Assembly of sensors on the left side: view from outside the pipe, on the right side: view from inside the pipe

3. Results and Discussion

As mentioned in the Experimental part, sensors are located in the thee locations ("Hallera", "Kopiec Kościuszki" and "Huta"), each point is monitoring of corrosion for different source water. Below each source water is shortly characterized:

Raba River – is water intake from the dam reservoir at Raba in Dobczyce. The Raba River is in 86% powered by mountain streams. From its sources to Myślenice it is typical mountain river with a stony bottom with a dense network of tributaries with large falls and narrow valleys. Below Dobczyce Reservoir (dam in Dobczyce) does not lose mountain features, meandering swiftly on gravelly ground. Closer to the estuary it flows in a regulated deep channel, but it is also difficult to find typical lowland sections. Shorly speaking Raba river as a mountain river is very soft and is characterized by quite low conductivity.

Bielany intake – is built by series of infiltration basins, supplied with water from the Wisła River (by Sanka River) to enrich the groundwater resources in the area of the intake – water pumped from the river filtered through the sandy bottom of the basins, depositing slurries and other contaminants on its surface (Fig. 3). Purified in this way, it penetrates the permeable layers of the ground, from where it is captured by deep wells. Wisła river is characterized by quite high level of chloride ions due to discharge of more mineralized mine water from coal mines into the rivers. This led to a high salinity level in the place where the mine water is discharged.

Dłubnia River – left-bank tributary of the Wisła. The Dłubnia river flows through the Upland in the Lesser Poland Voivodeship. It flows from a spring in the village of Jangrot. It flows through the agricultural areas then it flows into the Wisła. This river in rainy times contains runoff from farmlands and other agricultural activities.

Analitical tests of water from each intake were performed and are presented in the table 1.

Special attention should be devoted to the hardness, conductivity, chlorides, magnesium and sulphates. Water from Bielany intake is characterized by the lowest pH and the highest magnesium, chlorides, suphates. Dłubnia has the highest total alkalinity, hardness, conductivity, nitrates and the lowest potassium. The sample was collected in the dry season so the chemical composition in rain time can differ severly. Raba is characterized by the highest pH and the lowest hardness, total alkalinity,

TABLE 1

Physicochemical characterization of water from each intake

Tested parameter	Unit	Bielany Intake	Dłubnia River	Raba River
Measurement temperature	°C	21	20.5	22
pH	pH-meter CP-551	7.6	7.7	7.7
Hardness	$mg/dm^3 CaCO_3$	258	262	129
Total alkalinity	mmol/l	3.6	4.6	2.2
Conductivity	µS/cm	597	603	328
Calcium	mg/dm^3	88	101	42
Magnesium	mg/dm^3	7.7	7	5.3
Nitrates	mg/dm^3	10	19	3.9
Potassium	mg/dm^3	4	2.9	3.1
Chlorides	mg/dm^3	54	24	14
Sulphates	mg/dm^3	83	27	22
Phosphates	mg/dm^3	0.11	0.075	0.068
Iron	mg/dm^3	0.03	0.045	0.028

calcium, chlorides, iron, nitrates, phosphates, sulphates. Such a composition is quite typical for mountain river.

The Langelier and Ryznar Saturation Indices were calculated. Results are presented in the table 2. Explanation for Ryznar Saturation Index are in the table 3.

TABLE 2

Calculated Langielier and Ryznar Saturation Indices

Temp. °C	pH measurement			Langelier Index			Ryznar Index		
	1	2	3	1	2	3	1	2	3
0	7.53	7.90	8.11	0.23	0.66	0.24	7.07	6.57	7.62
5	7.47	7.84	8.05	0.25	0.69	0.27	6.96	6.46	7.51
10	7.42	7.79	7.99	0.28	0.72	0.29	6.85	6.36	7.41
15	7.37	7.74	7.95	0.32	0.75	0.33	6.74	6.25	7.30
20	**7.33**	**7.70**	**7.91**	**0.35**	**0.78**	**0.36**	**6.3**	**6.16**	**7.19**

Sample determination: 1 – Bielany, 2 – Dłubnia, 3 – Raba

Langelier Saturation Index results can be understand as LSI > 0 – non-aggressive water, LSI < 0 – aggressive water. The corrosivity of water increases mainly with the increase of the concentration of Cl^-, SO_4^{2-} and dissolved oxygen, with the reduction of its alkalinity.

Ryznar Saturation Index pointed Raba river as the most corrosive due to low hardness and total alkalinity. Dłubnia has the lowest value so should be the least corrosive.
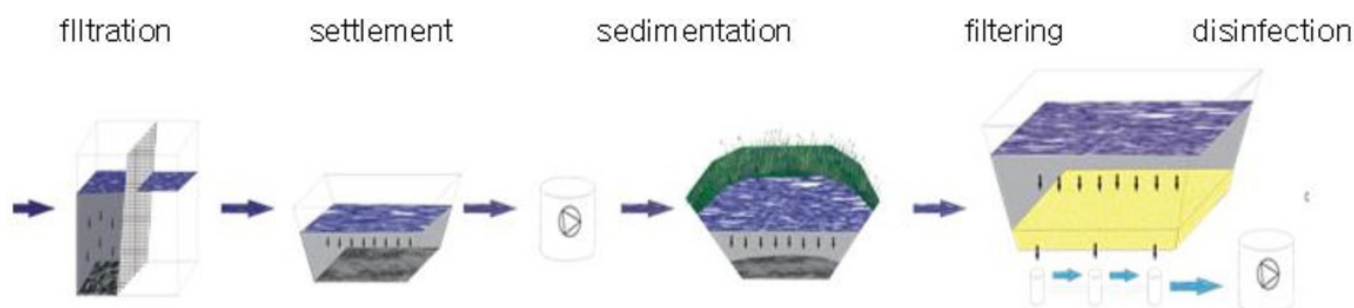

Fig. 3. Scheme of the series of proceses which undergo water from Sanka before getting to the water supply system

TABLE 3

Explanation for the Ryznar Saturation Index

RI	Indication (Carrier 1965)
4,0-5,0	Heavy scale
5,0-6,0	Light scale
6,0-7,0	Little scale or corrosion
7,0-7,5	Corrosion significant
7,5-9,0	Heavy corrosion
>9,0	Corrosion intolerable

Langelier Saturation Index shows different categorization than Ryznar, in this case the most corrosive is Dłubnia and Raba with Bielany has similar corrosivity.

Indication of corrosion aggresiveness of water limited to analysis of Saturation Indices is often insufficient like in this case. However implementation can find electrochemical methods.

Below are presented results from corrosion monitoring system for three locations measured for 150 days. First period is representative for summer, the latest period is representative for winter time.

Just for the record:
- Hallera location contains 100% Raba river,
- Huta location contais (average) 75% Raba river, 25% Dłubnia river,
- Kopiec location contains (average) 60% Raba river, 40% Wisła /Sanka river from Bielany Intake.
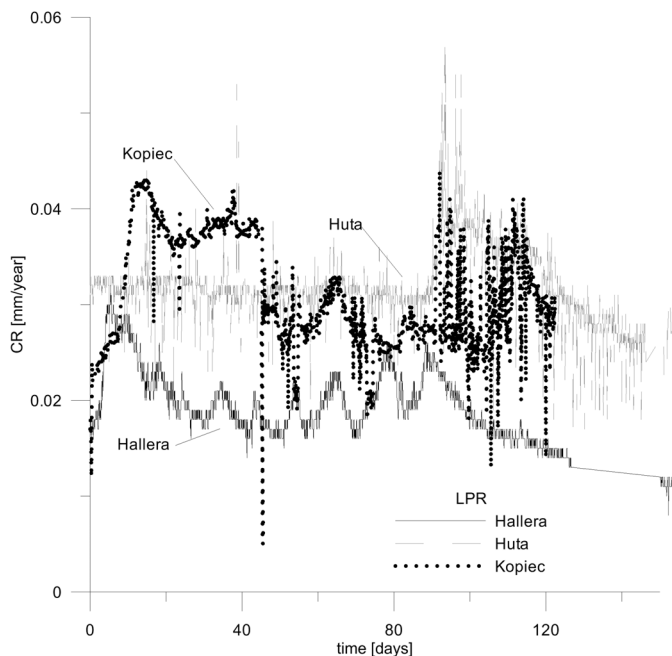

Fig. 4. Corrosion rate changes for water from three locations Hallera, Huta, Kopiec measured in 150 days

Figure 4 shows that corrosion rates in all locations are changing in time. It can be understand that Hallera represents the lowest corrosion rates. Concluding that pure Raba river has

the lowest corrosivity – differently from what was suggested by Saturation Indices. As it was said on the beginning that Raba river can be understood as mountain river so it is very soft. Has low ability to create protective layer of corrosion products on the inner surface of pipeline. However these pipelines in Krakow are quite old and already have old protective layer. In such a case soft water with low conductivity and low amount of corrosive species has low corrosion aggresiveness.

Corrosion rate describing water in Huta is quite constant with value of 0.033 mm/year. Corrosion rate depicting water in Kopiec is characterized by the most unstable corrosion rate in time. To find a reason of such a situation, analysis of the rest of data from other sensors was conducted.

Below are presented results from temperature (Fig. 5) and dissolved oxygen (Fig. 6) sensors.
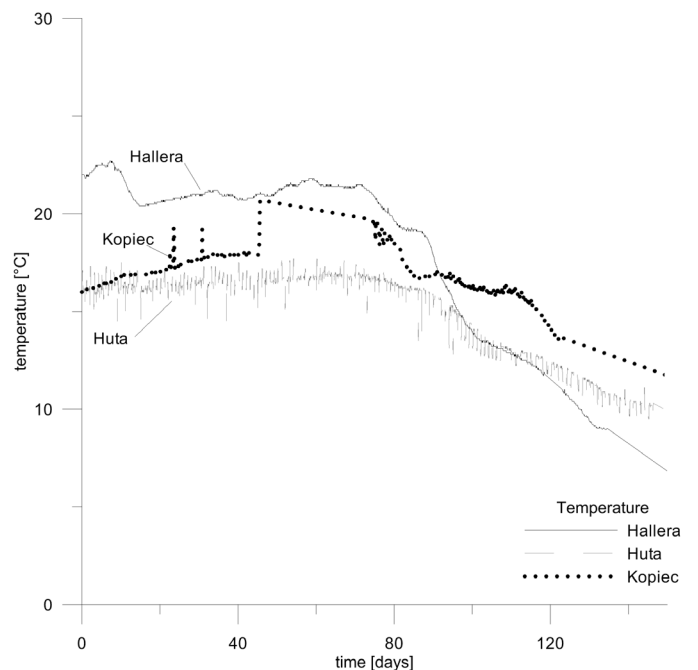

Fig. 5. Temperature changes of water from three locations Hallera, Huta, Kopiec measured in 150 days

It can be observed that corrosion rate is changing slightly with the decrease in temperature in all three location. Although the impact is not very intense.

Theoretically, dissolved oxygen increase corrosion rate up to some concentration as a substrate of corrosion cathodic reaction. Amount of dissolved oxygen increase when temperature decrease. Looking on the corrosion monitoring results it is true in the most of time except period between 50th and 80th day, when unusual decrease of corrosion rate in Kopiec location happened.

Normally, increasing values of both dissolved oxygen and temperature should increase corrosion rate. In the period of time when Kopiec is characterized by increse in this two values its corrosion rate drops down. The additional regular Tafel polarization measurements could give valuable informations, however on-line corrosion monitoring system installed in Krakow was based on non-destructive measurements. Tafel polarization due to
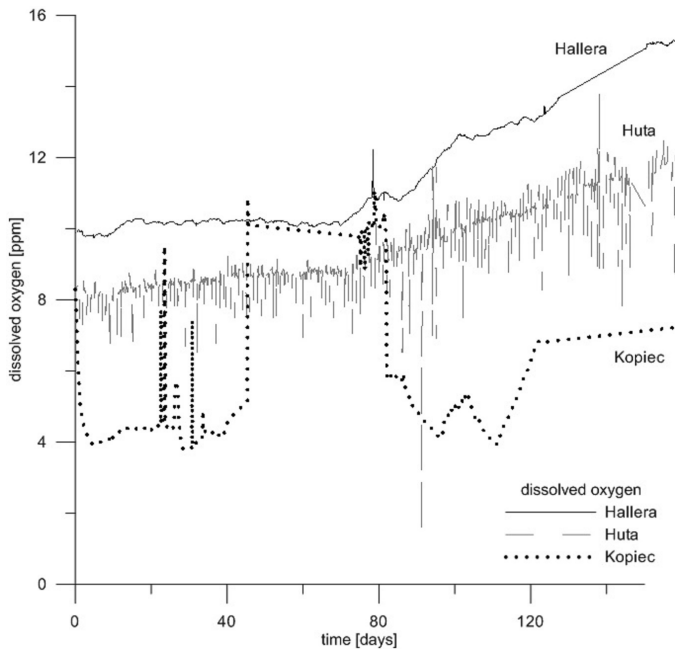
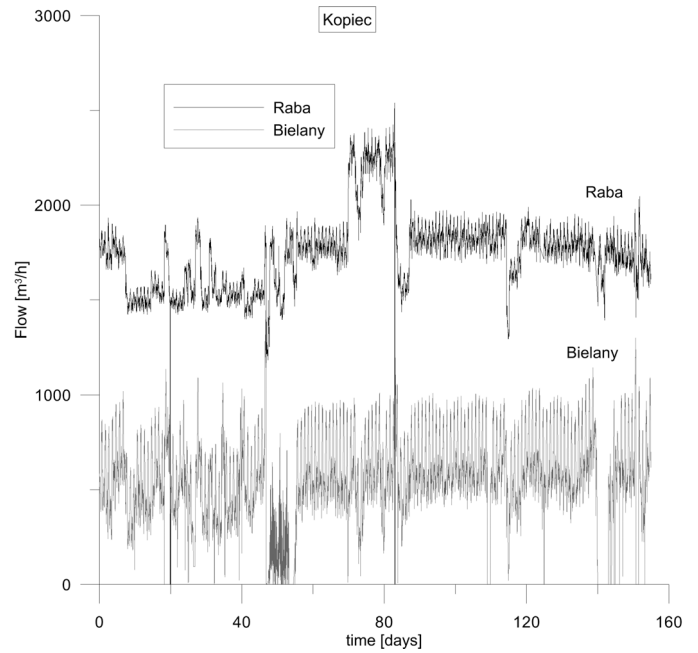Fig. 6. Dissolved oxygen content in water from three locations Hallera, Huta, Kopiec measured in 150 days

Fig. 7. Water flow diagram with composition of source water in the location of Kopiec

deep polarization has destructive influence on the metal surface. Such a measurements were done in the laboratory conditions on the base of sampled water but it cannot be assumed that amount of dissolved oxygen was preserved. Results of laboratory electrochemical measurements can be found in [15] and [16].

The explanation of this abnormal situation was found in the analysis of waterflow in the Kopiec location (Fig. 7).

Water flow diagram shows that in the time when Kopiec was characterized by the lowest corrosion rate, the ratio of Raba river to water from Bielany intake was much higher. This is another proof of the lowest corrosion agressiveness of Raba river.

Influence of the rain on the corrosion rate was also investigated on the example of Kopiec location (Fig. 8). For this

purpose analysed period of the time was limited for 30 days for better clearence.

Quite close relation of rain and increase in corrosion rate can be observed. The effect of the rain is slightly deleyed and extended in time. There are three teoretical possible explanation of increase corrosion due to rain:

•   **Acid rain**

Kraków in the time of anylysis was on the list of 20 most polluted cities in European Union according to World Health Organisation (WHO). The highest pollution in Kraków is observed during winter season due to combustion of coal in furnaces for house heating purposes. Acid rain by decreasing pH increase corrosion rate of the carbon steel.
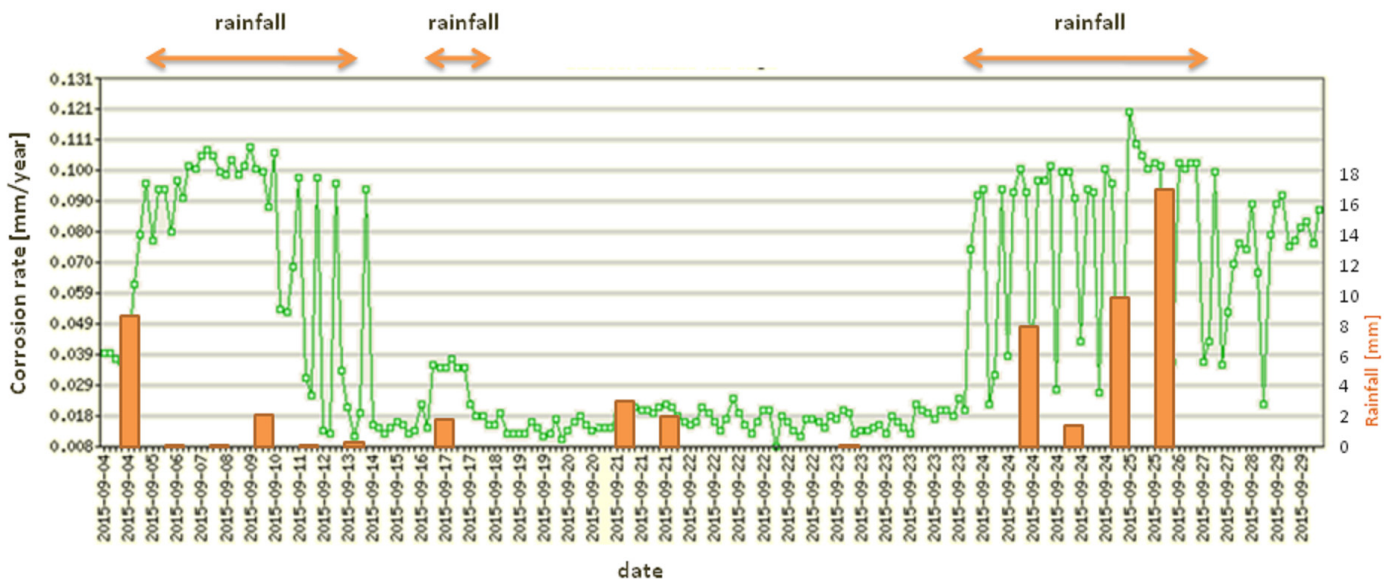

Fig. 8. Influence of rain on the corrosion rate in Kopiec location (orange bar – rainfall, green line corrosion rate)

- **Runoff from farmlands**

After heavy rains, a large amount of water travels to the surface layers of soil causing the migration of nitrates from fertilized fields, slurry, sewages and other products of agricultural activity to ground and surface water. Polluted water has much higher corrosion aggressiveness than clean water.

- **Disinfection – chlorination**

For cleaning and disinfection of water pipes, chemical agents are used. These are usually solutions of strong oxidants, such as: sodium hypochlorite, chlorine dioxide and hydrogen peroxide with peracetic acid. Sodium hypochlorite, although the most commonly used, does not guarantee removal of the bacterial biofilm, and its effectiveness is largely dependent on the pH value (the lower the pH, the higher the effectiveness of hypochlorite). Unfortunately, the reduction in pH entails the increase of corrosive properties, and hence the shortening of the service life of the installation and its greater susceptibility to biofilm formation. Often amount of disinfection agent used in the rain time is increased and can be also source of the increase corrosion in the rain time.

The installed online corrosion monitoring systems gives instant and valueable information of the corrosion phenomena taking place in water distribution system. However, there are weak sides of the system which should be noted:

1. Lack of CO_2 content analysis – due to the inability to perform this type of on-line measurement. Carbon dioxide has significant influence on corrosion agressiveness of the tested water.
2. Lack of measurements taking into account the separation of temperature changes from the dissolved oxygen content. As it was previously mentioned it was impossible to differentiate influence of temperature and dissolved oxygen. These two things are quite related, because when the temperature increase, solubility of the oxygen in water decrease. So, from the one hand corrosion rate should increase to due increase of temperature but it also should decrease due to limited dissolved oxygen content.
3. Lack of analysis of Tafel polarization continuously – Tafel measurement is destructive for measuring electrodes, so it can not be done in regular manner.
4. Lack of measurements by other methods verifying LPR measurements of corrosion rate (like ER probes oraz electrochemical impedance methods).

4. Conclusions

The changes of corrosion rates of the water distribution systems in Cracow made of carbon steel were investigated by analysis of online corrosion monitoring system results. Analysis of the results allowed to formulate the following conclusions:

- Indicating corrosion rate of water based only on Saturation Indices is insufficient.
- Corrosivity of water in the water supply systems strictly depends on the type of source water.
- The mountain water has the lowest corrosivity contrary to water from river running though region of high agricultural activity.
- Factors like: rain, temperatures, dissolved oxygen content have impact on corrosion rate.
- Increased corrosion in rainfall time can be due to acid rain, agricultural runoff and increase disinfection agent concentration.
- Weak sides of the system are lack of carbon dioxide content analysis, lack of Tafel coefficients knowledge, lack of corrosion rate verification method and impossibility of differentiation influence of temperature and dissolved oxygen on corrosion rate.

Corrosion monitoring system gives possibility of controlling corrosion rate by mixing waters from different sources in the way to obtain less corrosive mixture and enables:

- improvement of water quality by limiting its pollution with corrosion products,
- reduction of water consumption as a reduction of the number of failures,
- reducing the operating costs of the water supply network due to material savings and reducing the number of renovations.
- understanding of factors causing increased corrosion

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