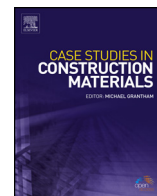




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## Case study

## Research on causes of corrosion in the municipal water supply system



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## ABSTRACT

This paper presents results of failure analysis study to characterize the corrosion damage that occurred in the water supply system in Krakow. This analysis includes: electrochemical noise, linear polarization and resistometric measurements. Water aggressiveness of four water intakes was defined using Langelier and Ryznar indices. Results from this indices did not reveal the causes of considerable corrosion losses in water systems. The corrosion rate measurements revealed that water from the one of water intakes is characterized by considerable corrosive aggression. In all studied water subsystems formation of protective layers limiting the corrosion rate was found. Overall analysis reveal the need to implement a on-line corrosion rate monitoring in the water supply system of the city of Krakow.

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## 1. Introduction

Detailed research on the operation of the water supply system in the city of Krakow has shown that the losses amount to 13.41% at the end of 2014 with 55 348 thousand m<sup>3</sup> having been pumped into the system over the whole year. In accordance with the register, failures caused by corrosion account for approx. 20% of the overall number of water supply failures. Failures of water main networks above  $\phi$  300 mm account for approx. 7%. A considerable number of failures of main networks are subject to local corrosion, which leads to perforation of pipe walls (Fig. 1).

Considerable costs connected with water losses and costs of removing failures have become grounds for research to explain the causes of corrosion processes. A significant problem in the analysis is the fact that water sent to the water supply system from the Water Treatment Plant (Zakłady Uzdatniania Wody) has various physicochemical properties and is characterized by varying values of the corrosivity index.

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Fig. 1. Local corrosion of a DN300 pipeline.

## 2. Experimental

Samples of water collected from four water intakes for the city of Krakow were selected for tests:

- Bielany
- Rudawa
- Dłubnia
- Raba

Analytical tests were performed using a Palintest 5000 spectrophotometer.

Tests of the corrosion rate were conducted on the basis of the following measurement techniques:

- linear polarisation measurement,
- resistometric measurement,
- measurements of electrochemical noise.

**Table 1**

Results of analytical tests of the tested samples of water.

Tested parameter	Unit	Bielany	Rudawa	Dłubnia	Raba
Measurement temperature	°C	25.6	25.4	24.8	25.5
pH	pH-meter CP-551	7.30	7.23	7.67	7.87
Hardness	mg/dm <sup>3</sup> CaCO <sub>3</sub>	70	56	56	52
Total alkalinity	mg/dm <sup>3</sup> CaCO <sub>3</sub>	188	183	233	103
Sulphides	mg/dm <sup>3</sup>	0.03	0.02	0.02	0.02
Silica	mg/dm <sup>3</sup> SiO <sub>2</sub>	0.02	0.82	0.08	0.06
Dry residue	mg/dm <sup>3</sup>	300	290	370	60
Conductivity	µS/cm	0.64	0.55	0.58	0.31
Calcium	mg/dm <sup>3</sup>	86	57.2	80	38.4
Magnesium	mg/dm <sup>3</sup>	6.4	6.0	4.8	5.7
Nitrogen	mg/dm <sup>3</sup>	1.3	1.8	0.58	0.80
Total copper	mg/dm <sup>3</sup>	0.20	0.13	0.20	0.10
Potassium	mg/dm <sup>3</sup>	5.3	3.9	2.4	6.0
Nitrates	mg/dm <sup>3</sup>	5.72	7.92	2.55	3.52
Chlorides	mg/dm <sup>3</sup>	46	42	45	32
Sulphates	mg/dm <sup>3</sup>	83	57	27	22
Phosphates	mg/dm <sup>3</sup>	14	16	11	16
Iron	mg/dm <sup>3</sup>	0.03	0.00	0.01	0.00
Zinc	mg/dm <sup>3</sup>	0.12	0.06	0.05	0.10
Bicarbonates	mg/dm <sup>3</sup>	229.36	223.26	284.26	125.66

Samples of structural steel were exposed in water (with a surface area of  $0.28 \text{ cm}^2$ ) in a three-electrode configuration selected on the basis of similarities between corrosion potentials. The corrosion rate of the samples was monitored over two months using two electrochemical techniques. Registration of electrochemical noise was complemented by measuring the polarization resistance. Electrochemical tests of linear polarization were performed using a system for electrochemical measurements—Gamry Reference 600. Measurements of electrochemical resistance were performed using an SCXI modular system manufactured by National Instruments, which consisted of the following components: SCXI 1141: an elliptical low-pass filter with attenuation at a cut-off frequency of 80 dB, used as an anti-aliasing filter, SCXI 1121: isolated signal amplifier, SCXI 1181 (marked as an I/U transmitter): an independently constructed current-to-voltage converter on a mounting plate on the basis of an operational amplifier OPA 128. The rate of synchronous sampling of potential and current sequences was 12 Hz, while the a signal duration cycle lasted 3 h. Resistometric tests were performed on the basis of the author's own low-ohm measurement system. A sensor in the form of a steel wire with a 2 mm diameter exposed in the environment of the tested water samples was the measuring element.

### 3. Results of research and their discussion

Results of analytical tests of the tested samples of water are presented in Table 1.

The results obtained were used for the analysis of Langelier and Ryznar corrosivity indices [1–4] (Table 2).

The results of the research have shown that water samples are not aggressively corrosive. Only for the water sample from the Rudawa intake at approx.  $0^\circ \text{C}$ , it is possible that water will have a limited ability to form calcium layers, which reduce the corrosion process. For results of analytical tests, it can be noticed that water from the Raba intake is characterized by the lowest content of calcium ions and hydrocarbons. Water from the Rudawa and Dłubnia intakes has similar corrosion aggression, while water from the Bielany intake has higher conductivity, hardness and the content of sulphates and calcium ions, which indicates that it may be the least aggressively corrosive of all of the tested types of water. Standard analytical tests conducted did not show unambiguously significant reasons for considerable corrosion-related losses. As a result, corrosion rate tests were performed. The results of resistometric tests are presented in Figs. 2 and 3.

Tests of corrosion rate of non-alloy steel, type S236JR using the resistometric method showed that water from the Raba intake was the most aggressive corrosive environment. The corrosion rate after 90 days is at the level of 0.28 mm a year. It is over 3 times higher than the recommended level ( $<0.1 \text{ mm a year}$ ), for which safe conditions of operation are adopted due to corrosive hazard. The corrosion rate of steel in water from the Dłubnia intake is at the level of 0.11 mm a year and from the Rudawa intake—0.08 mm a year. Water from the Bielawa intake is characterised by the lowest corrosive aggression—the corrosion rate for steel is 0.03 mm a year.

The results of corrosion rate tests using the linear polarisation method are presented in Fig. 4.

The tests have shown that the corrosion rate of non-alloy steel increases during use in water from the Raba intake, which shows that no layers are formed, which would limit the corrosion rate. The corrosion rate for steel water from the Raba intake after 90 days of exposure was approx. 0.35 mm a year. For research in the environment of water from the Bielany intake, the corrosion rate of non-alloy steel is reduced during the exposure time, which indicates that layers are formed, which reduce the corrosion rate. The protective layer formation process continues (for the exposure time of 90 days). The corrosion rate for steel water from the Bielany intake after 90 days of exposure was approx. 0.060 mm a year. Tests in the environment of water from the Rudawa and Dłubnia intakes showed that the steel corrosion rate for non-alloy steel at the initial period of exposure increased (approx. 30 days), a decrease in the corrosion rate in the time function can be observed later.

**Table 2**

Results of pH calculation analysis and water corrosivity indices as a function of water temperature.

Temperature ( $^\circ \text{C}$ )	pH measurement				Langelier index				Ryznar index			
	1	2	3	4	1	2	3	4	1	2	3	4
0	7.53	7.46	7.90	8.11	0.23	-0.02	0.66	0.24	7.07	7.51	6.57	7.62
5	7.47	7.40	7.84	8.05	0.25	0.00	0.69	0.27	6.96	7.40	6.46	7.51
10	7.42	7.35	7.79	7.99	0.28	0.03	0.72	0.29	6.85	7.29	6.36	7.41
15	7.37	7.30	7.74	7.95	0.32	0.06	0.75	0.33	6.74	7.18	6.25	7.30
20	7.33	7.26	7.70	7.91	0.35	0.10	0.78	0.36	6.63	7.07	6.16	7.19
25	7.30	7.23	7.67	7.87	0.39	0.14	0.82	0.40	6.53	6.95	6.03	7.08
30	7.28	7.21	7.64	7.85	0.43	0.18	0.86	0.44	6.41	6.84	5.91	7.07
35	7.26	7.19	7.62	7.82	0.48	0.23	0.91	0.49	6.29	6.73	5.80	6.97
40	7.25	7.17	7.61	7.81	0.53	0.28	0.96	0.53	6.18	6.61	5.69	6.74
45	7.24	7.17	7.60	7.80	0.59	0.34	1.02	0.59	6.06	6.49	5.57	6.62
50	7.24	7.16	7.60	7.79	0.65	0.40	1.07	0.64	5.94	6.37	5.45	6.50
55	7.24	7.17	7.60	7.79	0.71	0.46	1.14	0.71	5.81	6.24	5.33	6.38
60	7.24	7.17	7.60	7.80	0.78	0.53	1.20	0.77	5.69	6.12	5.20	6.26

Sample determination: 1—Bielany; 2—Rudawa; 3—Dłubnia; 4—Raba.

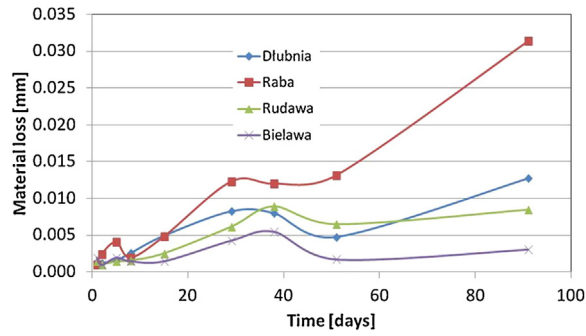


Fig. 2. Results of tests of corrosion losses on the basis of resistometric measurements.

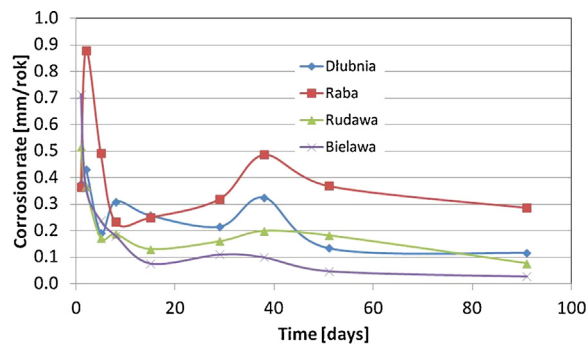


Fig. 3. Results of corrosion rate tests on the basis of resistometric measurements.

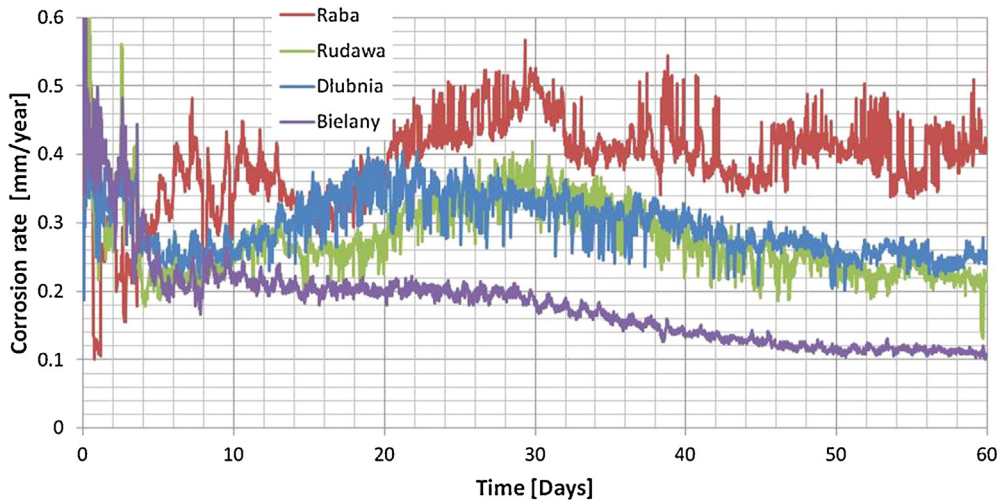
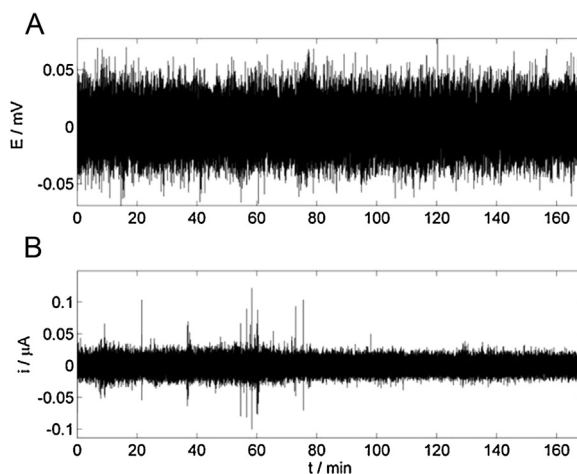


Fig. 4. Corrosion rate tests of non-alloy steel, type S236JR using the linear polarization method in an environment of tested water samples.

Electrochemical noise tests were also performed during resistometric tests and tests of linear polarization. Current and voltage registers were submitted to the procedure of trend removal, which influences the determination of the values of both noise resistance [5]. Sample potential (A) and current (B) noise registers after the trend removal procedure using polynomial matching is presented in Fig. 5.

The representations deprived of the multivariate component are characterised by normal distribution in all analyzed cases. Fig. 6 presents sample results in the form of histograms of the number of occurrences of individual values of potential

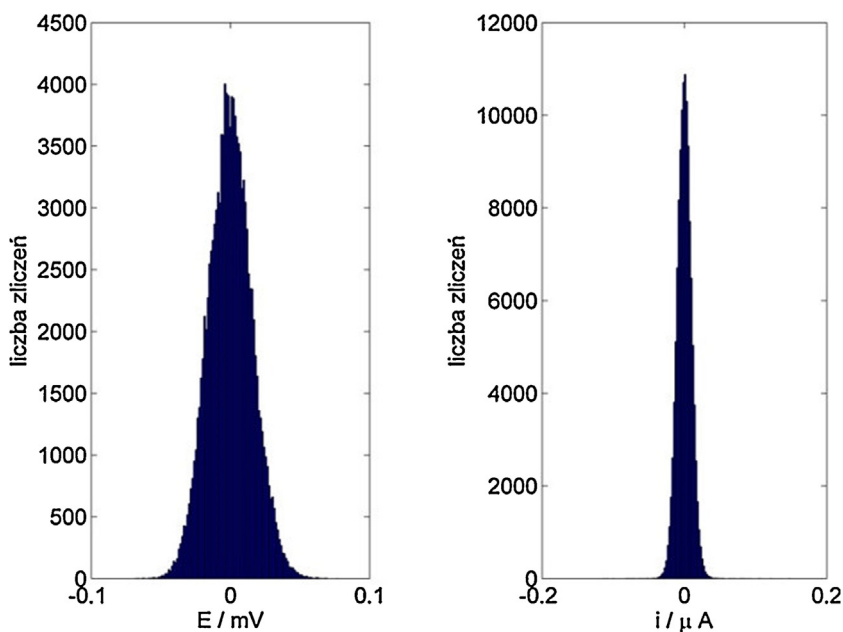


**Fig. 5.** Sample representations of potential (A) and current (B) electrochemical noise Registration rate 12 Hz, duration 3 h. Other technical details are presented in the text.

(A) and current (B), respectively. The Gaussian shape of both distributions is adopted as a requirement while using noise resistance (1), i.e. a measurement based on standard deviation.

Apart from noise resistance expressed by the dependence (1), a derivative measure was determined—spectral noise resistance, which was defined by the following formula (2). In practical estimation, the size of the spectral noise response was used, identical with the value of the impedance module in Bode's projection. A sample diagram is presented in Fig. 7. In accordance with the definition, the borderline low value of the spectrum frequency must be used. In the estimation of spectral resistance, the average value from the selected number of points of the spectrum in its low-frequency part.

Both measurements of general corrosion rate described above were confronted with the values of polarization resistance. The results registered in the assumed measurement regimen are presented in Fig. 8 with a division into 4 samples of water in accordance with determinations presented at the beginning of the chapter. Discrepancies between the results of various variants of measurement and analysis were observed. They result from various recording conditions and from different assumptions during the designation of the corrosion rate. The differences obtained do not diverge significantly from values encountered in the literature [6].



**Fig. 6.** Probability distributions of the potential and current representation.

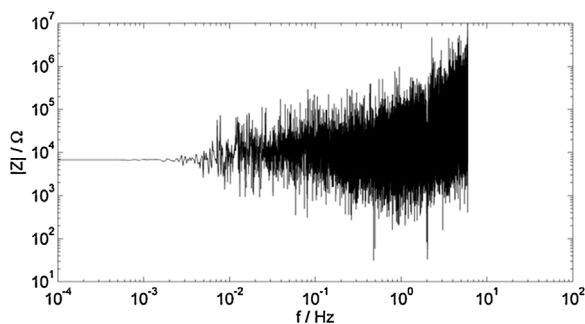


Fig. 7. The result of the spectral analysis of the representations presented in Fig. 5 in the form of the product of Fourier transformation modules with the dimension of electrode impedance.

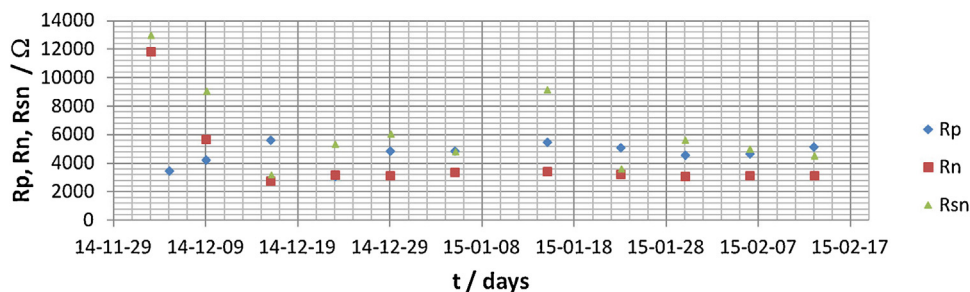


Fig. 8. Results of the monitoring of the corrosion rate in water from the Raba intake.

Similar values of resistance at the level of 3–5 k determined by means of three methods were observed for the sample (Raba)Ω. Better correlation can be observed between the values of spectral and polarization resistance than for noise resistance. Considerable discrepancies are observed only at the initial period of the corrosion rate monitoring.

For the Rudawa water sample, corrosive aggression is lower than in the case of the sample from the Raba intake, which is manifested by higher resistance values (4–10 kΩ). A virtually identical trend of changes was observed for both spectral and polarisation resistances, which indicates that corrosive aggression of the water sample decreases in time.

The Bielany water sample is characterized by still lower corrosive aggression (4–7 kΩ); however, as opposed to the sample described previously, the high value of resistance is kept at a constant level during the entire monitoring period. These values are randomly scattered, which makes it difficult to find any regularities concerning correlation between measurement techniques used (Figs. 9–11).

In one case (Dłubnia), significant discrepancy between the results obtained by means of the polarisation and noise techniques. At the final stage of monitoring, a distinct difference can be seen in the direction of corrosion rate changes. Considering the other exposure time, it can be concluded that corrosive aggression of the described water sample is similar to the previous one.

On the basis of the shape of the analysis of the noise spectrum, an additional conclusion can be drawn about the corrosion process mechanism. The obtained characteristics of the spectral noise response, as shown in Fig. 7 for example, are

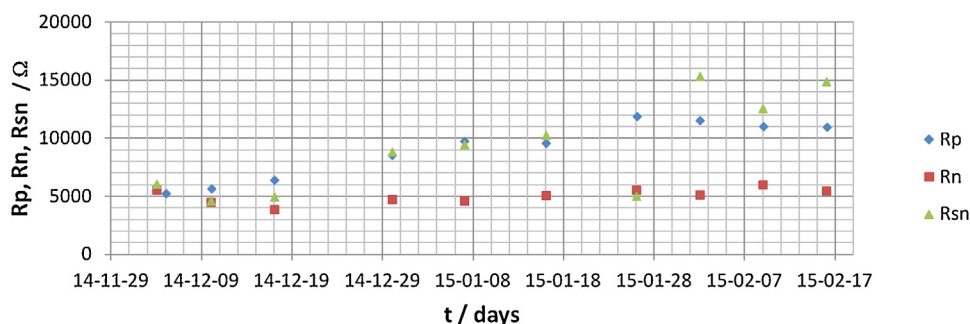


Fig. 9. Results of the monitoring of the corrosion rate in water from the Rudawa intake.

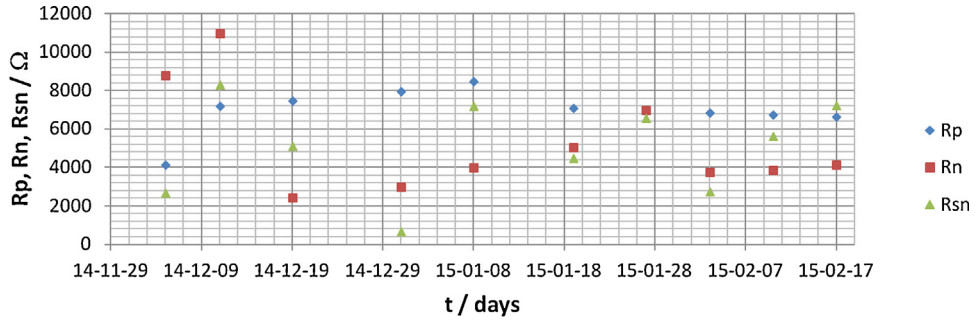


Fig. 10. Results of the monitoring of the corrosion rate in water from the Bielany intake.

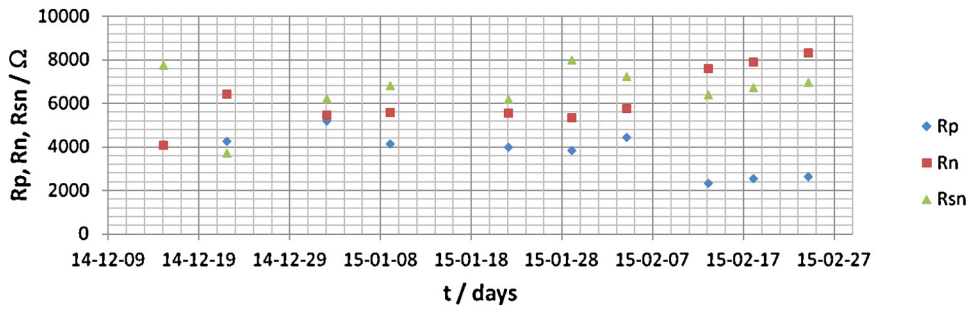


Fig. 11. Results of the monitoring of the corrosion rate in water from the Dłubnia intake.

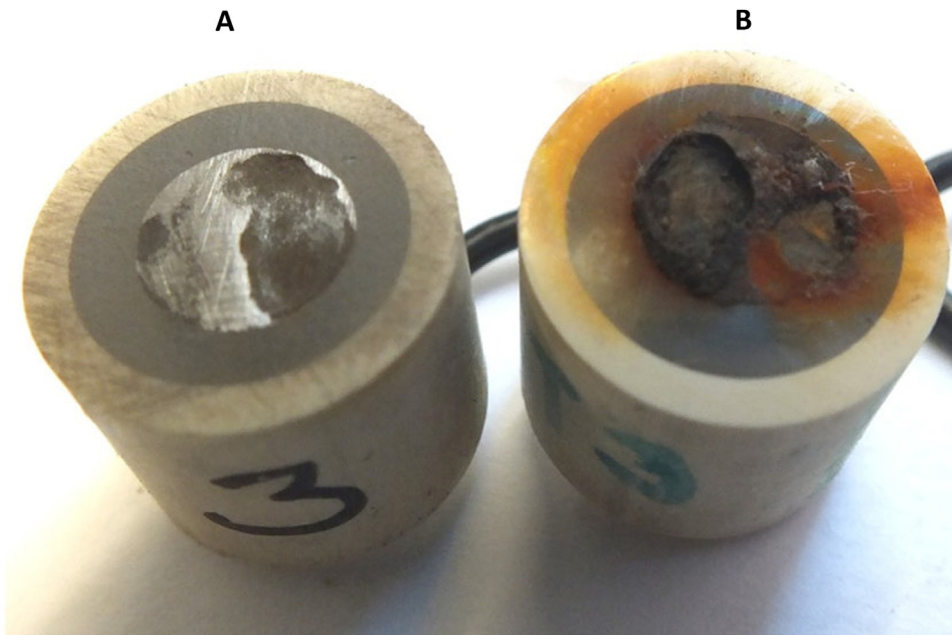


Fig. 12. S236JR carbon steel samples after the exposure in the tap water environment. Visible corrosion products (B) and damage to the sample after the removal of a layer of products (A).

characterized by zero inclination. This indicates an even course of the corrosive attack. After the planned exposure time, samples were assessed visually. The presence of a large number of corrosion products (Fig. 12B) was found in the form of sediments.

After removing a layer of corrosion products, the attacked metal was revealed with general corrosion characteristics (Fig. 12B).

The results obtained indicate similar values of the corrosion rate and the same trends of this value during the monitoring. It must be noticed that the presented results were obtained under laboratory conditions using specialist equipment for noise measurements. As a result, the conditions of the experiment are very different from the monitoring during the operation of the installation. Comparative measurements make it possible to conclude that the value of the corrosion rate obtained using a zero ammeter and a voltmeter without a developed conditioning system is similar. This shows that a cheaper and easier solution can be used, which is suitable for field conditions. An advantage of the described monitoring method includes the simplicity of the measurement procedure, which only involves passive recording which can be performed in a maintenance-free manner, apart from emergency situations.

#### 4. Summary

Tests of water aggression indices, which are the basis procedure for the assessment of water corrosiveness, did not reveal the causes of considerable corrosion losses in water systems in an unambiguous manner. The corrosion rate measurements performed using the resistometric method and the methods of linear polarization and electrochemical noise revealed that water from the Raba intake is characterized by considerable corrosive aggression. Sediments formed during the exposure of steel samples do not limit corrosion processes and contribute to the occurrence of a considerable corrosion rate. This requires changes in the technology of the water supply system. It is possible to change the water flow regulation to mix water from the Raba intake with other streams of water with lower corrosive aggression. In the case of the other water environments tested, formation of protective layers limiting the corrosion rate was found. Water from the Bielany intake is characterized by the lowest corrosive aggression. The results obtained indicate that it is advisable to start corrosion rate monitoring on-line in the water supply system of the city of Krakow.

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#### References

- [1] W.F. Langelier, The analytical control of anticorrosion water treatment, *J. Am. Water Works Assoc.* 28 (1936) 1500–1521.
- [2] T.E. Larson, A.M. Buswell, Calcium carbonate saturation index and alkalinity interpretations, *J. Am. Water Works Assoc.* 34 (1942) 1667–1684.
- [3] W.F. Langelier, Chemical equilibria in water treatment, *J. Am. Water Works Assoc.* 38 (1946) 169–178.
- [4] J.W. Ryznar, A new index for determining amount of calcium carbonate scale formed by water, *J. Am. Water Works Assoc.* 36 (1944) 472–483.
- [5] F. Mansfeld, Z. Sun, C.H. Hsu, Electrochemical noise analysis (ENA) for active and passive systems in chloride media, *Electrochim. Acta* 46 (2001) 3651–3664.
- [6] V.M. Salinas-Bravo, J. Porcayo-Calderon, J.G. Gonzalez-Rodriguez, Corrosion monitoring using electrochemical noise and linear polarization resistance in fuel oil combustion gas environment, *Russ. J. Electrochem.* 42 (2006) 560–565.

