

## Research Article

# Electrochemical Reduction of Industrial Baths Used for Electropolishing of Stainless Steel

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Long-term exploitation of industrial electropolishing baths may contribute to the emergence of surface defects and may limit the range of applicable current densities. Due to this, extending the time of use of industrial baths is a major challenge. The application of electrochemical reduction in the process of reduction industrial baths enabled to reduce its contamination and, as a result, to enhance the surface quality of electropolished samples of grade 304 stainless steel. The contamination influence of the electropolishing bath on such parameters of the electropolished samples as roughness, gloss, mass reduction, and corrosion resistance was compared. The conducted tests included reduction of the contaminated industrial bath with use of cathodic reduction and monitoring of bath contamination with use of emission spectrometry ICP-OES. Potentiodynamic tests in 0.5 M chlorine environment with the aim to determine the influence of electrochemical reduction of the plating bath on surface resistance demonstrated that the pitting corrosion resistance of samples electropolished in a bath after reduction was reduced by approximately 0.1 V in comparison with samples electropolished before reduction. The calculations conducted for 24 corrosion resistance measurements demonstrated that differences between the results were significant. Bath reduction leads to improved roughness and gloss, even by approximately 500 GU (gloss units). At the same time, mass reduction decreases even by 13% in comparison with the process conducted in the bath before reduction. This may have a positive influence by slowing down the bath contamination process and, as a result, it reduces negative environmental impact. Another argument that supports the reduction of industrial baths is slowing down the process of cathode contamination during the electropolishing process. In industrial conditions, this may extend the possibility to conduct the process without the need for cathode reduction or replacement.

## 1. Introduction

The practical use of the electropolishing process (EP) dates back to the 1930s. Nowadays, this technology is a widely known form of industrial surface processing used throughout the world. Along with the technology development, the demand for surfaces with a smooth, homogeneous, very clean, and corrosion-resistant surface increased. Currently, the electropolishing process is used both in the production of everyday objects and elements of special equipment [1, 2].

The applications of the electropolishing process described in the literature also include its use for surface processing of such elements used in biomedicine as stents or implants [3–8].

The electropolishing process allows for smoothening, glossing, and improving the appearance of element surface. It may also be preceded by mechanical polishing [9]. Electropolishing also enables smoothening modified surfaces from 316L grade steel manufactured in the ALM (additive layer manufacturing) process. There were also attempts at electropolishing of coatings manufactured with

use of TSC (thermal spray coatings). However, the obtained surface layer consisted of a mixture of  $\alpha$  and  $\gamma$  phases, which made it more difficult to electropolish [10]. Electropolishing may be supported by the influence of the magnetic field, which may improve surface roughness and, in some cases, corrosion resistance [11–13]. However, magnetic electro-polishing has not been widely applied in industries yet. Electropolishing also improves the surface corrosion resistance, due to the influence of the passive layer that contains, among others, chromium oxides and hydroxides [14, 15]. One of the main advantages of electrochemical processing is the possibility to obtain good surface quality even for elements of complex shapes. However, even after the electropolishing process, the surface may contain certain defects, including those resulting from long-term use of electrolyte, improper current density, or local overheating of the electrolyte. The most common defects include orange peel effect, shadows, smudges, and uneven polishing of the material [16, 17].

Intensive exploitation of phosphoric-sulfuric baths on an industrial scale and the contamination of such baths by metal ions have a significant influence on the extended time of the electropolishing process, deterioration of roughness and gloss of the obtained superficial layers [18]. Thus, it seems reasonable to search for ways to improve, even partially, the properties of contaminated processing baths, including the elimination of copper, nickel, iron, and chromium ions that migrate to the bath during anodic dissolution. The literature provides numerous publications whose authors have attempted to find reasonable ways of potential removal of metals from wastewater with use of electrochemical methods. Copper ions were efficiently removed from diluted industrial wastewater in an electrochemical reactor with the plate electrode [19]. The case of treatment of wastewater from a galvanizing facility is particularly interesting, as it resulted in practically complete reduction of copper from the solution. The process used an electrolyser with cathodic and anodic spaces separated by a membrane. The cathode was a grid made from stainless steel, while the anode was a titanium grate coated with ruthenium oxide [20]. Nickel may be recovered from wastewater with use of both electrochemical and chemical methods. Electrochemical methods allow obtaining relatively clean metal, but they cannot be applied with commonly used chloride-based solutions, as their reduction may lead to the emission of highly toxic gaseous chlorine. An example is the method of chemical destabilisation of used nickel coating solution, which resulted in cathodic reduction of nickel ions and the generation of nickel in form of powder [21]. The study by Khan [22] analyses the effectiveness of nickel and zinc ions removal from contaminated solution. The 50-hour process conducted with use of a stainless steel anode and aluminium cathode, led to a reduction of nickel ions in the solution by 70%. Bakaev et al. analysed the electrochemical regeneration of electrolytes used for electropolishing chromium steel with use of a regenerator with a membrane and carbon cathode of fibrous structure that allowed accelerating the process 10 times. As a result, approximately 50% of the iron was recovered [23].

The aim of the study was to evaluate the influence of reduction industrial phosphoric-sulfuric electropolishing baths on the surface quality obtained in the electropolishing process. The author analysed the influence of cathodic reduction on the gloss, surface roughness, and corrosion resistance of electropolished chromium-nickel steel.

## 2. Experimental Procedures

*2.1. Materials.* Tests were conducted on AISI 304 stainless steel of the following composition (wt.%): 0.037% C, 0.42% Si, 0.057% N, 1.28% Mn, 0.029% P, 0.002% S, 18.13% Cr, 8.04% Ni, and balance Fe. Samples were cut out from cold-rolled 1.5 mm thick stainless steel sheets.

Tests were conducted on three types of samples. The process bath reduction with use of cathodic reduction used rectangular samples 40 mm wide and 150 mm long, with two fastening holes of a diameter of 7 mm located in the upper part. In order to eliminate the influence of uneven immersion on the border between phases, the upper part of the electrodes was secured by a nonconductive PTFE tape providing exposure surface of 67 cm<sup>2</sup>. Before the electrolysis process, the electrodes were mechanically polished using polishing papers of grit size #400, #600, and #800.

Tests of surface quality after electropolishing were conducted on samples 30 mm wide and 90 mm long, with a hole of a diameter of 12 mm located 5 mm away from the upper edge. The upper part of the samples was protected with the PTFE tape, and the resulting exposure surface was 35 cm<sup>2</sup>.

The Metrohm corrosion test cell of a volume of 1 litre allows for the measurement of samples by providing an exposure surface area of 1 cm<sup>2</sup>. Due to this, tests were conducted on samples with a diameter of 16.7 mm and thickness of 1.5 mm, with a hole of a diameter of 1 mm at 1 mm from the edge of sample.

All types of samples were produced from the same piece of sheet metal. Before processing, the samples were degreased in an ultrasound washer in acetone for 20 minutes. After the reduction process, samples were washed in distilled water and after electropolishing, additionally in distilled water in an ultrasound washer.

*2.2. Experimental Circuit.* The reduction and electropolishing equipment consisted of the following elements: laboratory power supply unit KP-131 (KP-Elektronika), electric charge counter (KP-Elektronika), EUROSTAR 60 control mechanical mixer (IKA), water bath (Pilot ONE Huber CC-K12), and a designed circuit (Figure 1). The circuit was constructed with a 1.5 mm thick copper sheet. All connections were made in a way that ensures current flow by using copper bolted connections. In order to separate the cathode from the anode, nonconductive elements in the form of polyethylene cubes were used and connected with the frame with use of copper bolts.

For the cathodic reduction process, the cathode was placed in the centre of the frame, while the anodes were located 40 mm away from the central axis. For the

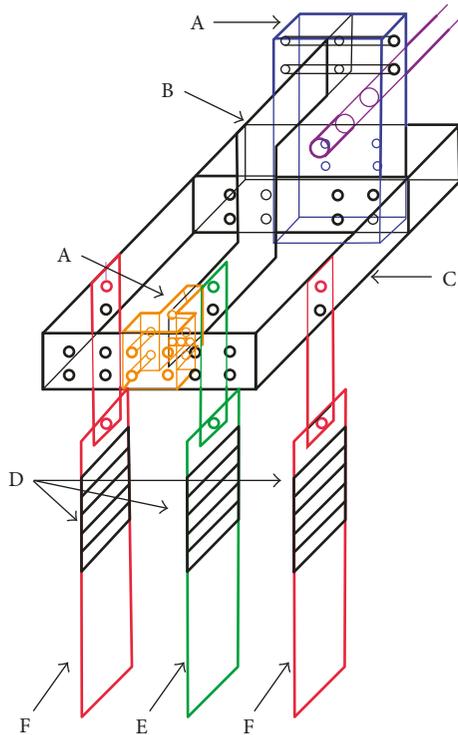


FIGURE 1: Diagram of the circuit used for tests: (A) polyethylene structural elements, (B) copper busbar of the electrode, (C) copper busbar of two electrodes, (D) PTFE insulation, (E) cathode electrochemical reduction variant, anode electropolishing variant, and (F) anode electrochemical reduction variant, cathodes electropolishing variant.

electropolishing process, the anode was placed centrally, while two cathodes were located at a smaller distance, that is, 20 mm from the central axis.

### 2.3. Reduction with Use of the Cathodic Reduction Method.

The conducted research covered the extent of reduction of the processing bath after the electropolishing process by means of cathodic reduction. The bath subjected to tests was used for industrial purposes for a long period of time, so its initial level of contamination was very high (ion concentration,  $\text{Fe}:\text{Cr}:\text{Ni}:\text{Cu} = 50:15:2.2:1.45 \text{ g}\cdot\text{dm}^{-3}$ ). The reduction process was applied to  $2000 \text{ cm}^3$  of the processing bath placed in a glass beaker in a water bath and mixed constantly with use of a mechanical mixer. The process took place in the following conditions: temperature  $50^\circ\text{C}$ , mixing speed 50 rpm, and current density  $0.0015 \text{ A}\cdot\text{cm}^{-2}$ . The duration of the reduction process consisted of 15 cycles of 12 hours each. The total duration of the electrolysis process was 180 hours. After the end of each cycle of 720 minutes of electrolysis, the electrodes were washed in distilled water, and the cathode was replaced with a new one. After proper mixing of the electrolyte, a sample of the volume of  $2 \text{ cm}^3$  was collected for ICP testing.

2.4. *Electropolishing.* The electropolishing process was conducted both for the bath without electrochemical

reduction (without ER) and with electrochemical reduction (with ER) in a glass beaker containing  $2000 \text{ cm}^3$  of processing bath, in the following conditions: temperature  $55^\circ\text{C}$ , mixing speed 50 rpm, and current density  $5 \text{ A}\cdot\text{dm}^{-2}$ . Three variants of process duration were tested: 45, 90, and 180 minutes. The obtained samples were washed in distilled water and subjected to surface roughness and gloss tests. Additionally, mass reduction as a result of anodic dissolution was determined.

2.5. *ICP Tests.* The collected samples were subjected to ICP-OES (inductively coupled plasma-optical emission spectroscopy) tests with use of the Thermo Scientific iCAP 7000 Series ICP-OES apparatus with an automated sample feeder and software manufactured by Qtegra Intelligent Scientific Data Solution.

2.6. *Gloss Tests.* Gloss was tested with use of the Rhopoint IQ goniophotometer that measures gloss at the angles of  $20/60/85^\circ$ .  $20^\circ$  angle gloss was selected as the main measurement from the available parameters of the equipment. According to the manufacturer's recommendations [24], the  $20^\circ$  measurement angle should be used for measuring high-gloss coatings and polished metals, as it allows obtaining enhanced accuracy and resolution. Six measurements were taken for each sample.

2.7. *Roughness Tests.* Roughness tests were conducted with use of the Mitutoyo SurfTest SJ-301 surface roughness test apparatus. Six measurements were taken for each sample, at the central axis, parallel to the upper edge of the sample, at equal distances.

2.8. *Optical Surface Profiler.* In order to provide a quantitative comparison of large-area undulations observed on the surface of the analysed samples, imaging was conducted with use of the Sensofar S Neox surface profiler that enables to obtain quantitative information about surface topography at a resolution of tens of nanometers on a length up to 10 cm. Whenever it was necessary to analyse an area that reached beyond the scanning range in a single course, the stitching process was conducted with use of dedicated SensoMAP Standard software. The same software was used to prepare visualisations of the recorded data. Quantitative assessment of the obtained profiles was performed with use of SPIP software manufactured by Image Metrology [25]. It should be noted that the quantitative analysis of changes in surface roughness caused by various factors was many times successfully used for the evaluation of the influence of a given medium on the analysed material [26–29].

2.9. *Corrosion Resistance Tests.* Pitting corrosion resistance of steel after electropolishing in a bath with ER and without ER was evaluated in potentiodynamic tests. The corrosion solution was 0.5 M NaCl with a temperature of  $25 \pm 1^\circ\text{C}$ . Tests were conducted with use of Solartron SI 1287

potentiostat manufactured by AMETEK. The Metrohm corrosion testing cell of a volume of  $1 \text{ dm}^3$  with a water curtain connected to the water bath was used. An arrangement of three electrodes was used, where the tested electrode was the analysed steel, the counter electrode was a platinum electrode, and the reference electrode was a saturated calomel electrode. The obtained data were analysed with use of dedicated CorrView software.

### 3. Results and Discussion

**3.1. Electrochemical Reduction of Process Bath.** The conducted ICP tests of the collected samples enabled to determine the content of metal ions (copper, nickel, iron, and chromium) both in the bath before electrochemical reduction and in various stages of the electrochemical reduction process. The results of tests conducted with use of this method are presented in form of diagrams of changes in the content of copper and nickel ions in the analysed solution (Figure 2). In spite of the perishability of contaminants that accumulate on the cathode during the process, a gradual removal of copper and nickel ions from the bath was observed as a function of the duration of electrolysis. The effectiveness of copper and nickel removal in the analysed process was 53% and 47%, respectively. The obtained results may constitute a basis for estimating the duration of the process required to remove the whole copper and nickel from the solution. For copper, the process should last for over 340 hours and for nickel over 380 hours. The realisation of such process on an industrial scale would be extremely time- and energy-consuming. In very acidic environment (pH of approx. 1), mainly copper and nickel can be removed from the solution. The attempt to remove iron and chromium in the analysed process was unsuccessful. According to initial expectations, their content in the solution remained practically the same. The obtained results demonstrate that it is possible to remove some of the contaminants on-site of their emergence, directly in the processing bath. However, in industrial conditions, conducting the bath reduction process would be very time-consuming. Thus, the authors of this paper considered increasing the surface of cathodes, because otherwise, the process would require too much effort and it would be unjustified in economic terms.

**3.2. Surface Studies.** Surface roughness and gloss were measured both for as received samples and for samples after the electropolishing process. In order to minimize the influence of surface quality of as received samples on the electropolishing results, all electropolishing tests were conducted on such row samples that were characterised by surface roughness of  $R_a = 0.16 \mu\text{m}$  (Figure 3). This allowed us to obtain the same initial conditions for all electropolished samples. The electropolishing process was conducted in two different variants of the bath: industrial bath without ER and with ER. For the bath without ER, the roughness value deteriorated after the electropolishing process in comparison with as received samples, while for the bath with ER,

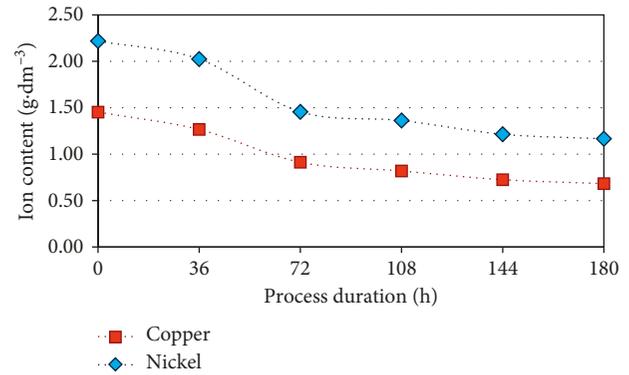


FIGURE 2: Content of copper and nickel ions in the electrolyte in specific stages of the cathodic reduction process ( $t = 0\text{--}180 \text{ h}$ ,  $I = 0.1 \text{ A}$ ,  $i = 0.0015 \text{ A}\cdot\text{cm}^{-2}$ , and  $T = 50^\circ\text{C}$ ).

a gradual improvement was noted with the prolonged duration of the process (Figure 3(a)). In individual series, the best surface roughness results both for the bath with ER ( $R_a = 0.13 \mu\text{m}$ ) and without ER ( $R_a = 0.18 \mu\text{m}$ ) were obtained for 90 minutes duration of the process. The results of the remaining amplitude roughness parameters, such as the skewness of surface roughness  $R_{sk}$  and the kurtosis  $R_{ku}$  (Figure 3(b)) were significantly improved after the electropolishing process. For samples subjected to electropolishing for 90 minutes and longer, the obtained  $R_{sk}$  and  $R_{ku}$  results were similar to the expected values ( $R_{sk} = 3$ ;  $R_{ku} = 0$ ).

The weight reduction of samples after electropolishing increased proportionally to the duration of the process. Considering the obtained results, it is not recommended to extend the time of the electropolishing process as the weight loss is high and the effects are only slightly improved at the same time. It was also found that samples subject to electropolishing in a bath with ER were characterised by lower weight loss than those processed in a bath without ER, which, if combined with the obtained lower roughness and improved gloss, is an important advantage (Table 1, Figure 3). As the duration of the process was extended, the differences between weight loss of samples with and without ER became smaller, although still significant. They were, respectively, 13%, 9%, and 7% for the process lasting 45 min, 90 min, and 180 min.

The best surface gloss results were obtained after electropolishing for a bath with ER and duration of 90 minutes—increase by approximately 500 GU. For bath without ER, the 90-minute duration also brought relatively best results, although in this case, the increase reached only 300 GU (Figure 4). An attempt to extend the process for a longer time (180 minutes) led to a deterioration of the obtained gloss results, both for bath with and without ER.

In the light of the conducted research, it is recommended to use relatively low current densities for industrial baths that are strongly contaminated with copper, iron, chromium, and nickel ions. The results obtained with use of the optical surface profiling method for current density of  $0.05 \text{ A}\cdot\text{cm}^{-2}$  demonstrated that samples electropolished in

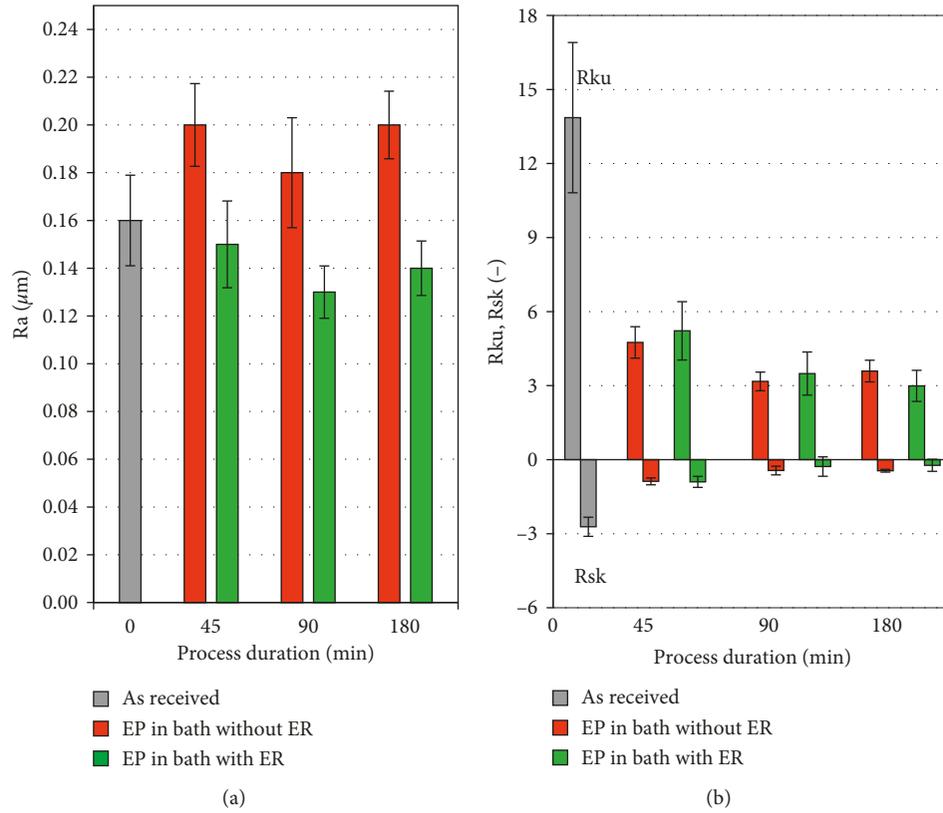


FIGURE 3: Comparison of the changes in surface roughness parameters of samples “as received” and samples after EP in a bath without ER and with ER (EP process parameters:  $t = 45\text{--}180$  min,  $I = 1.75$  A,  $i = 0.05$  A $\cdot\text{cm}^{-2}$ ,  $q = 2.25\text{--}9.00$  Amin $\cdot\text{cm}^{-2}$ , and  $T = 55^\circ\text{C}$ ): (a) arithmetical mean deviation of the assessed profile  $R_a$  and (b) skewness of the surface roughness profile  $R_{sk}$  and kurtosis of the profile  $R_{ku}$ .

TABLE 1: Presentation of the gloss and weight of samples “as received” and samples electropolished in a bath without ER and with ER (EP process parameters:  $t = 45\text{--}180$  min,  $I = 1.75$  A,  $i = 0.05$  A $\cdot\text{cm}^{-2}$ ,  $q = 2.25\text{--}9.00$  Amin $\cdot\text{cm}^{-2}$ , and  $T = 55^\circ\text{C}$ ).

$t_{EP}$ (min)	$q_{EP}$ (Amin $\cdot\text{cm}^{-2}$ )	Bath type	Gloss (as received) (GU)	Gloss (after EP) (GU)	Weight (as received) (g)	Weight (after EP) (g)
45	2.25	Without ER	153 ( $\pm 30$ )	345 ( $\pm 30$ )	24.822	24.404
		With ER	132 ( $\pm 20$ )	419 ( $\pm 10$ )	24.713	24.349
90	4.50	Without ER	144 ( $\pm 10$ )	459 ( $\pm 50$ )	25.026	24.210
		With ER	121 ( $\pm 10$ )	638 ( $\pm 40$ )	24.667	23.926
180	9.00	Without ER	133 ( $\pm 20$ )	365 ( $\pm 20$ )	24.857	23.281
		With ER	139 ( $\pm 10$ )	531 ( $\pm 20$ )	24.537	23.075

a bath with ER are characterised by a more smooth surface ( $S_q = 0.22$   $\mu\text{m}$ ;  $S_z = 0.770$   $\mu\text{m}$ ) than samples electropolished in baths without ER ( $S_q = 0.27$   $\mu\text{m}$ ;  $S_z = 1,044$   $\mu\text{m}$ ) (Figure 5).

**3.3. Influence of Current Density.** In order to analyse the influence of current density on the results of electropolishing, the process was conducted with use of the aforementioned baths without ER and with ER, for two different current densities. Surface roughness was measured both for as received samples and for samples after the electropolishing process. The applied current densities were, respectively,  $0.05$  A $\cdot\text{cm}^{-2}$  for  $I = 1.75$  A and  $0.20$  A $\cdot\text{cm}^{-2}$  for  $I = 4.00$  A. The exposed surface was adjusted so as to obtain the same unit load. For samples

electropolished at higher current densities, emerging smudges were noticed on the whole exposed surface, which resulted in a considerable deterioration of surface roughness of samples after electropolishing in comparison with as received samples, both for baths without ER and with ER.

Detailed inspection of the emerging defects allowed us to discover that elongated valleys emerged on the surface of the material. Their orientation with respect to the position of samples during electropolishing was vertical. The surface was analysed with use of a surface profiler to measure the distance between these valleys. The obtained results enabled a quantitative comparison of the observed results of the electropolishing process. The obtained profiles were the basis for calculating the following parameters:  $\Delta Z$ , maximum

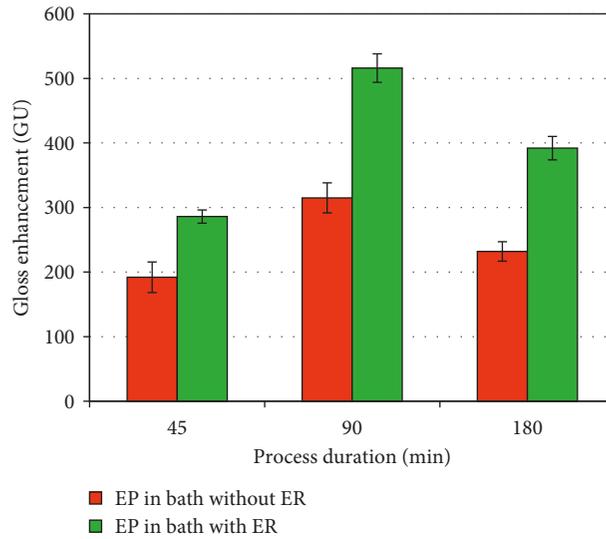


FIGURE 4: Enhanced gloss after electropolishing in a bath without ER and with ER (EP process parameters:  $t = 45\text{--}180$  min,  $I = 1.75$  A,  $i = 0.05$  A·cm<sup>-2</sup>,  $q = 2.25\text{--}9.00$  Amin·cm<sup>-2</sup>, and  $T = 55^\circ\text{C}$ ).

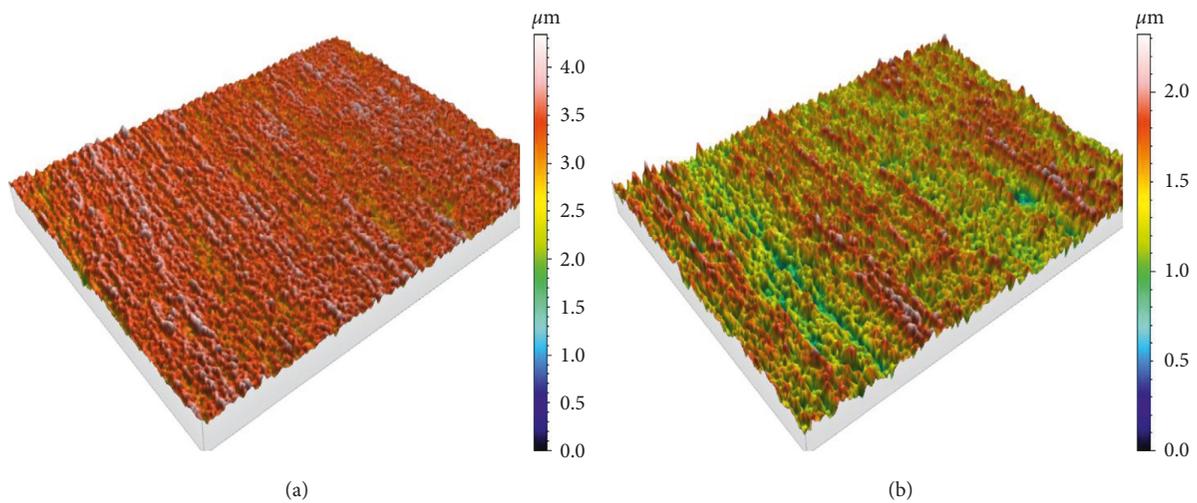


FIGURE 5: Topography of sample surface after electropolishing (parameters of the EP process:  $t = 180$  min,  $i = 0.05$  A·cm<sup>-2</sup>,  $q = 9.00$  Amin·cm<sup>-2</sup>, and  $T = 55^\circ\text{C}$ ): (a) in a bath with ER and (b) in a bath without ER.

difference in height within the sample;  $S_z$ , difference between levels in an averaged group of undulations;  $S_q$ , mean square roughness along the profile; and  $\text{FFT\_ampl}$ , total of the amplitudes of two first harmonic components FFT that define surface undulations in quantitative terms. Due to the specificity of each of these coefficients and the type of information they carry, their juxtaposition may be interpreted depending on the analysed problem. However, in terms of the noticed undulations, the differences are demonstrated most clearly by the  $\Delta Z$  coefficient. These values were assigned to the recorded surface profiles (Figure 6).

For samples electropolished at current density  $0.05$  A·cm<sup>-2</sup>, the difference in roughness  $R_a$  after the process was  $\pm 0.03$   $\mu\text{m}$ . At the same time, for samples electropolished at current density  $0.20$  A·cm<sup>-2</sup>, an increase in roughness even by  $0.1$   $\mu\text{m}$  was noted in comparison with the roughness

of as received sample. The presented parameters are similar in terms of trends. However, due to their sensitivity to characteristic morphological elements, some differences are visible. For example, the  $S_q$  roughness parameter takes into account, apart from undulations, also small morphological details to which other parameters are not sensitive. On the other hand,  $\text{FFT\_ampl}$  refers only to undulations detected in profiles by DFFT algorithms.

The authors analysed the threshold current density used for electropolishing at which defects emerging during the process can be noticed. For the temperature of  $55^\circ\text{C}$ , the threshold value is  $0.17$  A·cm<sup>-2</sup>. No smudges were noted at this current density. As the density increases, the effects are becoming more visible, from slight smudges at the bottom edge at  $0.18$  A·cm<sup>-2</sup>, through clear smudges at approximately  $1$  cm from the bottom edge at  $0.19$  A·cm<sup>-2</sup>, to noticeable

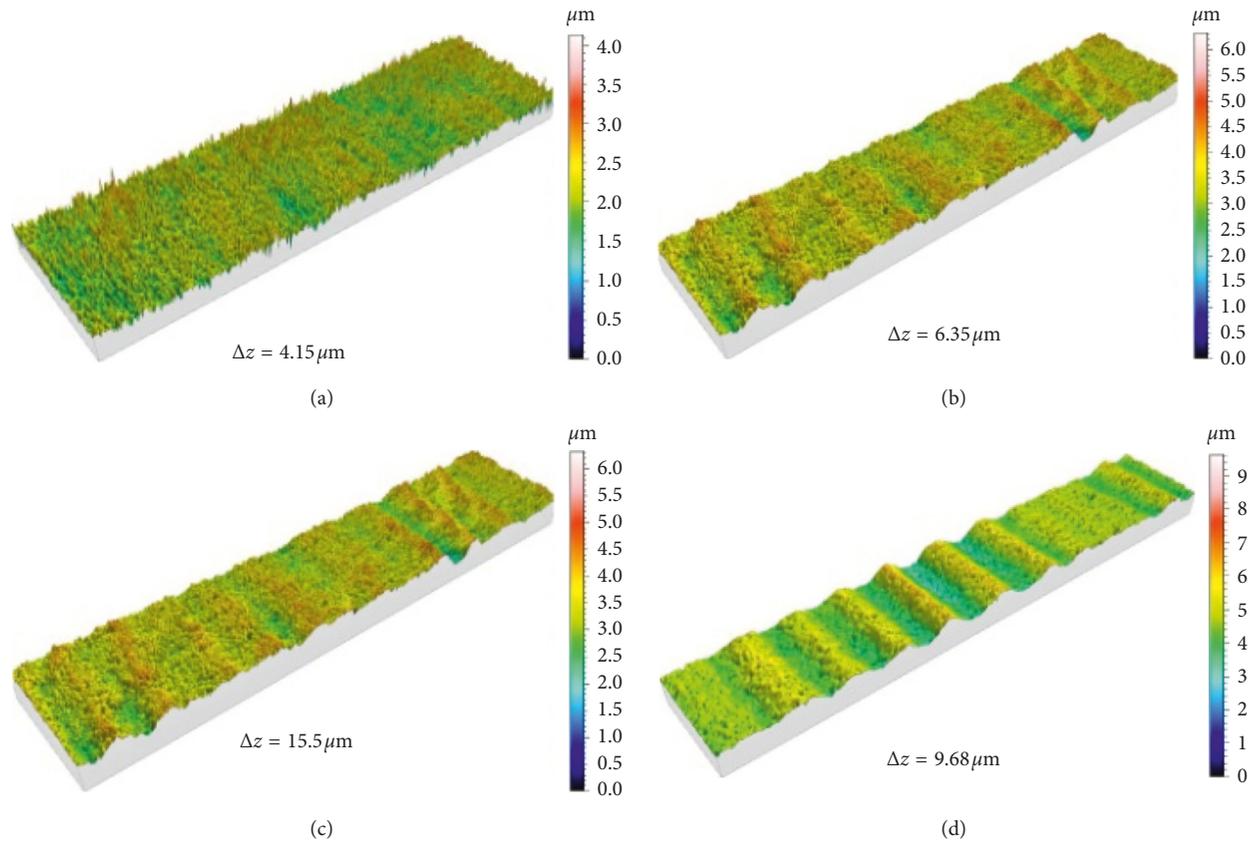


FIGURE 6: Topography of sample surface after electropolishing ( $T = 55^{\circ}\text{C}$  and  $q = 9.00 \text{ A}\cdot\text{min}\cdot\text{cm}^{-2}$ ) in a bath without ER: (a) sample without defects ( $i = 0.17 \text{ A}\cdot\text{cm}^{-2}$ ); (b) sample with defects ( $i = 0.19 \text{ A}\cdot\text{cm}^{-2}$ ); (c) sample with defects ( $i = 0.20 \text{ A}\cdot\text{cm}^{-2}$ ); and (d) after electropolishing in a bath with ER with defects ( $i = 0.20 \text{ A}\cdot\text{cm}^{-2}$ ).

smudges throughout the whole surface at  $0.20 \text{ A}\cdot\text{cm}^{-2}$  (Table 2).

The emergence of defects after the electropolishing process was also observed in 316L grade steel, where the application of a temperature of  $55^{\circ}\text{C}$  and current density of  $0.20 \text{ A}\cdot\text{cm}^{-2}$  led to emerging surface defects (smudges on the surface of electropolished samples) in the bath of sulfuric acid(VI), orthophosphoric acid, glycol, oxalic acid, and acetanilide.

At the same time, the application of high current densities during electropolishing of 304 or 316 grade steel in noncontaminated baths containing orthophosphoric acid (V), sulfuric acid(VI), and organic additives, that is, triethylamine, glycerol, triethanolamine, ethanolamine, diethanolamine, and butyldiglycol does not lead to the emergence of surface defects [30].

**3.4. Cathode Contamination after the Electropolishing Process.** After the conducted electropolishing processes of duration of 45, 90, and 180 minutes, a change in the appearance of cathodes was noticed, depending on the type of bath used. For baths with ER, there were considerably less contaminants accumulated on the cathode than for baths without ER (Figure 7).

In industrial conditions, contaminants that accumulate on cathodes during the process lower the attainable current

density range, which results in the necessity to clean or replace the cathodes periodically. Cathodes used in the reduced bath become contaminated after a longer time, as the content of copper ions in the bath is lower. This may have a positive influence on the course of the process in industrial conditions due to the fact that it is not necessary to clean the cathodes frequently after the process.

**3.5. Corrosion Resistance Tests.** Potentiodynamic tests in  $0.5 \text{ M NaCl}$  solution were used to determine the influence of bath reduction on the change in the pit development potential ( $E_{\text{pit}}$ ) and the potential of anodic-cathodic transfer ( $E_{\text{KA}}$ ) of samples after the electropolishing process (Figure 8). After determining the stationary potential of the analysed samples, potentiodynamic tests were conducted starting from a potential value lower by  $0.25 \text{ V}$  from the previously determined stationary potential. Tests were conducted at a scanning speed of  $1 \text{ mV/s}$ . After achieving the potential at which the current density increased by approximately three magnitude orders to the value of  $1 \cdot 10^{-4} \text{ A}\cdot\text{cm}^{-2}$ , the polarisation direction was changed, and measurement was continued until the moment when the returning curve crossed the original curve. Twelve measurements were taken in two series, for baths with and without ER. Then, the values of  $E_{\text{pit}}$  and  $E_{\text{KA}}$  were read from the obtained potentiodynamic curves (Table 3).

TABLE 2: Sample surface roughness in the area of noticed undulations.

Type of bath	$I$ ( $A \cdot cm^{-2}$ )	$q/s$ ( $Amin \cdot cm^{-2}$ )	Sq (nm)	FFT_ampl	$\Delta Z$ ( $\mu m$ )	Surface defects after EP
Without ER	0.20	9	547	547	15.50	+++
With ER	0.20	9	645	645	9.68	+++
Without ER	0.19	9	289	289	6.35	++
Without ER	0.18	9	170	170	2.32	+
Without ER	0.17	9	201	201	4.15	None
Without ER	0.05	9	271	271	2.31	None
With ER	0.05	9	218	218	4.33	None

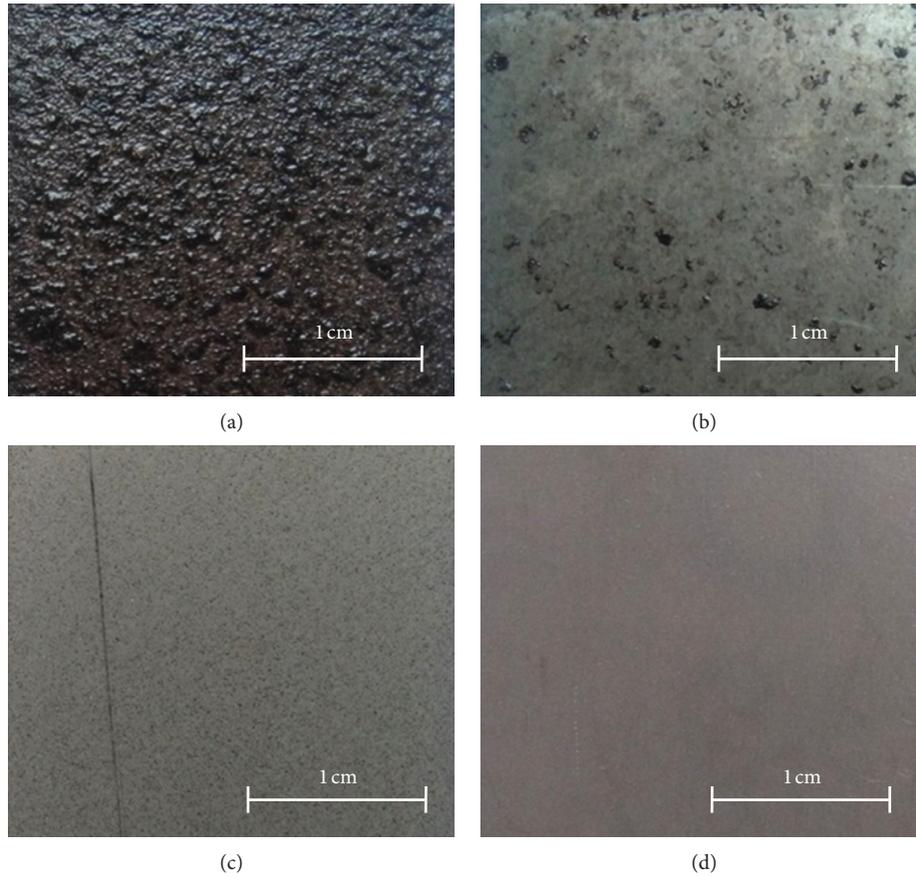


FIGURE 7: Contaminants accumulated on the cathode surface: in the bath without ER, (a) before DI water rinse and (b) after DI water rinse; in the bath with ER, (c) before DI water rinse and (d) after DI water rinse.

Basing on the measurements conducted for samples electropolished in baths without ER and with ER, it was noticed that the obtained  $E_{pit}$  results were approx.  $0.5 V_{SCE}$ , which was similar to the results obtained in previous studies [30]. At the same time, it was found that for samples electropolished in a bath with ER, many results were lower than  $0.5 V_{SCE}$ , while for samples electropolished in a bath without ER, most of the results exceeded this value. Due to this, the authors decided to analyse the significance of differences between the obtained results with use of data analysis methods used in various types of data evaluation, among others in medicine, chemical analysis, or engineering [31–34].

The normality analysis with use of the Shapiro–Wilk test did not show a significant deviation from normal

distribution. The analysis of differences between average  $E_{pit}$  values demonstrated that the average was significantly lower for samples electropolished in a bath with ER ( $0.462 \pm 0.056 V_{SCE}$ ) than in the bath without ER ( $0.552 \pm 0.13 V_{SCE}$ ). Additionally, the variance comparison demonstrated that the range of result variability was much higher in the group without ER (Levene test,  $p = 0.01$ ).

The obtained results demonstrate that the reduction of the process bath leads to deteriorated pitting corrosion resistance of the electropolished samples. However, it should be noted that the results obtained for this series were characterised by higher repeatability than those for baths without ER (Figure 9). The median and quartile range for samples electropolished in a bath with ER were, respectively,

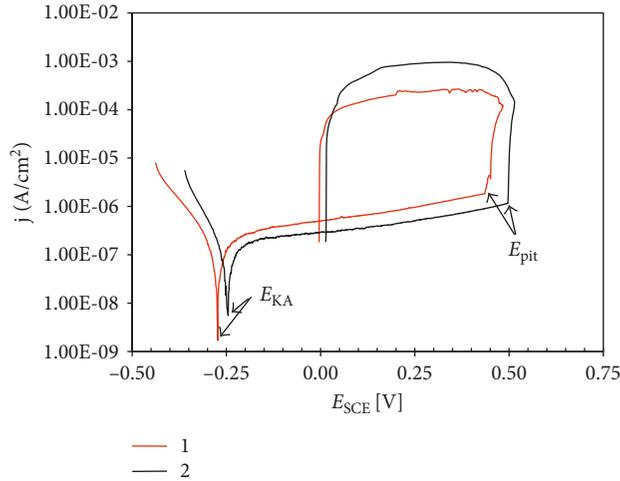


FIGURE 8: Potentiodynamic curves obtained in 0.5 M environment of NaCl solution for samples: 1, sample electropolished in a bath with ER; 2, sample electropolished in a bath without ER.

TABLE 3: Critical pitting development potential  $E_{pit}$  and the cathodic-anodic transfer potential  $E_{KA}$  for samples electropolished in baths with and without ER.

	Bath with ER		Bath without ER	
	$E_{KA}$ (V <sub>SCE</sub> )	$E_{pit}$ (V <sub>SCE</sub> )	$E_{KA}$ (V <sub>SCE</sub> )	$E_{pit}$ (V <sub>SCE</sub> )
Series 1	-0.27	0.44	-0.32	0.68
	-0.24	0.46	-0.28	0.59
	-0.26	0.36	-0.25	0.50
	-0.27	0.42	-0.23	0.37
	-0.25	0.45	-0.24	0.53
	-0.26	0.45	-0.32	0.65
Series 2	-0.22	0.53	-0.24	0.41
	-0.28	0.58	-0.27	0.55
	-0.31	0.50	-0.29	0.59
	-0.24	0.48	-0.26	0.33
	-0.24	0.42	-0.28	0.68
	-0.26	0.45	-0.27	0.74

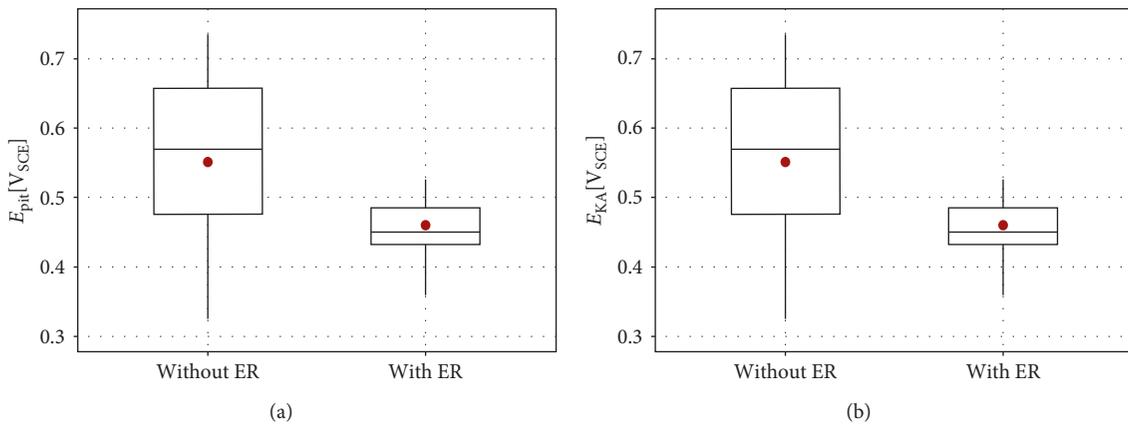


FIGURE 9: Comparison of  $E_{pit}$  and  $E_{KA}$  between groups with and without electrochemical reduction (dot-mean; line-median).

0.45 V<sub>SCE</sub> and 0.43–0.49 V<sub>SCE</sub>, and for baths without ER, 0.57 V<sub>SCE</sub> and 0.46–0.66 V<sub>SCE</sub>. A similar analysis as for  $E_{pit}$  was conducted for  $E_{KA}$ . No significant differences were found between the results for samples electropolished in baths with and without ER.

### 4. Conclusions

In the analysed processing bath reduction process with use of cathodic reduction, the effectiveness of copper and nickel removal was, respectively, 53% and 47%. The obtained results

allow us to estimate the duration of the process required for total removal of copper (340 h) and nickel (380 h) from the solution. However, the realisation of such a process on an industrial scale would be very much time- and energy-consuming.

For the bath without ER, the roughness value deteriorated after the electropolishing process in comparison with as received samples, while for the bath with ER, a gradual improvement was noted with the prolonged duration of the process. Surface quality tests after electropolishing demonstrated that the best results, both for baths with ER ( $R_a = 0.13 \mu\text{m}$ ; gloss 638 GU), were obtained for the electropolishing process lasting 90 minutes.

The weight reduction of samples after electropolishing increased proportionally to the duration of the process. It was also noted that samples electropolished in a bath with ER were characterised by lower weight loss in comparison with samples electropolished in a bath without ER, for all variants of the process duration. At the same time, for baths with ER, there were considerably less contaminants deposited on the cathode than for baths without ER. In industrial conditions, contaminants that accumulate on cathodes during the process lower the attainable current density range, which results in the necessity to clean or replace the cathodes periodically. Cathodes used in the reduced bath become contaminated after a longer time, as the content of copper ions in the bath is lower. This may have a positive influence on the course of the process in industrial conditions due to the fact that it is not necessary to clean the cathodes frequently after the process.

## Data Availability

The data used to support the findings of this study are currently under embargo while the research findings can be commercialized after the research is ended. Requests for data, 24 months after publication of this article, will be considered by the corresponding author.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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