STUDY OF CORROSION RESISTANCE OF CHROMIUM-NICKEL STEEL IN CALCIUM – HYPOCHLORITE SOLUTION PART 2. STEELS Č 4574 AND Č 4583

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Abstract

The paper shows the results of corrosion resistance investigations of different samples: chromium-nickel steels Č 4574 and Č 4583 in calcium-hypochlorite solution, using potentio-dynamic method. The paper presents continuation of investigations on steels URANUS B6 and Č 4578 published in reference [1]. Comparison of the obtained results is carried out, in order to detect steel, which quality is the best choice for calcium hypochlorite solution requirements.

Keywords: chromium-nickel, calcium-hypochlorite solution, numerical method of linear polarization, steel Č 4574, steel Č 4583.

1. Introduction

Corrosion resistance of chromium – nickel (special steels) specimen are tested in calcium-hypochlorite solution different solutions by fast electrochemical methods: numerical method of linear polarization, and polarization resistance method.

Chromium–nickel steels Č 4574 and Č 4583 (special steels) whose chemical composition is shown in Table 1. are used in this test.

Increase of $Ca(OCl)_2$ concentration leads to increase of pH value of the solution, as well as active chlorine concentration and corrosion activity of the medium. For investigations of corrosion resistance of steels Č 4574 and Č 4583, test was performed in 50 wt% $Ca(OCl)_2$ suspension and 10 wt% and 1 wt% $Ca(OCl)_2$ solution. Obtained results were compared with characteristics of steels URANUS B6 and Č 4578 [1].

2. Experimantal

2.1. Materials

Chromium–nickel steels (special steels), which chemical compositions are shown in Table 1, are used in this paper.

Table 1. Chemical composition of investigated steel.

Type of steel	Chemical composition in wt. %						
	C	Si	Mn	Cr	Mo	Ni	Cu
Č 4574	0.08	0.15	0.8	18.5	2.5	10.8	–
Č 4583	0.11	1.0	0.5	18.5	2.0	10.8	–

Electrodes for potentiodynamic measurement are made in the cylindrical shape plastic holder with steel specimen fixed on the one base. In that way constant surface of electrode is provided. Contact with electrode through plastic holder is provided by soldered copper wire. Working area of electrode is 0.1 cm^2 to 0.12 cm^2. Precision of test results depends on quality of pre-treatment of electrodes. Pretreatment electrode process consists of mechanic and chemical pretreatment.

Mechanic pretreatment consists of polishing of electrode with sandpaper

(so called, rough polish) and then, fine polish is done with sandpaper 220, 280, 400 and 600 type. After that, chemical pretreatment is done by degreasing in ethanol first, and than distilled water rinsing, alcohol rinsing and, finally, drying. Thus treated specimens (electrodes) are left in the atmosphere controlled vessel if they are not immediately tested.

Calcium–hypochlorite solutions were used as corrosive medium. Test was performed in 50% $Ca(OCl)_2$ suspension and 10% and 1% $Co(OCl)_2$ solution (in wt.%). Due to hypochlorite dissolving, solutions were prepared immediately before the test. Active chlorine content was found by iodinemetry method and pH value of solution was measured by pH meter.

2.2. The instruments and equipment

The following equipment was used for potentiodymanic measurement: Potentiostat-galvanostat type 273 PAR, *Princeton Applied Research*, USA, Hewlet–Packard computer, and X-Y type 7046A recorder, Houston Instruments, USA. We also used measurement cell of standard type for triple electrode system. Measurement cell is filled with corrosive solution where three electrodes are immersed: working electrode, counter electrode and reference electrode. Platinum wire preciously treated in mixed solution of concentrated nitric acid and sulphuric acid and then washed out in distilled water was used as counter electrode. Calomel electrode with +240 mV potential was used as reference electrode. Calomel electrode is connected to working electrode through agar–agar salt bridge.

3. Results and discussion

Potentiodynamic anode and cathode curves were registred on tested steels Č 4574 and Č 4583 from +2,0 V to –2,0 V in 50 wt. % $Ca(OCl)_2$ suspension, and 10 wt.% and 1 wt.% $Ca(OCl)_2$ solution (Fig. 2. and 3.).

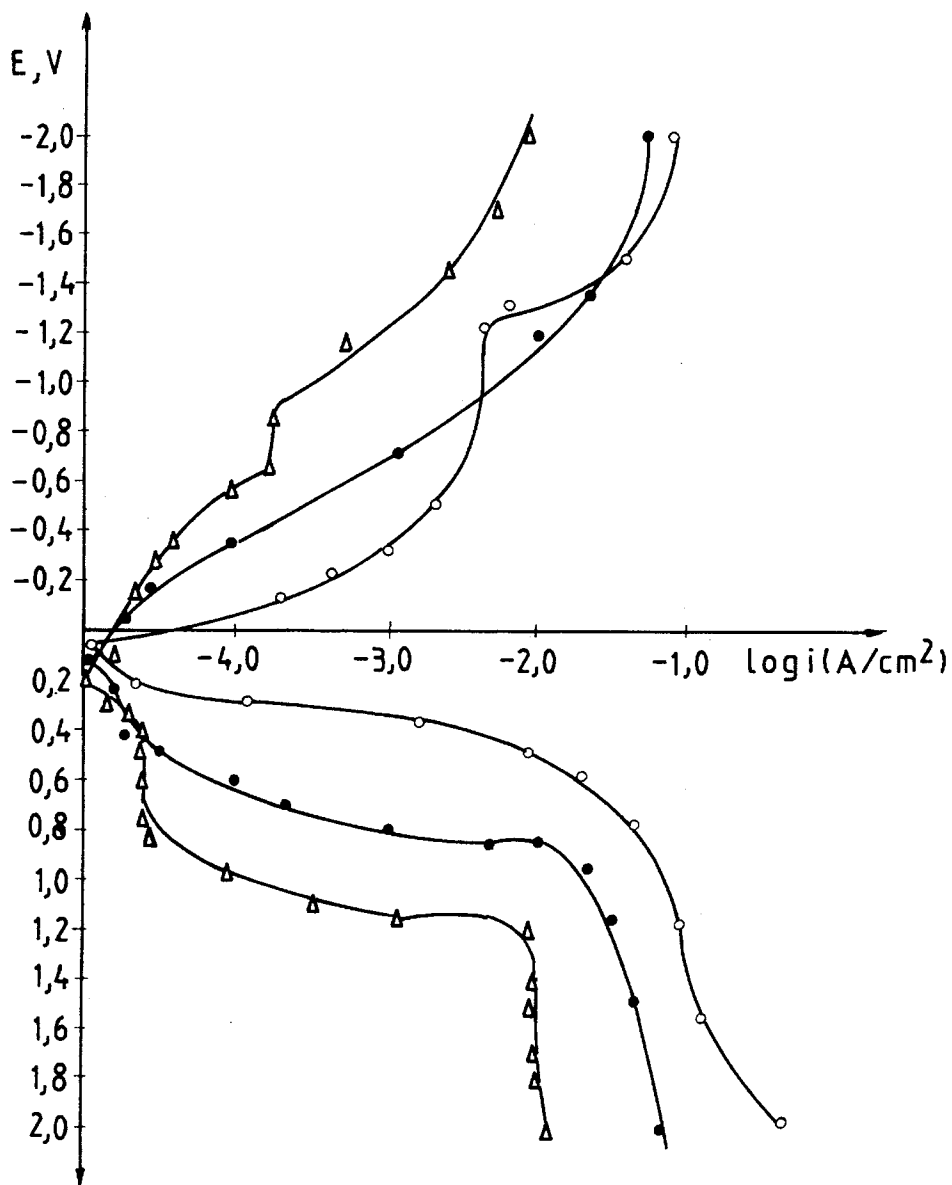Fig. 1. Potentiodynamic curves for steel Č 4574 in tested corrosive
media where: (o) Er = 60mV, (•) Er = 120mV, (Δ) Er = 186mV,
i.e. (o) - 50 wt. % suspension, (•) 10 wt. % solution i (Δ) 1 wt.
% solution.
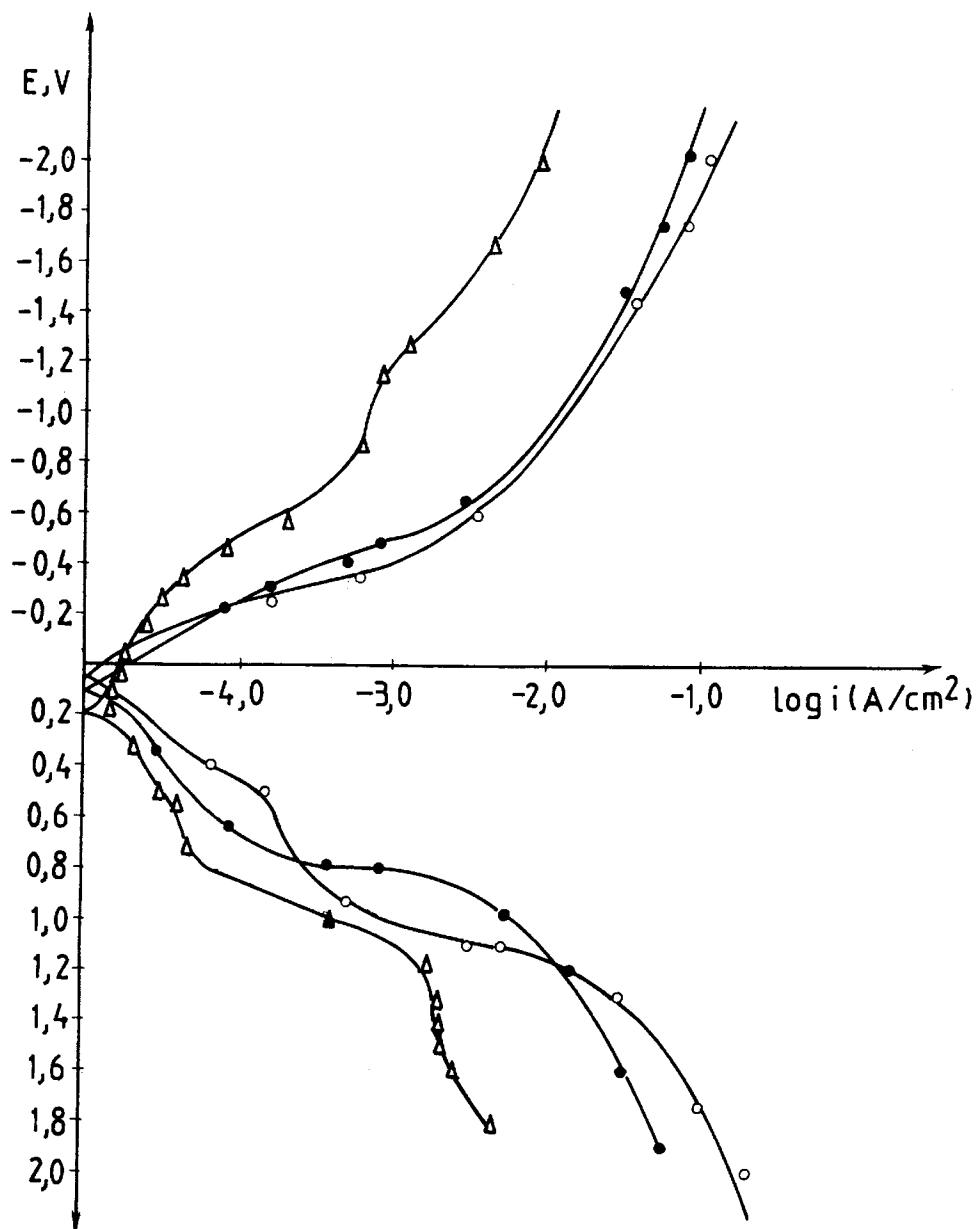
Fig. 2. *Potentiodynamic curves for steel Č 4583 in tested corrosive media where: (o) Er = 45 mV, (•) Er = 100 mV, (Δ) Er = 200 mV, i.e. (o) - 50 wt. % suspension, (•) 10 wt. % solution i (Δ) 1 wt. % solution.*

Anode polarization curves in potential interval from stetioned potential to +2,0 V for all four chromium–nickel steels in tested solutions are given on Fig. 3.–5.
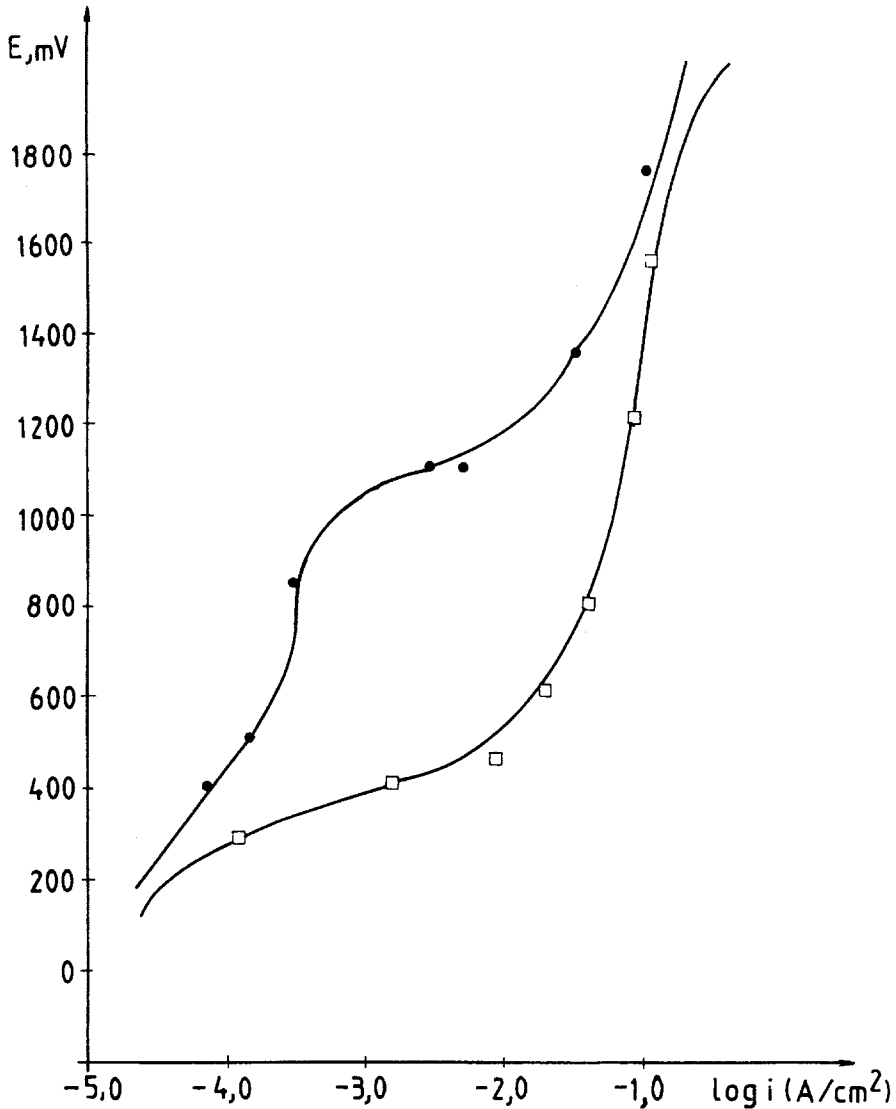

Fig. 3. Anode polarization curves in the 50 wt.% Ca(OCl)$_2$ suspension where: (•) - steel Č 4574, ( ) steel Č 4583.

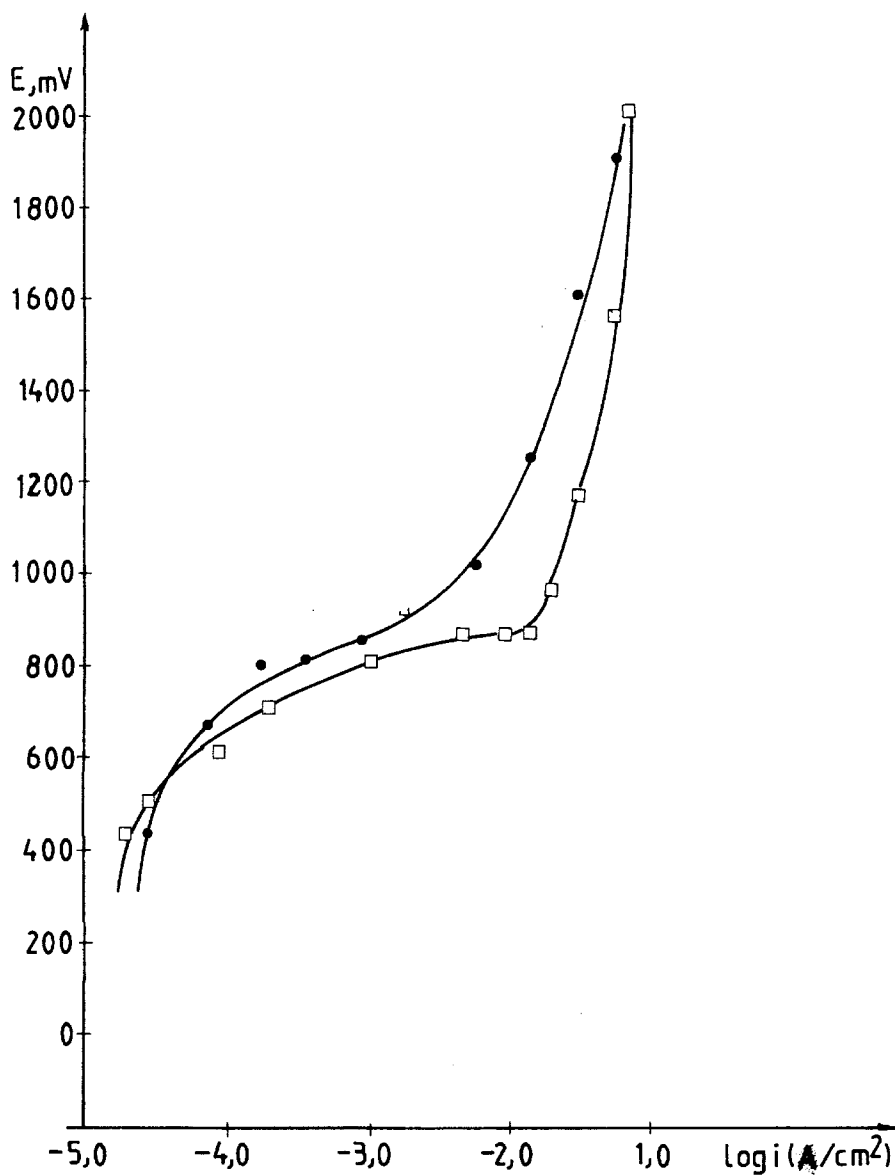*Fig. 4. Anode polarization curves in the 10 wt.% Ca(OCl)₂ suspension where: (•) - steel Č 4574, ( ) steel Č 4583.*

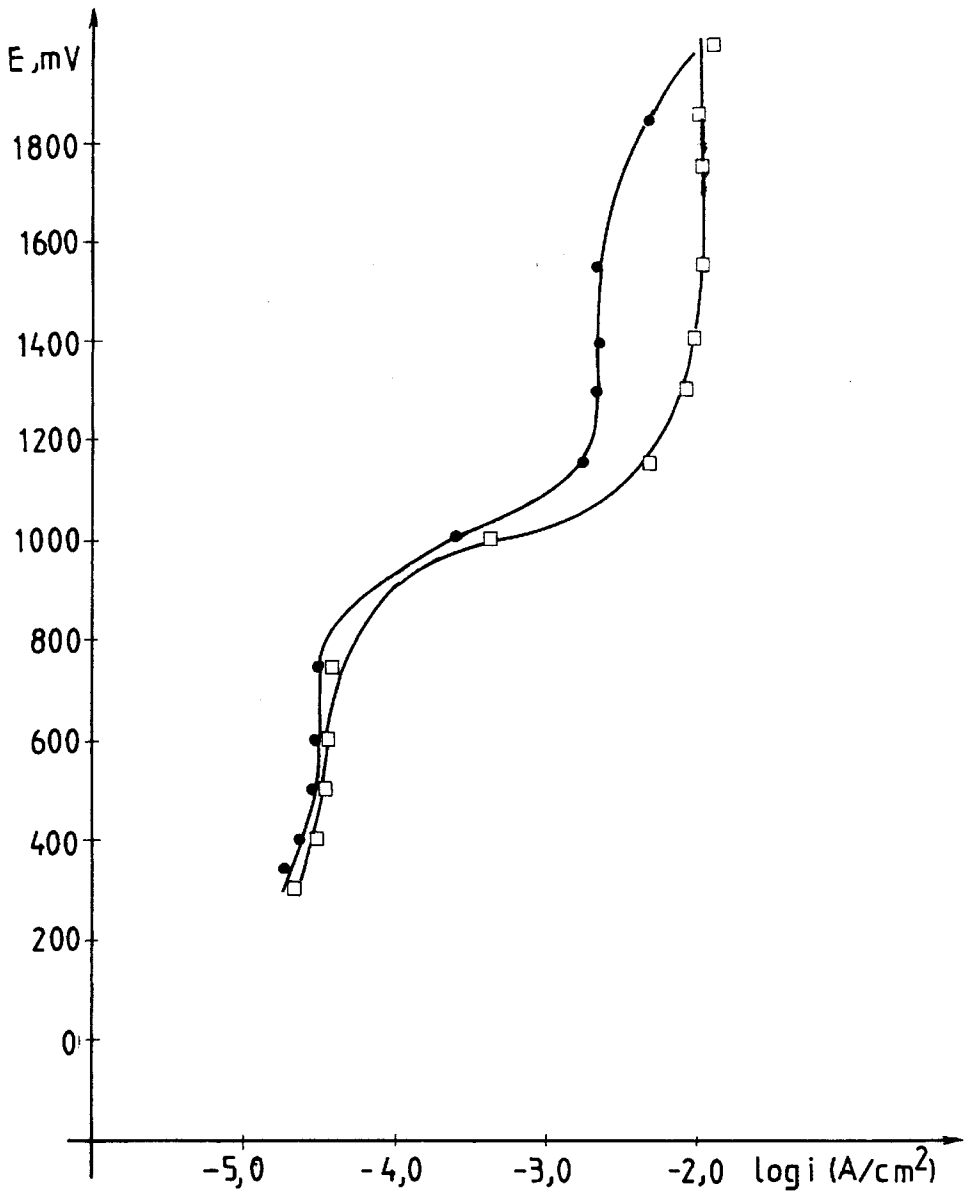*Fig. 5. Anode polarization curves in the 1 wt.% Ca(OCl)₂ suspension where: (●) - steel Č 4574, ( ) steel Č 4583.*

Corosion potential was measured after the working electrode was in contact with corrosive medium for 30 minutes for stabilization of potential [4].

Kinetic parameters of electrochemical reaction can be determined by graphic and numeric method based on polarization measurement. Corrosion current and corrosion potential are achieved in the section of Tafel lines e = f(log i) by graphic method of linear polarization. Fig. 6 shows Tafel lines for tested steels Č 4574 and Č 4583 in 50 wt. % suspension Ca(OCl)$_2$. Corrosion current and corrosion potentials are obtained analogously for the other two corrosion media.
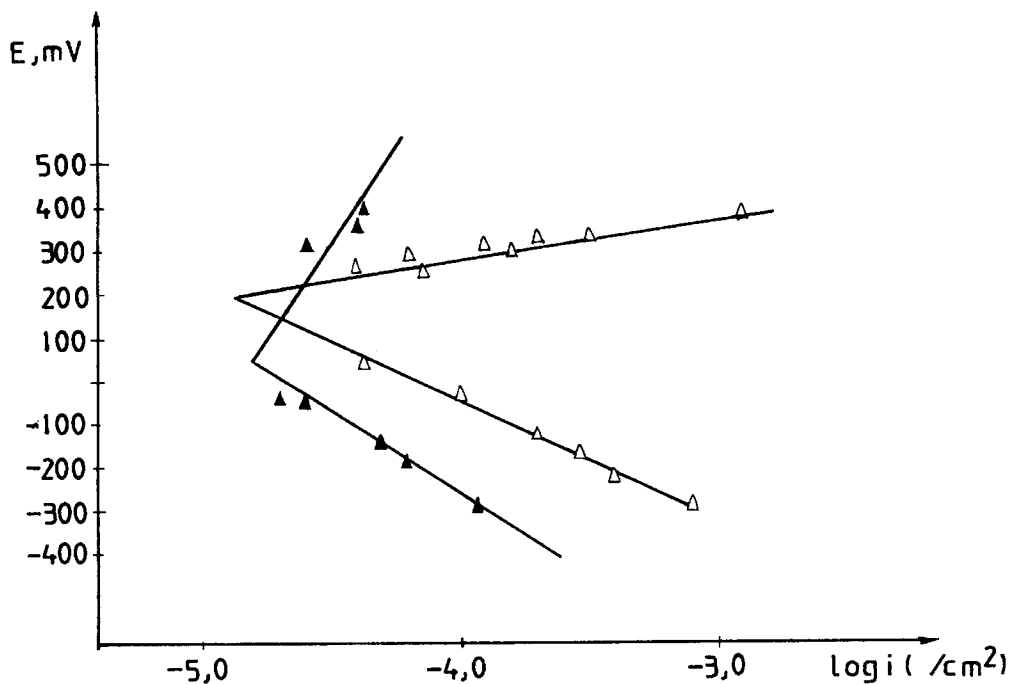

Fig. 6. Graphical determination of the corrosion current in the 50wt.% Ca(OCl)$_2$ suspension where: (Δ) - steel Č 4574, (▲) steel Č 4583.

Numerical processing of data obtained by polarization measurement consists of computer fitting of test results [3], showed in first part this paper [1].

Corrosion parameters resulting from the linear polarization method are shown in Table 2.

Table 2. Corrosion parameters obtained by numerical method of linear polarization

Type of steel	Concentrations of Ca(OCl)$_2$	Graphic methods		Numerical methods	
		i_{cor} (μA/cm^2)	e_{cor} (mV)	i_{cor} (μA/cm^2)	e_{cor} (mV)
Č 4574	50	12.58	100	12.60	202
	10	6.50	250	6.15	243
	1	1.26	– 30	1.15	– 19
Č 4583	50	16.00	30	15.00	94
	10	5.26	10	5.55	9.3
	1	1.50	50	1.20	– 22

Comparative method for determination of corrosion curent is polarization resistance [4,5]. Polarization resistance DE/DI is bend of polarization curve on corrosion potential. Anode and cathode Tafel coefficient b_a and b_k are determined from potentiodynamic curves (Fig. 1. and 2.). Corrosion current is estimated by Stern-Geary equation (1):

$$i_{cor} = \frac{b_a \cdot b_b}{2,3 \cdot (b_a + b_k)} \cdot \frac{1}{Rp} = \frac{B}{Rp} \tag{1}$$

Corrosion parameters for tested steel specimen Č 4574 and Č 4583 in 50 wt. %, 10 wt. % and 1 wt. % Ca(OCl)$_2$ solution determined by polarization resistance method are shown in Table 3.–5.

Table 3. Corrosion parameters of steels tested in the 50 wt. % Ca(OCl)$_2$ suspension.

Type of steel	b_a (mV/dek)	b_k (mV/dek)	$\Delta E/\Delta I$	i_{cor} ($\mu A/cm^2$)
Č 4574	180	290	3.20	15.08
Č 4583	250	330	3.79	16.30

Table 4. Corrosion parameters of steels tested in the 10 wt. % Ca(OCl)$_2$ solution.

Type of steel	b_a (mV/dek)	b_k (mV/dek)	$\Delta E/\Delta I$	i_{cor} ($\mu A/cm^2$)
Č 4574	170	250	6,50	6,75
Č 4583	250	300	6,13	8,50

Table 5. Corrosion parameters of steels tested in the 1 wt. % Ca(OCl)$_2$ solution.

Type of steel	b_a (mV/dek)	b_k (mV/dek)	$\Delta E/\Delta I$	i_{cor} ($\mu A/cm^2$)
Č 4574	250	300	53.19	1.11
Č 4583	240	300	50.00	1.40

Based on corrosion current calculated by equation 1 we determined corrosion rate by equation 2 [6–9].

$$V_{cor} = \frac{m}{\rho \cdot s \cdot \tau} = \frac{M}{\rho \cdot z \cdot F} \cdot i_{cor} \cdot 8,76 \cdot 10^4 \qquad [mm/year] \qquad (2)$$

where: V_{cor} - corrosion rate; mm/year; m – metal mass (g); r - metal density (for iron – 7.85 g/cm^3); i_{corr} - corrosion current density (A/cm^2); M – mol metal mass (for iron, 55.8 g/mol); F – Faraday constant (26.8 Ah/mol); S – electrode surface (cm^2); t – time, hours; z – electron number exchange in reaction.

Corrosion resistance of metal is evaluated according to GOST 5272–68, according by tenth unit scale. Table 6. shows corrosion current determined by numerical method (from Table II.) which helped us to calculate the corrosion rate by equation 2. Corrosion resistance level of tested steels is based on the calculated amounts of corrosion rate.

Table 6. Corrosion resistance of tested steels.

Type of steel	Concentrations of Ca(OCl)$_2$ wt. %	i_{cor} (μA/cm^2)	Corrosion rate (mm/year)	Unit of measurement of corrosion resistance *vs.* GOST
Č 4574	50	12.60	0.1463	6
	10	6.15	0.0714	5
	1	1.15	0.0133	4
Č 4583	50	15.00	0.1742	6
	10	5.50	0.0644	5
	1	1.20	0.0139	4

In thi spaper the corrosion current was determineed in several ways in this paper. Steel corrosion data calculated by equation (1) and (2) are obtained considering the anode dissolving mechanism by literature reference [10].

Agent corrosion concentration induces chromium–nickel steel corrosion resistance. All four tested steels show stability in 1 wt. % Ca(OCl)$_2$ solution because corrosion rate in those solutions is not higher than 0.10 mm/year. pH value in those solutions is 8.0 and it can be seen in diagram from the effect of pH value on HOCl, OCl$^-$, Cl$_2$, Cl$_2$O concentrations in Ca(OCl)$_2$ solutions (Fig.1. in the Part. 1 [1]) that hypochlorite ion and hypochlorite acid are present in equal amounts in solution as well as anhydride of hypochlorine acid in smaller amount. However, their concentration in solution is low, therefore this medium did not show corrosion activity.

In 10 wt. % Ca(OCl)$_2$ solutions both steels have same corrosion rate and they can be classified as less resistant material. pH value of these solutions is 9.5. The concentration of hypochlorine ion is higher with this pH value, while

the concentrations of hypochlorine acid and hypochlorine acid anhydride are somewhat smaller then in 1 wt. % solution.

In 50% Ca(OCl)$_2$ solution both steels Č 4574 and Č 4583 have corrosion rate from 0.10 to 0.50 mm/year and they can be classified as less resistant material (by measure unit of corrosion resistance). pH value of corrosion medium is 11.0. Solution with such pH value has OCl$^-$, HOCl and Cl$_2$O.

With higher Ca(OCl)$_2$ concentration active chlorine concentration also gets higher. Active chlorine is powerful oxidation solution which will lead to the higher corrosive activity of the medium.

In order to apply a material (steel) in a medium it is necessary for its potential to be in passive state in exploitation conditions [11].

Determination of passivation tendency of a system can be done through anode polarization curves and its characteristic points. It can be seen from anode polarization curve of tested steels in 50 wt. % Ca(OCl)$_2$ suspension that we do not have the passivation of any of the tested steels. The value of the stationed potentials is dropping in Č 4574 to Č 4583 steel. Dissolving currents are higher than in low concentrated hypochlorite and they are 85 mA/cm^2 for Č 4574 and 140 mA/cm^2 for Č 4583 with potential of +400mV.

All the areas of active passive conditions are nor expressed in anode polarization curves in 10 wt. % Ca(OCl)$_2$ solution. Stationed potential are more positive in relation to steels tested in 50 wt. % suspension and for Č 4574 and Č 4583 total is 120 mV, 100 mV, respectively. Potential passivation interval is from +400 mV to +600 mV. Active dissolving starts with + 600 mV potential, dissolving currents go from 50 mA/cm^2 for Č 4574 to 63 mA/cm^2 for Č 4583.

The tendency for passivation is higher with moving the beginning of passivation to negative area. Test data show that steels tested in 1 wt. % Ca(OCl)$_2$ solution have the same tendency.

Anode polarization curves show that the active area does not exist. Passivation potential interval is higher and it amounts from + 280 mV to + 850 mV. Based on the lower dissolving current in passive state it can be concluded that the passivation degree is getting higher, that is, metal corrosion rate is lower in passive state.

With potentials of anode penetration of protective layer (forming the pitting) Č 4574 to 32 mA/cm^2 for Č 4583.

Corrosion resistance of tested steels based on passivation. Passivation of Cr – Ni (special steels) dependes on content of Cr, Ni, Mo, Cu and other elements [12]. Steels Č 4574 and Č 4583 have the same Cr and Ni content while the Mo content is 2.5 wt. % - 2.0 wt. %. Lower corrosion current in Č 4574 in tested corrosion medium probably comes from the higher Mo content. As the alloyed element Mo has positive effect on all corrosion characteristics except the resistance to strong oxidation means [13]. The negative effect can be seen through higher corrosion current in transpassive state and also through moving of transpassive potential to negative values.

Mo significantly lowers the density of passivation current in Cr – Ni steels. That effect is detectable in 0.5 wt.% of Mo it can go to 6.0 wt. % Mo and even further [13].

4. Conclusions

Corrosion resistance of Cr – Ni (special steels) specimen is tested with fast electrochemical methods: numerical method of linear polarization, and polarization resistance method. Numerical method of linear polarization whose results obtained by potentiodynamic measurement are processed by computer, appeared to be very useful, because the influence of subjective factor is eliminated, and it is the fastest way to obtained the results of the corossion current intensity.

Anode polarization curves bring the ilustrative picture of corrosion resistance. In 1 wt. % $Ca(OCl)_2$ solution tested steels show passivity in potential area + 280 mV to + 850 mV whereas in 10 wt. % solution passivity area is considerable smaller, from + 400 mV to + 650 mV, while in 50 wt. % $Ca(OCl)_2$ suspension passive area cannot be found. The density of anode current disolving in + 600 mV is growing higher with higher $Ca(OCl)_2$ concentrations.

By higher $Ca(OCl)_2$ concentration pH value of the solution is also higher as well as active chlorine concentration and corrosion activity of the medium. Quantitative method of determining the corrosion resistance brought the conclusion that the steels tested in 1 wt. % $Ca(OCl)_2$ solution are resistant, in 10 wt. % solution constant, and in 50 wt. % suspension less resistant.

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