

# **STUDY OF CORROSION RESISTANCE OF CHROMIUM-NICKEL STEEL IN CALCIUM – HYPOCHLORITE SOLUTION PART 1. STEELS URANUS B6 AND Č 4578**

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## **Abstract**

*Corrosion resistance of Cr – Ni (special steels) specimen is tested by electrochemical methods, numerical method of linear polarization and polarization resistance method in calcium–hypochlorite ( $\text{Ca}(\text{OCl})_2$ ) solutions. With increasing of  $\text{Ca}(\text{OCl})_2$  concentration, pH value of the solution increases, as well as active chlorine concentration and corrosion activity of the medium. According to the quantitative method of the corrosion resistance determination it can be concluded that the steels tested in 1 wt %  $\text{Ca}(\text{OCl})_2$  solution are resistant, in 10 wt % solution constant, and in 50 wt % suspension less resistant. URANUS B6 showed the best corrosion resistance of all tested chromium – nickel steels in all tested corrosion mediums.*

**Keywords:** chromium-nickel, calcium-hypochlorite solution, numerical method of linear polarization, steel URANUS B6, steel Č 4578

## **1. Introduction**

Corrosion resistance steels are steels with chromium content bigger than 12%, additionally alloyed with Ni, Mo, Cu, Ti, N and other. Content of

these elements in corrosion resistance steels depends on corrosion medium activity degree and requirement for mechanical feature [1].

Corrosion activity is, by its nature, mostly affected by following electrolyte characteristics: dissociation, hydration ions, pH value, conductivity and oxidation ability of corrosion medium. Corrosion rate of metals in water solutions is different in acid, neutral and basic solutions.

Oxidation ability of corrosion solution is the most important sign of its corrosion activity. If the corrosion products or sediment insoluble corrosion products are formed on metal, as the result of media influence, corrosion process is slowed down. If the corrosion products are soluble or if the electrolyte ions are capable to destroy oxide passive layer on metal surface, corrosion will be intensified.

In water solution of calcium hypochlorite  $\text{Ca}(\text{OCl})_2$ , one can find more active components resulting from the following reactions:



The concentration of the components, mentioned above, is affected by pH value of solution as shown on Fig. 1 [2].

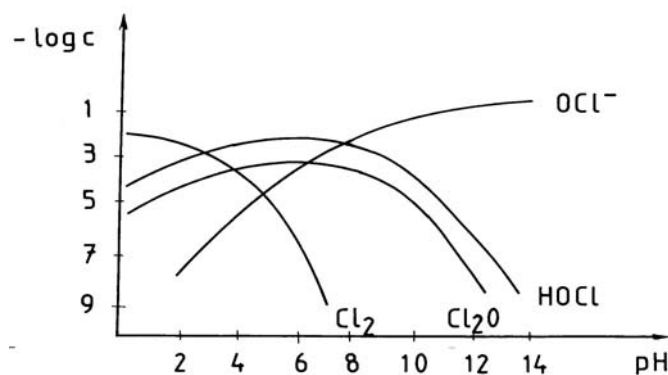
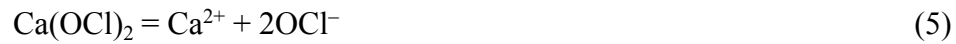


Fig. 1. The effect of pH value on HOCl, OCl<sup>-</sup>, Cl<sub>2</sub>, Cl<sub>2</sub>O concentrations in Ca(OCl)<sub>2</sub> solutions.

Oxidation activity of  $\text{Ca}(\text{OCl})_2$  comes mainly from  $\text{HOCl}$  resulting by hydrolysis and less from the  $\text{OCl}^-$  free anion.



Hypochlorite acid is weak acid with dissociation constant, as:



$$K_a = 3,2 \times 10^{-8}$$

which is known only for water solution. Being quite unstable, hypochlorite acid is dissolved with oxygen release, even in water solution:



Hypochlorite acid is strong oxidation substance, which can be seen from potential of partial redox-equation:



$$E^\circ = +1,63 \text{ V}$$

Since the chlorine is also oxidizing agent, reduction leads to chlorine.



$$E^\circ = +1,49 \text{ V}$$

From partial equation it can be seen that the hypochlorite acid is stronger oxidizing agent than chlorine itself. Hypochlorite ion is also an oxidizing agent:



$$E^{\circ} = +0,94 \text{ V}$$

Potentiodynamic measurements were used in this work for electrochemical testing of corrosion process by polarization current. Potentiodynamic anode polarization is the characteristic of metal specimen, which is the result of potential-current relation. Specimen potential goes slowly to positive direction thus acting as anode and corroding on forming oxide layer as such. These measurements are used for discovering corrosion characteristic of metal specimen. In liquid medium, complete current-potential specimen diagram can be measured in couple of hours or in some cases in couple of minutes.

When the metal specimen is saturated in corrosive medium both oxidation and reduction process are going on, on the surface. According to oxidation process, anode current appears on the metal surface, and on the other hand, cathode current appears as a result of a reduction process. Whatever the type of corrosion might be, it represents the result of anode current [3].

## **2. Experimental**

### **2.1 Materials**

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

Electrodes for potentiodynamic measurement were made in the cylindrical shape plastic holder, with steel specimen fixed on the one base, so constant surface of electrode was provided. Contact with electrode through plastic holder was provided by soldered copper wire. Working area of electrode was 0.1 cm<sup>2</sup> to 0.12 cm<sup>2</sup>. Precision of test results depends on a quality of pretreatment of the electrodes, which consists of mechanic and chemical pretreatment.

Mechanic pretreatment consists of polishing of electrode with rough sand paper and further, fine polishing with sandpaper of 220, 280, 400 and 600 type. After that, chemical pretreatment was done by degreasing in ethanol first, and than distilled water rinsing, alcohol rinsing and, finally, drying. Specimens (electrodes), treated in this way, were left in the atmosphere controlled vessel, if they are not immediately tested.

Table 1. Chemical composition of tested steel.

Type of steel	Chemical composition in wt. %						
	C	Si	Mn	Cr	Mo	Ni	Cu
URANUS B6	0,02	1,0	1,2	20	4,5	25	1,5
Č 4578	0,12	1,2	1,5	25	–	19	–

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

## 2.2. Instruments and equipment

The following equipment was used for the potentiodynamic measurements: Potentiostat-galvanostat type 273 PAR (*Princeton Applied Research*, USA) Hewlett–Packard computer, and X-Y type 7046A recorder (*Houston Instruments*, USA).

Measurement cell of standard type for triple electrode system was used also. Measurement cell was filled with corrosive solution, where three electrodes were immersed: working electrode, counter electrode and reference electrode. Platinum wire, previously 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 +240mV potential was used as reference electrode. Calomel electrode was connected to working electrode through agar–agar salt bridge.

## 3. Results and discussion

Potentiodynamic anode and cathode curves were registered on tested steels

URANUS B6 and Č 4578 from +2,0 V to -2,0 V in 50 wt %  $\text{Ca}(\text{OCl})_2$  suspension, and 10 wt % and 1 wt %  $\text{Ca}(\text{OCl})_2$  solution (Fig. 2 and 3).

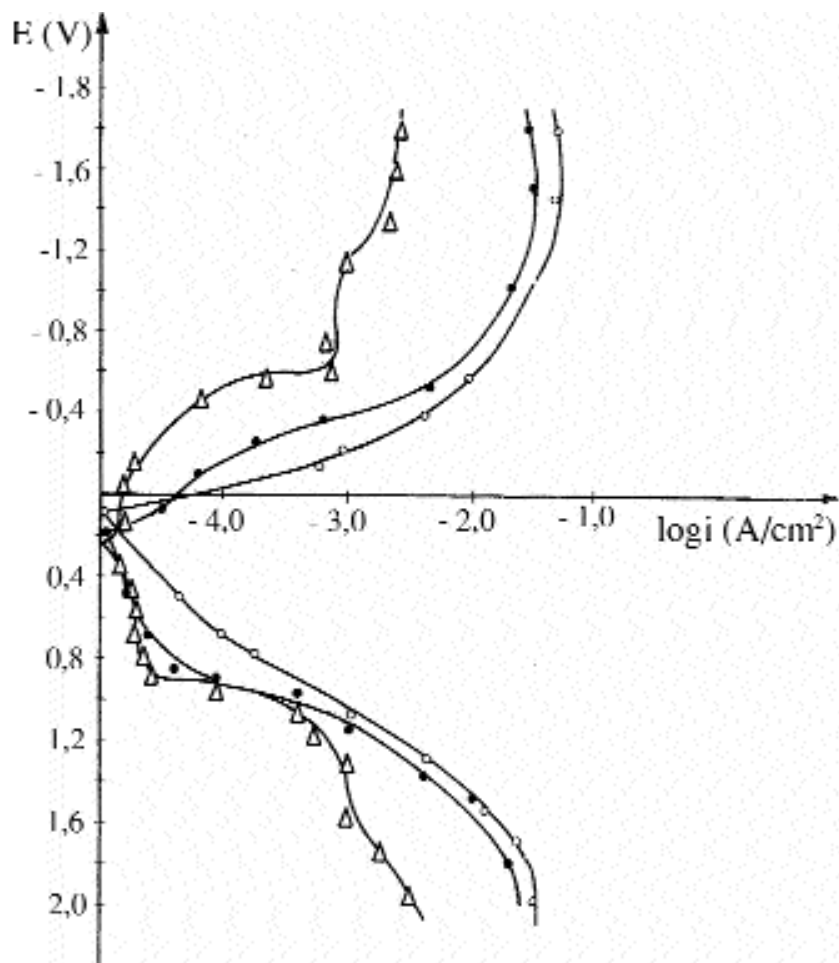


Fig. 2. Potentiodynamic curves for steel URANUS B6 in tested corrosive media where: (o)  $E_r = 100$  mV, (●)  $E_r = 186$  mV, ( $\Delta$ )  $E_r = 230$  mV, i.e. (o) – 50 wt % suspension, (●) 10 wt % solution i ( $\Delta$ ) 1 wt % solution.

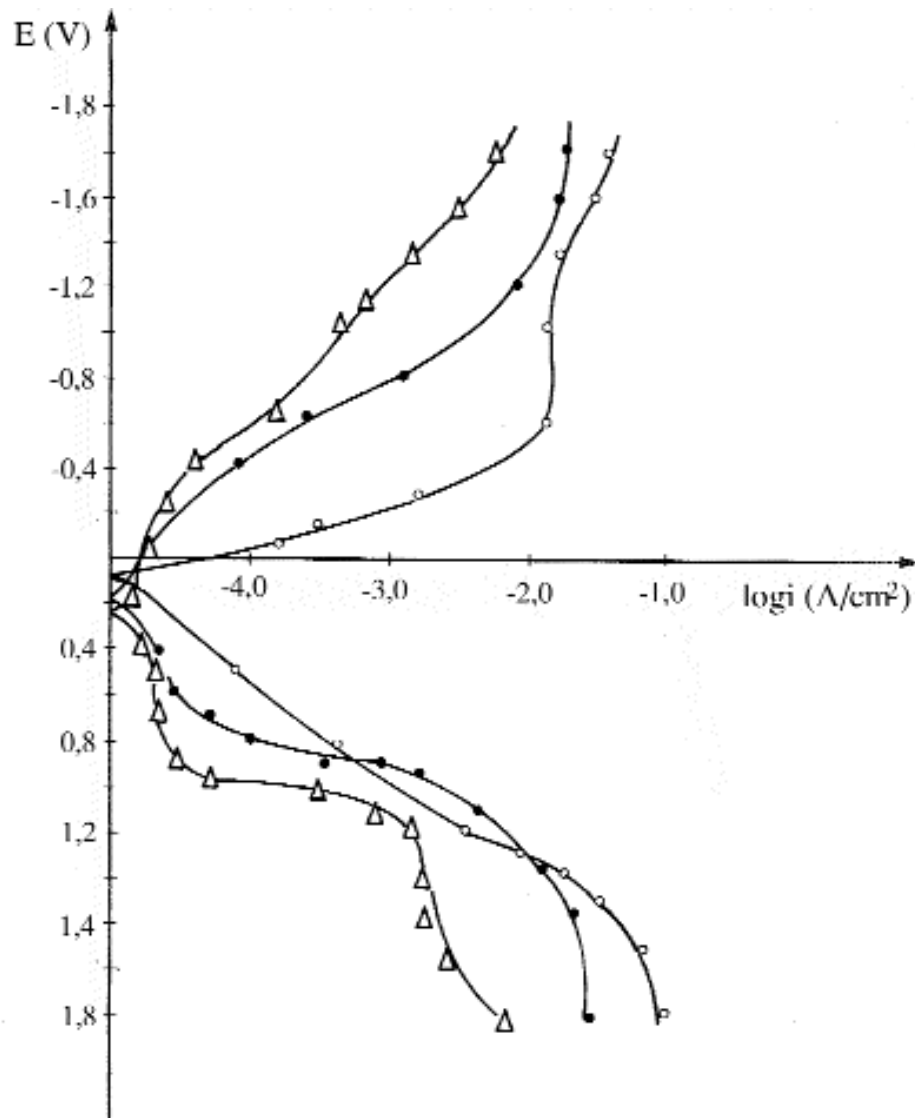


Fig. 3. Potentiodynamic curves for steel Č 4578 in tested corrosive media where:  
 (o)  $E_r = 80 \text{ mV}$ , (●)  $E_r = 180 \text{ mV}$ , ( $\Delta$ )  $E_r = 220 \text{ mV}$ , i.e. (o) – 50 wt % suspension,  
 (●) 10 wt % solution i ( $\Delta$ ) 1 wt % solution.

Anode polarization curves, in potential interval from stationed potential to +2,0 V for all four chromium–nickel steels in tested solutions, are given in Figs. 4.–6.

Corrosion 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 measurements. Corrosion current and corrosion potential are achieved in the section of Tafel lines  $e = f(\log i)$  by graphic method of linear polarization. Fig. 7 shows Tafel lines for tested steels in 50 wt % suspension  $\text{Ca}(\text{OCl})_2$ . Corrosion current and corrosion potentials are obtained analogously for the other two corrosion media.

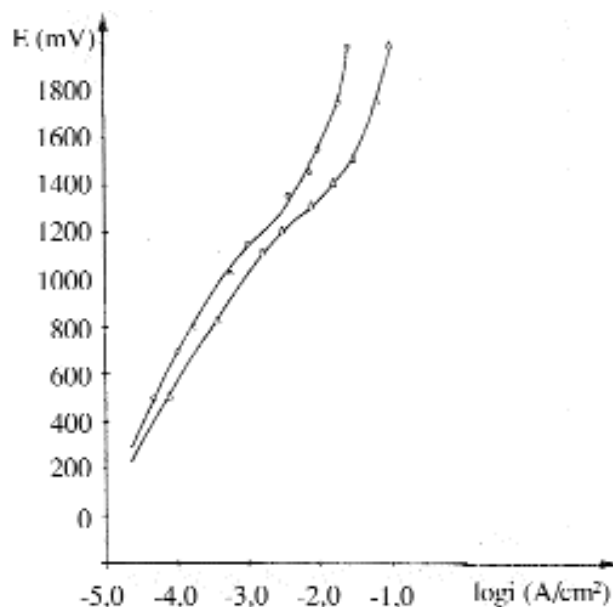


Fig. 4. Anode polarization curves in the 50 wt %  $\text{Ca}(\text{OCl})_2$  suspension where: (o) – steel URANUS B6, ( $\Delta$ ) steel Č 4578.



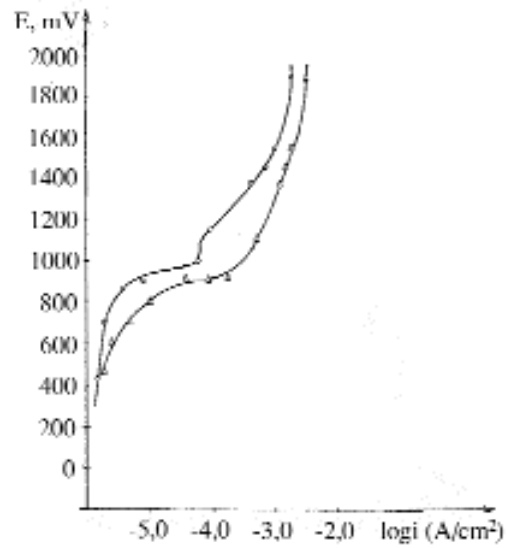


Fig. 5. Anode polarization curves in the 10 wt %  $\text{Ca}(\text{OCl})_2$  solution where: (o) – steel URANUS B6, ( $\Delta$ ) steel Č 4578.

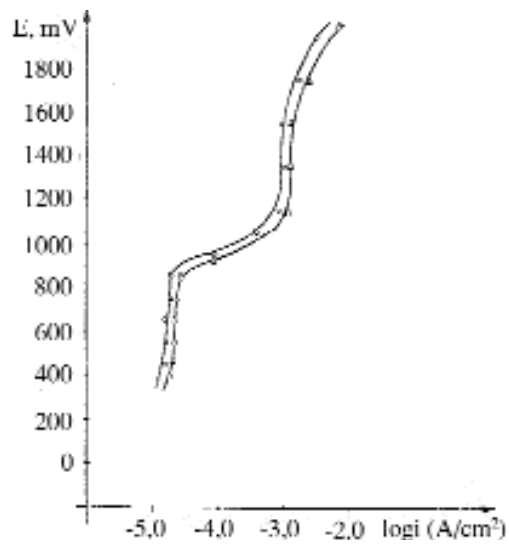


Fig. 6. Anode polarization curves in the 1 wt %  $\text{Ca}(\text{OCl})_2$  solution where: (o) – steel URANUS B6, ( $\Delta$ ) steel Č 4578.

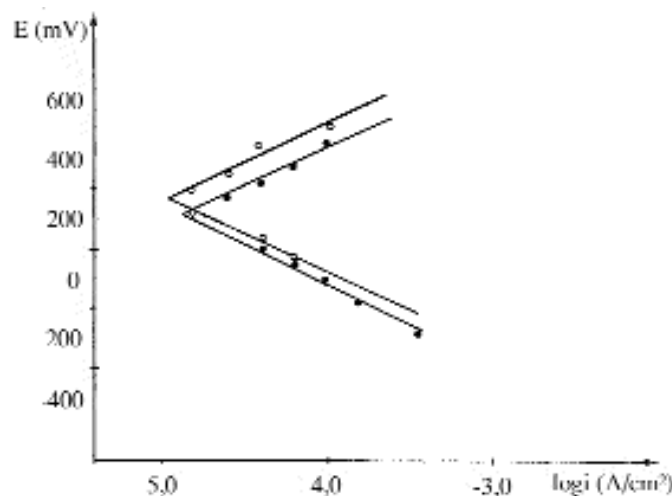


Fig. 7. Graphical determination of the corrosion current in the 50 wt %  $\text{Ca}(\text{OCl})_2$  suspension where: (o) – steel URANUS B6, (•) steel Č 4578.

Numerical processing of data obtained by polarization measurements consists of computer fitting of test results [5]. As a result of polarization measurements set of  $n$ -pairs of data  $e_i$  and  $i_i$  was obtained, where the current intensity was  $i = E(1, \dots, n)$ . Each of the test results has certain measurement error which leads to moving away from linear logarithm dependence. In order to avoid getting incorrect conclusion resulting from determining the coordination of neighboring points, it is necessary to determine the approximation of measurements results before determination of the shape of function. Approximation was done by smallest square method using the equation for the third degree polynomial:

$$F(x_i) = a_0 + a_1x_i + a_2x_i^2 + a_3x_i^3 \quad (13)$$

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) <sub>2</sub>	Graphic methods		Numerical methods	
		$(E_{mp}/A_{Li})=_{cor}i$		$i_{cor}$ (μA/cm <sup>2</sup> )	$e_{cor}$ (mV)
URANUS B6	50	11.35	270	11.50	275
	10	4.10	330	3.70	318
	1	0.16	240	0.14	235
Š 4578	50	12.34	200	12.85	170
	10	8.90	230	8.40	224
	1	0.69	30	0.75	Đ 15

Comparative method for determination of corrosion current is polarization resistance [6,7]. 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. 2 and 3). Corrosion current is estimated by Stern-Geary equation (14).

$$i_{cor} = \frac{b_a \cdot b_k}{2,3 \cdot (b_a + b_k)} \cdot \frac{1}{R_p} = \frac{B}{R_p} \quad (14)$$

Determination of polarization resistance for specimen URANUS B6 in 50% solution Ca(OCl)<sub>2</sub> is shown on Fig. 8.

Basic facts for polarization resistance  $R_p$  can be found in papers [10,11].

Corrosion parameters for tested steel specimen in 50 wt %, 10 wt % and 1 wt % Ca(OCl)<sub>2</sub> solution determined by polarization resistance method are shown in Tables 3–5.

Based on corrosion current calculated by Eq. (14) corrosion rate was determined by Eq. (15) [8–11], while the corrosion rate was calculated by Eq. (3).

$$V_{cor} = \frac{m}{\rho \cdot s \cdot \tau} = \frac{M}{\rho \cdot z \cdot F} \cdot i_{cor} \cdot 8,76 \cdot 10^4 \quad [\text{mm/year}] \quad (15)$$

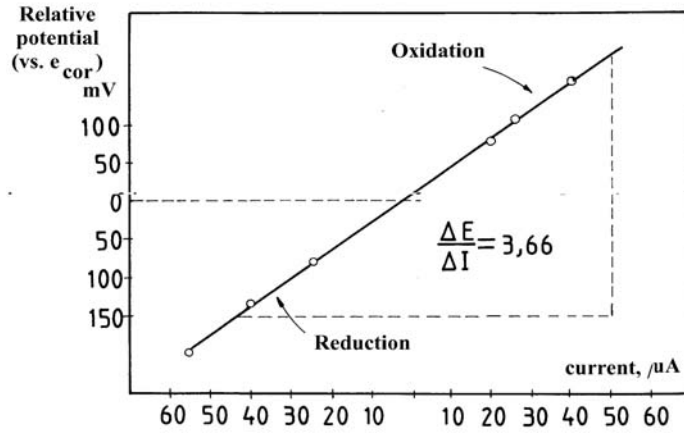


Fig. 8. Experimental determination of the polarization resistance.

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)	$\Delta E/\Delta I$	$i_{cor}$ ( $\mu A/cm^2$ )
URANUS B6	160	300	3.66	12.30
Č 4578	260	350	4.80	13.50

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)	$\Delta E/\Delta I$	$i_{cor}$ ( $\mu A/cm^2$ )
URANUS B6	160	300	9.11	4.97
Č 4578	260	350	5.90	8.84

Type of steel	$b_a$ (mV/dek)	$b_k$ (mV/dek)	$\Delta E/\Delta I$	$i_{cor}$ ( $\mu A/cm^2$ )
URANUS B6	200	300	292	0.18
Č 4578	200	300	50.0	1.04

Table 5. Corrosion parameters of steels tested in the 1 wt % Ca(OCl)<sub>2</sub> solution.

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

Corrosion resistance of metal was evaluated according to GOST 5272–68, by tenth unit scale. Table 6 shows corrosion current determined by numerical method (from Table 2), which enabled calculation of the corrosion rate by equation 15. Corrosion resistance level of tested steels was based on the calculated amounts of corrosion rate.

Table 6. Corrosion resistance of tested steels.

Type of steel	Concentrations of Ca(OCl) <sub>2</sub> wt %	$i_{\text{cor}}$ ( $\mu\text{A}/\text{cm}^2$ )	Corrosion rate (mm/year)	Unit of measurement of corrosion resistance vs. GOST
URANUS B6	50	11.50	0.1336	6
	10	3.70	0.0429	4
	1	0.140	0.0016	2
Č 4578	50	12.85	0.1492	6
	10	8.40	0.0975	5
	1	0.75	0.0087	3

Evaluation of corrosion quality of a material is given according to corrosion rate in mm/year. Corrosion rate of tested steels is determined by electrochemical method. All electrochemical methods are indirect, which points out to the importance of corrosion current determination. The accuracy of the parameters, determined indirectly, affects the accuracy of the calculated corrosion rate. For that reason the corrosion current was determined in several ways in this work.

Numerical method – computer data processing is used more and more for the processing of data obtained through potentiodynamic measurements [12,13]. This method provides fast and accurate processing of measurement results and removes the subjective influence of measurement to the processing of data.

Corrosion currents obtained through polarization resistance method are mainly of greater value related to the ones obtained through linear polarization method. In some papers [14,15] this method is preferred, because the measurement is done near corrosion potential and thus avoiding drastic changes of corrosion system features. This method is recommended in low corrosion rate materials (0.1mm per year, or less), which causes determination of corrosion stability of metal in tested corrosion medium to last only twenty minutes. Steel corrosion data, calculated by Eqs. (14) and (15), are obtained considering the anode dissolving mechanism [17].

Agent corrosion concentration induces chromium–nickel steel corrosion resistance. All four tested steels show stability in 1 wt %  $\text{Ca}(\text{OCl})_2$  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 (Fig.1) that hypochlorite ion and hypochlorite acid are presented 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.

There is a difference in corrosion resistance (Table 6). In 10 wt %  $\text{Ca}(\text{OCl})_2$  solutions, the lowest corrosion rate is obtained for URANUS B6. 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 than in 1 wt % solution.

In 50%  $\text{Ca}(\text{OCl})_2$  solution, both steels have corrosion rate from 0.10 to 0.50 mm/year and 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  $\text{OCl}^-$ ,  $\text{HOCl}$  and  $\text{Cl}_2\text{O}$ .

With higher  $\text{Ca}(\text{OCl})_2$  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 under the exploitation conditions [18]. Determination of passivation tendency of a system can be done through anode polarization curves and its characteristic points. From anode polarization curve of tested steels in 50 wt %  $\text{Ca}(\text{OCl})_2$  suspension, it can be seen that there is no passivation of any of the tested steels. The value of the stationed potentials is dropping from URANUS B6 to Č 4578 steel. Dissolving currents are higher than in low concentrated hypochlorite and they are  $31 \mu\text{A}/\text{cm}^2$  for URANUS B6 and  $60 \mu\text{A}/\text{cm}^2$  for Č 4578 with potential of + 400mV.

All the areas of active passive conditions are not expressed in anode polarization curves in 10 wt %  $\text{Ca}(\text{OCl})_2$  solution. Stationed potential are more positive related to steels tested in 50 wt % suspension and for URANUS B6 and Č 4578 total is 185 mV, 180 mV, respectively. Potential passivation interval goes from +400 mV to +600 mV. Active dissolving starts with + 600 mV potential, dissolving currents go from  $16 \mu\text{A}/\text{cm}^2$  for URANUS B6 to  $25 \mu\text{A}/\text{cm}^2$  for Č 4578. The tendency for passivation becomes greater by moving the beginning of passivation to negative area. Test data show that steels tested in 1 wt %  $\text{Ca}(\text{OCl})_2$  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, while metal corrosion rate is lower in passive state. With potentials of anode penetration of protective layer (forming the pitting potential) and transpassive dissolving current potential goes from  $10 \mu\text{A}/\text{cm}^2$  for URANUS B6, to  $16 \mu\text{A}/\text{cm}^2$  for Č 4578.

Better corrosion resistance of URANUS B6 steel, related to other tested steels, probably comes from higher content of chromium and nickel (20 wt %, and 25 wt %, respectively), as well as the presence of Mo and Cu (4.5 %, and 1.5 %). The effects of alloying of elements in steel and protective effects of Cu and Mo in steel were given by D.G.Trifunov [18].

#### 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, which results obtained by potentiodynamic measurement are processed by computer, appeared to be very useful, because the influence of subjective factor is eliminated. Also, it is the fastest way to obtain the results of the corrosion current intensity.

Anode polarization curves bring the illustration of corrosion resistance. In 1 wt %  $\text{Ca}(\text{OCl})_2$  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 %  $\text{Ca}(\text{OCl})_2$  suspension passive area cannot be found. The density of anode current dissolving in + 600 mV is growing higher with higher  $\text{Ca}(\text{OCl})_2$  concentrations.

By higher  $\text{Ca}(\text{OCl})_2$  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 enabled the conclusion that the steels tested in 1 wt %  $\text{Ca}(\text{OCl})_2$  solution are resistant, in 10 wt % solution constant, and in 50 wt % suspension less resistant. URANUS B6 showed the best corrosion resistance of all tested chromium – nickel steels in all three of tested corrosion medium. That is probably the result of higher Cr and Ni content, as well as the presence of additional alloyed elements like Mo and Co.

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