INFLUENCE OF CATHODIC PROTECTION ON PH AND CHANGE OF SOIL ELECTROLYTE COMPOSITION

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Abstract

Cathodic protection is applied especially to protection of coating fault on a buried pipe line in a soil. According to some authors, the mechanism of cathodic protection of carbon steel is a shift of open circuit potential into the *immunity* region or reducing of anodic reaction rate in the active state. The importance of change of pH and soil electrolyte composition during applying cathodic protection is sometime ignored.

The study deals with influence of cathodic protection on pH change and anions migration in soil electrolyte close to protected carbon steel surface. Concentration of chlorides, sulphates and hydrogen carbonates decreased about two orders of magnitude during applying cathodic protection. The migration rate of hydroxides during cathodic polarization is lower than their production by cathodic reduction of oxygen. As a result of cathodic reduction of oxygen, the pH of soil electrolyte close to protected surface gradually increases up to 12.

The final pH of soil electrolyte close to protected surface depends on the migration rate of anions, the diffusion rate of oxygen into soil electrolyte and neutralizing capacity of soil.

Keywords: Cathodic protection, soil electrolyte, migration

1.   INTRODUCTION

The corrosion of metals has mainly electrochemical character in aqueous electrolytes (natural and industrial or soil electrolytes). The corrosion rate of metals could be decreased by polarization of metal surface in either positive or negative direction from their open circuit potential (anodic or cathodic protection) [1].

A direct current is used for electrochemical protection of metals. Carbon steel is material, which is the most often electrochemically protected in aqueous and soil electrolytes. Cathodic protection is very often used as a protection of defects in insulating coating of buried carbon steel structures.

The principle of cathodic protection is explained relatively often inaccurately even though cathodic protection of carbon steel structures has been used for almost one hundred years. The existing explanation is based on a movement of open circuit potential to immunity region of metal or as a decrease of corrosion rate of metal in active state [2-4]. The change of pH and chemical composition of soil electrolyte close to the cathodically protected surface due to cathodic polarization is often ignored.

An increase of pH close to the cathodically protected surface is given by cathodic reduction of oxygen in soil electrolyte (1) and electrolysis of wather (2). The high alkalinity of soil electrolyte leads to cathodic passivation of protected carbon steel and it´s corrosion rate significantly decreases.

$$H_2O + \tfrac{1}{2}\, O_2 + 2\, e^- \rightarrow 2\, OH^- \tag{1}$$

$$2\, H_2O + 2e^- \rightarrow 2\, OH^- + H_2 \tag{2}$$

An observed presence of Fe_3O_4 adherent layer on the surface of buried carbon steel structures confirms that long time cathodic protection leads to cathodic passivation of protected carbon steel [5].

Total value of pH close to the cathodically protected surface is affected by concentration of dissolved ions in soil electrolyte. Average pH value of natural soil electrolyte is 6 - 8. The lower pH values 3.5 - 5.5 have only soil electrolytes of pseudogley, podzolic and loess soils [6].

In inorganic part, soil electrolyte contains mainly Cl^-, SO_4^{2-} and HCO_3^- anions and Na^+, K^+, Ca^{2+} and Mg^{2+} cations. An organic part of soil electrolyte contains mainly humic and fulvic acids [7].

Concentration of soil ions close to the cathodically protected surface is affected by rate of migration and diffusion. Ions migration rate during cathodic polarization is determined by their mobility. Ions mobility in electric field is directly proportional to their absolute rate, molar conductivity of electrolyte, value of charge transfer coefficient and inversely proportional to the intensity of electric field [8].

Total value of pH close to the cathodically protected surface is significantly affected by buffering and neutralizing capacity of carbonate system [9].

Observation of pH change and concentration of soil anions (Cl^-, SO_4^{2-}, HCO_3^-) in layers of clay during cathodic polarization of steel surface was aim of this study.

2. EXPERIMENTAL

The experimental cell was composed of anodic and cathodic sections, which were separated by ion-permeable membrane (**Fig. 1**). The cathodic section was saturated by oxygen through gas-permeable membrane.
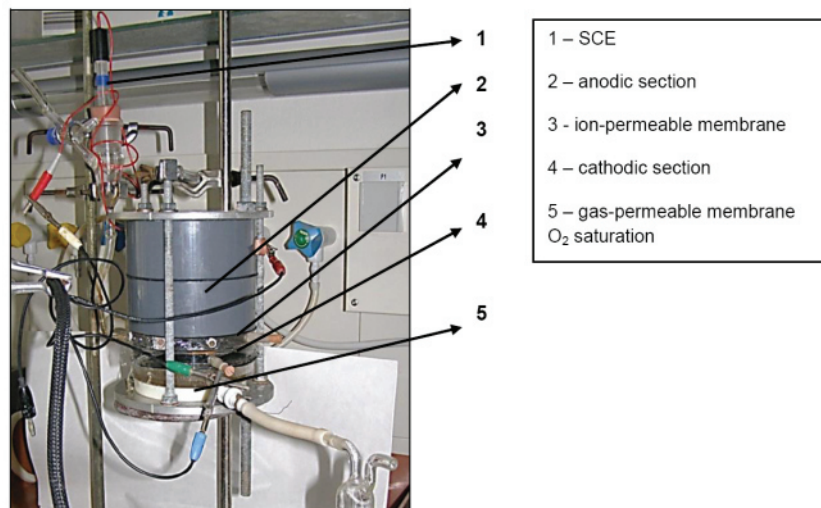
Stainless steel was used as a cathode. The area of the cathode was 113 cm^2. The cathodic section was divided into four layers by unwoven textile. The layers were filled with clay (grain size ≤ 2 µm) and soil electrolyte. Thickness of the layer was approximately

1 – SCE
2 – anodic section
3 - ion-permeable membrane
4 – cathodic section
5 – gas-permeable membrane O$_2$ saturation

Fig. 1 The experimental cell

2 mm (**Fig. 2**). The volume of soil electrolyte related to the area of cathode in layer of clay was 0.2 ml/cm^2.

Anodic solution
4. layer
3. layer
2. layer
1. layer close to the cathode

Fig. 2 Arrangement of the cathodic area and it´s cross section

The initial concentration of Cl^-, SO_4^{2-}, HCO_3^- in soil electrolyte are showed in **Table 1**. The initial pH of soil electrolyte was pH = 6.9.

Table 1 The initial composition of soil electrolyte

Anion	Concentration (mg/l)
Cl^-	216
SO_4^{2-}	284
HCO_3^-	90

A platinum wire was used as an anode. The anodic soil electrolyte flowed in a close circuit with volume 25 l. The rate of flow was 80 ml/min in the anodic section. A standard calomel electrode (SCE) was used as a reference electrode. Time of exposition was 72h of cathodic polarization at -780 mV/SCE. The potential -780 mV/SCE was kept using potentiostat Gamry PC3. The change of Cl^- and SO_4^{2-} concentration in layers of clay was determined by ion chromatography. The change of HCO_3^- in layers of clay was determined by titration with 0.1M HCl up to pH = 8.4 using phenolphthalein as an indicator and at lower value of pH by titration with 0.1M HCl using methyl orange as an indicator. The change of pH in layers of clay was determined using contact pH meter pH/ION 340i.

3.   RESULTS AND DISCUSSION

The highest pH value (11.8), in soil electrolyte was measured (after 72h of cathodic polarization) in the layer of clay close to the cathodically protected surface (**Table 2**). The pH value (6.9) in soil electrolyte of anodic section did not change.

Table 2 Value of pH in layers of clay after 72h of cathodic polarization at -780 mV/SCE

Layer of clay	-	1	2	3	4
pH value	initial 6.9	11.8	11.5	11.3	11.0

The pH value in the layers of clay did not change significantly with increasing distance from cathodically protected surface (**Fig. 3**).
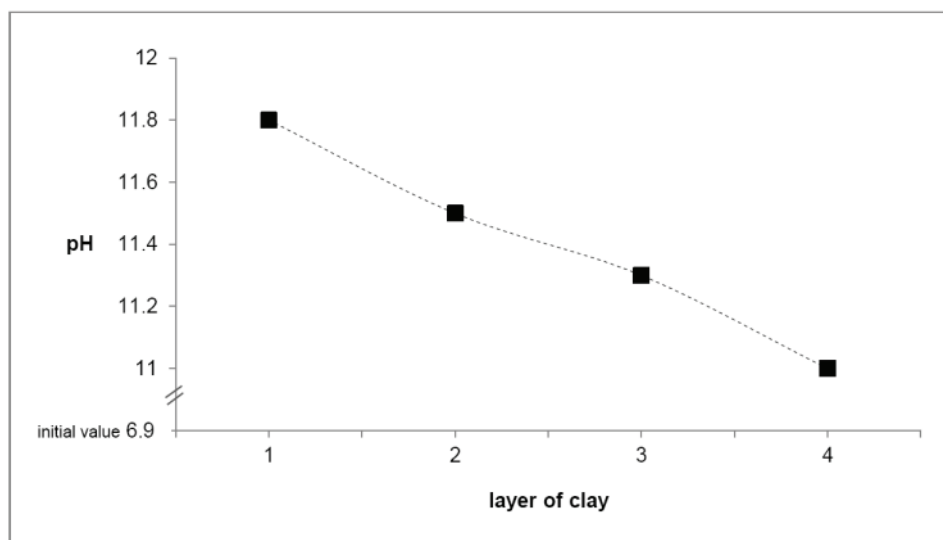

Fig. 3 The change of pH value in clay layers after 72h of cathodic polarization at -780 mV/SCE

The value of pH=11.8 in the layer of clay close to the cathodically protected surface corresponded to concentration of OH^- c_{OH^-} = 0.063 mol/dm^3. The value of charge was Q=488.2 C after 72h of cathodic polarization. The cathodic reduction of oxygen (1) at Q=488.2 C increased the concentration of OH^- in the soil

electrolyte up to $c_{OH^-} = 0.071 mol/dm^3$. The part of OH^- about concentration $c_{OH^-} = 0.008 mol/dm^3$ was probably used for reaction HCO_3^- to CO_3^{2-} (3).

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{3}$$

Concentration of Cl^- decreased due to migration by two orders of magnitude in the layer of clay close to the cathodically protected surface (**Table 3**).

Table 3 Concentration of Cl^- in clay layers after 72h of cathodic polarization at -780 mV/SCE

Layer of clay	-	1	2	3	4
Cl^- (mg/l)	initial 216	8.6	48.4	81.4	419.0

Concentration of Cl^- in the clay layers exponentially increased with increasing distance from cathodically protected surface (**Fig. 4**).
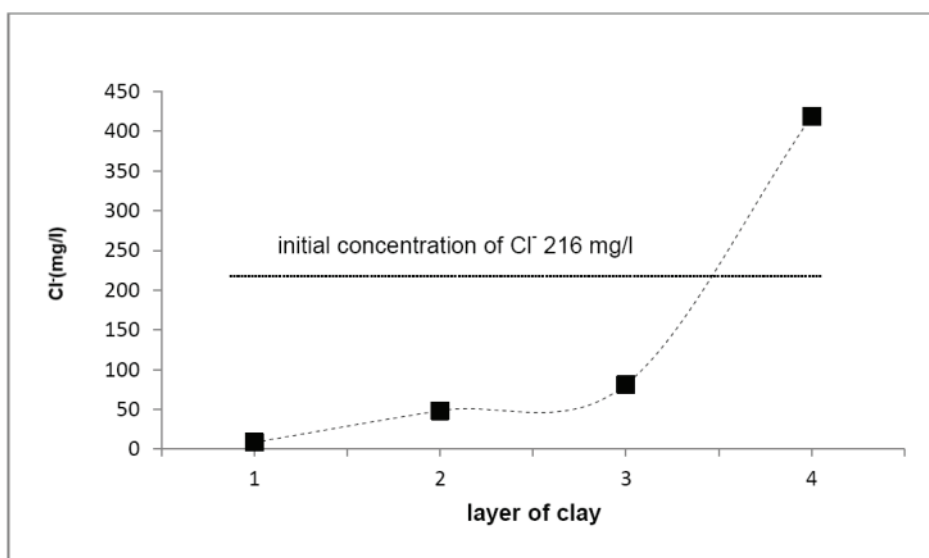

Fig. 4 The change of Cl^- concentration in clay layers after 72h of cathodic polarization at -780 mV/SCE

Concentration of SO_4^{2-} in the layer of clay close to the cathodically protected surface showed a similar trend as the concentration of Cl^- and decreased by two orders of magnitude (**Table 4**).

Table 4 Concentration of SO_4^{2-} in clay layers after 72h of cathodic polarization at -780 mV/SCE

Layer of clay	-	1	2	3	4
SO_4^{2-} (mg/l)	initial 284	5.4	68.8	113.0	208.0

Concentration of HCO_3^- in the clay layer close to the cathodically protected surface decreased due to migration up to one third of the initial value (**Table 5**).

Table 5 Concentration of HCO_3^- in clay layers after 72h of cathodic polarization at -780 mV/SCE

Layer of clay	-	1	2	3	4
HCO_3^- (mg/l)	initial 90	30	37	48	49

Concentration of SO_4^{2-} in the clay layers linearly increased with increasing distance from cathodically protected surface (**Fig. 5**).
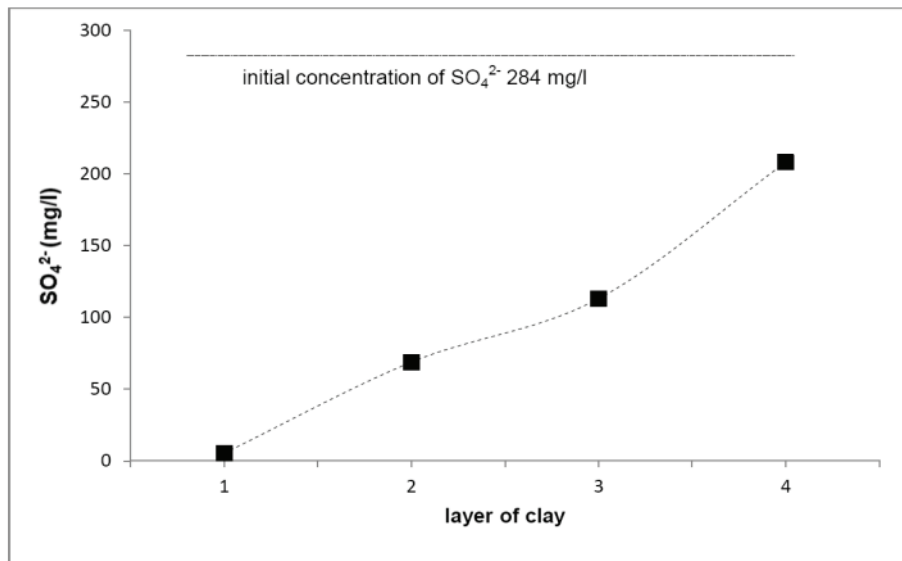
Fig. 5 The change of SO$_4^{2-}$ concentration in clay layers after 72h of cathodic polarization at -780 mV/SCE

Concentration of HCO$_3^-$ in the layers of clay did not change significantly with increasing distance from cathodically protected surface (**Fig. 6**).
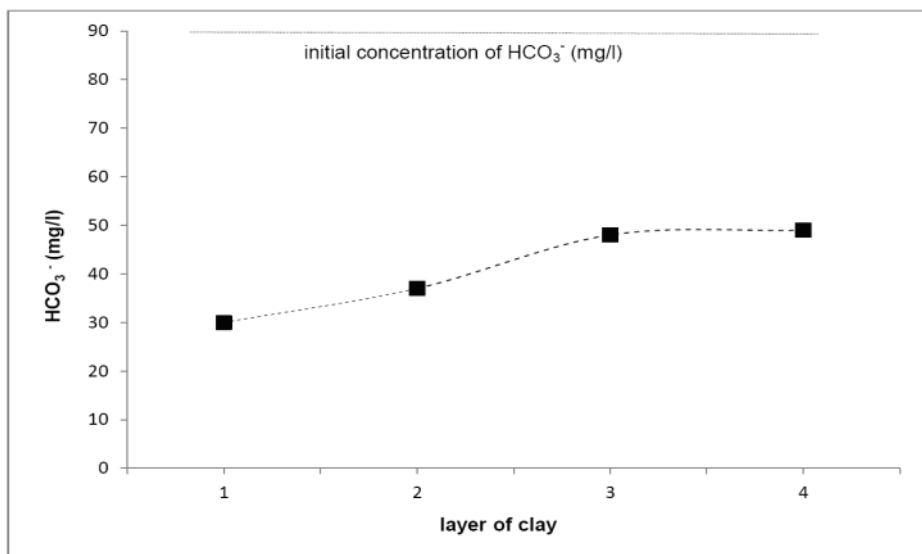

Fig. 6 The change of HCO$_3^-$ concentration in clay layers after 72h of cathodic polarization at -780 mV/SCE

Decrease of HCO$_3^-$ concentration is approximately ten times lower compared to decrease of Cl$^-$ and SO$_4^{2-}$ in the same layer of clay. The reason is probably different mobility of anions. The mobility of Cl$^-$(μCl$^-$ = 7.91.10^{-8}m^{2}s^{-1}V^{-1}) and SO$_4^{2-}$ (μSO$_4^{2-}$ = 8.27.10^{-8} m^{2}s^{-1}V^{-1}) in aqueous electrolyte at t = 25 °C is comparable. The mobility of HCO$_3^-$ (μHCO$_3^-$ = 4.61.10^{-8} m^{2}s^{-1}V^{-1}) in aqueous electrolyte at t = 25 °C is one half of the mobility of Cl$^-$ a SO$_4^{2-}$.

4. CONCLUSION

The pH value of soil electrolyte close to the cathode increased up to 11.8. The concentration of OH$^-$ in soil electrolyte increased due to reduction of oxygen in soil electrolyte (1) and electrolysis of water (2). The rate of migration/diffusion of OH$^-$, high mobility of OH$^-$ (μOH$^-$ = 20.52.10^{-8} m^{2}s^{-1}V^{-1}) and concentration of HCO$_3^-$ in soil

electrolyte had significant influence on the total pH value close to the cathodically protected surface. The concentration of Cl$^-$ and SO$_4^{2-}$ close to the cathode decreased about two orders of magnitude. Decrease of HCO$_3^-$ concentration close to the cathodically protected surface was approximately ten times lower. The reason is probably different mobility of anions. The high alkalinity of soil electrolyte and decrease of anions concentration due to migration led to cathodic passivation of the protected surface in the experimental set up mentioned above.

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