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## **pH Gradients Existing in Proximity of Cathodically Charged Steel Buried in Sediment**

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### **Keywords:**

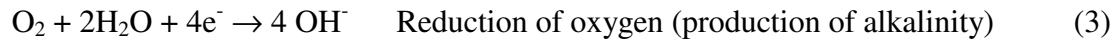
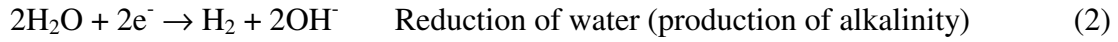
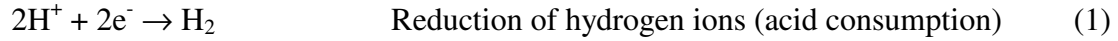
*Cathodic polarisation, pH-front, local environment, diffusion layer, precipitation*

### **Abstract**

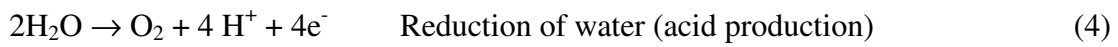
This paper describes observations on the pH- and potential profile evolving from a cathodically charged steel surface buried in a sand-sediment saturated with synthetic soil solution. An experimental set-up was established with a steel cathode placed in one end and an anode placed oppositely in a sand/soil solution-filled 90 cm long gutter. The steel was cathodically charged by 2.5 mA distributed over the 12.5 cm<sup>2</sup> area. Development in the pH profile evolving from the cathodically charged steel surface was followed, and ON-potential measurements with a reference electrode placed at distinct positions in the gutter was performed over a period of 19 days. After this, the current was shut off, and the pH and potentials measured additionally for a 15-days period without current. The pH measured during the period with current showed that a distinct alkalisiation front evolved from the cathode with a constant rate of 0.115 cm per hour with a final extension of 50 cm after 19 days. The pH behind the front was approximately 11, while the pH ahead of the front was as the initial pH (around 6.5). Based on the ON-potentials of the cathode measured in the distinct positions in the gutter throughout time, an assessment of the sand/solution resistivity was made. The measurements showed that the resistivity increased prior to passage of the alkalisiation front. From chemical equilibrium considerations this was attributed to chemical precipitation of earth alkaline hydroxides taking place prior to alkalisiation, and the chemical equilibria calculations justified that the precipitations formed in this particular environment consisted of Mg(OH)<sub>2</sub> rather than Ca(OH)<sub>2</sub>.

## Introduction

As a result of cathodic protection, the pH nearby a protected surface (cathode) usually increases due to electrochemical reactions such as:



At the anode, the electrons are produced primarily by water oxidation producing acid:



In all reactions (1-4) the ratio between electron flow and acid/alkalinity production is 1:1.

Considering a cathodically protected steel surface, the alkalisation (pH increase) is produced by the electrochemical reactions occurring directly at the surface. This sets up a pH gradient ( $\text{H}^+$  concentration gradient) in the proximity of the surface, and consequently diffusion processes initiates as described by Fick's laws of diffusion ([A] is concentration of diffusing species A):

$$j_A = -D \cdot \frac{\delta[A]}{\delta x} \quad (5)$$

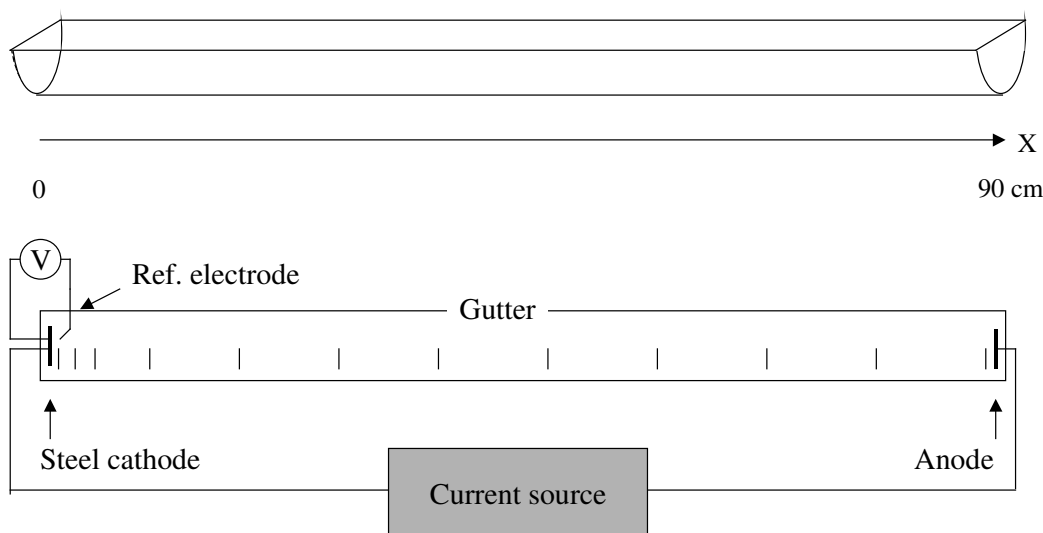
$$\frac{\delta[A](x,t)}{\delta t} = D \cdot \frac{\delta^2[A](x,t)}{\delta t^2} \quad (6)$$

Hence, diffusion processes renew  $\text{H}^+$  at the cathodically protected surface, whereas  $\text{OH}^-$  diffuses away from the surface, both causing a moderation of the pH increase otherwise taking place at the surface. The rate by which the diffusion can occur depends on the diffusion coefficients,  $D_A$ , for the diffusing species A in the particular environment.

The aim of the present investigation was to characterise the pH profile evolving at a cathodically protected steel surface exposed in a mixture of sand and artificial soil solution in terms of the conditions for diffusion and precipitation of solids in a mixture of sand and artificial soil solution.

## Experimental

The experiments were conducted in a 90cm long PVC-gutter filled with a mixture of sand and soil solution (figure 3).



*Figure 3. Sketch of the experimental set-up.*

A steel membrane (area = 12.5 cm<sup>2</sup>) was placed in one end acting as the cathode, and a titanium mesh (area = 100 cm<sup>2</sup>) was placed in the opposite end acting as the anode. The positions on a longitudinal axis of these electrodes were 0 cm (cathode) and 90 cm (anode). In between these end points, pH was measured throughout the experimental period using pH sensitive paper placed at 1, 3, 5, 10, 20, 30, 40, 50, 60, 70, 80, and 90cm positions. In addition the potential of the cathode and the anode was measured. ON-potentials of the cathode were measured placing the reference electrode in the above mentioned positions, whereas OFF-potentials were measured using the current interruption technique. A DC-current of 2.5 mA (0.2 mA/cm<sup>2</sup> with respect to cathode area) was passed between the anode and the cathode. The experiments proceeded with current for a period of 19 days with regular readings of potentials and pH. Subsequently, the current was shut off, and the readings of the potentials and the pH were continued for another 15 days.

The chemical composition of the soil solution is given in table 1. The initial pH of the soil solution was around 6.5. During the experiment, the gutter was equipped with a cover in order to prevent evaporation.

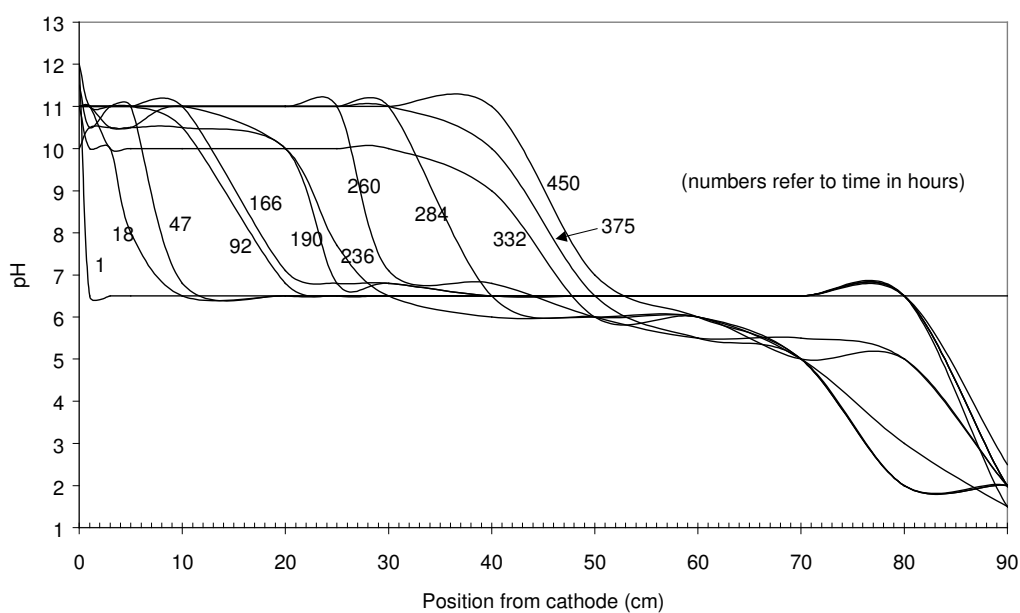
Component	Concentration (mg/L)	Concentration (mol/L)
MgSO <sub>4</sub> , 7H <sub>2</sub> O	617	2.5·10 <sup>-3</sup>
CaSO <sub>4</sub> , 2H <sub>2</sub> O	430	2.5·10 <sup>-3</sup>
CaCl <sub>2</sub>	554	5.0·10 <sup>-3</sup>

*Table 1. Chemical composition of the soil solution.*

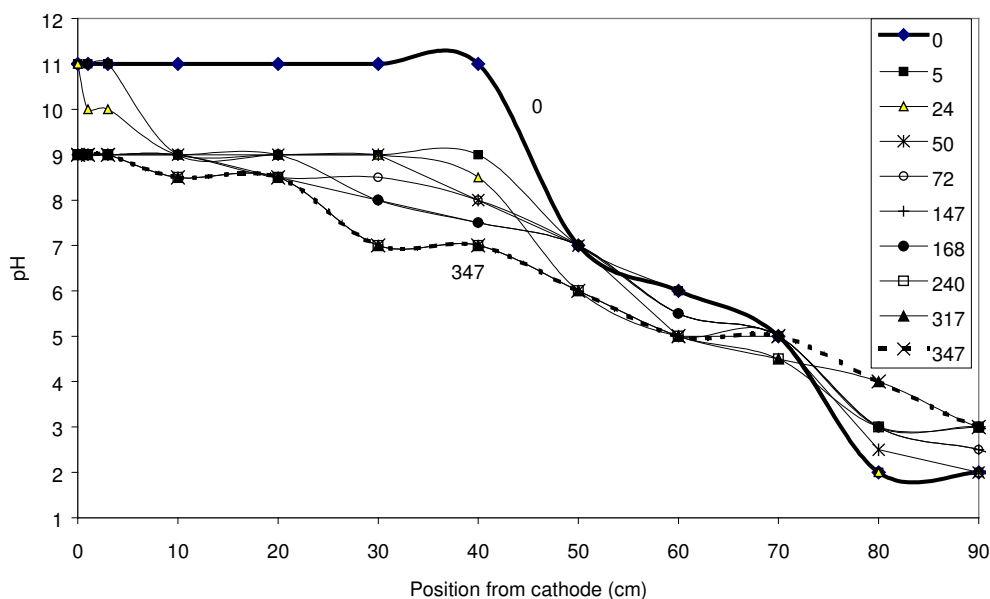
The SiO<sub>2</sub> sand used in the investigations had a grain size between 50 and 500 µm. A volume of 4L of sand was transferred to the gutter and mixed with 1.7L soil solution corresponding (saturation of the pores).

## Results

Figure 4 outlines the pH measured as a function of position relative to the cathode, throughout the period with current flow. As observed from the figure, an alkalisation profile evolves from the cathode, and an acidification profile from the anode. Figure 5 shows the equivalent pH distribution as a function of time after current shut off.

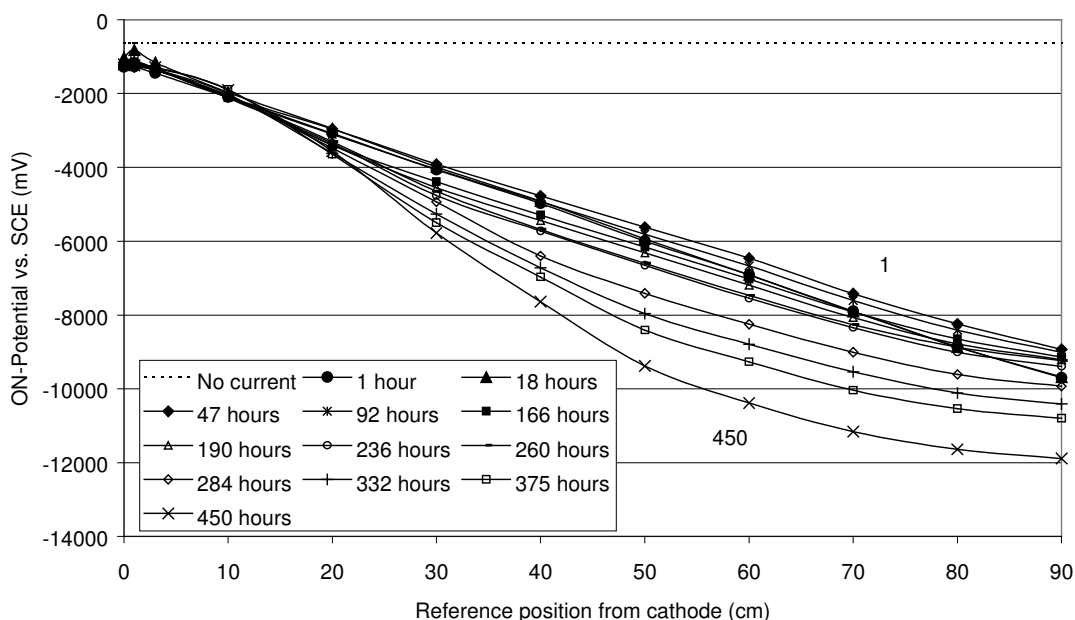


*Figure 4. pH throughout the period with current flow as a function of position relative to the cathode,*

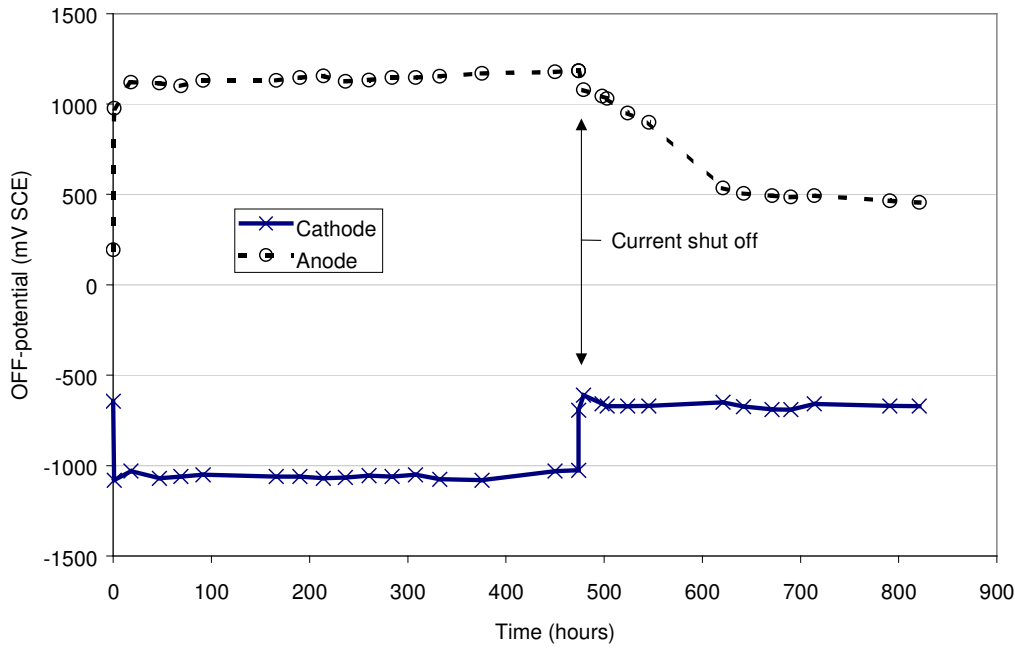


*Figure 5. pH as a function of the distance from the cathode after current switch off.*

The ON-potentials of the cathode throughout time with current flow measured with the SCE reference electrode placed in distinct distance from the cathode are presented in figure 6, indicating increasing IR-drop throughout time. OFF-potentials of the cathode and anode are presented in figure 7.



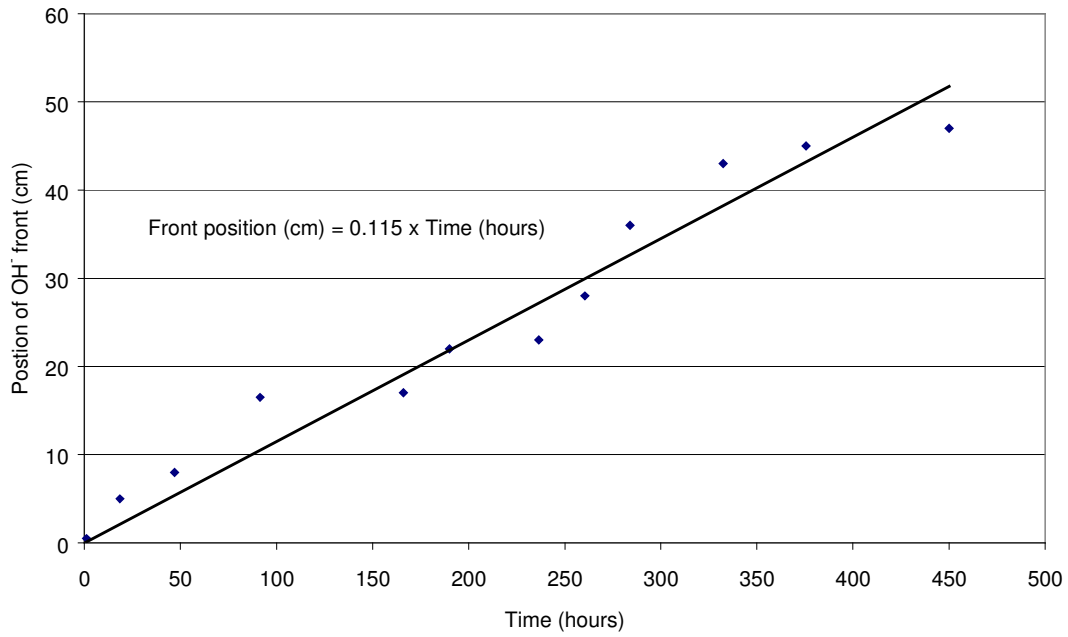
*Figure 6. ON-potentials of the cathode throughout time with current flow measured with the SCE reference electrode placed in distinct distance from the cathode.*



*Figure 7. OFF-potentials of cathode and anode throughout time.*

## Discussion

From figure 4 is observed that an alkaline front moves away from the cathode throughout time. The pH behind this front (including the surface pH of the cathode) stabilises around 11, whereas the pH ahead of the front equals initial pH around 6.5. The rate by which the front is moving may be assessed by drawing a line at pH 8 and use this line to assess the position of the front as a function of the time (where the profile intercepts with the pH=8 line). The result of this is illustrated in figure 8, showing a linear correlation between front position and time. The proportionality factor indicates that the alkaline front moves by a linear velocity  $V_{\text{front}} = 0.115 \text{ cm/h}$  or  $3.2 \times 10^{-5} \text{ cm/sec}$ . The pH of approximately 11 at the alkaline side of the front corresponds to a concentration of  $\text{OH}^-$  of  $10^{-6} \text{ mol/cm}^3$ , whereas the pH of around 6.5 at the other side of the front corresponds to a concentration of  $\text{OH}^-$  of approximately  $3.2 \times 10^{-11} \text{ mol/cm}^3$ . The difference almost equalising the  $\text{OH}^-$  concentration existing at the alkalisied side of the front,  $\Delta[\text{OH}^-] = 10^{-6} \text{ mol/cm}^3$ . Multiplying with the linear velocity of the front ( $V_{\text{front}}$ ), the flux of  $\text{OH}^-$  can be calculated to be  $j_{\text{OH}^-} = 3.2 \times 10^{-11} \text{ mol/(cm}^2 \cdot \text{sec)}$ .



*Figure 8. Position of the alkaline front as a function of time.*

A general  $\text{OH}^-$  mass balance across a volume element  $dV=dX \cdot A$  ( $A$  = cross sectional area) can be set up:

$$\text{OH}^- (\text{enter at } X) - \text{OH}^- (\text{exit at } X+dX) = \text{OH}^- (\text{accumulated}) + \text{OH}^- (\text{consumed}) \quad (7)$$

Directly at the cathode surface, the amount of  $\text{OH}^-$  entering the volume element equals the rate by which  $\text{OH}^-$  is produced by the cathodic current. The rate by which the  $\text{OH}^-$  is consumed is equal to the rate by which  $\text{OH}^-$  reacts with cations in the volume element. The consumption of  $\text{OH}^-$  proceeds only until equilibrium is achieved, hence – after a while, the consumption is zero. The pH in the volume element is controlled by the amount of accumulated  $\text{OH}^-$ , hence, in the equilibrium situation, this equals the difference between  $\text{OH}^-$  entering and exiting the volume element. Since a steady pH around 11 seems to exist behind the alkaline front, the accumulation behind the front is zero ( $\text{OH}^-$  diffuses right through the volume element). Consequently, accumulation and consumption takes place only across the alkaline front. In this particular volume element, the rate by which  $\text{OH}^-$  enters the volume element equals the rate by which  $\text{OH}^-$  is produced by the cathodic current:

$$\left( \frac{d[\text{OH}^-]}{dt} \right)_x = I_c \cdot n \cdot F \quad (8)$$

where  $I_c$  is the cathodic current,  $n$  is number of electrons producing  $\text{OH}^-$  (1) and  $F$  is the Faradays number.

The rate by which  $\text{OH}^-$  exits this particular element is very inferior to the rate by which  $\text{OH}^-$  enters the element since the concentration gradient approaches zero in this non-steady state condition. Accordingly, in the volume element across the alkaline front, the mass balance may be written:

$$\frac{I_c}{F \cdot V} \cdot \Delta t = [\text{OH}^-]_{\text{acc}} - [\text{OH}^-]_{\text{cons}} \quad (9)$$

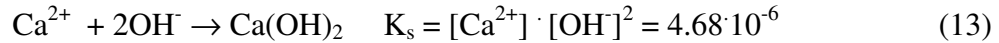
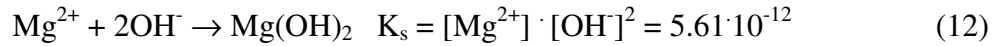
Considering a volume element of 0.0022 L (the volume of water included in the sand extending 0.115 cm along the X-axis in the gutter) and a time period of 1 hour, the amount of  $\text{OH}^-$  entering the volume element can be calculated as follows:

$$[\text{OH}^-]_{\text{enter}} = \frac{I_c}{F \cdot V} \cdot \Delta t = \frac{0.0025 \text{ A} \cdot 3600 \text{ s}}{96500 \text{ C/mol} \cdot 0.0022 \text{ L}} = 0.04 \text{ mol/L} \quad (10)$$

The concentration of accumulated  $\text{OH}^-$  can be calculated according to:

$$[\text{OH}^-]_{\text{acc}} = (10^{-(14-\text{pH})})_{\text{behind front}} - (10^{-(14-\text{pH})})_{\text{ahead of front}} = 0.001 \text{ mol/L} \quad (11)$$

Subtracting (11) from (10) necessarily leads to the conclusion that the vast majority (0.039 mol/L) of produced  $\text{OH}^-$  is consumed by chemical processes occurring prior to the pH increase. It can be suggested that these processes are precipitation of hydroxides according to the reactions (solubility product associated<sup>1</sup>):



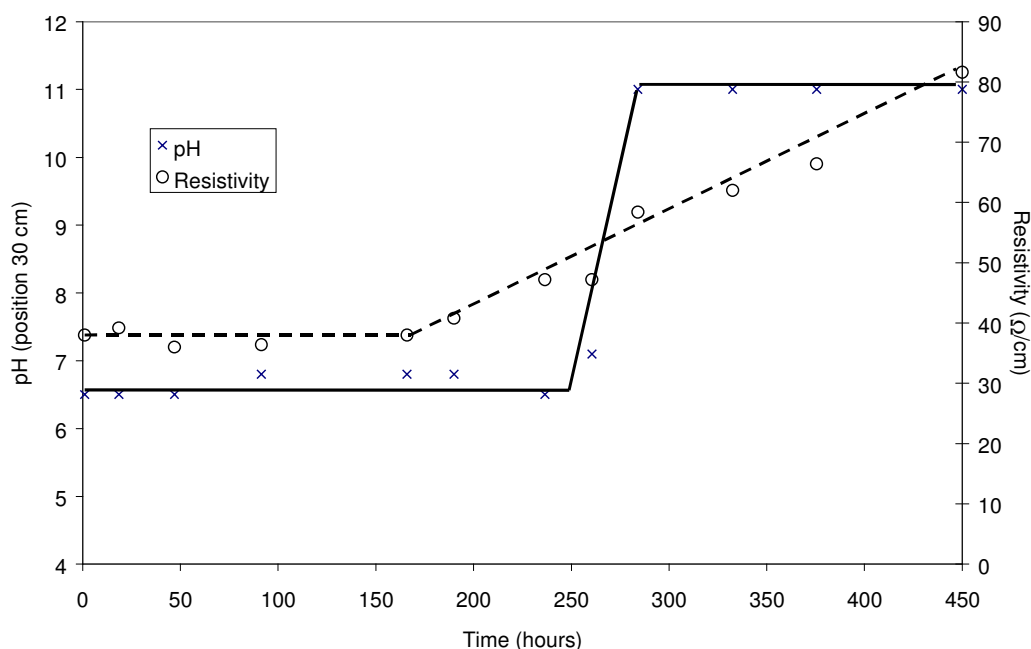
A calculation using the  $\text{Mg}(\text{OH})_2$  solubility product<sup>2</sup> shows that at pH = 11 ( $[\text{OH}^-] = 0.001 \text{ mol/L}$ ),  $\text{Mg}(\text{OH})_2$  precipitates until the  $\text{Mg}^{2+}$ -concentration decreases below  $5.61 \cdot 10^{-6} \text{ mol/L}$ , whereas the threshold concentration of  $\text{Ca}^{2+}$  is 4.68 mol/L. The initial concentrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in the solution were 0.0025 and 0.0075 respectively, hence, the calculations suggest that practically all  $\text{Mg}^{2+}$  is consumed in the alkalisied regions whereas no  $\text{Ca}^{2+}$  is consumed. In this case, the mass balance fits reasonably good, taking into account the inaccuracies introduced using the pH sensitive paper for the pH measurements.

If the produced  $\text{OH}^-$  reacts with  $\text{Mg}^{2+}$  initially and causes pH increase secondly, one should expect that prior to the passage of the alkalisiation front, the resistivity of the solution increases due to removal of  $\text{Mg}^{2+}$  ions. This may be confirmed by viewing the cathode ON-potentials measured with a reference electrode placed in various X-positions in the gutter throughout time (figure 6). Taking e.g. the X=30cm position as a control point, the resistivity as a function of time can be calculated taking the slopes of the  $E_{\text{ON}}\text{-X}$  curves from figure 6 in this particular position divided by the current. Figure 9 presents the resistivity versus time in this point in comparison with the pH, showing that the solution resistance actually increases prior to the passage of the alkalisiation front.

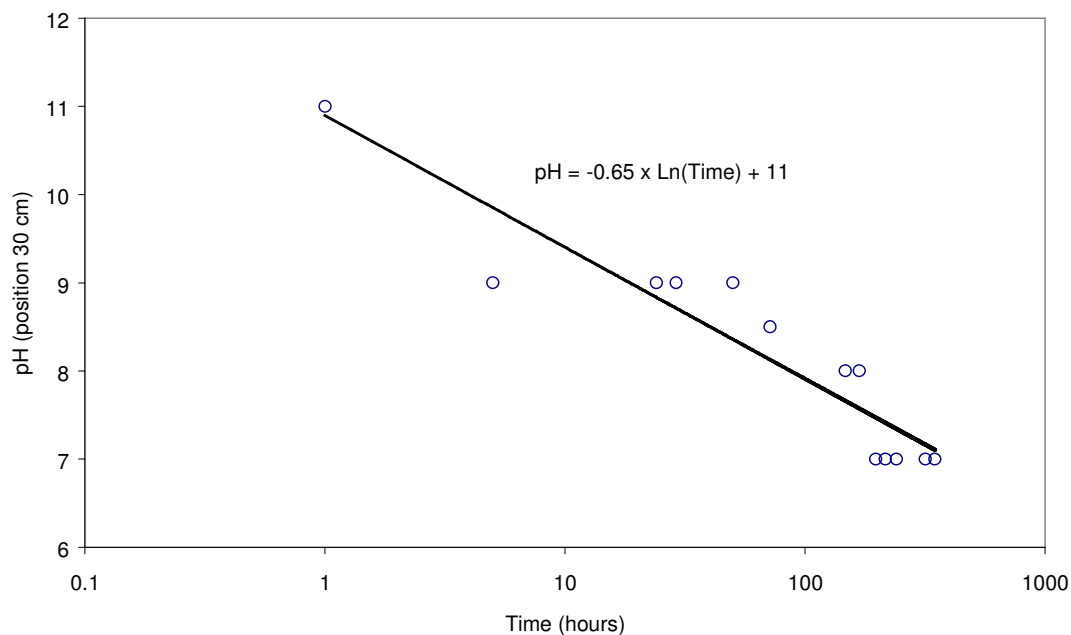
After current switch off, the pH profile does not have a distinct front associated, it rather forms a more uniform linear profile throughout the gutter with highest pH at the



cathode end and lowest pH at the anode end. This profile may eventually decay if the experiment was allowed to run for an extended period of time. Figure 10 shows the pH as a function of time at position X=30cm after current switch off. A linear pH log(time) behaviour may be indicated here.



*Figure 9. Comparison of the solution resistance and the pH in position X=30 cm as a function of time.*



*Figure 10. pH as a function of time at position X=30 cm after current switch off.*

Regarding the OFF-potentials of the cathode and the anode throughout time (figure 7), it is observed that although the anode area was 10 times larger than the cathode area, the anode polarises +1000 mV when the current flows, whereas the cathode polarises only -500 mV. Further, when the current is switched off, the cathode depolarises rapidly whereas the anode polarises throughout a period of 5 days. This observations are merely taken is an indication that diffusion processes are in control of the kinetics of the anode, while more rapid charge-transfer dominated processes are controlling the kinetics of the cathode.

## **Conclusions**

- An experimental set-up was established with a steel cathode placed in one end and an anode placed oppositely of a sand/soil solution-filled 90 cm long gutter. The steel was cathodically charged by 2.5 mA distributed over the 12.5 cm<sup>2</sup> area. Development in the pH profile evolving from the cathodically charged steel surface was followed, and ON-potential measurements with a reference electrode placed at distinct positions in the gutter was performed over a period of 19 days. After this, the current was shut off, and the pH and potentials measured additionally for a 15-days period without current.
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- Assessment of the sand/solution resistivity was based on the ON-potentials of the cathode measured in distinct positions in the gutter throughout time. The measurements showed that the resistivity increased prior to passage of the alkalisation front. This was attributed to chemical precipitation of earth alkaline hydroxides taking place prior to alkalisation, and chemical equilibria calculations justified that these precipitations consisted of Mg(OH)<sub>2</sub> rather than Ca(OH)<sub>2</sub>.

## **References**

1. Handbook of Chemistry and Physics, (David R. Lide, editor in chief), CFC press, 75<sup>th</sup> edition (1994).
2. L.V. Nielsen, Thermodynamical Considerations on the Local Chemistry Formed at the Steel-Soil Interface of Cathodically Protected Pipelines, Paper 1, this report, 2000.