2-13

Cathodic protection: A general discussion of the involved processes and their consequences for threshold values

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Korrosionsschutz ablaufenden Prozesse erforderlich. Die im Rahmen der Untersuchungen ermittelten grundsätzlichen Konzepte für den Mecha kathodischen Korrosionsschutzes und deren Konsequenzen auf die Grenzw diskutiert.

Résumé

La protection cathodique a augmenté la durabilité des conduites. Les limites util jugement de la protection cathodique sont éprouvées. Malheureusement sous courant constant ou alternative ils ne sont plus applicables. Pour l'evaluation des relevant et la discussion des valeur limites la compréhension des méc nécessaire. Ces concepts fondamental, leur relevance et leur conséquence po limites est discutée

It turned out that under a.c. interference a high cathodic protection curre
detrimental effects on the durability of cathodically protected structures.
These surprising observations in the case of a.c. and d.c. interference demor
profound understanding of the processes taking place on the steel surface is re
when the involved mechanisms are understood, the determination of parame
related thresholds is possible.

Experimental

For all electrochemical characterizations and potential measurements a Jaissle F
Galvanostat PCT 1002 in combination with a computer was used. The Coupons
surface of 1 cm^2 were used for all tests. Solutions were prepared from reagent g
chemicals and de-ionized water. The electrolytes used in this work were borate b
pH-value of 8.4 (0.075 M $Na_2B_4O_7 \cdot 10\ H_2O$, 0.3 M H_3BO_3), 0.1 M Na_2SO_4, 0.01
0.1 M NaOH. All potentials are referred to saturated Copper/Copper sulfate elect

presence of the oxidizing agent oxygen in the electrolyte. In the case of copper protection can be achieved by shifting the potential from the corrosion range of diagram (Fig. 1) to the immunity range.
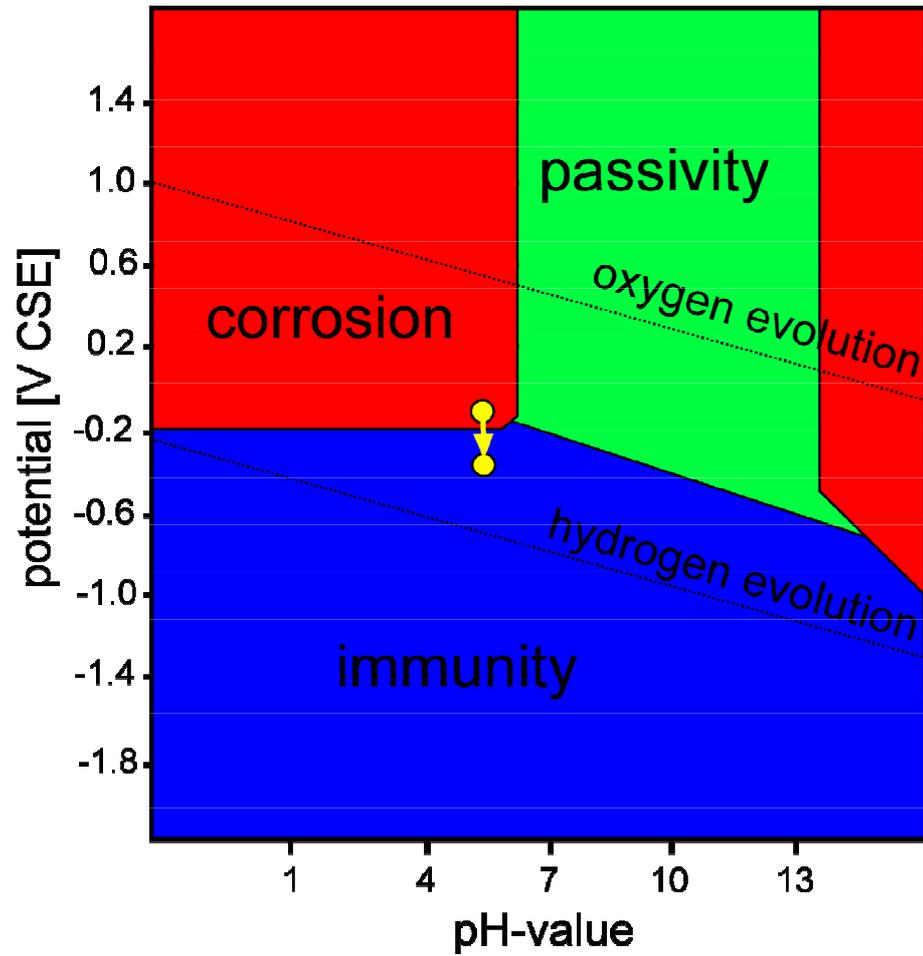

Fig. 1: *Pourbaix diagram for copper. Shift of the potential from the corrosion to range by the cathodic protection current.*
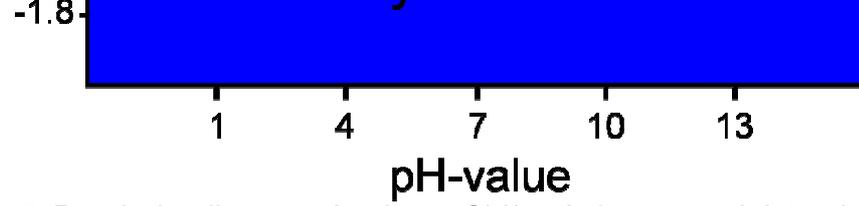
-1.8

| 1 | 4 | 7 | 10 | 13 |

pH-value

Fig. 2: *Pourbaix diagram for iron. Shift of the potential to the hydrogen evo...*
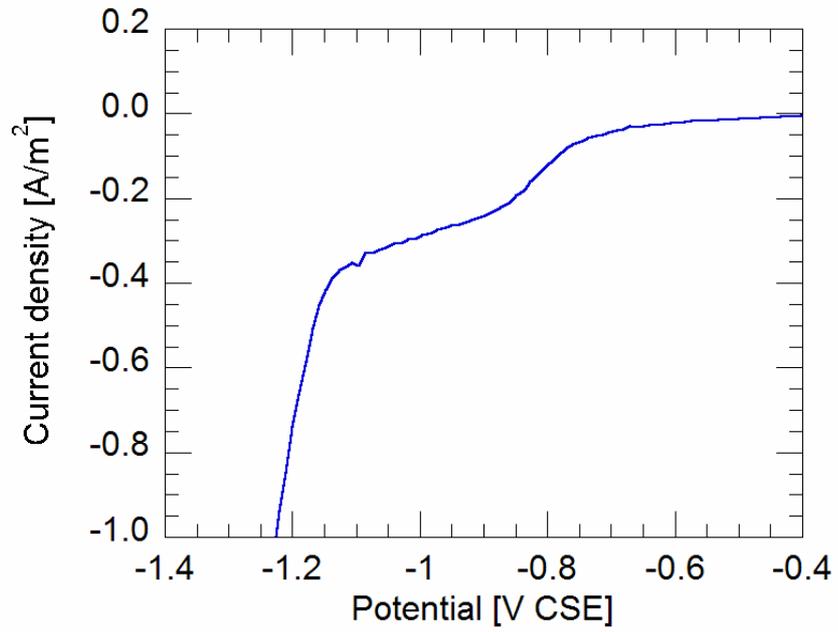*cathodic protection current.*

Fig. 3: *Cathodic polarization scan of steel in 0.1 M NaOH with pH 13.*

In Fig. 2 the Pourbaix diagram for iron is shown. It is important to note that th...
potential for the oxidation reaction (3), which is the transition from immunity to ...

2). In this range the formation of a protective passive film is thermodynamica...
When reaching the field of passivity the potential of the steel surface gets b...
CSE, which is the threshold value for the off potential. Since this value is not in...
range, the question arises regarding the protection mechanism. Clearly, the m...
different compared to the situation described for copper. There are several...
contribute to the corrosion protection of steel:

- Corrosion is only possible when the electrons formed in reaction (3) are co...
  predominant reducing agent is oxygen. Hence the depletion of oxygen...
  surface results in a decrease in the corrosion rate.

- The reduction reactions taking place on the steel surface increase the pH...
  surface. If the pH is sufficiently high, the steel surface is covered by...
  passive film that strongly decreases the corrosion rate.

- The lowering of the potential of the steel surface decreases the drivin...
  reaction (3). Therefore, the corrosion rate is decreased. Moreover, a...
  couples due to aeration elements along the pipeline are eliminated.

As a consequence, the positive effect of cathodic protection is caused by th...
contribution of all three effects. Based on the discussion of the processes taking...
cathodic protection, a potential below -0.85 V CSE can only be reached whe...
depleted and the alkalinity is sufficiently high to allow the formation of a prote...
film. As a consequence, the measurement of the off potential effectively is a ...
and oxygen measurement. This is illustrated by the potential measuremen...
electrolytes with different pH values (Fig. 4). The oxygen content of these e...
decreased by purging with nitrogen. Clearly the potential decreases rapidly whe...
content is lowered. In the case of the electrolyte with pH 12 the potential drops b...
CSE after a few minutes. This effect is even more pronounced at pH 14, wh...
solution the potential does not drop below -0.73 V CSE. This experiment ...
theoretical conclusions.

Corrosion due to a.c. interference
Now that the mechanism of the cathodic protection and the significance of t
value are discussed the question arises regarding their consequences for cathod
under a.c. interference. The involved mechanisms are described in detail in [4,
the corrosion mechanism is illustrated. The repeated complete formation and d
the passive film results in a corrosion rate of up to 70 mm/year and in the forma
layer.
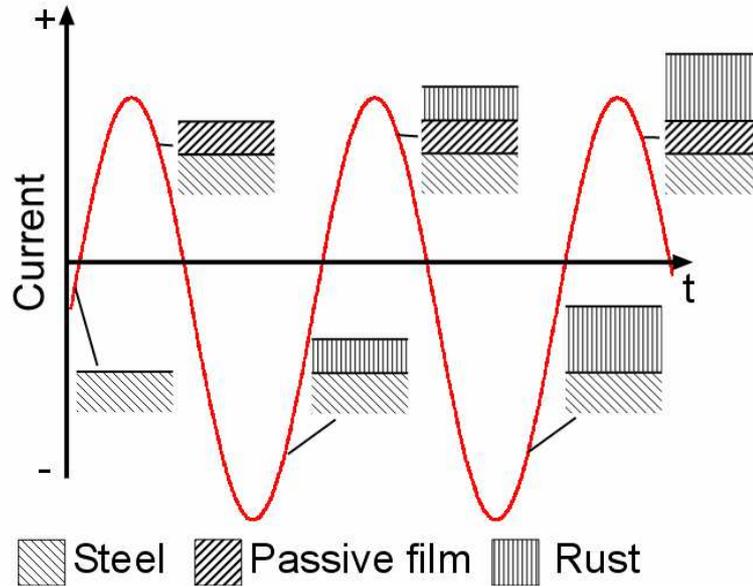

Fig. 5: Mechanism of a.c. corrosion.

This corrosion process can be stopped if the once formed passive film is r
anymore. This is achieved by decreasing the cathodic protection current. It is
note that a certain rust layer thickness is required for the consumption of the
cathodic charge of the a.c. current by reaction (5). In an extended field and la
the relevant threshold values were experimentally determined [6]. It was demc
the corrosion rate remains acceptable if the average on potential is more positiv

$$I_{d.c.} = \frac{E_{on} - E_{off}}{R}$$

In order to explain the experimentally observed threshold value of -1.2 V CS
potential, the effects taking place during cathodic protection have to be consider
the Pourbaix diagram (Fig. 6). As soon as the hydrogen evolution takes place
surface, the off potential is shifted along the equilibrium line for hydrogen evoluti
Fig. 6 it becomes clear that there is an intersection between the line for hydrog
and the line for an E_{on} of -1.2 V CSE. As a consequence, the difference between
according to equation (1) will go towards zero for high pH values, limiting the
density. This will limit the increase of surface pH and, therefore, equilib
established preventing an uncontrolled increase of the d.c. current density. In co
E_{on} of -1.3 V CSE the driving voltage can only go towards zero at unrealistic hig
and, therefore, the d.c. current density can strongly increase and cause a.c. co
important to note that the field of corrosion at high pH cannot be the primary
corrosion, since on potentials more negative than -1.2 V CSE in absence of a.c.
do not cause any corrosion.

Based on this discussion the question arises regarding the negative effect of the
In previous investigations it was demonstrated that the a.c. current density can
of the E_{off} to positive values [5]. This so called faradaic rectification is ca
asymmetry of the polarization curves (e.g. Fig. 3). This rectification becomes
a.c. current densities above 30 A/m^2 explaining the significance of this threshol
shift of the E_{off} to more positive values will additionally increase the d.c. cu
according to equation (1) and therefore cause a.c. corrosion. Based on this di
negative Effect of the a.c. current density in the case of low cathodic protec
primarily the increase of the d.c. current density.

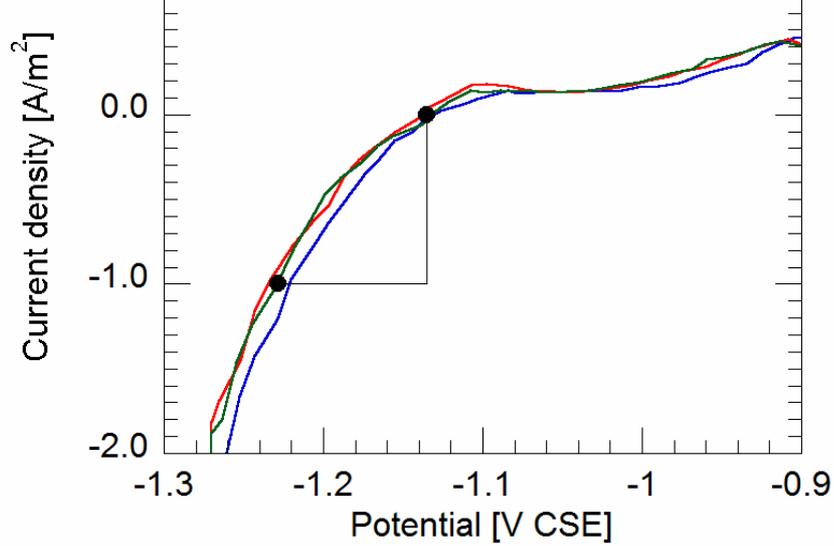Fig. 7: *Anodic polarisation scans of steel in 0.1 M NaOH (pH 13). The p*
associated with a cathodic current of 1 A/m² is 93 mV.

$$3Fe + 4H_2O \leftrightarrow Fe_3O_4 + 8H^+ + 8e^-$$

In field tests a threshold value of the d.c. current density at 1 A/m² is empirica
The question rises regarding its significance. Based on Fig. 6 it is clear that
potential is limited by the hydrogen evolution. However, at increased current
possible to further decrease the potential of the steel surface according to Fig.
the model concept described in Fig 5 the electrochemical reduction of the passi
main reason for the occurrence of a.c. corrosion. According to the Pourbaix dia
the dissolution of the passive film is thermodynamically possible at potentials in
range based on reaction (6). The potential difference between the equilibr
hydrogen evolution and the equilibrium line between immunity and passivit
Hence, a cathodic current that causes a potential shift of the steel surface of 8
capable of destroying the passive film and, therefore, cause a.c. corrosion.

excursions. The main difference is the frequency of the interference. Using th
could be assumed that similar mechanisms should take place during d.c.
Generally, an anodic interference is considered to be dangerous from the poi
corrosion. However, comparing the polarization scans in Fig. 8 it becomes clea
behavior is obtained both at pH 8.4 and 12. In contrast, at pH 7 no passivity is
interesting to note that the onset of the anodic current is at -0.85 V CSE a
elevated potentials an increase in current is observed for the passive sys
corresponds to oxygen evolution. Based on this result it can be concluded th
polarization primarily results in the formation of a passive film rather than co
anodic polarization even to significant potentials does not initiate any corrosio
these data it could be concluded that anodic currents do not adversely affect t
process of steel under cathodic protection. This is true as long as the pH value
high. This should be true if the off potential is more negative than -1 V CSE.
cathodic current causes the pH to decrease. Some anodic reactions strongly
pH. This is especially true for oxygen evolution that takes place at increased po
decreasing pH the conditions for passivity can be lost and corrosion can be in
consequence, the anodic current may only occur temporarily and the average cu
through the steel surface must be cathodic in order to assure a sufficiently high p
In the case of a.c. corrosion the repeated formation and dissolution of the passi
a high corrosion rate according to Fig. 5. The same process takes place in the
interference. However, the lower frequency is strongly limiting the corrosion ra
repeated formation and dissolution of the passive layer results in the format
layer, the amount of charge that can be consumed during the anodic ex
significantly increase. This is due to reaction (5) that can consume major
electrical charge without causing corrosion. This effect is reported by [2] for s
interference.

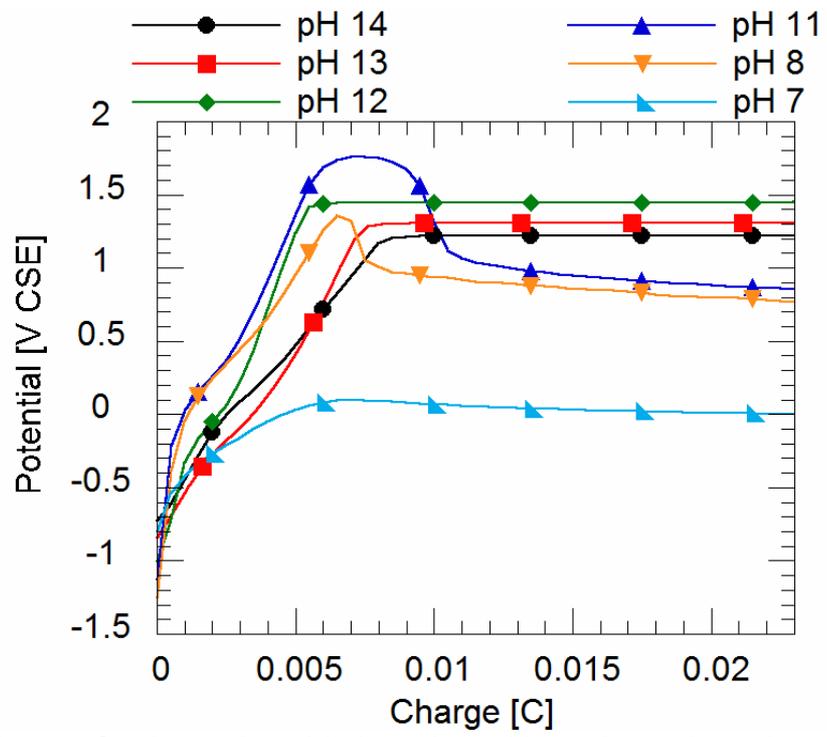Fig. 9: *Coulometric oxidation of steel in various electrolytes. The potential value ohmic potential drop.*

Based on this discussion it becomes clear that anodic charge and ano
excursions do not necessarily cause corrosion. Therefore, neither a potential
criterion is necessarily applicable for judging the risk of stray current corr
consequence, the currently used criteria according to EN 50162 are clearly cons
the risk of stray current corrosion is probably often overestimated.

A possible approach to the judging of the corrosion risk due to stray current in
the use of the coulometric oxidation [5, 7]. By applying an anodic current on a
potential evolution can be determined over time. An example is shown in Fig.
electrolytes. Based on these data it is clear that oxygen evolution can only be r
pH is sufficiently high to promote the formation of a protective passive film. The
can be followed by the increase of potential, while the oxygen evolution resu
independent potential value above 0.5 V CSE. Once the oxygen evolution is rea
starts decreasing which can cause initiation of corrosion. The corrosion initiatio
be detected by the drop of potential as demonstrated for pH 11 and 8. In the cas
passivation is observed at all since the potential does not rise up to oxygen evo
this short experiment the passivating properties of the soil in the vicinity of the
can be judged.

If repeated formation and dissolution of a passive film has taken place, a
accumulated on the steel surface. This rust layer can significantly increase th
charge that can be consumed during anodic polarization. In Fig. 10 an exampl
on a coupon connected to a pipeline is shown. A similar behavior as in Fig. 9
However, there is a larger amount of charge being before oxygen evolution is r
can be attributed to the oxidation of the rust layer according to reaction (5).

Conclusion

The processes taking place under cathodic protection of steel are discussed in
on this analysis it has to be concluded that the corrosion protection is not
polarization of the steel surface to the immunity range. Instead the positive effe

The coulometric oxidation, which was developed for investigating the a.c. ... suggested as a technique for characterizing the resistance of coupons tow... potential excursions and judge the corrosion risk of the pipeline under s... interference.

Acknowledgements

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