THE PERFORMANCE OF THERMALLY SPRAYED ZINC COATINGS AS ANODE FOR CATHODIC PROTECTION ON REINFORCED CONCRETE

WIRKUNG VON THERMISCH GESPRITZTEN ZINKÜBERZÜGEN ALS ANODE FÜR DEN KATHODISCHEN KORROSIONSSCHUTZ IM STAHLBETONBAU

L´EFICACITE DE LA METALLISATION AU ZINC SUR LE BETON ARME POUR LA PROTECTION CATHODIQUE ANTI CORROSIVE

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SUMMARY

Studies regarding the effectiveness of thermally sprayed zinc as galvanic and/or as impressed current anode showed good results under favourable conditions such as high zinc/steel area ratio and sufficient direct moistening. Cathodic protection with sprayed zinc on chloride containing concrete is achieved at least 2 years. With unfavourable zinc/steel area ratio and with temporarily inadequate moistening after one year a marked decline in the protective effect (galvanic anode) was observed. Subsequent operation with external current required steadily increasing voltage due to the increase of the internal resistance of the zinc/concrete interface.

ZUSAMMENFASSUNG

Untersuchungen zur Wirkung von auf Beton thermisch gespritzten Zinküberzügen zum Zwecke des kathodischen Korrosionsschutzes haben gezeigt, daß unter günstigen Bedingungen wie hohes Flächenverhältnis Zink/Stahl und genügende Befeuchtung ein ausreichender Schutz möglich ist. Bei einem ungünstigen Flächenverhältnis Zink/Stahl und mit zumindest zeitweise ungenügender Befeuchtung war nach einem Jahr ein deutliches Nachlassen der Schutzwirkung zu beobachten. Der anschließende Betrieb mit Fremdstrom erforderte wegen des ansteigenden Widerstandes an der Phasengrenze Zink/Beton zunehmend höhere Spannungen.

RESUME

Des études sur l'efficacité de la métallisation au zinc sur le béton pour la protection cathodique anti corrosive ont montré, qu'une protection suffisante est possible dans de bonnes conditions telles qu'une proportion importante de surface zinc/acier et d'humidification satisfaisante. Quand on avait une proportion défavorable de surface zinc/acier et une humidité temporairement insuffisante, on observait, au bout d'un an, une réduction de l'efficacité de protection. L'opération ultérieure avec le courant externe nécessitait une tension croissante due à l'augmentation de la résistance interne de l'interface de zinc/acier.

KEYWORDS: cathodic protection, thermally sprayed zinc, reinforced concrete, galvanic anode, impressed current anode, zinc

1. CATHODIC PROTECTION OF REINFORCED STEEL IN CONCRETE STRUCTURES

Corrosion of steel in concrete can be stopped or prevented by cathodic protection (CP). In civil engineering CP has been used for over 20 years [BAECKMANN, SCHWENK, 1989; POLDER, 1998]. The advantage of cathodic corrosion protection as compared with other protective measures consists in the fact, that concrete must be removed only in areas of advanced destruction. Chloride-contaminated zones do not need to be removed.

1.1 Protective Criteria for Cathodic Corrosion Protection on Reinforced Concrete

Protective Potential

As protective potential in DIN 30676 [DIN 30676, 1985] a potential of U_{NHE} = -0,43 V ist stated. The protective potential is limited downwards in order to avoid a loss of adhesion between reinforcement and concrete due to hydrogen evolution at lower potential values. However it is still uncertain wether commercial concrete types are actually affected [MENZEL, 1989]. In any case the possible danger of hydrogen embrittlement has to be considered in the case of prestressed structures. At a pH > 12 hydrogen evolution starts at about -0,7 V/NHE. Therefore, the protection potential should not exceed -0,65 V/NHE [BAECKMANN, SCHWENK, 1989; SHAW, 1965; PEDEFERRI, BERTOLINI, 1995]

Protective Current Density

The protective current density is limited to 20 mA/m² (steel surface). Usual current densities are between 1 and 15 mA/m² (steel surface).

100 mV-Criterion

A usual method for checking the effectiveness of cathodic protection is the 100 mV criterion. If, within four hours after the current has been switched off, the potential rises by at least 100 mV, sufficient protection is assumed [NACE Standard RP 0290-90]. However, studies show that in wet concrete and/or after some years of operation the 100 mV rise takes more than 4 hours [MIETZ, ISECKE, 1993] without loss of protection.

1.2 Anodes for Cathodic Corrosion Protection

In connection with reinforced concrete in most cases so far cathodic protection units with external current have been used. The anode is usually a conductive net (activated titanium wire mesh or conductive plastic cables with a copper core [BAECKMANN, SCHWENK, 1989]), embedded in a surface layer of shotcrete. In order to counter the problem of inhomogenous current distribution, repeated attempts have been made to apply conductive coatings [APOSTOLOS, 1983; WARNE, 1986; APOSTOLOS, CARELLO, 1985; CARELLO, 1986; MANNING, SCHELL, 1986; SCHELL, 1987; SEMINAR ON CORROSION IN CONCRETE, 1987; APOSTOLOS, 1987; MANNING, SCHELL, 1987; MANNING, 1990].

1.3 Zinc as an Anode

A possibility, already frequently used in practice for obtaining conductive concrete surfaces, consists in the application of sprayed zinc. As the zinc/concrete interface changes in the course of time zinc tends to passivate [HILDEBRAND, SCHWENK, 1986]. On the other hand, in concrete containing chloride, activation is possible so that, even without external current, cathodic protection will be successful [BAECKMANN, SCHWENK, 1989].

In the USA, field tests have already been carried out on bridges to test the effect of sprayed zinc films on concrete as a sacrificial anode (e.g. Florida Keys and Tampa Bay). The electric contact between zinc and reinforcing steel was partly assured by direct spraying onto exposed steel. It has been reported that the protective systems are still successfully working after 5 years in operation and that protective current densities of 1 µA/cm² are regularly achieved. The 100 mV criterion is still fulfilled also, however decreasing with time. As a limiting factor for adequate protection insufficient moistening is reported in some of the cases. In the vicinity of the sea splash water and frequent nebulousity ensures moistening for many years of protection. The effectiveness is directly related to the electric resistance of the concrete. In areas of high resistivity (very dry concrete) the protective effect is lower than in areas with a lower concrete resistance. [SAGÜÉS, POWERS, 1995; FUNAHASHI, DAILY, YOUNG, 1997].

Coatings of sprayed zinc have a number of advantages as compared with individual anodes or mesh anodes [SCHELL, 1987; APOSTOLOS, PARKS, CARELLO, 1987; MANNING, SCHELL, 1987]:

- They make possible a very good current distribution adapted to the particular conditions.
- They can be easily applied to surfaces with a complex design, in any direction.
- They only insignificantly change the appearance of the concrete.
- The film thickness can be adjusted to the particular conditions. After consumption of the zinc it can be renewed.

Mentioned as a disadvantage ist the fact that, for example in the case of inadequately low concrete cover in the case of protection with external current, short circuits are possible between zinc and reinforcing steel which lead to increased anode consumption and to an acid attack on concrete [WARNE, 1986; MANNING, SCHELL, 1986; SEMINAR ON CORROSION IN CONCRETE, 1987; APOSTOLOS, PARKS, CARELLO, 1987; MANNING, SCHELL, 1987]. However, if these circumstances are considered, sprayed coatings (applied by flame spraying and electric arc spraying) can be successfully used, as proved on pillars and bridge decks in marine environment [CARELLO, R.A., 1986; APOSTOLOS, PARKS, CARELLO, 1987]. In particular, the good long-term behaviour of the anode material is emphasised [MANNING, Schell, 1987].

As an anode, zinc is consumed. However, via the film thickness the protection duration as a function of the corrosive medium can be adjusted. On the basis of the studies for concrete structures exposed to chloride, film thicknesses of 200 µm are recommended [CARELLO, R.A., 1986].

In the case of protection with external current anodes, in [CARELLO, R.A., 1986] a protective current density of about max. 25 mA/cm² steel surface (during wet periods) and of min. 2 mA/cm² (in dry periods) is recommended by the same author. As the resistance of the zinc/concrete-interface increases with time due to growing layers of corrosion products, the voltage must be increased (adjusted) after a few years.

Initial problems of adhesion of zinc on concrete were improved by changing the process parameters of spraying (spraying distance, angles) and the preparation of the concrete surface. Thus tests and engineering applications already available showed that sprayed zinc films adhere very well to dry, blasted surfaces. Adhesion on "old" concrete proved to be best. Further studies showed that an increased surface temperature of the concrete (60-150 °C) during spraying markedly increases the adhesion of zinc. [APOSTOLOS, 1983; MANNING, 1990; BALDOCK, BROUSSEAU, ARNOTT, EVRAIRE, 1993; BROUSSEAU, FELDMANN,

DALLAIRE, ARNOTT, 1990; WIXON, 1993; BROUSSEAU, ARNOTT, DALLAIRE, FELDMANN, 1993]

2. INVESTIGATIONS / TEST METHODS

2.1 Pysical Protective Effect

2.1.1 Water Penetration Test

Regarding the physical protection, water penetration tests with zinc-sprayed and bare concrete surfaces were performed. Epoxi-coated concrete cylinders with metallized and bare bases were manufactured and stored in a water filled bath. The test conditions are shown schematically in fig. 1.

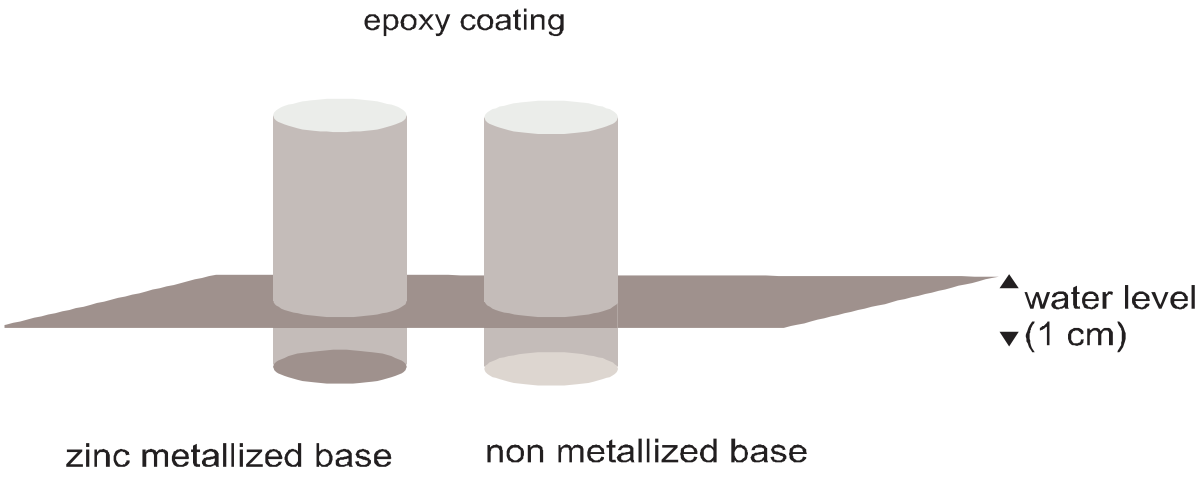

Fig. 1: *Water penetration test.*

2.1.2 Chloride Penetration Test

For testing the effectiveness of zinc as a barrier against chloride penetration metallized and bare concrete surfaces were sprayed with a 3-% sodium chloride solution once a week. The depth of chloride penetration was determined by analizing drilled samples taken from different depth.

2.2 Cathodic Protection

2.2.1 Specimens

Outdoor-Tests

In outdoor exposure-tests the influence of the following parameters has been taken into consideration:

- coverage ratio (metallized/bare surface)
- zinc-to-steel-surface-ratio,
- concrete cover.

To characterize the effectiveness of sprayed zinc as sacrificial and impressed current anode three concrete slabs of 1m x 1m x 0,1m with three or two layers of reinforcement were manufactured. The slabs were either totally or paritally coated with zinc. Details are given in figure 2.

The specimens were made of concrete class B25, containing 3 Wt.-% of chloride per cement weight. The chloride was added as sodium chloride.The water cement ratio amounts to 0,75.

The above figured concrete slabs were used for outdoor tests in Stuttgart. Concrete slab 1 was used as reference slab for measuring the free corrosion potential of zinc and steel. Zinc and reinforcement have never been shortcircuited in this case. The effectiveness of zinc as galvanic anode and as impressed current anode was tested on slab 2 and 3.

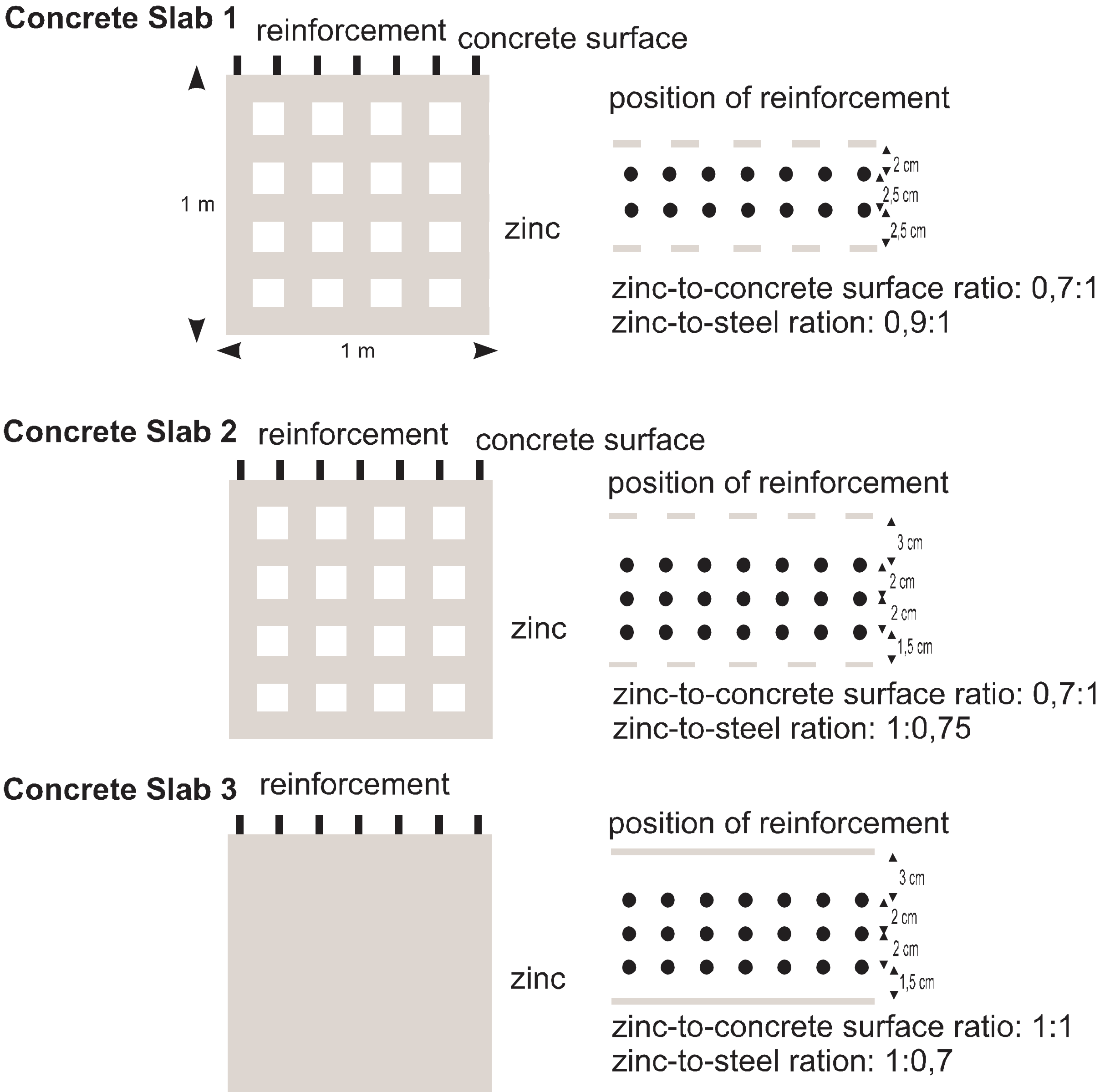

Fig. 2: *Concrete specimens for outdoor tests.*

Laboratory Tests

Small specimens (10cm x 7cm x 6cm) were manufactured for tests under constant environmental conditions (20°C, ca. 88% RH). One batch of specimens was chloride-containing (3% Chloride/cement weight), the other specimens were artificially carbonated after concreting and free of chloride. Afterwards on each of the samples two opposite surfaces were thermally sprayed with zinc (zinc-to-steel area ratio: 10:1). These specimens were used for testing the effectiveness of zinc as galvanic and impressed current anode.

2.2.2 Zinc Metallizing

Prior to metallizing the concrete surface was sand blasted. The blasting provides the surface roughness necessary to develop adequate bond strength between zinc and concrete. Prior to metallizing, the concrete surface was heated to 60 to 70°C by means of a propan gas burner. The zinc (flamesprayed) was sprayed to a thickness of about 450 - 550 µm.

2.2.3 Electrochemical Tests

Potentials were measured using a calomel electrode (+242 mV to NHE), contacted to the concrete either by means of a wet sponge or (for long term measurements) with silica gel inserted in a drilled hole. Short-circuit current was measured by means of a zero-resistance-ammeter.

3. RESULTS

3.1 Pysical protective effect

3.1.1 Water penetration test

The diagram in figure 3 shows the results up to a testing period of 160 hours. Obviously the zinc-coating obstructs the water penetration to some extent.

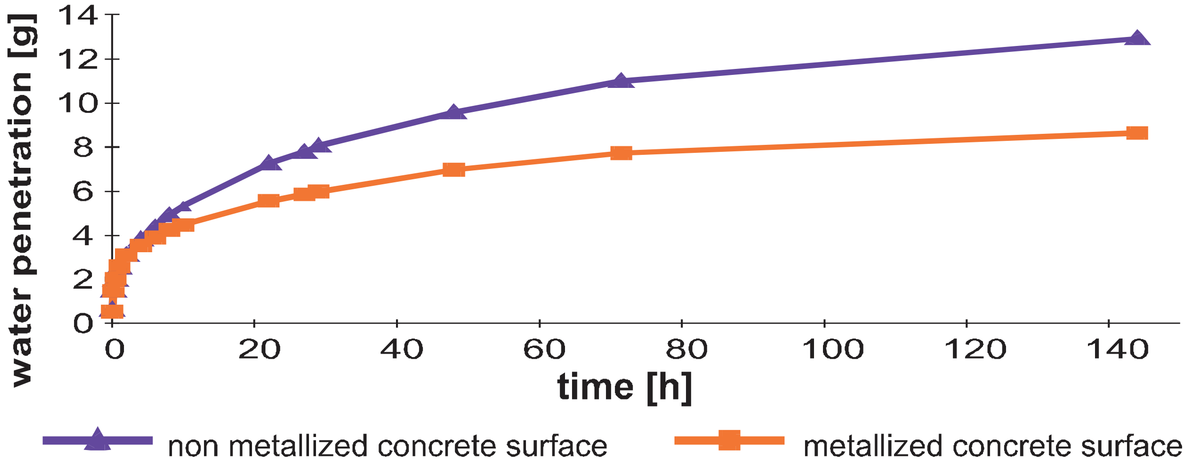

Fig. 3: *Water penetration test.*

3.1.2 Chloride penetration test

The results of the chloride analysis vs. concrete cover after 246 days are shown in figure 4. In case of metallized concrete the chloride content ist significantly lower than in case of the bare surface.

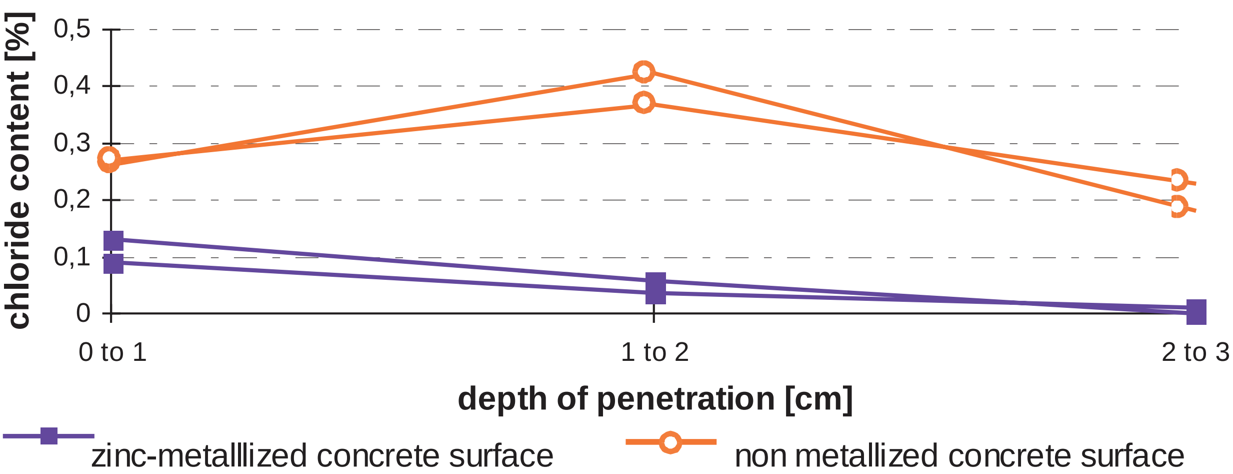

Fig. 4: *Chloride penetration test.*

3.2 Cathodic Protection

3.2.1 Outdoor Tests - Zinc as Galvanic Anode

Free Corrosion Potential of Zinc and Iron (no short-circuit)

The potential run of zinc not contacted to steel shows a primary decrease in potential up to -780 mV SCE, followed by a potential rise to values close to the free corrosion potential of the reinforcement (-400 mV SCE) after about 600 days (fig. 5).

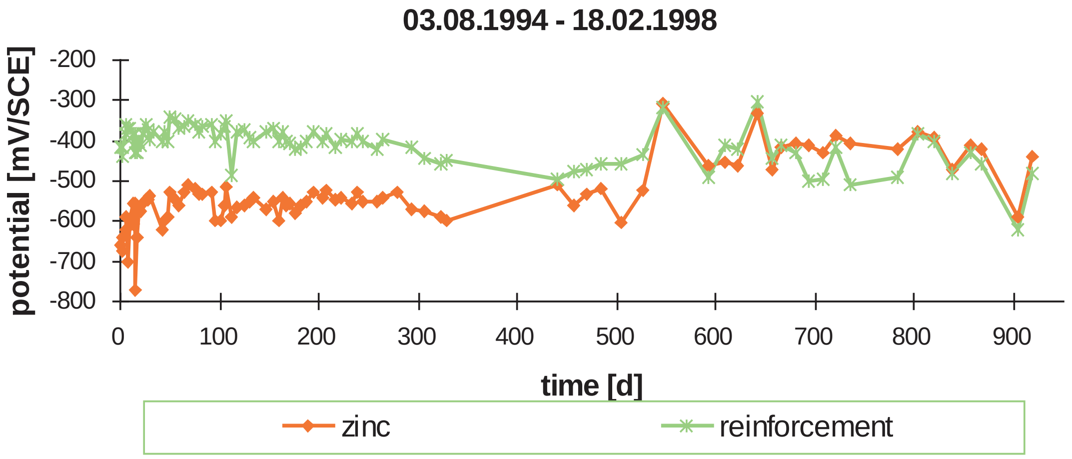

Fig. 5: *Free corrosion potential of zinc and reinforcement (no short circuit).*

Corrosion Potential of Fe-Zn-Short-Circuit-Couples

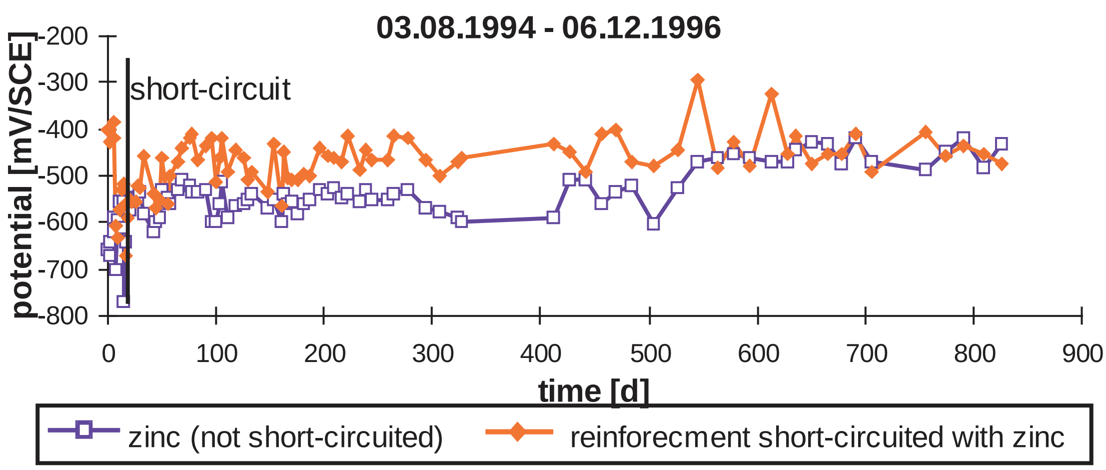

Fig. 6: *Potential of the reinforcement after short-circuiting with zinc.*

Figure 6 shows the potential of the reinforcement prior to and after short circuiting with zinc. Short-circuiting leads to a potential drop of the reinforcement of about 200 mV to values near the free corrosion potential of zinc. With time the potential rises to values about -400 mV SCE.

Polarization Decay Measurements

Polarization decay measurements show good results if evaluated by the 100 mV criterion for a period of about 9 months. The potential shift exceeds 100 mV within a few hours after opening the short-circuit between zinc and steel (fig. 7).

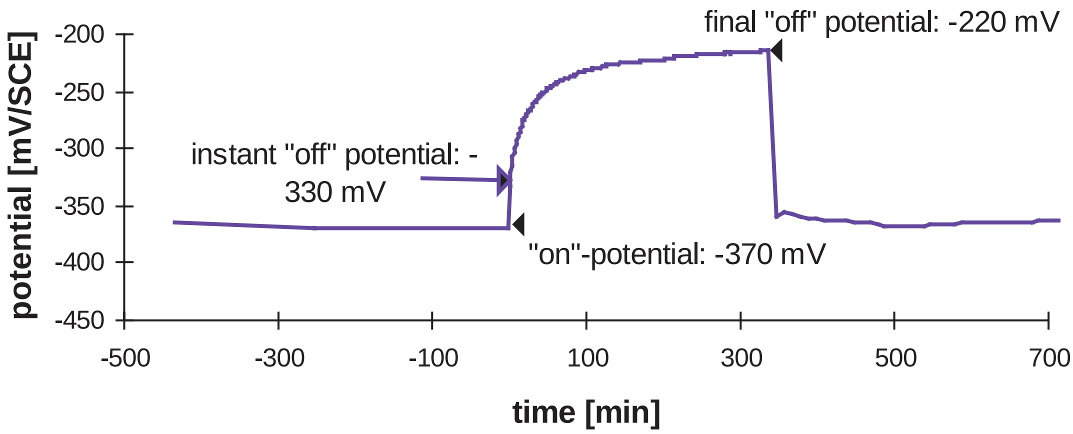

Fig. 7: *Polarization decay measurement 220 days after short-circuiting.*

From winter 1995 on the 100 mV-criterion was not fullfilled any more (fig. 8).

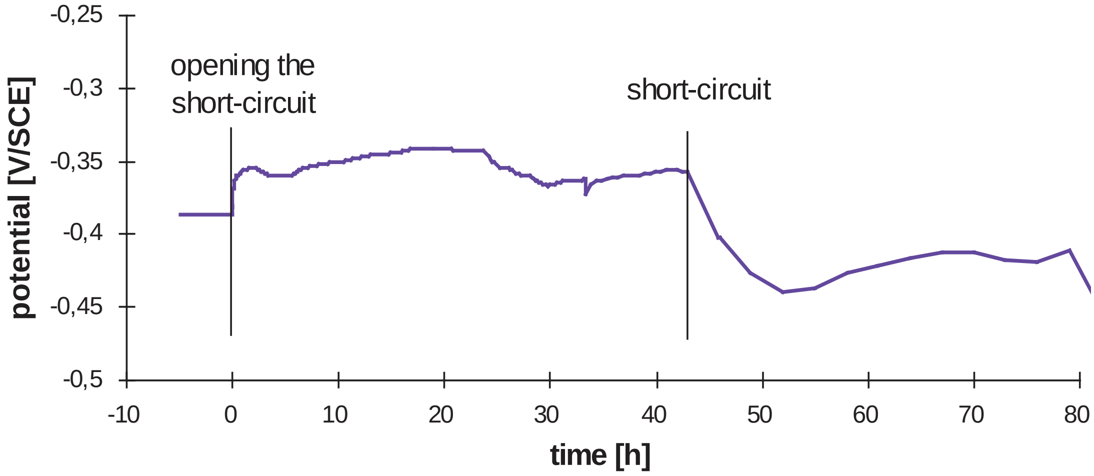

Fig. 8: *Polarization decay measurement 636 days after short-circuiting.*

Galvanic Current Densities

Current densities also show a time dependency. With increasing time the current density decreases (fig. 9). At the beginning the current density is about 2,6 µA/cm² (steel surface). 2,5 years later values about only 0,18 µA/cm² (steel surface) were reached.

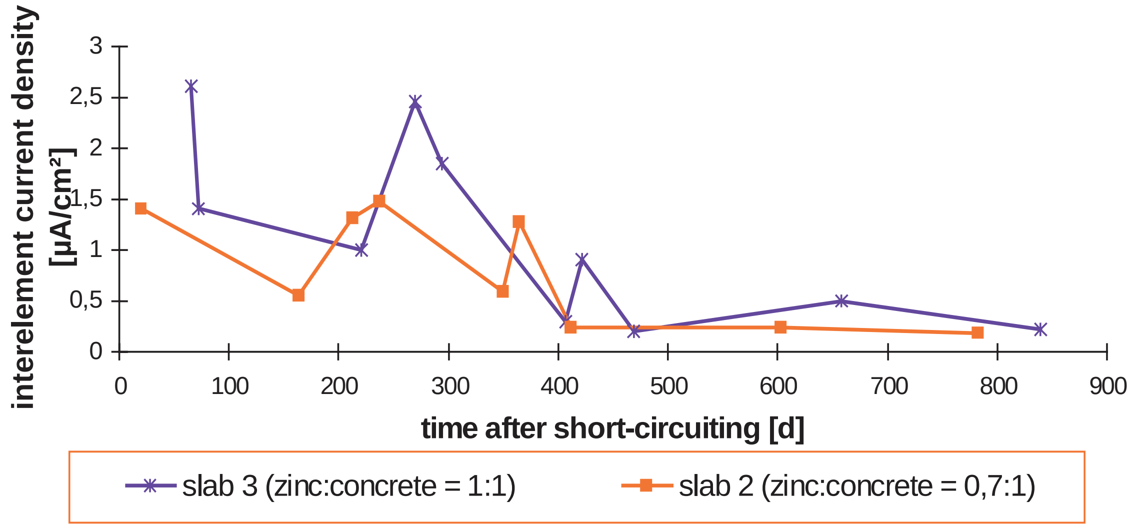

Fig. 9: *Galvanic current densities.*

3.2.2 Outdoor Tests - Zinc as Impressed Current Anode

After decreasing of the effectiveness of zinc working as galvanic anode tests with zinc as impressed current anode were started. By means of a potentiostat the potential of the reinforcement was regulated to -750 mV SCE and -800 mV SCE respectively. The required protective current was measured (fig. 10).

30 days after operating with external current the impressed current shows values of about 2 and 4 µA/cm² (steel surface). 10 weeks later the potential of the reinforcement could not be regulated to -800 mV SCE anymore. Obviously operation with external current required inadequately high voltage due to the increase of the internal resistance of the zinc/concrete interface.

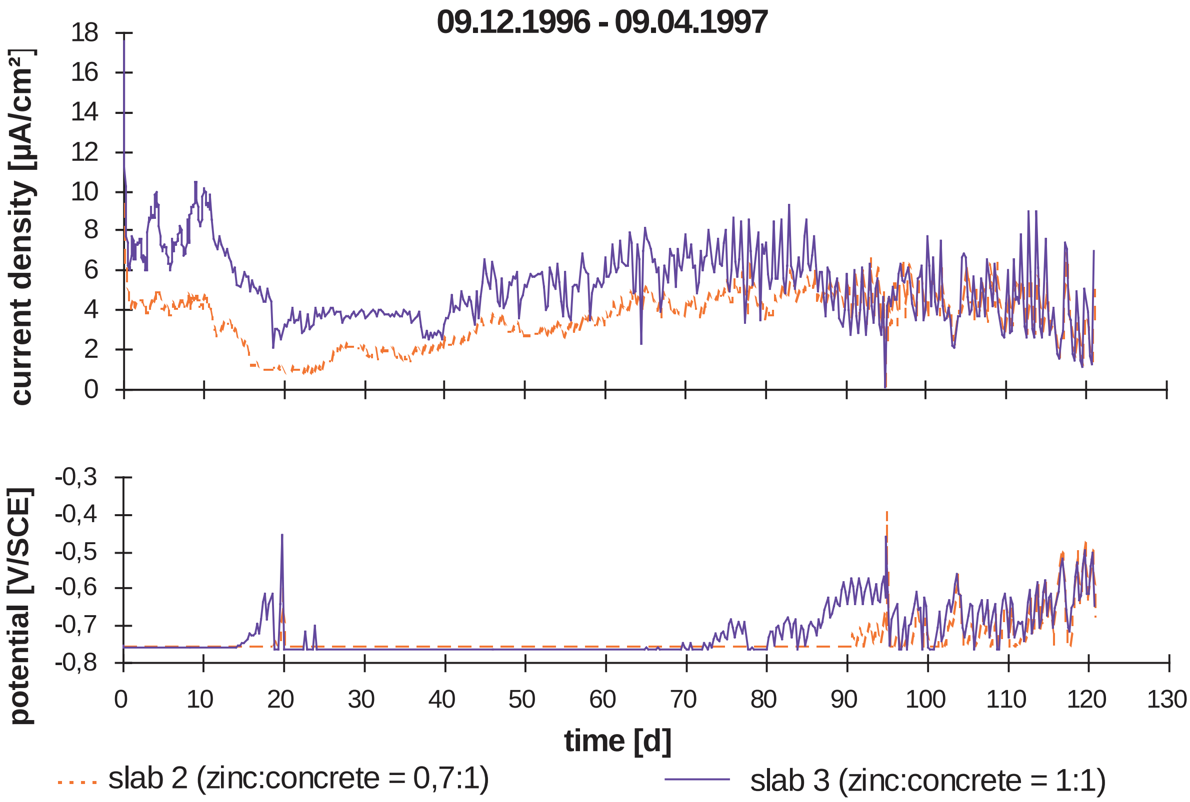

Fig. 10: *Potential and required current (external current source).*

3.2.3 Laboratory Tests - Zinc as Galvanic Anode

Chloride Containing Concrete

Two years after short-circuiting the potential shows values about -750 mV SCE in chloride containing concrete, indicating sufficient protection (fig. 11). This can be confirmed by polarization decay measurements (fig. 12).

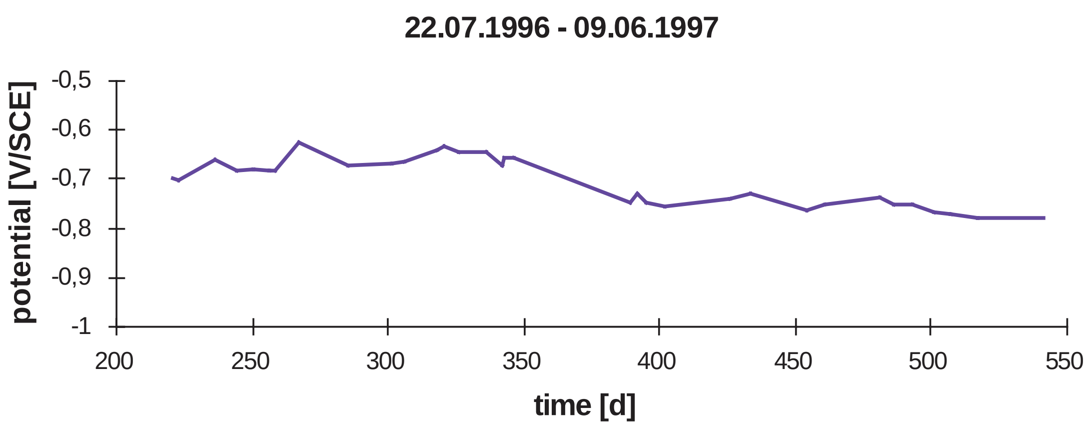

Fig. 11: *Potential run of the reinforcement short-circuited with zinc in chloride containing concrete.*

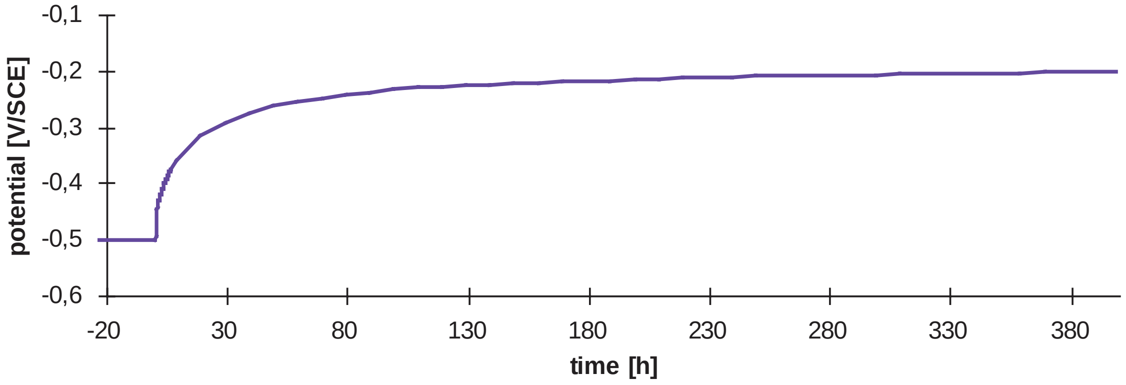

Fig. 12: *Polarization decay measurement 342 days after short circuiting (chloride containing concrete).*

Carbonated Concrete

The potential of the short-circuited couple (zinc-reinforcement) in carbonated concrete shows no constant run (fig. 13). The 100 mV criterion is barely fullfilled (fig. 14).

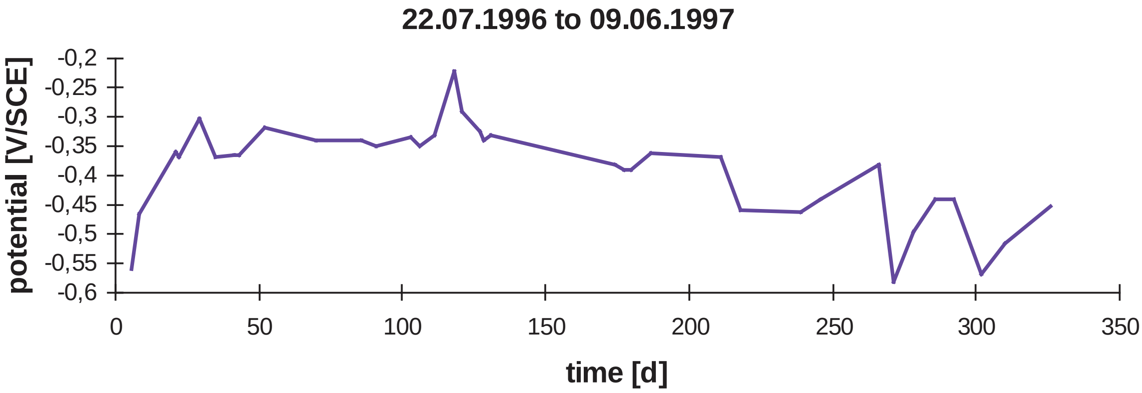

Fig. 13: *Potential run of the reinforcement short-circuited with zinc in carbonated concrete.*

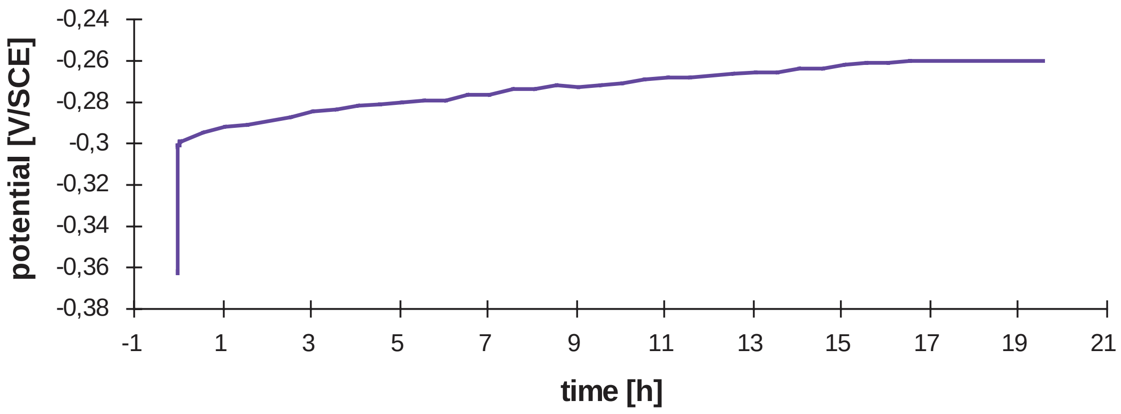

Fig. 14: *Polarization decay measurement 326 days after short circuiting (carbonated concrete).*

3.2.4 Laboratory Tests - Zinc as Impressed Current Anode

Chloride Containing Concrete

Under constant environmental conditions cathodic protection with zinc as impressed current anode was assured for 1,5 years at least. Figure 15 shows the required impressed current for regulating the potential of the reinforcement to -800 mV SCE.

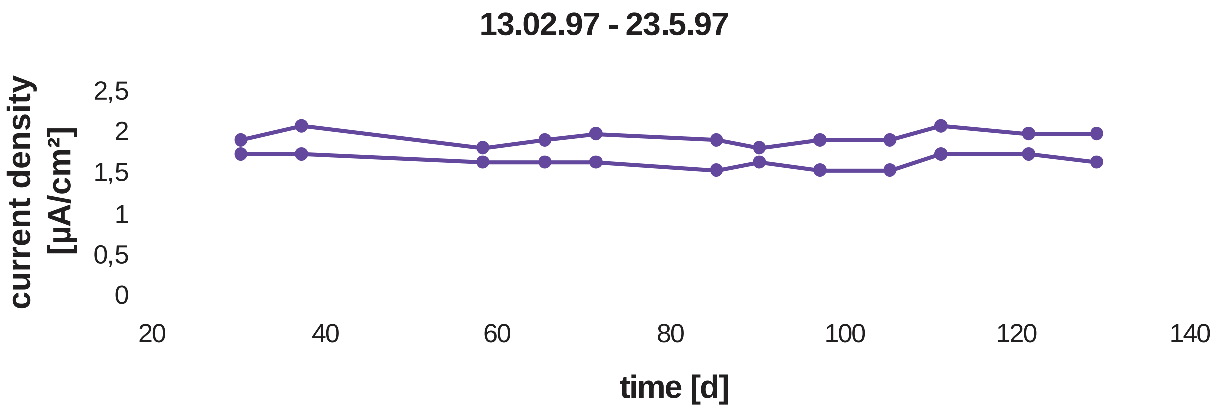

Fig. 15: *Impressed current (chloride containing concrete).*

Carbonated Concrete

For regulating the potential to -800 mV SCE an impressed current of 0,2 to 0,7 µA/cm² is required in carbonated conrete (fig. 16).

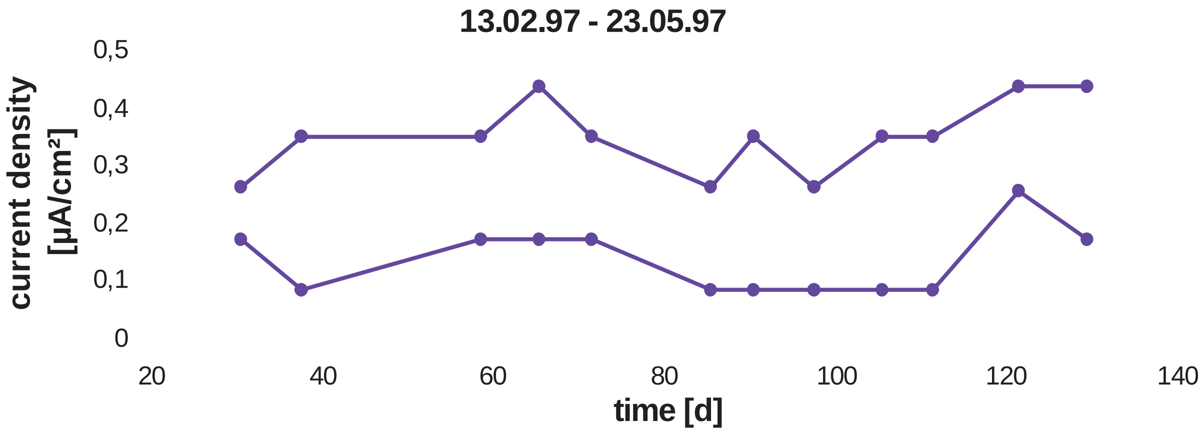

Fig. 16: *Impressed current (carbonated concrete, two identical samples).*

4. DISCUSSION

The exposure and laboratory-tests reveal both limitations and possibilities of CP with zinc sprayed anodes.

By outdoor exposure in rural/town atmosphere full protection (according to potential- or 100mV-decay criteria) is restricted to a period of about one year as far as the parameters chosen in this experiment (zinc-to-steel ratio 1:0,4 to 1:0,6; 3% chloride) are realistic. The loss of effectiveness is due to zinc passivation (in case of galvanic anode) and increase of the ohmic resistance of the zinc-concrete interface (in case of impressed current anode). Delamination or significant loss of adhesion of the zinc cover was not observed during the three years of exposure.

The results of the laboratory experiments (high and constant humidity, high zinc-to-steel area ratio and chloride contaminated concrete) confirm the good results reported from marine environment. Until now the electrochemical parameters are almost stable and in the range of full protection.

In carbonated concrete, CP does not perform satisfactory because of zinc passivation and the high internal resistance of the circuit.

5. ACKNOWLEDGEMENTS

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