

NOVEL TYPE OF DISCRETE GALVANIC ZINC ANODES FOR THE PREVENTION OF STEEL REINFORCEMENT CORROSION INDUCED BY PATCH REPAIR

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1. ABSTRACT

Corrosion of steel reinforcement as a result of repair of concrete damages induced by reinforcing steel corrosion is a common and well documented result of “patch repairs”. The corrosion is caused by the transformation of cathodic areas near the corroding steel reinforcement into “incipient anodes”. Cathodic protection (CP) is one safe method to prevent the formation of incipient anodes. Very often, repairs have to be executed on locally limited areas where CP is not economical. Incipient anodes may be prevented by embedding discrete galvanic anodes into the patch repair close to the interface repair/old concrete, shifting the steel potentials of the passive steel towards sufficiently negative potentials to eliminate or at least minimize macro-cells. Considering the fact that the electrochemical potential of zinc is more negative than even the corrosion potentials of pits on reinforcement, discrete zinc anodes offer a thermodynamically sound possibility to prevent incipient anodes. Reports based on field tests of discrete galvanic yielded mixed results on the durability and reliability of the prevention of corrosion of steel reinforcement adjacent to patch repairs, proving thermodynamics is no guarantee that systems work in reality. The main issues regarding durability and reliability of galvanic zinc anodes are passivation of the zinc anode and the formation of anodically formed zinc hydroxide forming an ion-transport barrier. A novel type of discrete galvanic zinc anode will be presented that addresses and solves these issues. The novel discrete galvanic zinc anode system is composed of a novel type of composite zinc mesh embedded into a proprietary matrix that solidifies into an electrolyte with ion exchange properties. The combination of the novel composite zinc anode and the solid matrix containing additives that prevent passivation of the zinc anode assures high and durable galvanic activity of the discrete galvanic zinc anode.

Keywords: Galvanic Corrosion Protection of Steel Reinforcement, Discrete Galvanic Anodes, Incipient Anodes, Patch Repair

2. Introduction

Corrosion of the steel reinforcement is one of the major causes for increased maintenance and repair costs and subsequently for the reduction of the service life of concrete structures. The major causes for the corrosion of the steel reinforcement are ingress of chloride into the concrete overlay due to the application of de-icing salts, due to exposure to sea water (Bertolini et al. 2013a, Raupach et al. 2006, Cigna et al. 2003) or due to carbonation of the concrete (decrease of pH). Corrosion initiated by de-icing salts or sea salt is due to the formation of macrocells, coupling corroding anodic sites with passive cathodic sites. Due to the macro cell coupling, corroding zones are acting as a galvanic anode providing a degree of cathodic prevention to the surrounding passive steel (Bertolini et al. 2013, Raupach et al. 2006, Cigna et al. 2003, Broomfield 1997, Dugarte et Sagües 2009). Consequent and lasting repair involves the removal of the macro cells, requiring the replacement of the chloride contaminated concrete entirely with repair mortar or shotcrete, or to apply cathodic corrosion protection on the affected areas of the concrete member. However, in many cases, local corrosion damages repaired by patch repairs in which only the concrete in the surrounding of the visible corrosion induced damages is removed and replaced. The durability of such repairs is affected by the “halo effect” (Broomfield 1997) wherein the steel within the

new repaired area serves as a cathode generating accelerated corrosion of the steel in the surrounding area of the patch repair (Dugarte et Sagües 2009). Formerly anodic zones no longer provide protection, and corrosion can initiate in the areas surrounding the repaired zones (these have been called “incipient anodes” (Sergi & Page 2001, Bertolini et al. 2013b). For the purpose of forestalling the “halo damage”, small galvanic an-odes (“point anodes”, “discrete galvanic anodes”) are available commercially and have been applied since 1999 (Dugarte et Sagües 2009, Sergi & Page 2001, Bennet & McCord 2006). The most comprehensive report on the performance of “galvanic point anodes” – two different types of commercially avail-able anodes were tested over a period of 3 years - was made available in 2009 by the Department of Transportation of Florida (Dugarte & Sagües 2009). The main conclusions of the report were that the activity of the anodes decreased over time significantly and the anodes were estimated to function up to 1/3 to 1/4 of the theoretical consumption limit. Installed in a concrete containing 1.5 % chloride/weight of cement, the point anodes tested over 480 days, showed only modest to negligible polarization of the reinforcement bars and were not sufficient for the prevention of initiation of corrosion. The efficiency of galvanic corrosion protection depends on the lasting activity of the zinc anode. Deposition and agglomeration of the anodic products or contact with calcium hydroxide in the pore solution may passivate the zinc anode surface (Schwarz et al. 2014). A novel discrete galvanic zinc anode system, composed of a of composite zinc mesh embedded into a proprietary matrix that solidifies into an electrolyte with ion exchange properties and containing additives that prevent passivation of the zinc anode assuring high and durable galvanic activity of the discrete galvanic zinc anode is presented in this paper.

3. Concept

Incipient anodes in patch repairs are generated when the initially corroding steel rebars, embedded into the repair mortar of the patch repair, passivate and get coupled with the steel rebars embedded into adjacent concrete with modest chloride contamination. The prevention of the formation of incipient anodes by discrete galvanic point anodes is not achieved by shifting the potentials of the corroding reinforcement bars as in cathodic corrosion protection but by maintaining the potential of the reinforcement bars embedded into the repair mortar in the patch repair area at potentials equal or more negative than the steel potentials of the reinforcement bars in the adjacent chloride contaminated concrete, preventing the formation of the macro cell formed by the patch repair (Bruns 2015) as shown in figure 1.

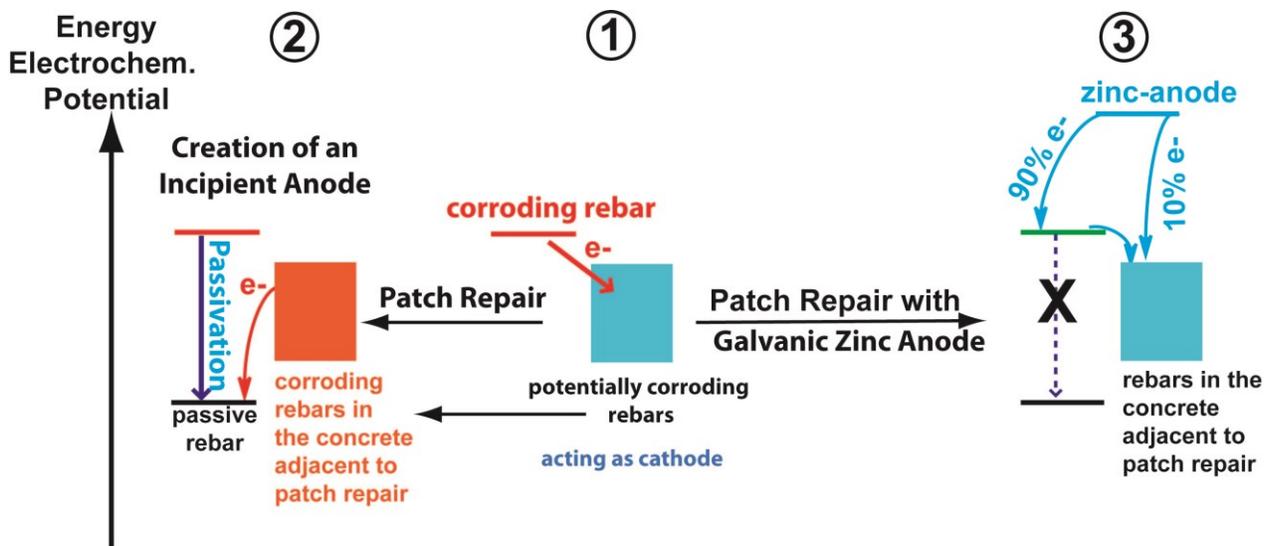


Figure 1: Schematic presentation of (1) corroding rebar causing concrete damage, (2) patch repair creating an incipient anode, (3) prevention of the formation of incipient anodes by galvanic discrete point anodes attached to the rebar in the patch repair

The activity and efficiency of galvanic anodes depend on the lasting activity of the zinc anode. Zinc tends naturally to passivate by formation of an impermeable zinc oxide/hydroxide layer. Depassivation of zinc is achieved either by embedding the zinc in a high pH matrix ($\text{pH} > 13$) or in a low pH matrix ($\text{pH} < 6$). As a result of the galvanic consumption of zinc in a high alkaline matrix OH^- is consumed and has to be provided either by 170 g KOH/100g Zinc or by 73 g LiOH/100g Zinc. If the pH drops below pH 13, the zinc anode will passivate. Depassivation in an acidic environment may lead to further acidification and autocorrosion of the zinc anode. Deposition and agglomeration of the anodic products at the anode surface or contact with calcium hydroxide in the pore solution may also passivate the zinc anode surface.

The anodic products formed need more space than the zinc-metal, e.g. zinc hydroxide consumes 2,34 times more space than zinc metal. Therefore, the anodic products may clog pores and hinder or even block ionic transport to and from the anode surface consequently passivating the zinc anode. The main factors controlling long term activity and durability of discrete galvanic point anodes are: a) prevention of passivation of the zinc anode surface, b) providing enough space for the anodic products formed and c) prevention of auto-corrosion of the zinc an-ode. The novel discrete galvanic zinc anode system relies on the following basic concepts:

- (1) The activity and depassivation of the zinc anode surface is assured by embedding the zinc anode in a proprietary binder matrix described elsewhere in detail (Schwarz et al. 2014). The binder solidifies into a matrix with ion exchange properties containing additives that prevent passivation of the zinc anode assuring high and durable galvanic activity of the discrete galvanic zinc anode.
- (2) The zinc anode itself is composed of a zinc-mesh matrix providing a high galvanic available surface from which only part is galvanically active and therefor assuring a nearly constant galvanic active surface over about of 90% of the theoretical service time.
- (3) The surface/volume and zinc metal volume/anode volume ratio is such that there is enough space for anodic products formed to be accommodated without impeding ion transport and therefore galvanic activity. Besides the geometric volume ratio this is assured by a volumetric porosity of the binder matrix of at least 35 Vol.%.
- (4) The electrochemical environment of the solidified binder matrix contains additives that reduce autocorrosion to negligible values.
- (5) Two galvanized wired brackets are integrated into the anode allowing and assuring optimum and quick electrical connection to the steel reinforcement bars (figure 2).



Figure 2: Sika® FerroGard® ICM discrete galvanic zinc an-ode (SFG-anode) for the prevention of the formation of incipient anodes induced by patch repairs

4. Experimental Setup

To evaluate the performance of galvanic anodes, measurements were performed in galvanic cells that simulate the conditions in a real concrete environment and allow accelerated testing. The set-up of the galvanic cell is shown in figure 3.

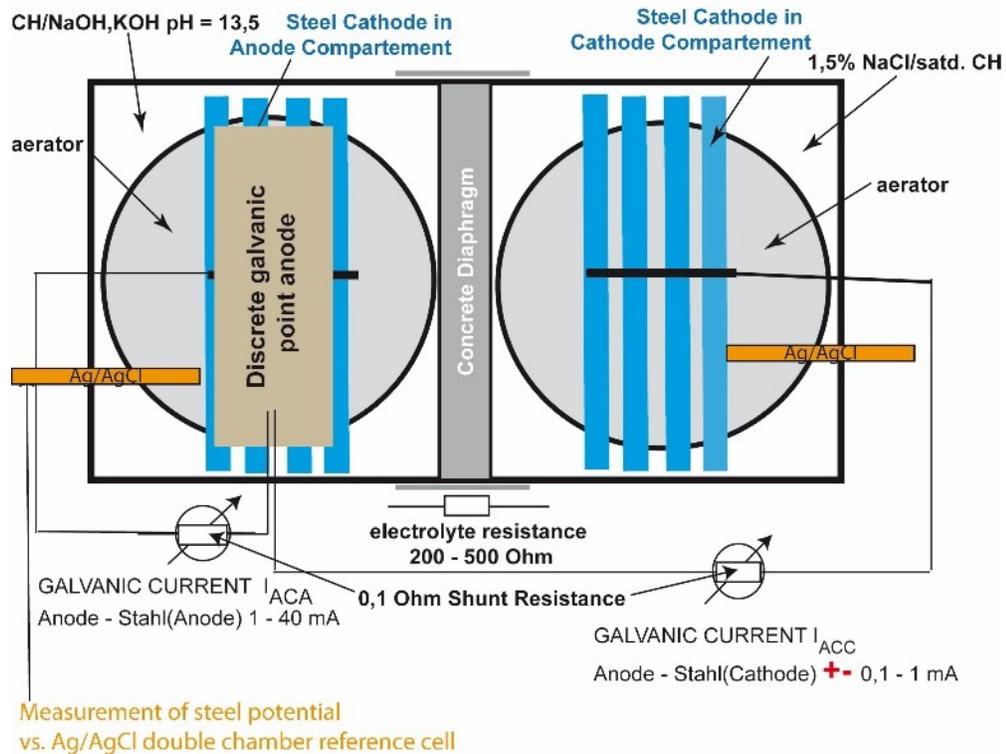


Figure 3: Scheme of the set-up of the galvanic cell simulating a real concrete environment for discrete galvanic point anodes embedded into patch repairs. The concrete diaphragm is prepared from Sika MonoTop®-412 N (Wenk 2013).

The steel electrodes consisted of 4 steel reinforcement bars (Ø 10 mm) connected by welding to a steel rod (Ø 6 mm) with a total steel surface of 200 cm^2 . The concrete cell separator was cast with a re-pair mortar, 1-component CC mortar complying to EN 1504-3 as R4 mortar and having a resistivity similar to the host concrete. The electrolyte in the anode compartment consisted of a simulated concrete pore solution (pH 12.8 – 13.5), the catholyte consisted of a 1.5 – 2.0 % NaCl solution, initially saturated with calcium hydroxide (CH). The current and steel potentials were measured and recorded online with the CAS MO-DAC monitoring and control system. Data were recorded every 30 min.

The galvanic cell shown schematically in figure 3 simulates the set-up of a patch repair in a concrete member: The SFG anode is connected to the rebar in the passivating environment of the patch repair simulated by the artificial pore solution with a pH of 12.8 – 13.5, separated by a 3 cm thick mortar slab (made from repair mortar) from the adjacent rebar immersed into a moderately corroding salt solution (1.5 % NaCl, satd. CH, pH kept > 9) – simulating the “old” concrete. The steel reinforcement bars are intensely aerated in both compartments. This set-up creates an environment that is very harsh in comparison to the real situation with respect to oxygen transport to the steel rebar surface and with respect to ion transport which is fast in solution but slow in concrete. Data received so far compared with published data (Dugarte & Sagües) indicate that the time scale in the galvanic cell set-up is about ten times faster than in a concrete environment.

The galvanic performance of the anodes for corrosion protection of steel reinforcement bars in chloride environment (3 % NaCl) was evaluated in an electrolytic cell consisting of a 3-litre bucket in which an aerator, steel reinforcement bars and reference cell as shown in figure 3 were immersed in 1.5 litres of 3 % NaCl.

5. Results of Galvanic Cell Measurements

The galvanic performance of an SFG anode (approx. 150 g zinc/anode, 650 cm² galvanically available surface, 127 cm² galvanically active surface, open circuit potential (OCP) -1160 mV vs. Ag/AgCl) was evaluated in the galvanic cell set-up described above and shown in figure 3. Results are shown in figure 4. The high initial current output of about 6 mA temporarily decreases to about 2 mA (period 1), increases again to currents in the range from 3 – 5 mA (period 2) after increasing the chloride content in the cathodic compartment by 0,5% NaCl.

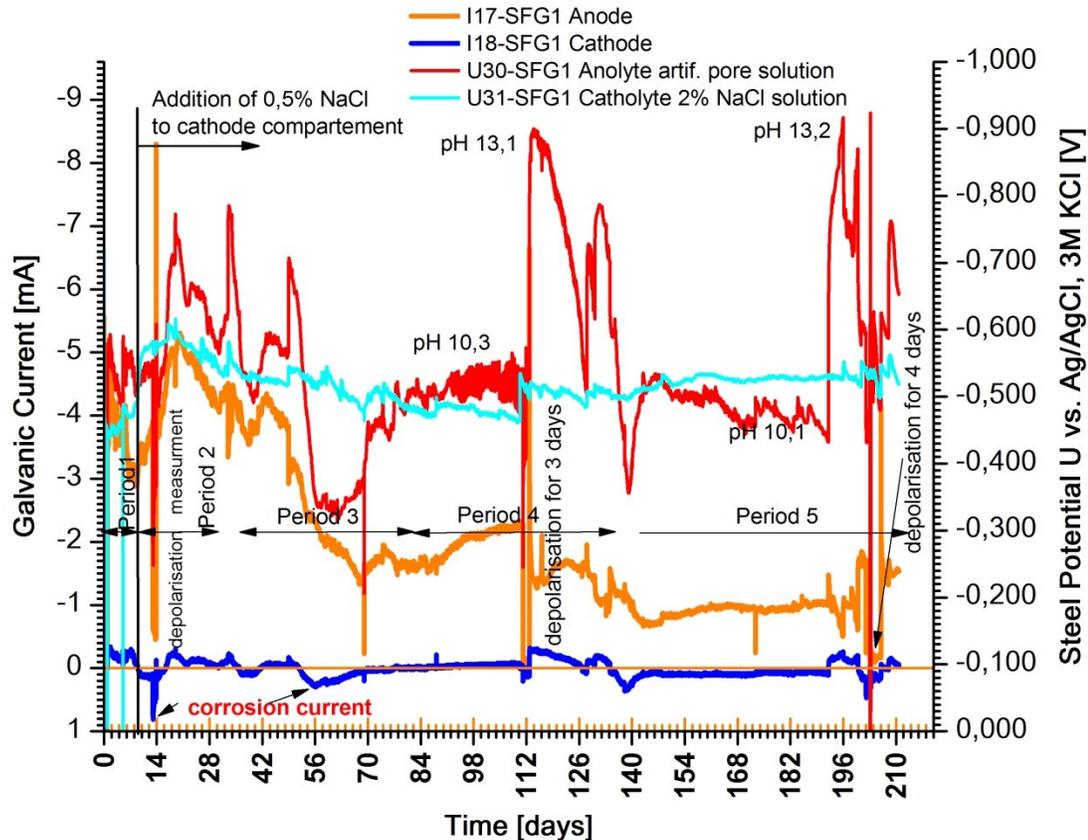


Figure 4: Galvanic performance of Sika® FerroGard® ICM discrete galvanic zinc anode (SFG-anode)

After about 1 month, the galvanic current decreases again (period 3) and stabilizes at about 2 mA (period 4). After a depolarization (interruption of galvanic current) for three days, the galvanic current stabilizes at about 1,5 mA (period 5), typical for SFG anodes. The galvanic current to or from the steel rebars in the cathodic compartment (figure 4, I18 SFG1 Cathode) is in the range of - 0.23 to + 0.25 mA. Negative values indicate corrosion protection – current flows towards the steel rebars, positive values reveal corrosion, 0,2 mA correspond to a loss of cross section of 11 $\mu\text{m}/\text{year}$. The galvanic current is consumed by about 95 % by the rebar in the passivating environment of the anode compartment, only 5 % is consumed by the reinforcement bars in the moderately corroding environment in the cathode compartment.

The galvanic current shifts the potential of the reinforcement bars in the “patch repair” environment (U30-SFG1) from -240 mV vs. Ag/AgCl by about 300 mV to the level of the potential of the reinforcement bars in the corrosive environment (U31SFG1, about - 550 mV vs. Ag/AgCl), efficiently eliminating the “corrosion cell”, even slightly cathodically protecting the reinforcement bars by currents of about 1 – 3 mA/m² steel surface. The cathodic protection cedes temporarily by increasing the “corrosivity” of the environment in the cathodic compartment by increasing the NaCl concentration from 1.5 % to 2.0 %

inducing a shift of the steel potentials towards more negative values by about 250 mV (period 1/period 2). The steel potentials of the reinforcement bars in the patch repair environment shift temporarily to values slightly positive of the potentials of the reinforcement bars in the corrosive environment. Incipient anode induced rebar corrosion is efficiently prevented as long as the steel potential in the patch repair area (U30-SFG1) is more negative or at least close to the steel potential in the moderately corrosive environment of the catholyte (U31-SFG1), corresponding to the non-repaired concrete. The potential measured depends strongly of the pH of the electrolyte in the “anodic” compartment as demonstrated in figure 4: An increase of the pH from pH 10,1 to pH 13,2 induces a potential shift by about 450 mV, far larger than expected ($-0,056$ mV/pH unit). The potential measured in the cell compartment in which the SFG zinc anode is immersed into the artificial pore solution is a mixed potential composed of the potential of the zinc-anode and of the steel cathode. The pH in the electrolyte apparently influences also the potential of the zinc anode. The results indicate that high pH, as observed in a patch repair mortar environment, significantly improves the efficiency of SFG anodes in preventing the formation of incipient anodes. The change of pH in the electrolyte is due to carbonation caused by the forced aeration of the electrolyte. Alkalinity is restored by adding small amounts of calcium hydroxide.

The performance of the SFG anode in preventing incipient anodes is illustratively shown by the depolarization measurements executed by disconnecting the SFG anode from the system. Complete depolarization in solution is obtained within 3 hours (fig. 5) which is different from concrete where it usually takes 24 hours. Depolarization leads to an shift of the potential of the steel in the artificial pore solution to values positive of the steel in the 2% NaCl solution, resulting in corrosion of the steel in the compartment simulating the steel in the adjacent concrete. Corrosion is immediately stopped if the SFG zinc anode is reconnected.

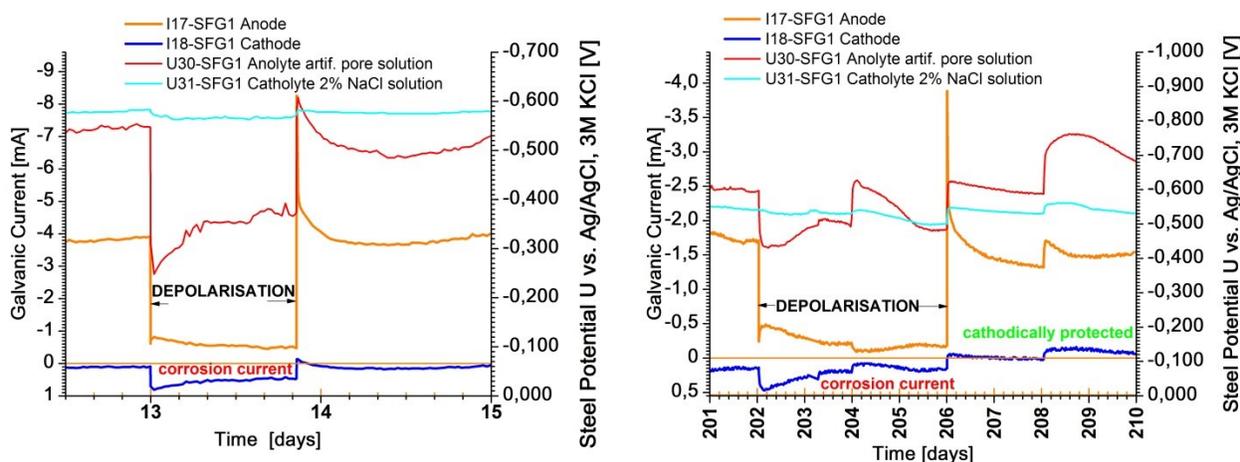


Figure 5: Current and steel potentials during depolarization measurement of a Sika® FerroGard® ICM discrete galvanic zinc anode (SFG-anode) in artificial pore solution two weeks after start up (left) and after 7 month of operation (right)

Depolarization 2 weeks after start up – indicates at least temporary passivation of the steel rebars in the artificial pore solution. Whereas depolarization about 7 month after start up yield instant off steel potentials in the non-passive range of potentials, the 130 mV shift towards negative potentials may indicate onset of passivation reaction of the steel rebars. The steel rebars in the simulated patch repair area are moderately polarized to about -500 mV vs. Ag/AgCl during start-up whereas after about 7 month of operation the steel rebars are polarized to about -600 mV vs. Ag/AgCl. Eventually, during startup, polarization of the steel potentials may be near the Flade potential (Strehblow 2006) allowing passivation whereas steel potential values more negative than -600 mV vs. Ag/AgCl lead to the dissolution of the passive film.

The steel reinforcement bars in the corrosive environment shift by about 20 mV towards positive values, showing that the main effect of the discrete galvanic point anodes is the elimination of the macro cell by

maintaining the potentials of the reinforcement in the patch repair at potentials equal or more negative than the potentials of the steel rebars in the adjacent concrete rather than by protecting the reinforcement bars in the adjacent old concrete by cathodic polarization. Depolarization establishes the incipient anode inducing a corrosion current (about 1,5 - 3.5 $\mu\text{A}/\text{cm}^2$) flowing between the steel reinforcement bars in the corrosive and passivating environment. The corrosion current shifts the potential of the steel rebar in the patch repair environment towards more negative values as observed in real patch repairs (Wenk 2013). The currents measured are mirror inverted as the current flows between the steel-rebars. The corrosion current is immediately eliminated by reconnecting the SFG anode to the steel rebar electrode. The data shown in figure 4 demonstrate illustratively the mode of operation of the SFG discrete galvanic point anodes: Incipient anodes are eliminated and prevented by polarizing the reinforcement bars in the patch repair areas to levels nearly equal to the potentials of the steel reinforcement bars embedded into the concrete adjacent to the patch repair

The course of the potentials of the steel reinforcement in the patch repair environment is not always proportional to the galvanic current flowing to the steel reinforcement, especially during the time period 3 & 4 (figure 4): The steel potential remains nearly constant despite decreasing galvanic current and its value shifts to more negative values during period 4 while the current remains nearly constant. This might indicate passivation of steel rebars during time period 3.

The evaluation of the performance of the SFG discrete galvanic anode for corrosion protection of reinforcing steel immersed and aerated in 3% NaCl solution, yielded at the beginning galvanic current of about 25 mA, corresponding to 1.2 A/m² steel rebar surface, stabilizing after about 2 month of operation at 3.7 ± 0.7 mA (185 \pm 45 mA/m²) (figure 6).

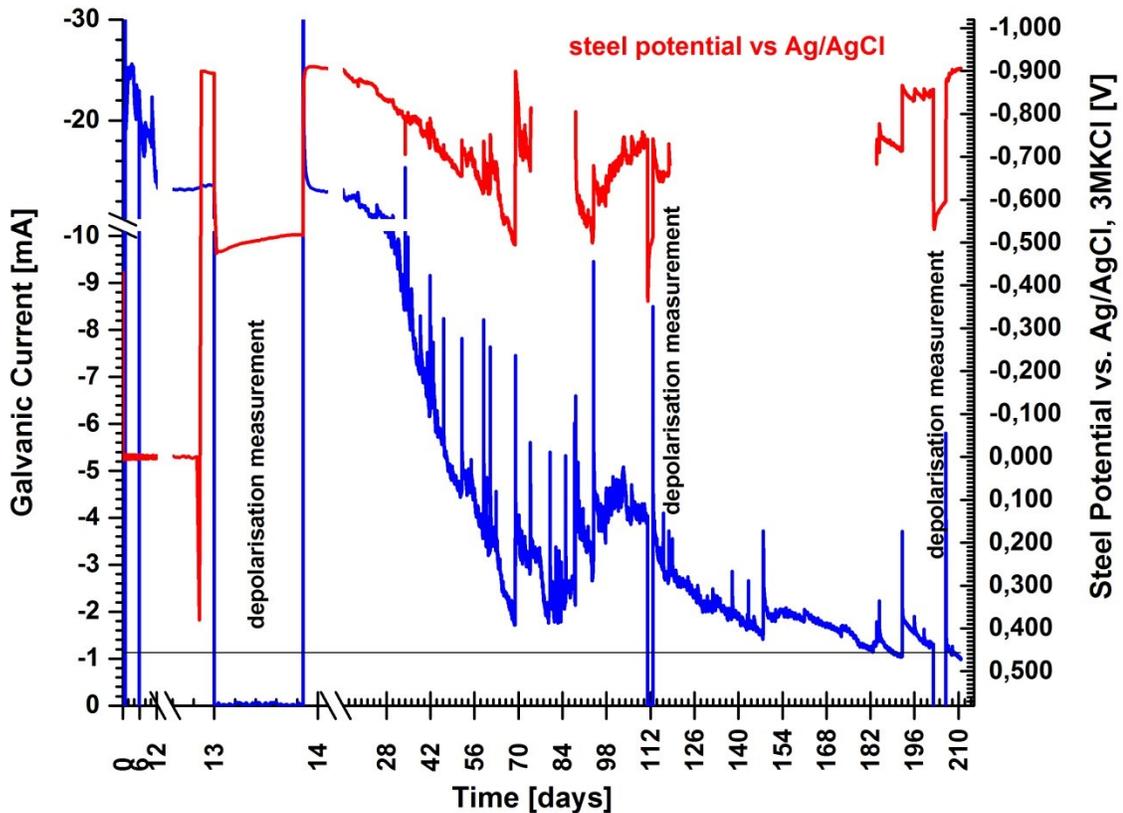


Figure 6: Galvanic performance of Sika® FerroGard® ICM discrete galvanic zinc anode (SFG-anode connected to an aerated reinforcing steel cathode, both immersed into 3% NaCl

In this range, current densities depend strongly on the intensity of aeration of the steel rebars – explaining the “current spikes” in figure 6. The steel-reinforcement bars were polarized at the beginning to about – 900 mV vs. Ag/AgCl yielding 4 hours depolarization values of 400 mV during start-up and 370 mV after about 7 month of operation. The decrease of the galvanic current after about 4 month of operation to values of about 1 mA is due to the strong polarization of the steel rebars to values near the open circuit potential of the SFG zinc anode (~ - 1100 mV vs. Ag/AgCl) therefore reducing the driving voltage to values of about 150 mV.

The high galvanic current output is due to the low cell resistance of 4.5 Ohm due to the low resistivity of the binder matrix in which the zinc anode is embedded. However, in a concrete environment, cell resistances between point anodes and steel reinforcement bars in distances up to 30 cm are in the range of several hundred Ohms.

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6. Conclusions and Outlook

Patch repairs of steel rebar corrosion induced damage to concrete members are a common solution despite the fact that these techniques do not lead to a sustainable solution. Therefore there is a general need to eliminate the incipient anodes generated by the patch repairs. The formation of incipient anodes may be prevented by embedding suitable discrete galvanic point anodes into the mortar of the patch repairs adjacent to the concrete. Numerous galvanic anodes are on the market. However, to offer these galvanic anodes as an essential part of a sustainable concrete repair technique, these anodes have to be reliable in long term performance and durable in current output over a time period of at least 12 – 15 years.

The novel discrete galvanic zinc anode presented here was developed based on a concept accepted to assure the above defined requirements. The results of the physicochemical and preliminary accelerated laboratory tests in galvanic cells indicate strongly that the novel galvanic point anodes fulfill the defined requirements. However, the obtained results have to be corroborated and complimented by tests in the field and in pilot test set-ups. These tests are underway covering different environmental conditions and concrete qualities and exposures.

Furthermore, a scientific based criterion may be formulated: Discrete galvanic point anodes should shift the steel potentials of the steel reinforcement bars in the patch repair mortar to potentials nearly equal to the steel potentials of the steel reinforcement bars in the adjacent concrete. Usually, the required potential shifts are in range of 150 – 250 mV. The effect of galvanic anodes on the passivation of steel rebars should be evaluated.

7. References

- Bennet, J. & Mc Cord, W. 2006. Performance of Zinc Anodes Used to Extend the Life of Concrete Patch Repairs , Paper No 06331, Corrosion/2006, NACE International Houston
- Bertolini, L., Elsener, B., Pedferri, P., Redaelli E., Polder, R. 2013. Corrosion of Steel in Concrete, 2nd Edition, Wiley-VCH, Weinheim
- Bertolini et al. 2013, pp 130
- Broomfield, J. P. 1997. Corrosion of Steel in Concrete, Under-standing, Investigation and Repair, Taylor & Francis, London
- Bruns, M., August 2015. Ingenieurbüro Raupach, Bruns, Wolff GmbH & Co. KG, private communication
- Cigna, R., Andrade, C., Nürnberger, U., Polder, R., Weydert, R. , Seitz, E. (eds.) 2003. Corrosion of steel in reinforced concrete structures – Final report, Cost Action 521, European Communities

- Dugarte, M. & Sagües, A. 2009. Galvanic Point Anodes for Extending Service Life of Patched Areas Upon Reinforce Concrete Bridge Members, Contract No BD 544-09, Final Report to the Florida Department of Transportation, 30 September 2009, NTIS Springfield, VA 22161
- Raupach, M., Elsener, B., Polder R., and Mietz, J. (eds.) 2006. Corrosion of reinforcement in concrete, Mechanisms, monitoring, inhibitors and rehabilitation techniques, European Federation of Corrosion Series EFC 38, Woodhead Publishing Limited, Cambridge, UK.
- Schwarz W., Müllner, F., van den Hondel, A. 2014, Maintenance and Repair of Steel Reinforced Concrete Structures by Simultaneous Galvanic Corrosion Protection and Chlo-ride Extraction” in Grantham, M. Muhammed Basheer ,P.A., Magee, B., Soutsos, M. (Eds.), Concrete Solutions, CRC Press, London, pp 223 -228
- Sergi, G. & Page, C.L. 2001. Sacrificial anodes for the cathodic prevention of reinforcing steel around patch repairs applied do chloride-contaminated concrete, in Mietz, J., Polder, R., Elsener B. (eds.) Corrosion of Reinforcement in Concrete, Mechanisms and Corrosion Protection, The European Federation of Corrosion Publication number 31, The Institute of Materials, London, pp. 93 – 100
- Strehblow H-H., “Passivity of Metals” in Advances in Electrochemical Science and Engineering, Vol 8, Alkire R. C., Kolb D. M. (Eds.), John Wiley & Sons, 2006, pp 304
- Wenk, F. 2013, “Sika MonoTop-412 N, Measurements of spe-cific electrical resistivity”, Report Version 01, 16 October 2013, IBU Institut für Bau und Umwelt, CH 8640 Rapperswil