PREVENTION OF INCIPIENT ANODES INDUCED BY PATCH REPAIR BY A NOVEL TYPE OF DISCRETE GALVANIC ZINC ANODES

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ABSTRACT: Corrosion of steel reinforcement as a result of repair of concrete damages 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 anodes yielded mixed results on the durability and reliability of the prevention of corrosion of steel reinforcement adjacent to patch repairs, proving that only the 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.

1 INTRODUCTION

Corrosion of the steel reinforcement is one of the mayor 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 deicing salts or sea salt is due to the formation of macro cells, 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 are 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 cathode generating accelerated corrosion of the steel in the surrounding 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 anodes ("point anodes", "discrete galvanic anodes") are available commercially and 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 available 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.

2 CONCEPT

Incipient anodes in patch repairs are generated by the coupling of the passivated steel reinforcement bars in the patch repair with the reinforcement bars 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 shifting the potential of the passivated reinforcement bars towards potentials equal or more negative than the steel potentials of the reinforcement bars in the adjacent chloride contaminated concrete, eliminating the macro cell formed by the patch repair (Bruns 2015) as shown in figure 1.

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 (pH > 13) or in a low pH matrix (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.

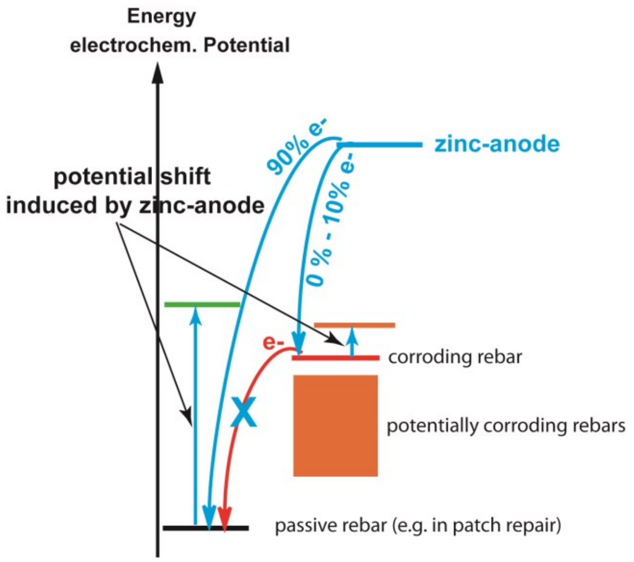

Figure 1: Schematic presentation of the prevention of the formation of incipient anodes by shifting the steel potential of the steel rebar passivated in the patch repair by attached galvanic discrete point anodes

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 time 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 anode. 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 anode (SFG-anode) for the prevention of the formation of incipient anodes induced by patch repairs.

3 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.

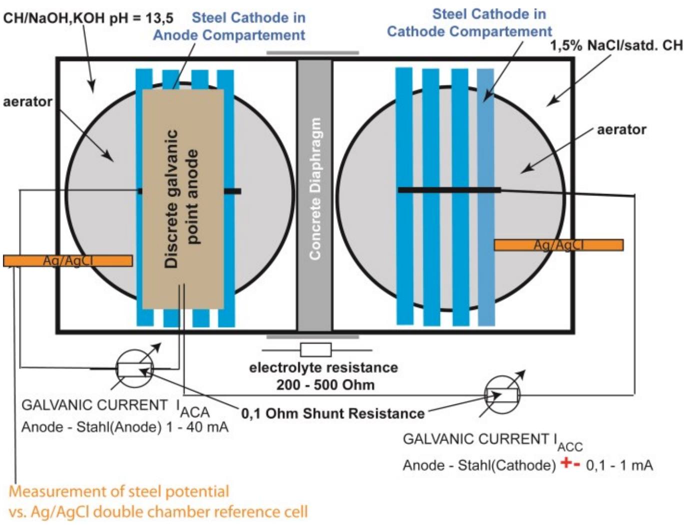

Figure 3: Scheme of the set-up of the galvanic cell simulating a real concrete environment for discrete galvanic point anodes embedded into patch repairs. The concrete diaphragm is prepared from Sika MonoTop®-412 N (Wenk 2013).

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 casted with a repair mortar, 1-component CC mortar complying to EN 1504-3 as R4 mortar and having a resistivity similar to 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 > pH 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 a electrolytic cell consisting of a 3 liter bucket in which an aerator, steel reinforcement bars and reference cell as shown in figure 3 were immersed in 1.5 Liters of 3 % NaCl.

4 RESULTS OF GALVANIC CELL MEASUREMENTS

The galvanic performance of an SFG anode (approx. 150 g zinc/anode, 650 cm^2 galvanically available surface, 127 cm^2 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) which is characteristic for SFG anodes.

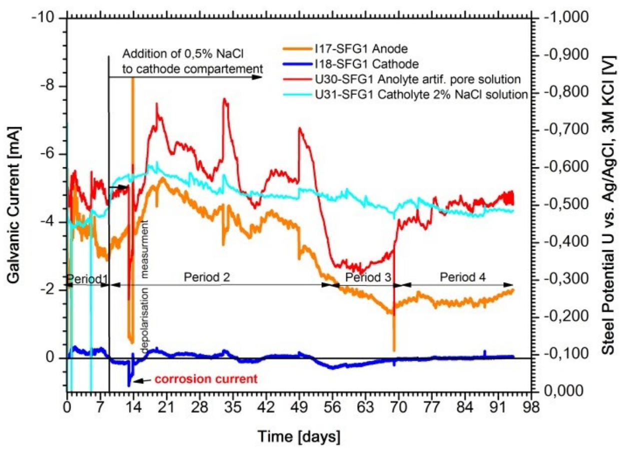

Figure 4: Galvanic performance of Sika® FerroGard® ICM discrete galvanic zinc anode (SFG-anode)

After about 1 month, the galvanic current decreases again and stabilizes at about 1.8 -2 mA (period 2 & 3). 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 + .,25 mA. Negative values indicate corrosion protection – current flows towards the steel rebars while the positive values reveal corrosion. The galvanic current is consumed by about 95 % by the rebar in the passive 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 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/m^2 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. 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.

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. The potential of the steel rebar in the patch repair environment shifts by about 300 mV rapidly towards the potential of a steel rebar in a passive environment (- 260 mV).

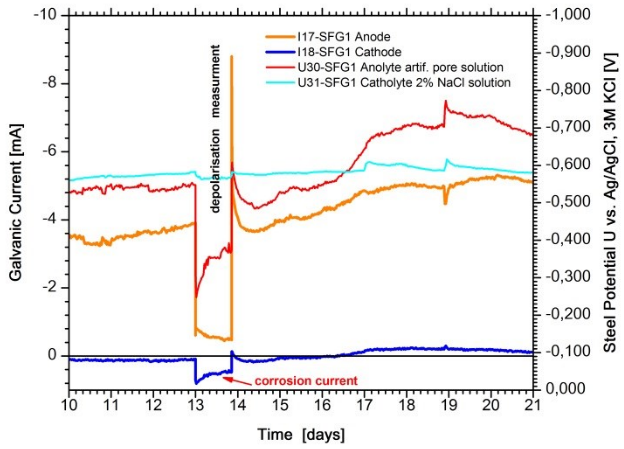

Figure 5: Current and steel potentials during depolarization measurement of a Sika® FerroGard® ICM discrete galvanic zinc anode (SFG-anode) in artificial pore solution.

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 shifting the potentials of the passivated reinforcement bars rather than by protecting the reinforcement bars in the adjacent old concrete by cathodic polarization.

Depolarization establishes a macro-cell with a throwing power of about 300 mV and a corrosion current (about 3.5 µA/cm^2 steel surface) flows between the steel reinforcement bars in the corrosive and passivating environment. As a consequence a classic macro-cell is established. 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 corrosion current decreases due to that shift stabilizing at values of about 0,5 mA corresponding to 2,5 µA/cm^2 steel surface. The currents measured are mirror inverted as the current flows between the steel-rebars.

The macro cell and consequently the corrosion current are 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: Macro cells are eliminated and therefore the formation of incipient anodes is 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 to the patch repair adjacent concrete.

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 currents of about 25 mA, corresponding to 1.2 A/m^2 steel rebar surface, stabilizing after about 2 month of operation at 3.7 ± 0.7 mA (185 ± 45 mA/m^2) (figure 6). 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. The steel potentials are approximately proportional to the galvanic current stabilizing at – 600 ± 40 mV vs. Ag/AgCl.

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 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 while the galvanic corrosion protection is effective until about 100 Ohms.

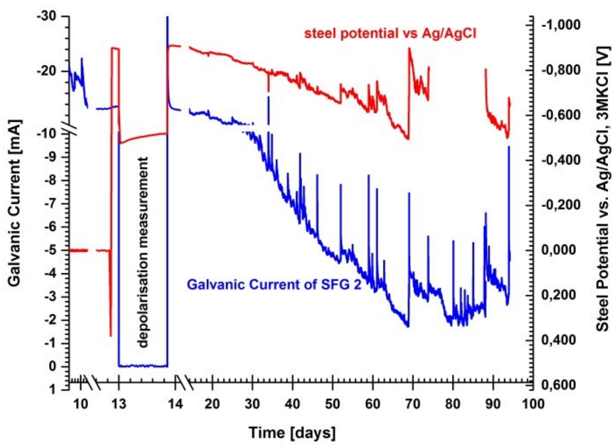

Figure 6: Galvanic performance of Sika® FerroGard® ICM discrete galvanic zinc anode (SFG-anode connected to an aerated reinforcing steel cathode, both immersed into 3% NaCl

5 CONCLUSIONS AND OUTLOOK

Patch repairs of steel rebar corrosion induced damages to concrete members are a common solution despite the fact that these technique leads not 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 physico-chemical 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.

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