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A New Silane System for Corrosion Reduction of Steel Reinforced Concrete

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Abstract

Buildings, bridges, parking decks- steel reinforced concrete structures represent major private and public investments. The useful life of and maintenance expenses for concrete buildings are often decisively influenced by corrosion of the steel reinforcement. In unfavourable cases severe damage appears only a few years after construction of the building, especially if the chloride load is high, as is the case near the sea or where de-icing salts are used. For this reason corrosion inhibitors are widely used, but their effectiveness in certain cases is debatable, particularly when they are applied to the surface of the concrete. The requirements for an effective corrosion inhibitor works on both chloride and carbonation induced corrosion, is effective in high humidity environments, changes the electrical properties of the concrete, has a long service life, is effective on concrete with micro-cracks and the effectiveness is proven by laboratory and field tests. This paper will discuss the performance of a new organofunctional silane system, called Protectosil® CIT, which penetrates deeply into the concrete and acts manifold against corrosion, as it excludes water and chloride ions and can strengthen the passive layer of the steel reinforcement. The results of two field tests indicate that this silane system decreases active corrosion and is effective over many years. This liquid silane system is easy to apply to the concrete surface via a conventional spraying process.

1 Introduction

Corrosion of steel reinforcement is a frequent cause of damage in concrete buildings. Steel normally does not corrode in concrete because, on account of the high pH of the concrete matrix, a passive layer on the steel surface protects it from corrosion. However, if the passive layer is damaged by reduced pH or penetration of chlorid ions, the situation becomes critical. If the steel surface is no longer protected by a passive layer, water and oxygen can begin their destructive work according to eq. (1).

$$4Fe + 2H_2O + 3O_2 \rightarrow 4FeOOH \tag{1}$$

Hence the primary goal in obtaining durable structures is the prevention of carbonation of concrete and the penetration of chlorides. The most common approach is the use of sufficiently high concrete cover. A coating impervious to gases and water can achieve the same effect, but this of course has the disadvantage that the treated component (the facade, for example) can no longer breathe, which means that permeation of water vapour is strongly inhibited. Moreover, coatings are susceptible to mechanical damage such as scratching and erosion, to attack by the UV radiation in sunlight, and to chemical attack by, for example, water and acid rain.

There are other ways to protect the steel reinforcement in concrete from corrosion. The most important of these is direct treatment of the rebars with coatings. Layers of this type are normally applied directly to the steel reinforcement. This is relatively expensive, and the risk of mechanical damage occurring during the process is high.

The use of stainless steel (Cr-Ni steel) is a more effective, but also much more expensive form of protection.

The use of corrosion inhibitors (chemical substances that reduce the corrosion rate of a metal), on the other hand, is now common practice [1]. Nitrites, for example, efficiently passivate steel surfaces and can be added directly to the concrete in the manufacturing process. The disadvantages are the relatively high quantities required, as the entire amount of concrete must contain the corrosion inhibitor in sufficient concentration, and the fact that the rheological properties of the liquid concrete are changed, requiring the use of further additives. This complicates the mix design, which is then difficult to control. Additionally, the use of corrosion inhibitors of this type is often toxicologically and environmentally questionable, particularly when there is a risk of being washed out of the concrete matrix.

The use of liquid corrosion inhibitors, such as amino alcohols, that are applied directly on the concrete surface is very simple. In order to obtain suf-

ficient effectiveness the liquid is required to penetrate into the concrete, to spread through it, and, when the depth of penetration is sufficiently high, to come into contact with the steel reinforcement. Chemical reactions between the inhibitor and the steel surface should then lead to the required passivation effect. A prerequisite here is that an adequate concentration of the inhibitor must be ensured at the steel reinforcement.

2 Corrosion inhibiting action of organofunctional alkoxysilanes

On account of their unique chemical structure (see Figure 1), organofunctional alkoxysilanes can react with the concrete matrix as well as with the steel surface [2-4]. A simplified representation of this is shown in Figure 2 and 3.

$$C_2H_5$$
 $R-S_1-OC_2H_5$
 C_2H_5

Figure 1: Structural formula of a monomeric organofunctional alkoxysilane

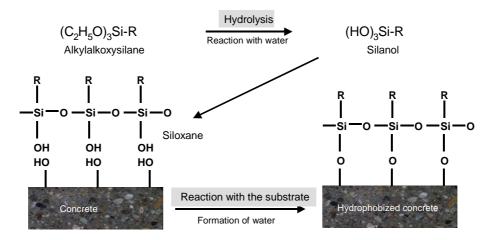


Figure 2: Reaction of an organofunctional trialkoxysilane with the concrete matrix (schematic representation)

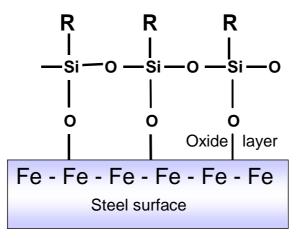


Figure 3: Steel surface coated with organofunctional alkoxysilane (schematic representation)

Monomeric organofunctional silanes possess excellent penetration power on account of their small molecular size. In the case of alkyltrialkoxysilanes, the concrete matrix becomes hydrophobized as a result of chemical modification. However, there is no closure of the pores; in contrast to the action of coatings, the breathing activity of the construction material, and therefore its ability to transport water vapour, remain entirely unaffected. The exclusion of liquid water dries out the concrete, and this also reduces corrosion of the steel reinforcement because the corrosion reaction is significantly controlled by the concrete resistance. Moreover, the reduction of capillary controlled water uptake by the hydrophobic concrete significantly reduces the penetration rates of chlorides dissolved in the water or already present in concrete. Chlorides destroy the passive iron layer even at high pH, and often result in high corrosion rates of up to 1 mm/year.

Degussa has developed a corrosion inhibitor based on an organofunctional alkylalkoxy silane system. The mode of action of this corrosion inhibitor can therefore, according to the above models, be multi-pronged and described as follows:

- interaction of the organofunctional alkoxysilane molecules with the passive layer (oxide layer) of the steel surface,
- hydrophobisation of the concrete matrix resulting in exclusion of water, which results in an increase of concrete resistance,
- exclusion of chloride ingress by hydrophobization.

3 Measurement of corrosion currents

The corrosion extent of steel reinforcement in concrete is best assessed by measurement of the corrosion current or corrosion rate (corrosion current per unit surface area). The higher the corrosion current, the higher is the extent of the corrosion. Active corrosion is here defined as continuing corrosion which, unless controlled, could result in a condition that is detrimental to public safety.

In the case of corrosion in concrete at least part of the corrosion current can be readily measured since the anodic metal dissolution is separated from the cathodic oxygen reduction due to the formation of a macro cell (Figure 4).

The overall reaction indicated in eq. (1) can be subdivided into constituent cathodic and anodic reactions. Electrons are transported between cathode and anode, constituting the flow of current. The cathode and anode can be formed within a single rebar (the cathode, for example, in the upper area of the rebar and the anode in the lower, as is shown in Figure 4) or between different rebars; this type is known as mat-to-mat corrosion.

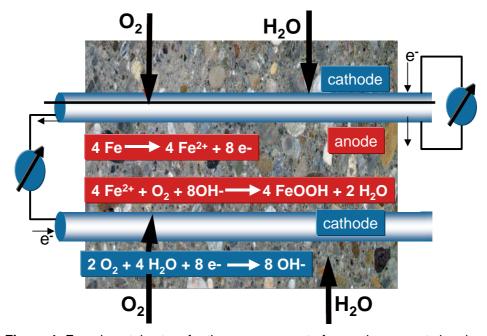


Figure 4: Experimental set-up for the measurement of corrosion currents in reinforced steel. Cathodic and anodic areas are formed. Corrosion always occurs in the anodic areas

4 Effectiveness of corrosion inhibitors based on organofunctional trialkoxysilanes in field tests

4.1 Field test at Monroe County Parking Garage in Stroudsburg, Pennsylvania, USA

The indirect measurement of corrosion currents is possible even on existing objects with relatively little effort and by using portable, battery-operated measuring equipment. A commonly used method is that of linear polarisation. Suitable devices are commercially available from a number of manufacturers.

The relationship between measurable corrosion rate and the degree of corrosion in a certain structure is shown in Table 1. For a corrosion current of less than $0.2~\mu\text{A/cm}^2$ the corrosion of the steel reinforcement is negligible (the region above indicates active corrosion); for a high corrosion current (> $1.0~\mu\text{A/m}^2$) visible damage is to be expected within the next two years. In 1996, high chloride values were found in the region of the steel reinforcement of the 30-year-old Monroe County Parking Garage in Stroudsburg (Pennsylvania, USA). Measurements of corrosion current also gave cause for concern (> $0.6~\mu\text{A/cm}^2$, see Figure 5). Among the maintenance measures it was decided to treate the chloride-loaded areas with an organofunctional silane. This system was applied via an airless spray gun in two coats, for each approximately $0.203~l/m^2$ is used. After the treatment the corrosion currents were checked again and a significant reduction down to negligible values (< $0.1~\mu\text{A/cm}^2$) was found. The effectiveness of the treatment was checked annually. The result is shown in Figure 5.

 Table 1: Relationship between degree of corrosion and measurable corrosion rate

| Rate of corrosion [µA/cm²] | Degree of corrosion | Visible damage after |
|----------------------------|-----------------------|----------------------|
| < 0.2 | negligible | - |
| 0.2 – 0.5 | low | > 10 years |
| 0.5 – 1.0 | moderate 3 - 10 years | |
| > 1.0 | high | < 2 years |

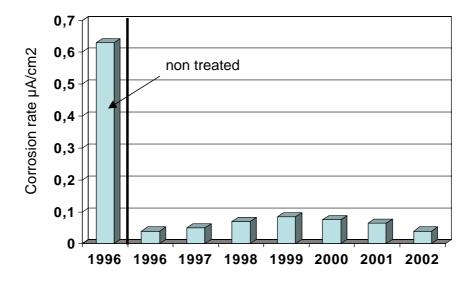


Figure 5: Field trial Monroe County Parking Garage

Despite the existence of a chloride load, there were neither appreciable corrosion currents, nor visible corrosion damage after several years of the silane application [5].

4.2 Field test at the gallery Cianca Presella on the Swiss highway A13

4.2.1 Set-up of measurements

The characterization of the effectiveness was tested by means of corrosion sensors embedded in concrete. The corrosion behavior was investigated with a continuous data acquisition system. Hence, the effectiveness of the corrosion inhibitor was determined as a function of time, the climatic conditions etc. The corrosion current is determined by measuring the current flow between the rebar of the structure and the sensor element. A detailed description of the experimental setup is given elsewhere [6].

The used sensor elements and their treatment are shown in Table 2. Each of the elements contains 3 rebars. The concrete cover is 10 mm. Hence a fast transport of the aggressive substances is achieved. The measurement of the corrosion potential allows to determine the corrosion initiation, while the monitoring of the macrocell corrosion current enables the measurement of the corrosion rate.

Table 2: Location and pre-treatment of sensor elements

| Equipment | Location | Chlorides | CIT Treatment |
|-----------|----------|-----------|---------------|
| 3 rebars | Presella | X | Х |
| 3 rebars | Presella | Х | - |

The elements were soaked with 2 M NaCl solution in order to monitor the corrosion behavior of an existing structure with already present corrosion damage. The elements built into columns of the gallery Presella were pretreated with the corrosion inhibitor Protectosil® CIT. The elements were exposed to a humidity of 75 % for 4 months. Two days prior to the treatment the humidity was lowered to 40 %. 2 g of product were applied on each element in two different treatments on the surface exposed to the environment. This equals an amount of 0.5 kg/m². Then the elements were stored at 80 % relative humidity. They were installed on the 14th of January 2002 and the measurement was started immediately. The elements were installed in different columns. Since the pretreatment did not affect the cathode, the silane based corrosion inhibitor was applied via airless spray guns on the entire column (which included the treated elements) on the 7th of September 2002. The application rate of the product was 0.5 kg/m².

4.2.2 Results

The results of the investigation are presented in Figure 6 and 7. On each element the corrosion potential of one rebar sensor and the corrosion current between the two other rebar sensors and the rest of the reinforcement mat of the column was registered.

In Figure 6 (left side) the corrosion currents are displayed. Starting from low temperatures in January the corrosion current continuously increased in spring. This effect is primarily a result of the increased concrete conductivity in the warmer season. Additionally, the strong effect of the daily temperature cycles is visible. In general, the sensors treated with the silane based corrosion inhibitor show a slightly smaller corrosion current compared to the non treated sensor element.

For a more detailed analysis the whole corrosion current shown in Figure 6 (left) was integrated and from the electrical charge the amount of corroded steel was calculated (Figure 6, right side). This allows to estimate the development of the corrosion damage. The sensors treated with the silane based corrosion inhibitor show a smaller increase of the steel dissolution within the investigated time range. Further, the slope of the mass loss curves is smaller after the second silane treatment in September 2002. During fall

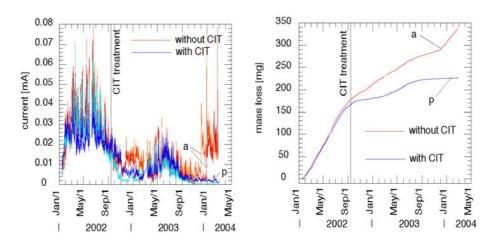


Figure 6: left) Corrosion current of the chloride treated sensors right) Mass loss calculated from the current data of the different sensors shown left

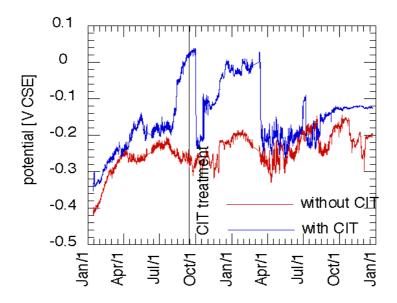


Figure 7: Corrosion potential of the chloride treated sensors

2003 the curves of the silane treated part clearly flatten. Overall, the difference in the corrosion loss between the treated and the non-treated sensors is about 20 %.

Based on the development of the corrosion potential (Figure 7) of the sensors it can be concluded that the sensor treated with the silane based corrosion inhibitor repassivated repeatedly while the non-treated sensor remained in the active corrosion state. The stable potential of the sensor with silane treatment (since August 2003) is an indication for repassivation, while the non-treated sensor is still in active state.

Based on the data available to date the following conclusions are possible: In the gallery Cianca Presella a clearly smaller corrosion degradation is observed on the sensors with corrosion inhibitor treatment.

The influence of the Protectosil[®] CIT allows the temporarily repassivation of an active corrosion sensor as can be concluded from the corrosion potential.

5 Outlook

Organofunctional alkoxysilanes can be effective in reducing corrosion of steel reinforcement in concrete. In many cases a reduction of more than 90 % is observed in the measurable corrosion currents. Application of the liquid product is relatively easy; it is applied directly to the concrete surface, with no need to expose the steel reinforcement. The use of Degussa's new corrosion inhibiting silane systems therefore represents a highly attractive possibility of reducing maintenance expenditure on concrete buildings.

6 References

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