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Transport of a surface-applied corrosion inhibitor in cement paste and concrete

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Abstract

Surface-applied corrosion inhibitors are a kind of repair material and usually contain an aminoalcohol and a component forming a salt with the aminoalcohol. According to the manufacturers, this type of inhibitor penetrates very rapidly into concrete; however, the transport mechanisms have not been sufficiently investigated so far. The major part of the study therefore focused on the transport of the ingredients of an inhibitor in cement paste and concrete, which contained an aminoalcohol and a phosphorous compound. It has been shown that the latter forms an insoluble calcium salt in the environment of cement and precipitates quantitatively. It is thus unable to penetrate from the outside into the alkaline concrete zone and cannot develop its inhibiting effect there. The aminoalcohol, on the other hand, is not bound by cement, but remains largely dissolved in the pore liquid, thus providing optimal conditions for high mobility. The analysis of the transport mechanisms involved has revealed that diffusion in the dissolved state is by far the most efficient transport mechanism. While basically the transport of the aminoalcohol via the gaseous phase is possible, it does play an inferior role only. Surprisingly, the substance had hardly been absorbed by concrete by capillary suction, but at first remained close to the concrete surface.

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1. Introduction

Corrosion inhibitors, by definition, are substances whose presence impedes corrosion in a medium of attack. They act like negative catalysts and have become indispensable in a variety of applications such as cooling cycles in industry or engine cooling systems. In the building sector, corrosion inhibitors have received attention for the past three decades or so. From among the substances that basically have proven to be suited, attention has focused in particular on the nitrites [$NaNO_2$ and, in particular, $Ca(NO_2)_2$], which are salts of the nitrous acid. They are candidates, for example, if no chloride-free raw materials are available and reinforced concrete can thus not be constructed chloride-free. This is the case, for instance, in several coastal regions with arid climate. However, since nitrites are toxic, efforts have been made to develop inhibitors that are largely free from health risks. They contain active ingredients of organic nature, mostly aminoalcohols. In landlocked countries where there are sufficient noncontaminated raw materials, inhibitors have hardly been an issue so far. However, since substances for subsequent application onto existing structures have been offered on the market, interest in them has been rising rapidly. They are considered to be a kind of repair material that is supposed to have a preventive effect, or to restore lost corrosion protection. They are sold in liquid form (aqueous solution), are low in price, and easy to apply by spraying, rolling, or painting onto the surface. Yet there have been a number of questions whose solution seems to be imperative, such as their speed of penetration in cement or concrete as well as the respective mechanisms involved, since only an active ingredient that has passed all the way to the reinforcement can actually become effective there. This paper describes briefly the initial situation and then the author's own studies, which have been performed within the EU project COST 521, using the product of a European company. They have focused on the active ingredients of this product (an aminoalcohol and a phosphorus compound) and include (i) the binding in cement, (ii) the diffusion behavior in cement paste and concrete, (iii) the transport of aminoalcohol via the gaseous phase, (iv) the penetration into

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concrete by capillary suction, and (v) the transport behavior in carbonated concrete.

2. Initial situation

Organic inhibitors are described as fast-penetrating ones. For example, it is mentioned in a report by Mott MacDonald [1] that the product FerroGard 903 of the company SIKA penetrates into concrete at a speed between 2.5 and 20 mm/day, depending on the quality of the concrete. The explanation commonly offered for this fast penetration is that the organic active ingredient is transported not only by way of capillary suction and diffusion but via the gaseous phase as well. However, as there were hardly any test results available supporting this theory, the question itself suggested as to whether such a transport behavior is possible at all and by which mechanisms the substance is transported within the concrete.

A review of the literature showed that the question of the mobility of surface-applied inhibitors had been investigated repeatedly [1–4]. In all papers available, the aminoalcohol content of the concrete—determined usually from its nitrogen content—was used as a measure for the total inhibitor content. However, these inhibitors usually do not just contain aminoalcohol, but a second organic or inorganic inhibiting component (frequently an acid), which forms a salt with the aminoalcohol. This should, above all, prevent the aminoalcohol from evaporating from the concrete surface rather than penetrating into it. Unfortunately, nobody has investigated whether the salt-forming component is transported to the same extent as the aminoalcohol. As many acids form insoluble calcium salts, the precipitation of the acid component in the concrete (i.e., its immobilization) cannot be ruled out according to Elsener et al. [5]. Considering that some aminoalcohols develop their effects only in the presence of a second component, efficiency is most likely to decrease when the two active ingredients are separated—this question is a very crucial one.

The findings obtained in practice were similarly unsatisfactory. Unfortunately, the reports, the majority of which were quite promising, did not contain sufficient information for an evaluation of the products [6–9]. In most of them, the decrease in corrosion current density is attributed entirely to the inhibiting effect of the product without considering other possible factors of influence, such as changes in humidity or the effect of a coat of paint applied onto the top of the concrete, etc. As comparative studies (e.g., by using water instead of the inhibitor while employing the same procedure) had not been found, it was not possible to assess as to what extent the measured effect was to be attributed to the ingredients of the product. It was, therefore, not possible either to determine whether the positive effect on the respective object noted can be generalized, or whether it was merely due to the special conditions prevailing in a given case.

3. Cooperation with the producer of the investigated product

For the intended studies on the transport of such products, measuring the concentration of their ingredients in the pore solution of cement paste and concrete appeared to be the most appropriate approach.

Investigations like these can only be carried out if the composition of the commercially available inhibitor is known. As this was not the case with organic inhibitors because the composition is kept secret by the producers, the author offered his collaboration to a European manufacturer. The company responded positively, expressed its interest in such investigations, and offered to reveal the composition of its product provided that it would be kept secret. However, it can be said that the product contained, besides an aminoalcohol, a phosphorus compound as a salt-forming component. The part of the company was to determine the concentration of the active ingredients of their product in the samples that are investigated. The samples were sent to the company in coded form and the results were evaluated by the author, so that impartiality was ensured. Contact was established with this company only because the products offered by other companies basically work in a very similar way.

4. Binding of the active ingredients of the inhibitor in cement

Since an active ingredient is truly mobile in unbound state only, it is most important for the understanding of the transport processes in concrete to know how much of it is not bound and remains dissolved in the pore solution of cement or concrete. This was the main reason why, firstly, the concentrations of the ingredients of the product were studied in the pore solution of hardened cement paste samples. Three different types of cement from Austrian manufacturers were included in the study: (a) normal Portland cement (PZ-375-EZ; this is an OPC); (b) EPZ (it contains about 30 Mass% blast furnace slag, BFS); and (c) HS cement (sulfate-resisting cement). First, the inhibitor was dissolved in the mixing water, and then the cement was added. The cement pastes, which were produced by manual mixing with a spoon, were filled into plastic containers with tight caps and rotated until hardened (over night) to avoid demixing. Until testing, the containers were stored in closed state at 20 °C. The pore solution was expressed at a sample age of 28 days. The device that had been used is described in Ref. [10].

It was shown that the concentration of the salt-forming compound was below the detection limit. This indicates that this component had been completely bound and/or that it had precipitated. It is to be concluded from this result that the phosphorus component segregates from the liquid phase in concrete at the transition from the carbonated peripheral zone to the noncarbonated concrete at the latest, and that the

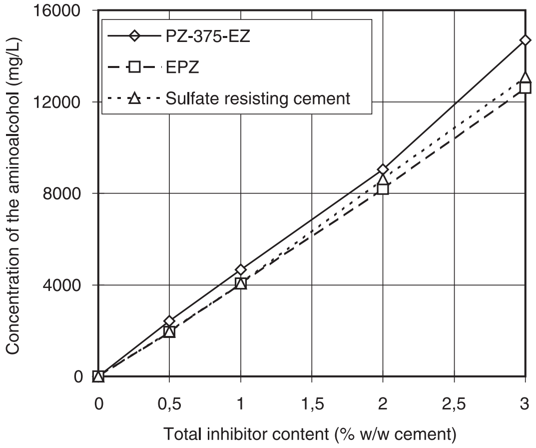

Fig. 1. Aminoalcohol in the pore solution versus total inhibitor content.

corrosion of the reinforcing steel down in the deeper layers of the concrete cannot be inhibited by this compound.

Fig. 1 shows the concentration of aminoalcohol in the pore solution of three different cements (w/c ratio, 0.6; age of the sample, 28 days) with dependence on the total inhibitor content. The concentrations were highest in PZ-375, followed by HS cement and EPZ. The aminoalcohol concentration was almost 90% higher in the pore solution of the PZ-375-EZ than in the mixing water [11].

This corresponds to the concentration that established itself due to water binding in the hardened cement and the consequent loss in free water. The content of unbound water was probably higher in the other cements after 28 days than in the PZ-375-EZ, so that the concentration of aminoalcohol was unable to rise to an equally high level. This suggests that the aminoalcohol was not bound, but remained more or less completely in the pore solution. Further studies showed the expected result—namely that the concentration of the aminoalcohol in the pores decreased as the w/c ratio increased, and that it rose with the rising age of the sample (continued water binding). The aminoalcohol thus meets the requirement for maximum mobility.

5. Transport of the aminoalcohol via diffusion

Cylindrical samples (200 mm in diameter and 240 mm in height) were produced from PZ-375-EZ with w/c ratios of 0.55 and 0.70. The moulds for the sample preparation were plastic sewer pipes, which were provided with rubber gaskets 30 mm before the two openings and could be closed tightly with two plastic caps. After the lower end had been closed, the respective pipe was filled with cement paste up to the top end gasket, then the second cap was put on. Via a hole (Ø 20 mm) that was drilled through the top cap, the pipe was then filled up completely. The hole was closed with a rubber plug. To avoid demixing of the cement paste, the container was put on a rotary stand and turned until hardened (overnight). Since it was not possible to remove the caps after hardening, the pipes were cut parallel to the base at the level of the upper rubber gasket with a stone saw after a hardening period of 28 days, during which they were stored at room temperature. In order to be able to apply a layer of the inhibitor onto the cutting surface, plastic strips, which protruded above the cutting surface by at least 30 mm, were wound around the pipes and fastened with hose binders. First, the cutting surfaces were exposed to water for 7 days to fill the pores. This was necessary because the transport of the ingredients by diffusion was to be determined and an intake into the shrinkage pores by capillary suction had to be avoided. After exposure to water, the water still present in the plastic extension of the pipe was poured off and replaced by the inhibitor. To avoid the evaporation of the volatile constituents of the product, the samples were placed into plastic bags, which were tied, for further storage. On the scheduled date of testing, slices of 1 cm thickness were cut off parallel to the exposed base and examined for their concentration of aminoalcohol in the pore solution. A concentration profile was thus established. The tests were carried out after 2, 7, 14, and 50 days of exposure. It was found that some specimens contained less aminoalcohol after 50 days of exposure than at earlier dates of testing, which suggests that the penetration of aminoalcohol must have been inhibited by some mechanism. The clogging of pores by the phosphorus compound of the product, which is insoluble in the alkaline environment of cement, was excluded as a potential cause then since penetration tests with chloride ions showed that Cl^--ions penetrated into the cement pastes at the same speed regardless of whether they had been exposed to the inhibitor or not [12]. Further studies showed that the product solidified like a gel without the precipitation of solids if a synthetic pore solution had been added [a mixture of NaOH, KOH, and $Ca(OH)_2$; pH value of approximately 13.5; because of the high pH value, $Ca(OH)_2$ precipitated immediately as a solid, rendering the solution milky and turbid]. However, as this was the case only in the presence of $Ca(OH)_2$, it is assumed that the phosphorus component reacted to form an insoluble calcium compound whose individual particles were probably stabilized in colloidal distribution, rather than settling as a precipitation because they adsorbed water so heavily that the solution altogether solidified into a gel (hydrophilic colloid). It is also likely that during exposure of the cement paste samples, such a gel layer, although probably a thin one only, developed through which the aminoalcohol could neither easily enter nor exit. To corroborate the assumption that this product was inhibited from penetrating, samples were exposed to an aqueous solution of pure aminoalcohol of a concentration lower than in the product. After 28 and 50 days of exposure, a concentration profile of the aminoalcohol in the pore solution was established. The results obtained in samples with w/c ratio 0.55 are shown in Fig. 2.

As can be seen, although the concentration of aminoalcohol in the solution used was lower than in the product, considerably more penetrated from the solution of pure

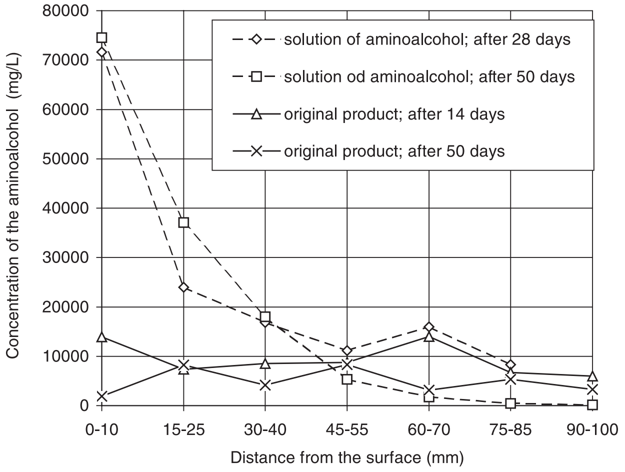

Fig. 2. Concentration of the aminoalcohol in the pore solution of cement paste samples ponded to (i) a solution of aminoalcohol and (ii) to the original product.

aminoalcohol than in the case of exposure to the original product. This provides evidence that the penetration of aminoalcohol from the product was obstructed indeed. This is most likely to be attributed to the formation of a gel as described above. The absence of a difference in chloride uptake between samples exposed to the product and the nonexposed ones was most probably due to the fact that the gel layer had been removed upon contact with water (at the end of exposure and during exposure to the chloride solutions, respectively) [12]. Further studies showed that gel formation took place only on fresh, alkaline-reacting surfaces while this was not the case in carbonated concrete (see Sections 7 and 8).

6. Transport of aminoalcohol via the vapor phase

Samples were used as described before and dried at ambient temperature for 5 days, during which some cracks already developed due to shrinkage. As shown schematically in Fig. 3, each sample was then pushed all the way up to just below the rubber gasket, with its cutting surface down, into a lid into whose lateral surface a hole had been drilled, and fastened in this position.

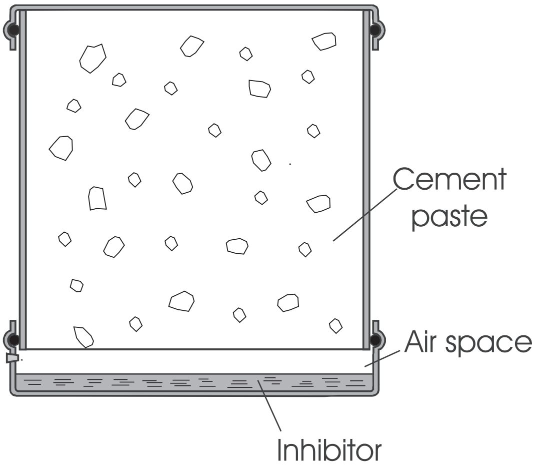

Fig. 3. Schematic representation of the experimental set up.

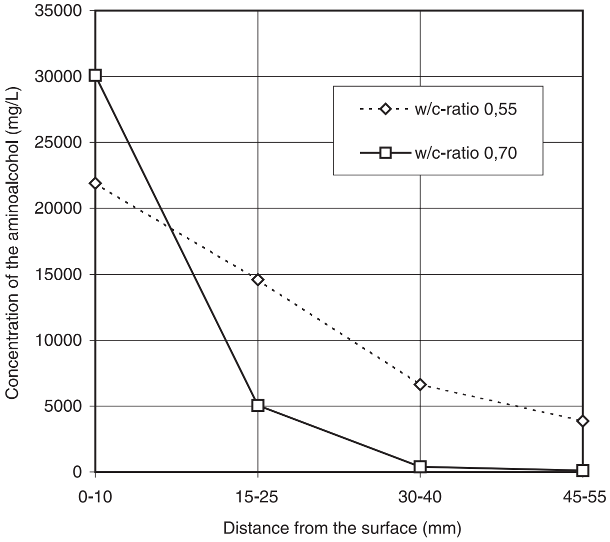

Fig. 4. Aminoalcohol concentration in the pore solution of cement paste samples after 6 months of storage above the inhibitor.

After the samples had been taken to their final place of storage (20 °C), approximately 3 cm of the inhibitor was filled in through the hole, which was then closed immediately with a rubber plug to prevent vapor from escaping. After a storage period of 6 months, the test was completed and the concentration profile of aminoalcohol was determined in the pore solution. The results are shown in Fig. 4.

As can be seen, aminoalcohol was transported into the samples. However, a comparison with Fig. 2 shows very clearly that considerably less had penetrated than by diffusion from the solution of pure aminoalcohol. This provides evidence that, although vapor phase transport does occur, no appreciable quantities are being transported within a short period of time. It is assumed that the relatively slow transport was due to the fact that the vapor above the product contained probably little aminoalcohol and that the dried up pores of the samples were chiefly filled via capillary condensation, with the water evaporating from the product. This can be safely assumed because water has a higher vapor pressure than aminoalcohols. Hence, the less easily evaporating aminoalcohol most probably hit primarily pores that had been refilled with water, was dissolved in the pore solution, and then transported in the liquid phase down to lower depths by diffusion.

7. Penetration of the inhibitor into carbonated concrete

As it turned out that the phosphorus compound is not soluble in alkaline cement paste, the question itself sug-

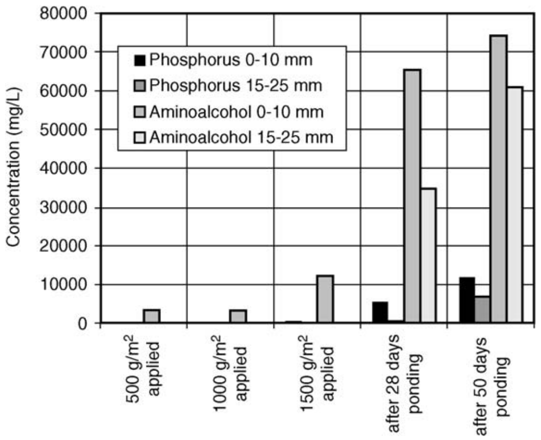

Fig. 5. Concentration of the ingredients of the inhibitor in the pore solution of carbonated concrete.

gested whether the product penetrates more readily into carbonated concrete and whether the phosphorus component is soluble there. First it was examined whether the addition of $CaCO_3$ powder to a diluted solution of the inhibitor results in a decrease in phosphorus concentration. As expected, the concentration of aminoalcohol remained unchanged while the phosphorus compound concentration at a dilution of 1:10 dropped by more than 60% within 28 days. This demonstrates that the phosphorus component is not completely soluble in concrete, not even in the carbonated peripheral zone.

To study the penetration behavior of the inorganic component into carbonated concrete, five samples of 25 cm in length were cut off from a reinforced concrete beam of 14 cm in height and 13 cm in width. The beam belonged to a building constructed around the year 1900 and had to be removed during alterations. It was completely carbonated. The samples were stored at room temperature and dried that way. Then 500 g/m^2 inhibitor (as recommended by the manufacturer) was applied onto the surface of one sample, twice the amount onto another sample, and three times the recommended quantity onto a third sample with a brush according the guidelines of the producer. After a waiting period, during which the samples were kept in plastic bags and stored at 20 °C, slices were cut off from the samples and their pore solution was expressed. The two remaining samples were first saturated with water and then exposed to the inhibitor in a ponding test. After 28 and 50 days of exposure, slices of 1 cm in thickness were cut off from the samples and their pore solution was expressed. The results of the pore solution analyses are summarized in Fig. 5.

The figure illustrates that the aminoalcohol was present in the samples exposed to 500, 1000, and 1500 g/m^2 inhibitor in appreciable quantities only in the pore solution of the outermost zone. The concentration of the phosphorus compound was almost negligible, even in these highly absorbent samples. The results shows in particular that apparently nothing or very little only had penetrated into the well air-dried samples by capillary suction. This was a big surprise, and additional tests performed on bricks, which revealed that this inhibitor was absorbed much more slowly than distilled water [12], provided some explanations.

When the product was applied onto water-saturated samples for 28 and 50 days, comparable quantities of aminoalcohol had penetrated as into alkaline cement paste samples out of a solution of pure aminoalcohol (Fig. 2). This indicates that in carbonated concrete, there is no formation of a gel blocking the penetration of aminoalcohol. The phosphorus component penetrated as well; however, its concentration in the pore solution was very low compared to that of aminoalcohol because the phosphorus compound does not dissolve easily, not even in carbonated concrete, and thus had largely precipitated.

8. Penetration of the product into the concrete of an existing structure

A hall made of reinforced concrete, which in the past had served as a storage depot for deicing salts, was used. Therefore, the concrete was partly heavily chloride-contaminated. Bore cores (Ø 200 mm) have been taken from two test areas onto which the inhibitor was applied. From these bore cores, which were extracted 1 day after the application of the product and 3 months after, slices of 1 cm thickness were cut off parallel to the base in the laboratory. As the samples were not saturated with water, moistened cellulose was wrapped around the sections to fill the concrete pores with water. After 2–3 weeks, the pore solution was expressed and analyzed. The results are shown in Fig. 6.

As can bee seen, the pore solution contained very little aminoalcohol 1 day after application. The phosphorus concentration was below the detection limit in all samples. This result is in agreement with the findings obtained from carbonated concrete samples and shows that no capillary absorption had occurred here either. Apparently, the substance had remained on the concrete surface and was washed off by the cooling water when the bore cores were extracted. However, what was surprising was that after 3 months, aminoalcohol concentrations were measured in the

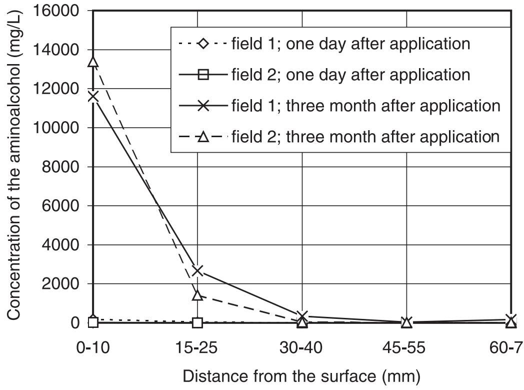

Fig. 6. Concentration of aminoalcohol in the pore solution of concrete.

outermost sections, which roughly corresponded to the concentration one might expect based on the quantity applied, and that a clear concentration profile existed, with values decreasing from the outside to the inside. It is quite obvious that the aminoalcohol had been transported mainly via diffusion into the concrete. The phosphorus concentration was below 100 mg/l in the outermost zone down to a depth of 1 cm and below detection limit in the lower zones.

9. Summary and conclusions

The study on the binding of the ingredients of the investigated inhibitor by cement showed that the aminoalcohol had not been bound by cement but remained completely dissolved in the pore solution, thus providing optimal conditions for high mobility. However, the phosphorus component forming a salt with the aminoalcohol was insoluble in the alkaline environment of cement paste and precipitated quantitatively from the liquid phase. It was thus unable to penetrate from the outside into the alkaline concrete zone and could not develop its inhibiting effect there. As Elsener et al. [5] found that the salt-forming component of the product of other manufacturers precipitated in contact with cement as well, it seems that this is not restricted to the investigated product because the products of other manufacturers contain comparable ingredients. Therefore, the found interactions seem to be (qualitatively) transferable to other products as well. As was shown, the salt-forming component of the investigated product hardly penetrated, not even into carbonated concrete, and was poorly soluble therein only. From this, it can be inferred that this component is hardly effective as an inhibitor, even if the product is applied according to the manufacturer's instructions. It cannot be said whether the salt-forming components of other products are soluble in the carbonated zone or not (i.e., if they can inhibit corrosion when applied onto carbonated concrete).

As regards the transport mechanisms involved, diffusion in solution has turned out to be by far the most effective one. While basically transport of aminoalcohol via the gaseous phase is possible, the latter plays an inferior role only. This can also be transferred to other products. The aminoalcohol, however, penetrates much more slowly than expected at the beginning, with a speed comparable to that of chloride ions [2].

The author does not believe that the major obstacle to assessing the inhibiting effect of surface-applied inhibitors is the slow penetration of the aminoalcohol into the concrete, but the question of whether the aminoalcohol contained in the products alone (i.e., without the salt-forming component) is able to develop a sufficient inhibiting effect. So far, no explicit answer could be provided to this question. There is hardly any literature to corroborate this, and the data contained in two patents are contradictory [13,14]. Nevertheless, inhibitors intended for subsequent application continue to be an interesting subject because of their low costs and their versatility of application. However, it remains to be seen whether the products can be improved in a way that the existing uncertainties concerning their ability to inhibit corrosion when applied onto the surface of reinforced concrete structures can be removed.

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