Even concrete is not as hard as it looks. Sea water, salt on icy roads, and indirectly even carbon dioxide from the air can corrode the steel of the reinforcing bars and so threaten the strength and integrity of a bridge pier, jetty, or viaduct. Dessi Koleva, a chemical engineer from Bulgaria, spent her doctoral research at the Faculty of Civil Engineering and Geosciences devising a method for the cathodic protection of steel rebars. The method is cheaper and also has fewer side effects on the microstructure of concrete.

Joost van Kasteren
There is no need to derust reinforcing steel before the concrete is poured, since a very thin protective layer will eventually form that prevents the steel from corroding. Where things go wrong is when the protective layer breaks down.

Many salts used for de-icing are chlorides that in the long term will cause corrosion in concrete structures.

The service life of concrete structures sometimes falls far short of the normal life expectancy, due to corrosion of the reinforcing steel. In the 1970s and 1980s for example, a wave of concrete decay swept over the Netherlands. This was caused by the practice, common in the 1960s and 1970s, of adding calcium chloride to the concrete mix to accelerate the setting process. The chloride ions in the accelerant proved to have a disastrous effect on the reinforcing bars, which started to corrode. Since rust has a much greater volume than steel, the concrete started to flake, and in some cases the steel rebars even became exposed.

Although the use of calcium chloride in concrete is now prohibited, this has not removed the problem of corroding reinforcing steel and concrete decay. A few years ago a viaduct across the Tilburg – Eindhoven motorway had to be replaced for this reason, and concrete sections of the approaches of a bridge near Krimpen aan den IJssel were found to be cracked. These will certainly not be the last of such cases. Research by Gerard Gaal, who was awarded his doctorate last year at the Faculty of Civil Engineering and Geosciences, shows that the Netherlands is in for a prolonged spell of decaying bridges and viaducts.

De-icing

The main cause of the decay is the salt that is used to de-ice Dutch roads during the winter. In most cases this is ordinary cooking salt, sodium chloride. The chloride ions penetrate the concrete and – just like the chloride ions of the setting accelerant did a few decades ago – corrode the reinforcing bars. The corrosive power of chloride ions used to be underestimated. It was assumed that corrosion of the reinforcing steel was practically impossible because concrete forms a highly alkaline environment in which the high pH value (approximately 13) would offer sufficient protection. A logical supposition in itself, if it weren’t for the fact that chloride ions can penetrate this type of protection. The ions infiltrate through the protective layer and can cause a festering, pitted corrosion of the steel.

In addition to de-icing salt, carbon dioxide from the air can also affect the reinforcing steel, albeit indirectly. This particular phenomenon can often be found on concrete balconies that are exposed to the full blast of the weather. The chemical process involved is complex but basically, at the boundary between air, water and concrete, carbon dioxide from the atmosphere dissolves to form an acid (bicarbonate). The bicarbonate reacts with calcium compounds in the concrete to form calcium carbonate. As a result of the carbonation of concrete the acidity can increase to the point where the alkaline protection breaks down and the reinforcing steel starts to corrode.

Electrochemistry

Various methods are being tried to prevent the corrosion of reinforcing steel and the subsequent deterioration of concrete structures and buildings. Bridges and viaducts are now given an improved cover (a thicker layer of concrete), premature drying of the concrete is prevented (post-treatment), and sometimes an impermeable layer is included that closes off the pores. In addition, these days high-strength concrete, which is almost impossible for chloride ions to penetrate, is used more often. An alternative that was developed in the early 1970s is cathodic protection, in which a continuous weak direct current of a few milliamps flows between the reinforcing steel and the encasing concrete.

Cathodic protection is based on the fact that corrosion is an electrochemical process in which the dissolving of iron (the anodic reaction) is linked with the production of hydrogen and oxygen. As the iron dissolves, two electrons are released which convert oxygen and hydrogen into hydroxyl groups (OH-) through a complex series of reactions. The iron ions (Fe²⁺) react with these hydroxyl groups to produce a form of iron hydroxide which, after some intermediate stages, is transformed into the familiar dark brown flaking material, rust.

Combined with the adsorbed water molecules the volume of rust is about six times that of steel. The result is that the corrosive action pushes away the concrete, causing cracks to form and finally, pieces of concrete to break away.

Hydrogen

The application of a small electric current renders the reinforcing steel immune to corrosion, as it were. The currents involved are very low. Higher currents are sometimes applied to the reinforcing steel to force chloride ions away from the boundary between concrete and steel or conversely, to stimulate realalkalisation of the boundary layer. These higher currents can
only be applied for short periods at a time, due to the risk of hydrogen forming as the result of the separation of water. If the hydrogen cannot escape this will render the reinforcing steel brittle, which is not the intended effect.

"However, at low currents chloride extraction and realkalisation can be a welcome side-effect of cathodic protection," says Dessi Koleva. Trained as a chemical engineer at the University of Sofia, the capital of Bulgaria, she came to the Netherlands a few years ago at the invitation of Van der Heide Corrosion Protection and Engineering BV. Funded by the European Union through a Marie Curie Host Fellowship she is currently doing research on cathodic protection. A prerequisite for this type of scholarship is that the research must be scientifically interesting as well as being relevant for the industry.

Microstructure Cathodic protection works by connecting one pole of a current source to the reinforcing steel and the other to a metal (e.g. titanium) screen that is attached to the concrete surface and which acts as an anode. The screen is usually covered with an epoxy resin coating. Instead of titanium, a conductive mortar or coating can also be used to act as the anode. Although the method has been in use for some decades (albeit on a limited scale in the Netherlands), the exact details of why cathodic protection is so effective remained unknown. Koleva has done extensive fundamental research on the subject. Contrary to common practice in this type of research, she used standard methods such as resistance measurements, but she also looked into the microstructure of concrete and reinforcing steel and into the changes at the boundary between steel and concrete.

For her research Koleva used cylindrical test pieces 100 mm long with a diameter of 40 mm, made using normal Portland cement with a water/cement ratio of 0.6 and a sand/cement ratio of 3:1. At the centre of the cylinder was a rebar of 6 mm diameter. The bottom third of a test set of cylinders was immersed in a saline solution. A number of these cylinders were cathodically protected, whereas the remainder were left to corrode. A third set of cylinders acted as reference and was immersed in demineralised water.

Platelets Interesting differences in morphology and microstructure were observed between the protected and the unprotected samples. The test pieces, both with the oxidised and the cathodically protected rebars, were expected to contain a mix of iron oxide, hydroxides and iron hydroxides. However, the protected samples were found to contain a lot fewer crystals of all these oxides than the unprotected samples. Also, corrosion products such as high-valency oxides (hematite and magnetite) were found. In addition, the crystalline structure of the corrosion products was found to differ greatly. In the unprotected concrete the corrosion products were found to have formed what appeared to be platelets. The resulting increase in volume is to a great degree responsible for the forming of microfissures in the concrete. In the case of the cathodically-protected reinforcing steel, however, few or none of these platelets were observed to form. In other words, the effect of cathodic protection lies mostly in preventing the formation of large-scale morphological changes such as the platelets.

Having demonstrated what the efficacy of cathodic protection is actually based on, Koleva used the same techniques of analysis to investigate whether the protective action could be improved by applying the electric current as a square-wave pulsed direct current instead of continuously. One of the drawbacks of cathodic protection with a continuous current supply is that the heterogeneity of the concrete causes the current to be non-uniformly distributed. This results in areas that are overprotected, at the cost of other areas. The porosity of the concrete also changes, in particular at the steel/concrete boundary. This can cause small cavities to form, which in turn can lead to the formation of microfissures.

"All in all," says Koleva, "reason enough to see whether the application of a pulsed current might at least alleviate the problem."

Pulse The use of a square-wave pulsed current is nothing new in itself. The technique is already in use to prevent rising damp in brickwork and concrete. A screen of titanium is applied to the affected concrete or masonry, and close to the wall a copper rod is driven into the ground. A current source is then used to apply low-voltage pulses, which extract the water molecules from the wall. This Electro-Osmotic Pulse (EOP) system has been used since the 1990s, but with only limited success. A breakthrough came in 2004 when Gert Van der Heide at the University of Twente demonstrated that the inorganic electrolyte can be replaced by the organic electrolyte dimethyl ethylene diamine (DME). This damps the rising damp almost completely, even in situations where conventional methods have failed. The mechanism of action of the DME solution is essentially the same as that of the EOP, but the DME solution can be applied to the wall much more easily.

The process of rust-forming and cracking as the result of electrochemical processes.
and according to Internet advertisements will show results within a fortnight. What is new about Koleva’s research – and which has been covered in a patent application – is the use of a specific square-wave pulsed current supply for the cathodic protection of reinforced concrete. Pulse techniques are also used to protect underground pipelines.

In order to demonstrate the improvements over the traditional cathodic protection methods, Koleva again used cylinders, but this time they contained two rebars to see what the effect of the distance between them was on the electrical resistance. In addition she prepared a number of prisms of non-reinforced concrete. To make these, she used demineralised water in one set, a saline solution in the next, and a mix of both in the rest. The electrical resistance, or rather the electrical resistivity (specific resistance), of each of the prisms was measured, and at set intervals their chemical composition was analysed. This enabled Koleva to measure the transport of ions over time, both as a function of continuous and of square-wave currents.

**Electron microscope** To begin with, the cylinders of reinforced concrete were exposed to a saline solution to initiate the corrosion process. Next, some of the samples were cathodically protected using a continuous current, while others were protected using a square-wave current. Several methods were then used to catalogue the electrochemical parameters of the reinforcing steel. In addition, the microstructure was visualised using an ESEM electron microscope. Thanks to a technique developed by colleague Jing Hu (who has since gained her doctorate) Koleva was able to quantify the structural properties of the material based on the two-dimensional images produced with the electron microscope. Finally, the morphology and the chemical composition of the samples of reinforced concrete were analysed at regular intervals.

Electrical pulses protect concrete
Koleva’s research shows that there is a clear difference between the effects of continuous and of square-wave currents on the microstructure of reinforced concrete. A continuous current causes undesirable changes in the microstructure, as the heterogeneity of the bulk material clearly increases, while the porosity decreases. As a result the specific resistance increases, so more electricity is required. The hypothesis is that the most important change occurs at the boundary between concrete and rebars. The electron microscope images clearly show that a cavity, a zone of increased porosity, is being formed between the steel of the rebars and the concrete, as well as between the cement and the gravel aggregate. The cavity in turn serves as the starting point for the formation of microfissures.

The square-wave current cause hardly any of these microstructural changes, either in the bulk material or at the boundary between the reinforcing material and the concrete.

Koleva: “On the one hand the application of a square-wave pulsed direct current appears to offer sufficient cathodic protection, while on the other it causes little or no undesirable changes in the microstructure. And because a pulsed current requires less electricity, it is also cheaper, which is particularly important to commercial users.”

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