

# **Electrochemical treatment of cementations water storage tanks**

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## **Abstract**

In the storage of drinking water repeatedly the formation of soft stains on the surface of mortars and concrete in contact with water has been observed. The practical experience has shown, that this softening of the cement matrix and the associated decrease of alkalinity can be slowed down or even stopped by the use of an electrochemical treatment. The issue of the formation of the soft stains and the related mechanisms are discussed. Additionally related practical experience is presented.

## **Zusammenfassung**

Wiederholt wurde in Wasserreservoirs mit Zementmörtelauskleidung oder Betonoberflächen Fleckenbildung beobachtet, welche zu einer Aufweichung der des Zementsteins geführt hat. Die praktische Erfahrung hat gezeigt, dass diese Aufweichung durch eine elektrochemisches Verfahren in den meisten Fällen verlangsamt oder gar gestoppt werden kann. Die Problematik der Fleckenbildung und die zugrundeliegenden Mechanismen werden diskutiert. Weiter werden konkrete Praxiserfahrungen aufgezeigt.

## **Résumé**

Dans le cadre du stockage de l'eau potable, on a observé à plusieurs reprises la formation de taches molles à la surface des mortiers et bétons au contact de l'eau. L'expérience pratique a montré que ce ramollissement de la matrice de ciment et la baisse d'alcalinité qui en découle pouvaient être ralenties, voire arrêtées, grâce à un traitement électrochimique. Le problème de la formation des taches molles et les mécanismes liés sont examinés. De plus, une expérience pratique connexe est présentée.

## 1. Introduction

In the past years numerous cases with formation of stains in the mortar lining or the concrete surface of water storage tanks were observed. These stains are not only characterized by an impairment of visual appearance of the reservoir surface but also by a softening and a decrease of alkalinity of the cement stone. The latter increases the risk for the formation of a biofilm. An example for the formation of stains is shown in Fig. 1.



**Fig. 1: Formation of stains in a drinking water reservoir with mortar lining**

Still there is significant disagreement regarding the origin of the formation of the stains. It is generally accepted that the stains result from the neutralization of the cement pore solution, the formation of calcium carbonate and its successive dissolution. However, the explanation for the heterogeneous formation of stains include diffusion processes for calcium and hydroxyl ions in large pores, an accelerated transport process due to the pressure variations during filling and emptying of the reservoir, accelerated transport due to migration in the electrical field caused by galvanic processes, or a chemical attack due to an excess of aggressive carbon dioxide in the water.

While it is not clear how the various mechanisms contribute to the formation of stains and whether a combination of several factors is required to generate them, the practical experience has shown that the use of cathodic protection can influence the stain formation process. The possible influencing factors are discussed in the following. Additionally some case studies demonstrating the effect of an imposed electrical current on the degradation process are presented.

## 2. Basics

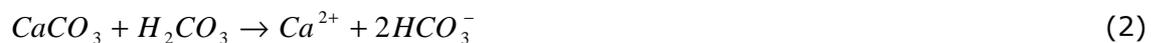
### 2.1. The chemical dissolution of concrete and mortar

Concrete or mortar exhibit a porous structure. The pores may have diameters from nanometers (gel pores) over micrometers (capillary pores) to millimeters (air pores). These pores form an interconnected network that is spreading throughout the entire concrete structure. The pores contain essentially  $\text{Ca(OH)}_2$ , which is dissolved in the pore solution but also as a precipitated salt. It is responsible for the high alkalinity of the pore solution and therefore for the passivity of steel embedded in concrete. Additionally, it has a buffering action with respect to chemical attack by carbonic acid.

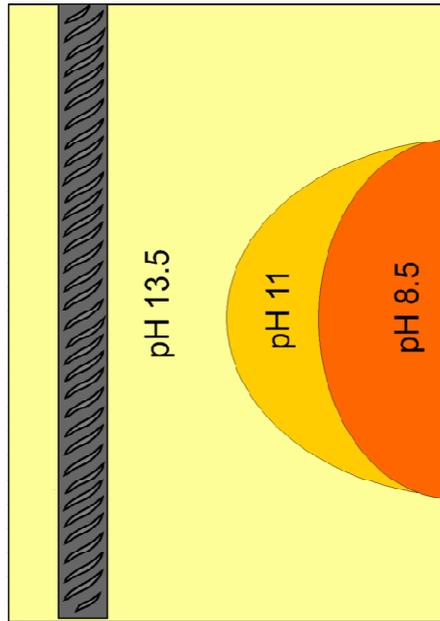
The chemical attack of concrete is proceeding through two stages. First carbonic acid will react with the calcium hydroxide and form calcite according to reaction (1).



The neutralization reaction (1) causes the filling of the concrete pores with calcium carbonate and the increase of the compressive strength. Additionally, a decrease of the pH in the range of 11 is observed. With proceeding neutralization of the concrete pores, reaction (2) becomes more and more dominant.



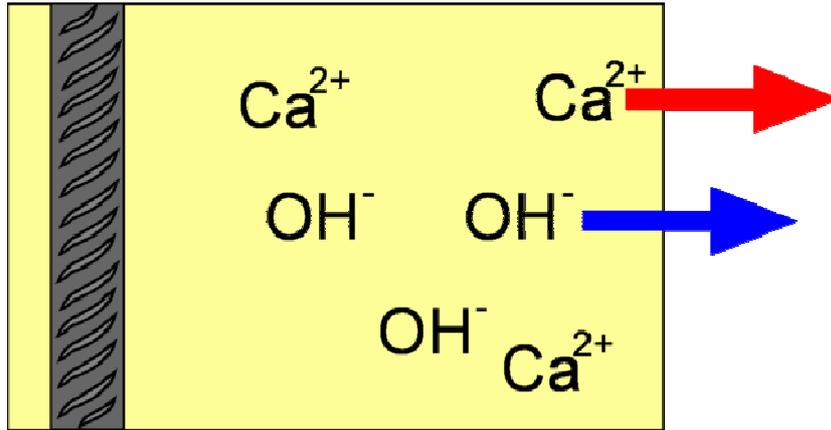
Reaction (2) decreases the alkalinity even further but also results in a chemical dissolution of the cement stone structure. The concrete or mortar surface becomes soft and the pH decreases to the range of 8.5. If this process continues over time, the soft stains can extend for several centimetres into the concrete structure. Eventually they reach the surface of the reinforcing steel and result in the initiation of corrosion. The schematic process caused by the chemical reaction of concrete with carbonic acid is shown in Fig. 2.



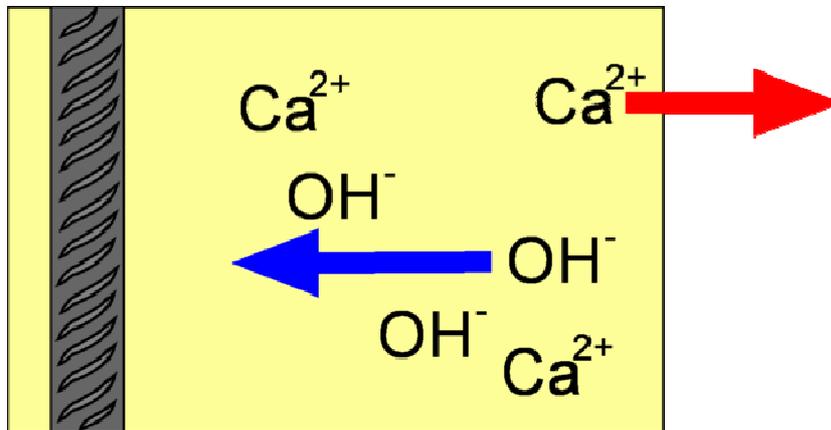
**Fig. 2:** Schematic representation of the process of stain formation according to reaction 1 and 2.

Based on the discussion of the mechanism of chemical attack of concrete it becomes clear that the presence of  $\text{Ca}(\text{OH})_2$  is critical for the resistance of concrete towards chemical attack. As a consequence, all processes that decrease its concentration in the pore solution result in a decreased buffer capacity and hence in an acceleration of the neutralisation reaction. The most relevant mechanisms are discussed in the following:

- The concentration difference between the drinking water and the concrete will result in diffusion of  $\text{Ca}(\text{OH})_2$  as shown in Fig. 3. As a consequence, a decrease in concentration in the concrete surface layers is expected over time.
- Pressure variations due to differences in filling level of the water reservoir can cause filling and emptying of larger pores causing a transport of  $\text{Ca}(\text{OH})_2$  due to water flow. Again this will cause a decrease in its concentration over time (Fig. 3).
- An electrical field can result in a migration of ions. Depending on the electrical current significant transport rates can be obtained. The electrical current can have various sources such as dc traction systems or galvanic corrosion processes. The contribution of an electrical current that is leaving the concrete surface is shown in Fig. 4.



**Fig. 3:** Transport of hydroxide and calcium ions by diffusion or pressure variations.



**Fig. 4:** Transport of ions due to an electrical current which is leaving the concrete surface.

## 2.2. Mitigation measures

### 2.2.1. Porosity

All discussed processes that result in a decrease  $\text{Ca}(\text{OH})_2$  concentration and that increase the susceptibility for chemical dissolution are influenced by the pore size and pore distribution of the concrete or mortar. Therefore, an increase of porosity and of pore diameter of cement based materials will result in an acceleration of the transport process. In contrast, the decrease in porosity will generally decrease the chemical attack and improve the durability. However, it is very difficult to obtain a homogeneously low porosity distribution due to manufacturing restrictions. But also temperature differences and condensating water during the curing of concrete or mortar were found to influence the surface properties and therefore the susceptibility with respect to the formation of stains.

### 2.2.2. Galvanic separation

Since electrical currents can contribute to the mass transport and a decrease of  $\text{Ca}(\text{OH})_2$  in the pore solution of the cement based materials, it can be beneficial to decrease or eliminate all galvanic couples that contribute to the galvanic current or cause it. This can be achieved by galvanic separation of all stainless steel surfaces, reinforcing steel, metallic pipelines, and earthing systems. This will not only decrease the risk of related galvanic currents that can support the formation of stains, but also decrease the potential risk of galvanic corrosion. Therefore, the migration of hydroxide ions away from the concrete surface into the bulk and the related decrease of surface pH can be decreased.

### 2.2.3. Saturation index

Based on the above discussion of the mechanism of stain formation it becomes clear that the alkalinity of the cement based material represents a buffer capacity towards chemical dissolution by carbonic acid. The discussed processes of  $\text{Ca}(\text{OH})_2$  transport, therefore, only represent a decrease of the buffer capacity. Even if migration, diffusion and flow of the  $\text{Ca}(\text{OH})_2$  out of the pore solution is completely stopped, the formation of stains is not necessarily eliminated. In the presence of aggressive water with an excess of carbonic acid the chemical dissolution of the cement based material according to reaction (1) and (2) can only be slowed down by a highly alkaline pore solution. But it will not be possible to stop it.

Therefore, an efficient method for increasing the durability is to modify the water in a way that it favors deposition of  $\text{CaCO}_3$ . The problem with most water storage facilities is, that the mixture of two different waters which are both in equilibrium with respect to the calcite carbonic acid equilibrium (reaction 2) will result in a water that is aggressive towards calcite. As a consequence, the water will have to be modified e.g. by addition of  $\text{NaOH}$  or  $\text{Ca}(\text{OH})_2$ . The increase in alkalinity will shift reaction (2) to the left and prevent the dissolution of calcite. In presence of an equilibrated water or water that is calcite depositing, the chemical dissolution of the cement matrix is expected to be strongly limited.

In addition to increasing the pH the increase of water hardness in the case of the addition of  $\text{Ca}(\text{OH})_2$  will additionally result in a better durability of the cement based material.

### 2.2.4. Electrochemical realkalisation

Instead of increasing the alkalinity of the water in order to adjust its calcite depositing properties it can be beneficial to generate the alkalinity just at the surface of concrete or mortar. This can be achieved by applying a cathodic current to the reinforcing steel. This is achieved by positioning an anode in the drinking water and imposing a driving voltage. The cathodic current on the reinforcing steel results in reduction of oxygen according to reaction (3) or the evolution of hydrogen according to reaction (4).



Both reactions result in the formation of hydroxide ions and therefore in an increase of pH at the steel surface. The current flow between the reinforcing steel and the anode will result in the migration of negative ions towards the concrete surface. This will cause an inversion of the transport direction shown in Fig. 4. As a consequence, the neutralization reaction between

carbonic acid and  $\text{Ca}(\text{OH})_2$  will be compensated. Moreover, the increase of surface pH can shift reaction (2) to the left and result in the formation of a dense surface layer of calcite.

### 2.2.5. Conclusions

The application of the discussed mechanisms for limiting the loss of alkalinity result in an improved durability of the cement based material in contact with drinking water. There is significant experience in the use of electrochemical realkalisation. Although the interaction with the drinking water composition and the detailed processes are not fully understood, it has proved to be an efficient way for limiting the chemical dissolution of the surface of cement based materials. Selected examples will be discussed.

## 3. Practical experience

Around 200 cementations water storage tanks have been successfully protected in Switzerland. Typically, mixed oxide titanium anodes were installed in the reservoir. They do not produce any anode sludge and allow imposing a controlled current via the control unit of the DC current source (Fig. 5).



**Fig. 5:** Anodes installed in a water reservoir



**Fig. 6:** Local formation of calcium carbonate at the concrete surface due to high protection current. Left side: no steel in concrete and no protection resulting in the formation of stains; right side steel wires embedded as cathodes in the concrete without formation of stains.

To limit the formation of stains current densities between 1 to 10 mA/m<sup>2</sup> are needed. As cathode connection the reinforcing steel is used. It has to assured, that all reinforcing steel in the storage tank is interconnected. The protection current is able to stop the growth of soft stains due to the increase in alkalinity at the concrete surface and possibly the formation of a dense calcite layer on the concrete surface. The two examples show that it is possible to realkalize the concrete.

In case 1 heavy stain formation occurred as shown in Fig. 1. The applied electrical current allowed for stabilizing the stain formation. However, in some areas with locally too high current the formation of calcium carbonate was found.

Case 2 significant formation of stains was observed also on the bottom of the tank, which did not contain any reinforcing steel making it impossible to realkalize the concrete surface of the bottom. As a consequence steel wires were embedded in the concrete surface as cathodes in order to insert the cathodic current. In Fig. 6 the effect of these local cathodes is clearly visible. On the left side no protection current could be inserted while on the right side the stain formation could be eliminated. On the right side the locally high current directly over the cathodes resulted in the deposition of calcium carbonate. Nevertheless, the growth of the soft stains could be stopped due to the electrochemical realkalisation.

#### **4. Conclusion**

The formation of soft stains in water reservoirs represents a serious problem not only because of the impaired visual appearance of the surface, but also because of a local drop of pH in the cementitious material. This favors the growth of microbiological cultures and in certain cases the local decrease of pH for several centimeters into concrete. This can result in the activation of corrosion of the reinforcing steel. Hence,

The stain formation is relevant for the hygienic conditions in the tank and in extreme cases for its structural integrity.

While the decrease of porosity is critical for the control of the problem, the effect of water hardness and saturation index may not be underestimated. The decrease of the pH of the pore solution, which may additionally be accelerated by pressure variations and galvanic currents, favours the chemical dissolution of the cement matrix.

In numerous cases the application of an electrochemical realkalisation of the concrete surface allowed for limiting the formation of stains and the formation of calcite on the surface. Moreover, the increase of the surface pH is expected to limit also the growth of microbiological colonies.