

103669

TREATED AND TERMINATED: SULPHURIC ACID ATTACK

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Mineral coatings protect waste-water treatment plants from the destruction of biogenous sulphuric acid corrosion "The stench is unbearable!". As residential areas are built up and populated more and more densely, local waste-water treatment plants often give rise to bitter, yet totally justified complaints by local residents. Many communities have obviously opted to solve an urgent problem quickly, only to find themselves in more trouble with high amounts of follow-up costs: foul-smelling clarifiers are frequently simply capped or enclosed. However, this supposedly safe measure creates new dangers, if there is no additional concrete protection as well. What kind of chemical processes can develop in these enclosed environments and how can damage to the concrete structure be avoided?

1. Introduction

Without a doubt, concrete has been the primary building material of the last and present century. Concrete is highly durable, in supply almost everywhere, easy to mould, and above all, inexpensive. 70 percent of post-war construction has been built with concrete. In the construction of water and waste-water treatment plants concrete is also the building material used most frequently. In fact, contemporary waste-water treatment plants could not be built in their present form without concrete.

The national capital investment of a country such as Germany, which is based in no small measure on over 10,000 communal waste-water treatment plants, is of almost inconceivable dimension. The maintenance of existing structures as well as the protection of new constructions is one of the major challenges that public authorities face today. It is an area where forward-planning and prudent actions are required, so that only sensible investments are made that utilize the latest technology and expertise that is available.

2. What Causes Damage to Concrete?

A high degree of industrialization, using water more sparingly, as well as new methods for freshwater and waste-water treatment, poses ever higher demands on the durability of concrete. Though concrete can withstand high mechanical and thermal stress, being an alkaline material has its limitations when coming under chemical acid attacks. A pH-value of 5 is the critical limit for unprotected concrete.

Municipal waste-water, which is fed into the treatment plant with a pH-value of 6.5...7, according to regulations, does initially not really attack concrete. This means, a primary attack through waste-water does not take place. However, as the waste-water moves through the various stages of treatment and sludge processing, there is a potential for secondary attacks through concentration of toxins or biological processes, which can cause a lot of damage to concrete.

In the case of domestic waste-water, the organic substances released during the biological cleaning phase are changed into biomass as carbon dioxide (CO_2) and hydrogen sulphide (H_2S) are separated. CO_2 , a gas that occurs naturally in our atmosphere at 0.03 Vol. %, is the trigger for the much-feared carbonation of concrete. This process does, however, not occur in the wet environment of a waste-water treatment plant.

H_2S is also a rather non-aggressive gas with regard to concrete, but is highly poisonous and the cause for the bad smell that was mentioned earlier. The odour threshold is as low as 0.1 ppm (parts per million), from 1 to 10 ppm odour is perceived as unpleasant. If a concentration of 0.1 Vol. % is reached, cramps and unconsciousness occur; only a few minutes' exposure to such a mixture can potentially be life-threatening.

In order to minimize the unpleasant and dangerous effects of hydrogen sulphide it frequently becomes necessary to cover or encapsulate the respective treatment stages. As a result of this structural change it is quite common for secondary biological processes to develop, especially when there is insufficient ventilation above the water level, the so-called 'headspace'. In these processes the micro-bacterial oxidation of *Thiobacillus* changes H_2S into the more concentrated sulphuric acid (H_2SO_4). In just a few months this can cause a rise in pH value, reaching from 1 to 2.5. This biogenous sulphuric acid is highly aggressive towards concrete, as it attacks the concrete in two ways: on one hand it has a dissolving effect, *i.e.* the cement stone matrix dissolves, on the other hand as a propulsive attack through the solidified waste product, *i.e.* the plaster that is created as a consequence of the chemical reaction. The ensuing crystal growth leads to an implosion within the concrete. Cracks appear, the damaging acid can penetrate even deeper into the concrete and destruction is accelerated.

3. Which Type of Coating Gives Effective Protection from Acid Attack?

Under these conditions unprotected concrete deteriorates rapidly. But which materials are suitable for preventive concrete protection that is safe, effective and durable up to a pH value of 1? Recent studies have shown that organic coating materials, such as epoxy resins and polyurethane, which give effective surface protection when bonding with substrates, have serious disadvantages in permanently wet conditions of waste-water treatment plants. Current findings of long-term observations in treatment plants confirm: the diffusion resistant organic coating systems are prone to a loss of bonding to the substrate because of internal water vapour pressure in

treatment basins – usually in contact with the ground – causing blistering and large surface de-bonding of the coating. Many treatment plants have experienced this phenomenon.

In addition, osmotic processes (the auto-balancing of concentration of concrete pore water content and water contained in the basin) lead to osmotic pressures that can also result in the de-bonding of organic coating systems, subsequently leading to blister formation and, finally, eliminating any kind of protection.

The ZTV-W regulations, regulating concrete repair measures for structures in connection with hydraulic engineering, have ruled out the use of organic coating systems in structures that are under constant influence from water for some time now. Similar active principles apply in sanitary engineering. Another serious disadvantage of organic coating systems: is represented by the fact that their resistance to abrasion is limited and, in the medium term, any damage to the surface renders the overall surface protection ineffective.

4. How Do Mineral Systems Operate that Are Open to Water Vapour Diffusion?

Mineral protection systems that are water vapour permeable on the basis of C₃A-free cements (see box) at least guarantee durable adhesion with the concrete substrate, so that water vapour permeability is ensured and the root cause for damage is avoided, as long as the coating is applied correctly. Their use in open treatment plants is highly effective.

However, what is needed is a system that is open to water vapour diffusion while at the same time being highly acid-resistant to pH < 3.5. In areas of treatment plants where such high levels of acid attacks occur, polymer silicate mortars have been successfully used for more than 10 years. These are purely mineral, cement-free protection systems that allow water vapour diffusion, in which an amorphous silicon gel forms a solid matrix that cannot be penetrated or damaged by acid and that lastingly bonds with the concrete. They are also able to withstand mechanical stress, in contrast to synthetic systems. Polymer silicates, also known as hydrogels, have excellent form and volume stability. They pose no health hazards for operators, have high thermal resistance and are also highly resistant to attacks from frost and de-icing salts.

5. How Are Polymer Silicate Systems Applied?

The polymer silicate system Konusit KK 10 by MC consists of a powder and a liquid component that are mixed together at a specified ratio. It is subsequently applied either by hand or spray application to the primed concrete substrate. The surface may well be damped at the time of application. It is important, however, to achieve the required layer thickness of 8 mm to ensure the relevant impermeability of the system against liquids. After just 7 days of hardening the system is fully operational.

The use of this protective system in treatment plants has been monitored for more than 10 years, recording the experiences of plants and testifying the impressive and lasting effectiveness of the system. Time lapse tests have shown that the polymer silicate mortar Konusit KK 10 is resistant to sulphuric acid attacks with a pH value of 1 for several decades, if applied accurately. A fact that has been attested by numerous independent institutes.

For several years MC has been in the process of establishing a licensed product distribution system around the world for Konusit KK 10. Today Germany has a sufficient number of specialist applicators, who are experts in the application of polymer silicate technology. These companies receive detailed instructions and application training and benefit from annual follow-up training sessions. This is a highly sophisticated surface protection system and in this way quality standards are ensured.

6. What Are the Costs for Concrete Protection?

Given the high costs for the repair of secondary damage, investing in durable concrete protection makes economic sense. In capped processes only the headroom and the corresponding water transfer zone need to be treated and not the entire internal basin surface. The cost of a polymer silicate system only amounts to 0.5 to 1% of the overall construction sum of a newly-built treatment plant.

The subsequent application of a protective system usually causes additional costs, which are significantly higher than the actual repair costs, as it becomes necessary to shutdown basins or pump equipment during maintenance works or because the waste-water flow has to be diverted into alternative waste-water treatment plants.

7. Conclusion

To protect concrete in treatment plants with open basin systems, where in addition to the waste-water itself, thermal effects (freeze-thaw cycle) and biological growths in the water transfer zone are the typical culprits, highly impermeable and hardened cement mortars such as MC-RIM or MC-RIM-F can be used which are resistant to strong acid attacks (up to $\text{pH}=3.5$). These protective systems have been designed on the basis of C_3A -free cements and are sulphate compatible. The reprofiling mortar Nafufill GTS or Nafufill KM 250, which are part of the MC-RIM or MC-RIM-F protective system, have also been formulated on the basis of C_3A -free cements, providing a complete and optimized repair package for any conceivable requirement in the area of waste-water technology.

Received, February 4, 2008

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R E F E R E N C E S

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PROTEJAREA BETONULUI LA ACȚIUNEA ACIDULUI SULFURIC

(Rezumat)

Stratificarea minerală protejează instalațiile de epurare împotriva coroziunii distrugătoare biogene provocate de acidul sulfuric.

Instalațiile de epurare provoacă, în regiuni dens populate, plângeri în masă și total îndreptățite ale locuitorilor. Anumite comune au rezolvat această problemă evidentă rapid provocând astfel supărare și cheltuieli: bazinele de limpezire urât mirositoare sunt de cele mai multe ori doar acoperite. Totuși această măsură, care se presupune a fi sigură, aduce cu sine, fără protecția betonului, noi pericole. Ce procese au loc sub capac și cum pot fi evitate efectele dăunătoare asupra elementelor de construcție din beton?

Fără îndoială betonul este materialul de construcție al secolului trecut și al secolului acesta. El este de o durabilitate ridicată, disponibil aproape peste tot, ușor modelabil și mai presus de toate avantajos ca preț. 70 la sută din substanța construită după război a fost realizată din beton. Betonul este de asemenea materialul de construcție cel mai utilizat la construcția instalațiilor de alimentare cu apă și evacuare a apei uzate. Fără beton nu ar putea fi construite instalațiile de epurare în forma în care este posibilă astăzi. Proprietatea națională într-o țară ca Germania, care a construit peste 10 000 de instalații de epurare a apei, are o dimensiune neînchipuită iar întreținerea substanței construite existente, cât și protejarea noilor instalații, prezintă una din cele mai mari provocări pentru finanțările din fonduri publice. Aici este necesară, în special, o procedură prevăzătoare și înțeleaptă pentru a introduce investiții într-un mod util și pentru a lua în considerare toate cunoștințele și experiența disponibilă în prezent.