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# Sulphur Attack, Key Factor in Concrete Works Safety and Environment Protection

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## Abstract

*The main aspects in correlation with concrete works degradation as the origin of aquatic environment salinity due to sulphur, the premises and types of concrete corrosion, and the sulphur corrosion are presented. This study focused on the drinkwater and wastewater treatment constructions in concrete that are exposed to corrosion induced by the sulphur compounds. The theoretical aspects constituted the base of a study carried-out on sulphur corrosion and its evolution at concrete works of drinking water treatment plant in Botosani County, in Northeast Romania, during the fifteen-year period and also the wastewater concrete works. The results were useful to choose the opportune feed-before measures for constructions, people and environment.*

**Key words:** sulphur corrosion, hydraulic parameters, premises and types of concrete corrosion

## 1. Introduction

The hydrotechnic constructions are different from other engineering constructions, especially by the aquatic environment (dynamic or static, aggressive or neutral) with that are in contact (permanent or intermittent) and by the socio-economic disaster as unsafe operation outcome.

These aspects give to the hydrotechnical works some specific features regarding the constructive solutions, the execution technology, calculation methods, materials, their technical conditions and also the importance class. The main materials used in the hydrotechnical constructions are the concrete and the steel.

The operation safety of a concrete hydrotechnic work is continuous diminished in time by the independent or the simultaneous action of the external aggression and of the internal changes of concrete matrix. The external elements may be of physical, chemical or biological nature, but the most destructive are the environment corrosion and erosion, repeated freeze – thaw cycles, recurrent variations in humidity. The alkali – aggregates reactions, the volume variations produce, by the distinct thermal characteristics of aggregates and cement paste, the expansion of some damaging constituents that are found excessively in cement and the permeability represent the main internal factors.

## 2. Origin of Aquatic environment salinity due to sulphur

By their destination, the hydrotechnic works are in contact with waters of different qualities. Thus, the seaside constructions are in contact with seawater, having an increased mineral and organic content; the inland waterway constructions and the bridges - with poor mineralised waters but with high organic content; the drinking water systems - with river or lake waters having aggressive variations in time and space of mineral content, and the wastewater treatment plants - with water very rich in organic and inorganic compounds, and pathogen agents. The river harbour constructions, retention constructions, raw water pipes, water reservoirs, tubes and structures from sewage network and plant offer favourable conditions for micro-organisms to develop on the concrete surfaces.

The constructions for drinkwater or wastewater treatment are exposed to chemical corrosion induced by the acid character of coagulant solutions, oxidant products etc. and/or to biochemical degradation.

The presence of soluble salts in waters or soils is expressed by salinity. The occurrence of salinity depends on several factors, the most important of which are the characteristics of the landscape, the climate, and the effects of human activities.

The natural sources are: rainfall which carries low concentrations of salts that have accumulated in the atmosphere over thousands of years; erosion of surface rocks; groundwater that has soaked through sediments and sedimentary rocks that originally formed in marine environment. The salts content varies from 35 g/l for oceans, to 15 g/l for Romanian Black Sea coast, to scanty salinity for rivers. Water's noxiousness increases in the area of the industrial water discharge.

The chemical content of the surface water issues from contact processes at the water-air and water-land interface. At the atmosphere-water interface, the particles of the atmosphere (gases -  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{CO}_2$ , mineral and organic powders in suspension) are carried by the rainfall within the surface waters. At the water - land interface, the water dissolves the minerals and the rocks, in a process which depends, quantitatively and qualitative, by their composition, by the surface and the period of contact, the environment's temperature. Some minerals (alkaline chlorides, limestone, gypsum) dissolve in water without some chemical reactions being needed, other dissolve as a result of some complex process (hydrolysis, hydration, redox, micro-organisms' activity).

### 2.1. Dissolution

In nature, the common dissolution of minerals, without changing properties or without the participation of other compounds, is very rarely. The quartz is the most important mineral which dissolves in this way. The minerals as  $\text{NaCl}$ ,  $\text{CaSO}_4$  suffer a simple dissolution.

#### 2.1.a. Dissolution by hydration

Mineral hydration is a form of chemical weathering that involves the rigid attachment of  $\text{H}^+$  and  $\text{OH}^-$  ions to the atoms and molecules of a mineral. When minerals take up water, the increased volume creates physical stresses. For example, the hydration of anhydrite ( $\text{CaSO}_4$ ) forms gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

#### 2.1.b. Dissolution by hydrolysis

Hydrolysis is a chemical weathering process affecting silicate minerals especially. The weak acids salts with strong basis, the strong acids with weak basis or weak acids with weak basis suffer the reaction of hydrolysis, meaning that they create with water weakly-dissociated

compounds. The result of hydrolysis is the dissolution. For instance, some reactions regarding sulphur compounds:  $\text{FeSO}_4 + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + \text{H}_2\text{SO}_4$ ;  $\text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} = 2\text{Al}(\text{OH})_3 + 3\text{H}_2\text{SO}_4$ ;  $\text{CuS} + 2\text{H}_2\text{O} = \text{Cu}(\text{OH})_2 + \text{H}_2\text{S}$ .

## **2.2. Oxidation**

In the horizons prone to alteration, many elements change their bonds through valence, yet only four elements are important from a quantitative point of view: carbon, sulphur, iron and oxygen.

### **2.2.a. Sulphur oxidation**

The sulphur in lithosphere is divided almost equally between sulphates (gypsum and anhydrite are very important) and sulphides (iron pyrite is the most important).

During alteration, gypsum and anhydrite dissolve, but pyrite and other sulphures of iron oxidize ( $\text{Fe}^{2+}$  turns into  $\text{Fe}^{3+}$ , and  $\text{S}^{2-}$  into  $\text{SO}_4^{2-}$ ). The hydrogen ions released during this process attack a range of minerals from the soil. If carbonates are present, these tend to neutralize the sulphuric acid, so:  $\text{CaCO}_3 + 2\text{H}^+ + \text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2$ . In silicate soils,  $\text{H}_2\text{SO}_4$  reacts with these ones to extract out  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  ions, originating from silicates and ferromagnesian minerals especially.

## **2.3. Other processes responsible for the concrete deterioration**

The concrete alteration may be produced by dissolution under the influence of pH and bacteria, by entraining some constituents, adsorption and ionic change.

### **2.3.a. Dissolution due to the pH**

The waters which contain high quantities of humic acids, carbonic acid, and **hydrogen sulphide** render soluble the alkaline rocks (oxides, carbonates). But the waters which contain high quantities of earthy-alkaline carbonates ( $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ), having alkaline character, render soluble the rocks with acid minerals (sulphates and nitrates).

### **2.3.b The involvement of some compounds**

The clay content in soluble salts is poor, so the water can render soluble only the salts existing on the clay's surface. Higher the water content in alkaline chlorides the bigger is the action to render soluble the gypsum and limestone.

### **2.3.c. Adsorption and ionic change**

Two characteristic aspects may be distinguished: a) adsorption of mineral ions by the colloidal substances in suspension or deposited; b) ionic change between aqueous solution and the contact rocks.

The colloidal particles from water, mainly formed of humus and clay minerals, adsorb at their surface  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  ions, respectively  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  ions.

## **3. Premises and types of concrete corrosion**

The size and stability of contact surface between concrete and water are different on the structure height and, so, four areas may be delimited:

- up to the water level, that is never wet, but exposed to bad weather, atmospheric temperature-humidity changes;

- at the water level variations, exposed to waves action, freeze – thaw cycles, water penetration, biological aggression;
- submerged area, exposed to mechanical, chemical and bio-chemical aggressiveness of water;
- underground area, exposed to groundwater chemical action.

The water chemism (mineralization, nutrients concentration, organic load, oxygen regime, toxic substances presence) have a hard influence on the areas at 2-nd and 3-rd position.

The concrete processing (mixing, curing, placing, finishing, and maintenance) matters a good deal in concrete durability. The composition and compactness of the concrete, and the W/CM ratio play a significant role in the total porosity of future structure.

The hydrodynamic parameters of contact water (depth, flow velocity, hydraulic state, size and duration of pressure gradient) influence the concrete corrosion, also.

In natural or industrial conditions, very rarely can be met the isolated manifestation of a single type of corrosion. The hydrotechnic works in concrete are simultaneously exposed to more types of corrosion which amplify each other, even if apparently there is a prevailing cause.

The concrete corrosion is the effect of:

- a) selected dissolving of mineral constituents of cement stone, firstly of calcium hydroxyl with their gradual transformation in gels, predominating the hydrated silica gel;
- b) chemical interaction of the cement constituents with aggressive environment, that leads to easy-soluble salts or amorphous salts, lack of binding properties;
- c) chemical processes between the cement compounds and the aggressive salts from water, resulting products that lay down and crystallise in the capillary pores and fissures of the concrete, destroying the concrete matrix.

## 4. Sulphate corrosion

### 4.1. Sulphate ions responsible for concrete weathering

The sulphate ions ( $\text{SO}_4^{2-}$ ) react with hydration products present in hardened cement such as tricalcium aluminate  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ , calcium hydroxide  $\text{Ca}(\text{OH})_2$  and calcium silicate hydrate  $(\text{CaO})_3(\text{SiO}_2)_2(\text{H}_2\text{O})_8$ . The chemical mechanisms of sulphate-related deterioration are expressed by expansive reactions between cement stone constituents and sulphate ions, originated from internal or external sources. The expansion may be a result of oriented crystal growth, crystallization pressure, swelling phenomena etc. The sulphate ions arise from dissociation, in solution, of the sulphur acid and its salts (alkaline sulphates, calcium and magnesium sulphate, ammonium sulphate) which are noxious to the concrete. The aggressiveness due to the sulphate ions depend on also the kind of cations. The water insoluble sulphates (i.e. barium sulphate, lead sulphate) are inoffensive, and no affect the concrete matrix.

The presence of sulphate ions in water increases the solubility of cement components, favouring the corrosion by dissolution, leaching and swelling. As well, the sulphate ions may induce double replacement reactions, resulting amorphous salts lacked of binding properties, associated with decalcification of cement paste in concrete.

In the first phase of corrosion, the sulphates from solution react with calcium hydroxide from concrete, creating calcium sulphate (gypsum):  $\text{SO}_4^{2-} + \text{Ca}(\text{OH})_2 + 2\text{HOH} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \downarrow + 2\text{H}_2\text{O}$ . The formation of gypsum makes the concrete softer and can lead to failure and collapse of the concrete structure. But, the presence of some substances could increase or decrease the

gypsum solubility. So, the sodium chloride in concentration of 2 - 4% increases the calcium sulphate solubility 2.5 - 2.8 times, but CaO decreases the calcium sulphate solubility in water with 20%.

In the next stage of chemical interactions between sulphate solutions and cement, the sulphate ions can react with calcium hydroaluminates, creating a complex salt of calcium hydro-sulphate-aluminate type. So, from the reaction with sodium sulphate results the etringite (hexacalcium aluminate trisulphate hydrate):  $3(\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}) + 2(3\text{CaAl}_2\text{O}_3 \cdot 12\text{H}_2\text{O}) \rightarrow 3\text{CaO Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31 \text{H}_2\text{O} + 2\text{Al}(\text{OH})_3 + 6\text{NaOH} + 17\text{H}_2\text{O}$ . The reaction is accompanied by big crystallisation forces making a strong expansion, cracking and destruction of the hydrated paste. The mortar or the concrete loses its resistance, then, by swelling, detachment and decomposition, it completely degrades. Damage develops in time.

The magnesium sulphate reaction with hydrosilicates and calcium hydroaluminates, as well as with calcium hydroxide is  $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O} + 3\text{CaO} \cdot 2\text{SiO}_2 \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Mg}(\text{OH})_2 + \text{SiO}_2$ .

The cation character of sulphatic substances from the aggressive solutions is another condition for the intensity of sulphate ions penetration in cement stone. So, the diffusion of  $\text{SO}_4^{2-}$  ion came from a  $\text{MgSO}_4$  solution of a certain concentration (which doesn't suppose important deposits of  $\text{Mg}(\text{OH})_2$ ) will have a higher speed than in the case of a  $\text{Na}_2\text{SO}_4$  solution of the same concentration, due to the higher energy of the double replacement reactions between magnesium salts and the cement stone hydrates. When forming the etringite occurs, the amplitude of the solid phase growth depends on the nature of hydro constituents it came from. When the reaction starts from tricalcium hydroaluminate, the volume increase is 1.63 times, and in saturate solutions of  $\text{Ca}(\text{OH})_2$  this growth is 2.27 times higher with concrete destruction.

From thermodynamic point of view, the forming and the stability of sulphataluminate hydrates depends on environment's pH, the favourable one being  $\text{pH} \geq 10.8$ , while gypsum crystallization is possible on almost every pH.

The ammonium sulphate presents a very intense aggressivity; it forms, with calcium hydroxide, gypsum and ammonia, the sulphatic corrosion, connected to that produced by ammonia.

The sulphatic corrosion speed over concrete is higher with the solution's concentration and the process permanence. It is influenced by the water's pressure which contains sulphates, by its action over the concrete elements, by the way of exposure, temperature, the alternation drying-humidity. The concrete submitted to sulphate aggression has a whitish specific aspect, and the degradation starts regularly with the element's borders and corners, being followed by cracking and progressive exfoliation.

Regarding the sulphate solutions actions whose constituent cations form soluble hydroxides, the corrosion's intensity grows with the concentration, without establishing a direct proportionality. Regarding the solutions of magnesium, copper, calcium, and potassium or the sodium sulphates, in the conditions of an absence of the protective role of  $\text{Mg}(\text{OH})_2$  and  $\text{Cu}(\text{OH})_2$  deposits, a certain regularity in the corrosive intensity of these sulphate salts can be observed, depending on the metallic ions' character, corresponding to the series:  $\text{Mg}^{2+} \approx \text{Cu}^{2+} > \text{Ca}^{2+} > \text{K}^+ \approx \text{Na}^+$ .

A parallelism can be observed between the corrosion intensity and the ionic potential of metallic cations constituent of sulphate salts. The growth of ionic potential indicates a decrease of cations' basicity, so a decrease of the solubility of respective hydroxides and this fact involves an intensification of the reactions:  $\text{Ca}(\text{OH})_2 + \text{MSO}_4 \xrightarrow{+\text{H}_2\text{O}} \text{M}(\text{OH})_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Ca}(\text{OH})_2 + \text{M}_2\text{SO}_4 \xrightarrow{+\text{H}_2\text{O}} 2\text{MOH} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  with the consequences they imply over further reactions and over chemical processes accompanied by expansion. Then when the protective effect of the insoluble hydroxides deposits manifests, the order of corrosive action above mentioned modifies, the solutions of magnesium sulphate and copper sulphate being less. In practice, the degradation with sulphates is less severe than in the laboratory, as a result of the inhibitor effect of the chlorides in water.

## 4.2. Other sulphur compounds action

Sulphur gases (sulphur dioxide  $\text{SO}_2$ , sulphur trioxide  $\text{SO}_3$ , hydrogen sulphide  $\text{H}_2\text{S}$ ) present a corrosive action of worthy consideration. In high environmental humidity, sulphur gases act through acid aggressivity, because, directly or by oxidation, can become sulphuric acid ( $\text{H}_2\text{SO}_4$ ) whose action supposes the association of acid aggressivity with sulphatic corrosion.

The sulphuric acid reacts with the concrete, increasing the permeability. This type of deterioration is known as "crown rot".

Elemental sulphur sometimes is used as an additive to concrete, to improve its properties, but the conventional concretes can be susceptible to attack by sulphates.



**a.** **Fig. 1.** Radial settler D 25 m. **a.-** Cracks in the crain-beam and columns due to sulphatic corrosion and level variations; **b.-** Detail **b.**

## 4.3. Biochemical corrosion of concrete with sulphur involvement

The bio-chemical corrosion of concrete is due to the acidic action (acetic, formic, and lactic acid) of bacteria, alga, and lichen on the calcium hydroxide from the cement stone and aggregates as well as due to the modifications made to some substances of the environment.

### 4.3.a. Biological weathering

Lichens, mosses, algae, bacteria grow on essentially those surfaces in contact with water and create a more humid chemical microenvironment. The attachment of these organisms to the concrete surface enhances physical as well as chemical breakdown of the surface micro layer.

### 4.3.b. Bacteriogenic acid corrosion

The bacterial acid corrosion may result in aerobic or anaerobic medium, but in different ways.

**The anaerobic bacteria** reduce the sulphur compounds from organic matter existing in water till hydrogen sulphide gas that interacts with calcium hydroxide and forming calcium sulphide:  $H_2S + Ca(OH)_2 \rightarrow CaS + 2H_2O$ . In moist environment, this calcium sulphide is oxidized in calcium sulphate that by expansion destroys the concrete mass:  $CaS + 4H_2O \rightarrow CaSO_4 + 4H_2$ .

This type of sulphur attack is the predominant one in wastewaters treatment plant. The septic tank is a biochemical reactor, where anaerobic reactions occur to break down solids into gaseous compounds, which are primarily  $CO_2$  (carbon dioxide) and  $CH_4$  (methane). In wastewaters high in sulphates or sulphides, the anaerobic bacteria produce hydrogen sulphide.

**The aerobic bacteria** oxidize sulphide hydrogen to sulphur acid, ( $H_2SO_4$ ) producing acidic corrosion:  $H_2S \xrightarrow{\text{oxidation due to the aerobic bacteria}} H_2SO_4$

The presence of oxygen from wastewater inflow or from the air space in the septic tank and the moisture on the concrete sidewall tank allow aerobic bacteria to grow and to convert the exsolved hydrogen sulphide into sulphuric acid which corrodes the concrete.



Fig. 2. Surface-aerated basin. a.- sidewalls deteriorated by bio-corrosion; b., c.- details

## 5. Case study

These theoretical aspects were the base of a study carried-out on the deterioration evolution at reinforced concrete constructions from Water supply system in Botosani County, during a period of 15 years.

The degradation' surveillance produced by sulphur compounds over concrete constructions was one of the followed objectives.

It was found out that the most damaged are the buildings of drinking water treatment plant and of wastewater treatment plant. The degradations are not produced only by sulphur attack, but are the consequence of the synergical action between numerous human and natural agents.

Near the monitoring data, an important archive of photo-documents was obtained, from which some are presented in this paper.

For example, at the clarifier  $D = 35$  m,  $H = 6.7$  m, made up of prefabricated elements of reinforced concrete, technological errors (concrete segregation, pouring deficiency, cracks in

prefabricated elements, the lack of external finishing) favoured and accelerated the degradation of the building by sulphatic corrosion.

At the radial settler  $D = 25$  m, the crain-beam and columns have suffered from water acidity and level variations (Fig. 1).

In the wastewater treatment plant, the sidewalls of surface-aerated basins were deteriorated by bio-corrosion (Fig. 2).

## 6. Conclusions

The engineering constructions must give both resistance-stability and durability. Beside, the hydrotechnical constructions must resist to the physical - chemical destructive action of the water, to the biological aggressiveness and to the action of waves, ices and alluvia.

The sulphur attack on concrete leads to detrimental chemical - physical changes, increasing permeability and decreasing mechanical properties of the concrete.

It is necessary to pay more attention to environmental factors and operating agents during the design and construction stages, so as to prevent the need of major investments during the operation or rehabilitation stages of concrete hydrotechnical structures.

The monitoring data and the studies were useful to choose the opportune feed-before measures (prevention, protection and repair) for constructions, as well as for people and environment.

## References

1. Blăgoi O., Georgescu M. – *Sur l'utilisation du sulfate d'aluminium dans les petites et moyennes stations de traitement*. In Proc. I-st International Conference „Gândirea Științifică Modernă. Realizări și perspective“, Sect. II, p. 76-85, Chișinău, Rep. Moldova, 1997.
2. Georgescu M. – *Research on the safety of the concrete constructions from water supply system (Botosani)* PhD thesis, (in Romanian), „Gh. Asachi” Technical University of Iasi, 2006.
3. Ionescu I., Ispas T. – *Proprietățile și tehnologia betoanelor*. Ed. Tehnică, București, 1997.
4. Oneț T. – *Durabilitatea betonului armat*. Editura Tehnică, București, 1994.
5. Teodosiu C. – *Tehnologia apei potabile și industriale*. Editura MATRIX ROM, București, 2001.
6. Patraș B., Blăgoi O., Georgescu M. et. al. – *Aging by Corrosion of Hydraulic Concrete Constructions, Major Risk Factor*. Proceedings of International Scientific Conference “VSU’2007” of Higher School of Civil Engineering “Lyuben Karavelov”, II Session “Building Structures”, Vol. I, p. II.113 – II.117, Sofia, Bulgaria, 15-16 May 2007.
7. Varduca A. – *Hidrochimie și poluarea chimică a apelor*. Editura “H.G.A”, București, 1997.

## Atacul sulfului, factor cheie în siguranța lucrărilor din beton și protecția mediului

### Rezumat

*Se prezintă principalele aspecte legate de degradarea construcțiilor din beton precum originea salinității produse de sulf în mediul acvatic, premisele și tipurile de coroziune a betonului, coroziunea produsă de sulf. Atacul sulfului asupra betoanelor duce la modificări fizico-chimice defavorabile. Particularizarea se îndreaptă spre construcțiile din beton pentru tratarea apei potabile și apei uzate care sunt expuse la coroziunea produsă de compușii sulfului. Aspectele teoretice au stat la baza unui studiu efectuat timp de 15 ani, privind coroziunea construcțiilor din beton din stația de tratare a apei din Botoșani, care a fost oportun pentru alegerea măsurilor de reabilitare a construcțiilor, de protecție a populației și mediului.*