DEGRADATION OF BRICKS AND TILES

PART 1 - A REVIEW OF PROCESSES

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INTRODUCTION

Degradation of bricks and tiles is a problem whose solving requires application of knowledge from a few different fields of science and engineering, such as chemical-, civil- and environmental- engineering, architecture, economy, etc. This paper considers chemical- engineering aspects only. It considers degradation of material due to parallel and/or consecutive chains of chemical reactions and related physical changes. First and the most important step towards understanding of such kind of degradation are investigation of processes (and their mechanisms) which cause deterioration of materials.

Essential factors which influence responses of material to any attack from environment are its composition and structure. As everybody knows, during production of bricks and tiles (especially, during sintering) stable initial raw materials (clays, microcline, albite, quartz and other minerals) transform into complex, high temperature compounds (wollastonite, diopside, gehlenite, anortite, sillimanite, mullite, etc.). When exposed to water influence, these complex compounds become unstable and tend to return previous form. Very often, degradation is caused by appearing of certain, new compounds - products of chemical reactions among constituents of bricks and tiles and aggressive ions, such as SO₄, NH₃, CO₃, etc., dissolved in water. Particularly sensitive are aluminosilicates that contain: Ca, Mg, K, Na, Fe, etc. So, hydrates, sulphates, carbonates and other compounds might appear, which is undesired due to the various reasons. They can provoke further chemical reactions and/or can dissolve thus developing the degradation.

Solubility of both groups of compounds, primary present and secondary obtained by degradation, is great problem that will be specially analyzed. When such

compounds are exposed to direct influence of rain, they can be leached out and washed away from the surface parts of bricks or tiles. Cumulative results, visible after longer period of time, are serious damages due to the fact that certain parts of walls and roofs were physically removed and taken away. In this way, chemical degradation directly causes physical degradation, so that an expression: "chemically induced physical degradation" can be used.

Not only newly formed compounds decrease general stability of material but they usually contribute to the change of volume of the system. It decreases or increases thus causing contraction or expansion. Since the system is rigid, it is exposed to deformation stresses and, as a consequence, smaller or greater cracks may appear. So opened system is less resistant in many ways. It is particularly less resistant to further water and frost action. Obviously, physical degradation is related to chemical degradation and vice versa. However, there is degradation that can be regarded as pure physical. It is degradation due to frost attack. Finally, degradation of material due to development of various microorganisms and plants is possible. This kind of material deterioration is known under the term: "biodegradation".

CHEMICAL DEGRADATION

Influence of composition and structure

In the presence of water, oxygen, carbon dioxide and other acidic gases, stability of the compounds formed at high temperatures decreases. This fact can be proved by considering the natural degradation (so called alteration) on rocks and stones [1,2]. Such systems were obtained by solidification of magma that had temperatures among 1200 °C and 700 °C. In this

way many minerals, such as olivine, fayalite, pyroxen, feldspars, zeolite, etc., appear. They all have tendency towards degradation due to hydrolysis, hydration, oxido- reduction, silification and wash away of alkaliand earth-alkali- metals from the crystal lattice. They easily react with water and some dissolved gasses (carbon dioxide, SO₂, etc., [3]). Table 1 illustrates the conversion of high- temperature minerals to the low-temperature compounds, caused by water, at particular stages of degradation.

According to the level of their stability, degradation products can be classified as in table 2. At

the top, one can put unstable, high-temperature minerals (found in earth), while the low-temperature minerals (which are hydrated and therefore more resistant to water influence) take the positions at the bottom. Stability of the aluminosilicates increases with the increase of degree of polymerization of the SiO₄⁴-tetrahedrons. This is very well illustrated by the table 3. It contains examples that show possible structures of the aluminosilicates. A kind of ranking given in table 3 contributes to better understanding of the degradation processes illustrated by tables 1-2.

Table 1. Products of degradation of minerals and compounds by water.

degradation level	mineral	free ions	degradation products
early stage	olivine	Fe ²⁺ , Mg ²⁺	clays, hematite, limonite
·	pyroxen	Fe^{2+} , Ca^{2+} , Mg^{2+}	clays, hematite, limonite
	amphibole	Fe^{2+} , Ca^{2+} , Mg^{2+}	chlorites, zeolites, clays
	K-feldspars	K ⁺	clays
	Ca, Na-feldspars	Na^+ , Ca^{2+}	clays
	calcite	Ca^{2+} , CO_3^{2-}	calcite
	gypsum	Ca^{2+}, SO_4^{2-}	gypsum
intermediate stage	micas	K ⁺ , SiO ₂	hydroxymica, clays
	zeolites	Mg^{2+} , Ca^{2+} , K^+ , Na^+	clays
	clays	Mg^{2+} , Ca^{2+} , K^+ , Na^+	boxite, hematite, limonite
late stage	clays	SiO,	gibbsite
	gibbsite	-	gibbsite
	quartz		quartz
	hematite		hematite

Table 2. Relative stability of particular silicate minerals. (Stability increases towards the bottom end of the table.)

olivine: (Mg,Fe),SiO, Ca-plagioclase: CaAl₂Si₂O₈ fayalite: Fe₂SiO₄ gehlenite: Ca₂Al₂SiO₇ augite: Ca, Na-plagioclase: (Ca, Na)(Mg, Fe, Al)(Si, Al)₂O₆ CaAl₂Si₂O₈ - NaAlSi₃O₈ chornblende: Na, Ca-plagioclase: $Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$ NaAlSi₃O₈ - CaAl₂Si₂O₈ biotite: Na-plagioclase: $K(Mg, Fe)Si_3(Al, Fe)O_{10}(OH)_2$ NaAlSi₃O₈

> K-feldspar: KAlSi₃O₈

 $\begin{array}{c} muscovite: \\ KAl_2AlSi_3O_{10}(OH)_2 \end{array}$

zeolite: gismondine: CaAl₂Si₂O₈ 4H₂O

clays:

montmorilonite: (Na, Ca)_x(Al, Mg)₂Si₄O₁₀(OH)₂ nH₂O halloysite: Al₄Si₄O₁₀(OH)₈ 4H₂O kaolinite: Al₄Si₄O₁₀(OH)₄

opal: SiO₂ nH₂O quartz: SiO₂

While sintering of bricks and tiles, the compounds, similar to the mentioned minerals found in nature, appear [4, 5]. Therefore, there is an analogy among their behaviour. So, tendencies of chemical reacting with water show many calcium silicates, calcium aluminates and calcium aluminosilicates, present in bricks and tiles. Thermodynamically, hydration is fa-

vouring process, that gives more stable products than the reactants. Unfortunately, such compounds do not posses satisfied mechanical characteristics. It makes them rather undesired with regard to durability. Besides that, water absorption can effect an extension of volume of molecules thus causing physical destruction of the system.

Table 3. Structures and types of silicates present in bricks and tiles.

structure of the SiO ₄ -tetrahedra	formula	type and comment	Si:O ratio	example
\triangle	SiO ₄ ⁴	orthosilicate (nesosilicates)	1:4	olivine: (Mg,Fe) ₂ SiO ₄ fayalite: Fe ₂ SiO ₄ sillimanite: Al ₂ SiO ₅
	Si ₂ O ₇ ⁶⁻	pyrosilicate (sorosilicates)	1:3,5	gehlenite: Ca ₂ Al ₂ SiO ₇
	Si ₃ O ₉ ⁶⁻	cyclosilicate (sorosilicates) -not present in bricks & tiles	1:3	benitoite: BaTiSi ₃ O ₈ cordierite: (Mg,Fe) ₂ Al ₄ Si ₅ O ₁₈
	$(SiO_3^2)_n$	pyroxene (inosilicates)	1:3	enstatite: MgSiO ₃ diopside: (Ca,Mg)SiO ₃
	$(Si_4O_{11}^{6-})_n$	amphiboles (inosilicates)	1:2,75	tremolite: $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$
	$(Si_4O_{10}^4)_n$	chlorites, micas, serpentines, clays (phyllosilicates)	1:2,5	muscovite: KAl ₂ (AlSi ₃ O ₁₀)(OH) kaolinite: Al ₄ Si ₄ O ₁₀ (OH) ₈
	$(Si_{4-x}Al_xO_8^{x-})_n$	feldspars, zeolites (tectosilicates)	1:2	orthoclase: KAlSi ₃ O ₈ anortite: CaAl ₂ Si ₂ O ₈ margarite: CaAl ₄ Si ₂ O ₁₁ nH ₂ O gismondine: CaAl ₂ Si ₂ O ₈ 4H ₂ O
	(SiO ₂) _n	silicium-dioxide (tektosilicates)	1:2	opal: SiO ₂ nH ₂ O quartz: SiO ₂

As for the sulphates, the main sulphate bearing compounds in bricks and tiles are anhydrite (CaSO₄) and gypsum (CaSO₄ 2H₂O). They might be brought by raw materials or might appear after sulphate attack from the environment [6, 7]. Chemically polluted air in cities and industrial zones is almost always characterized by high contents of sulphurdioxide (SO₂) which, after photochemically induced oxidation, converts into sulphurtrioxide (SO₃). Sulphurtrioxide easily reacts with moister from air giving sulphuric acid (H₂SO₄). Acid rains and acid water precipitations in early morning hours bring diluted sulphuric acid to bricks and tiles. The chemical reactions between H₂SO₄ and mineral phases that contain alkali- and earth--alkali-metal ions are instantaneous. Some of the products of these reactions are soluble (Na₂SO₄, NaHSO₄, MgSO₄), but CaSO₄ is insoluble (its solubility is approximately: $\approx 2 \text{ g dm}^{-3}$). Therefore, the presence of CaSO₄ usually does not result in major problems. Under static conditions it will remain chiefly as solid constituent. However, under excessively wet conditions (i.e., wet underground retaining walls) CaSO₄ will be mobilized as a result of the ionic exchange reaction [8]. In this reaction, CaSO₄ (in the bricks) and the sodium and potassium hydroxides (either in the bricks or in the nearby bedding mortars) produce much more soluble alkali sulphate. When water transporting soluble salts evaporates from the surface of the brick (thereby depositing the salts on or below the surface), so called efflorescence arises. If the salts crystallize on the surface an unsightly efflorescence result that is not harmful to the brickwork. If the salts precipitate below the surface as crypto- efflorescence, then the crystallization forces produced can result in delamination.

Other undesired, sulphate bearing compound (mostly in mortars but in brickwork walls, as well) is ettringite. Here is presented mechanism of ettringite formation under the influence of strong, aggressive ammonium sulphate solution [9]. As a result, two phenomena occur: dissolution of Ca(OH)₂ and sulphate expansion due to following reactions:

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^-$$
 (1)

$$(NH_4)_2SO_4 \Leftrightarrow 2NH_4^+ + SO_4^{2-}$$
 (2)

$$NH_4^+ + OH^- \Leftrightarrow NH_4OH \Leftrightarrow NH_3 + H_2O$$
 (3)

$$Ca^{2+} + SO_4^2 + 2H_2O \Rightarrow CaSO_4 2H_2O$$
 (4)

$$3\text{CaO Al}_2\text{O}_3 6\text{H}_2\text{O} + 3\text{CaSO}_4 2\text{H}_2\text{O} + 20\text{H}_2\text{O} \Rightarrow$$

$$\Rightarrow 3\text{CaO Al}_2\text{O}_3 3\text{CaSO}_4 32\text{H}_2\text{O}$$

$$\text{ettringite}$$
(5)

or

$$4\text{CaO Al}_2\text{O}_3 \ 13\text{H}_2\text{O} + 3\text{CaSO}_4 \ 2\text{H}_2\text{O} + 14\text{H}_2\text{O} \Rightarrow$$

$$\Rightarrow 3\text{CaO Al}_2\text{O}_3 3\text{CaSO}_4 \ 32\text{H}_2\text{O} + \text{Ca(OH)}_2$$
ettringite
(6)

As the next compound, associated with sulphate attack, calcium silicate sulphate carbonate hydrate- thaumasite (CaO.SiO₂.CaSO₄.CaCO₃.15 H₂O) was identified, almost 30 years ago. One of the possible mechanisms of its formation was suggested by Halliwell and Crammond [10] on an example of brickwork retaining walls. Sulphation problems might start to occur when excessive quantities of water begin percolating through the walls and mobilizing the reservoir of sulphates present in the bricks. During certain period of time, movement of these sulphates might lead to efflorescence, disruptive delamination of the brick faces and the attack of the brickwork mortar, reducing its strength to zero at the locations of attack. The reason the strength might be reduced is appearance of thaumasite which possesses no binding capability. This example shows that the deterioration problems in building can not be considered separately for various building materials due to the fact that degradation phenomena on particular materials and components are mutually dependent.

Analysis of stability with respect to solubility and chemical bond strength

It has been already emphasized that certain compounds- constituents of bricks and tiles- dissolve in water, which significantly contributes to deterioration of their structure and causes total degradation [11-18]. Variations in the acidity of environment (expressed by pH- factor) undoubtedly affect solubility of particular compounds (as presented in figure 1). Due to the fact that building materials are rarely exposed to direct influence of chemicals (which can drastically change pH of the system), it might be expected that acidity for bricks and tiles varies about pH values determined by both partial pressure of CO₂ from the environment and its solubility in water. Influence of extreme pH values to solubility of brick components is minimal. Presence of particular alkali- and earth-alkali- metal oxides, built in the crystal lattice of silicates, could not radically change pH of bricks. Pure rain, with pH among 5.5 and 5.7 due to dissolved CO₂, can not severely influence degradation of building materials due to low concentration of carbonic acid. On the other hand, when SO₂ is dissolved, the pH of rain can decrease to values around 2 and then one has a serious corroding agent.

Mullite and sillimanite do not degrade in a way typical of minerals that contain cations such as: Ca, Mg, Fe, K, Na and others. These cations are very important factors of degradation processes. They are easy to remove by washing away from minerals and compounds. That occurs with different rates for different cations (see table 4). Composition of the

(7)

system changes towards quartz- SiO_2 and Al_2O_3 that are the main building components of mullite, sillimanite and similar, high temperature products. Mentioned compounds do not contain cations so that their degradation processes do not occur by chemical changes (reaction (7)) but do occur by dissolving in water.

$$10SiO_2 + 2Al_6SiO_{11} + 12H_2O \Rightarrow 3Al_4Si_4O_{10}(OH)_8$$

Solubility of quartz, mullite and sillimanite is very low. So, degradation processes on these minerals are hardly noticed for long period of time (for example, see solubility of quartz in figure 1). Unfortunately, at sintering temperatures lower then 980 °C only small quantities of these compounds appear.

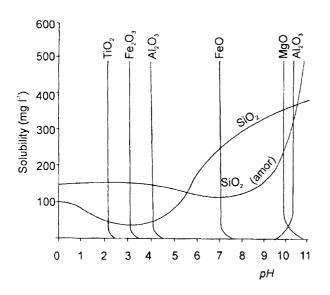


Figure 1. Solubility of particular components from aluminium silicates as a function of pH values

Table 4. Relative mobility of particular metals from their oxides, in relative units from 1 to 10000 [19].

type of oxide	formula	relative mobility	comment
seskvioxides	Al ₂ O ₃	2	1 - 100
	Fe_2O_3	30	low mobility
	Cr_2O_3	60	
dioxides	TiO_2	10-100	100 - 500
	SiO_2	300	average mobility
oxides of	Na ₂ O	1 000	500 - 10 000
alkali- and	K_2O	100-1 000	high mobility
earth-alkali-	CaO	500-2 000	
metals	MgO	300-2 000	

There is another physico- chemical property important for an interpretation of degradation processes. That is: strength of chemical bond between cation and oxygen in matrix of aluminosilicate (table 5). Those elements which bonds with oxygen are strong enough and which valences are high enough will be hard to remove from aluminosilicate matrix by washing away and will be less mobile (table 4).

Table 5. Strength of metal - oxygen bond.

bond	strength (kJ mol ⁻¹)	
Ti(IV) - O	647	
Al(III) - O	582	
Si(IV) - O	464	
Ca(II) - O	423	
Mn(II) - O	389	
Fe(II) - O	389	
Mg(II) - O	377	
Na(I) - O	256	
K(I) - O	278	

PHYSICAL DEGRADATION

Physical degradation could be divided into two distinct processes: 1. chemically induced physical degradation and 2. frost attack.

Chemically induced physical degradation

One of very important reasons for chemically induced physical degradation is the volume change due to formation of degradation products. Once again, an analogy between degradation of natural minerals and compounds from bricks and tiles could be used. The examples that follow are only models, since chemical composition of the natural minerals could never completely match formulas used in this text. Nevertheless, the main physico-chemical processes could never be disobeyed.

In table 6, physico-chemical data for some of the minerals found in bricks and tiles or in clays and sends, raw materials for brick production, are listed. The most important chemical degradation processes are represented by reactions from (8) to (17). All these reactions are spontaneous and they have a negative volume change ($\Delta V_{\rm reaction} = \Sigma V_{\rm products} - \Sigma V_{\rm reactants}$). The results are based on data represented in table 6.

Empirical experiences have proven that kaolinization is usually a dominant degradation reaction in most of the natural systems. It is assumed that this process is affecting also artificial products, such as bricks and tiles, which by their chemical composition and crystal

Table 6. Some important physico-chemical parameters for various minerals and chemical species [20].

mineral	formula	$\Delta G_{\rm f}^{\rm o}$	V _{mole}
		(kJ mol ⁻¹)	(cm³ mol-¹)
muscovite	$KAl_3Si_3O_{10}(OH)_2$	-5600	140.7
sericite	$KAl_3Si_3O_{10}(OH)_2$	-5900	140.7
biotite	K(Mg,Fe) ₃ AlSi ₃ O ₈ (OH) ₂	-4810	159.0
chlorite	$(Mg,Fe)_6Si_4O_{10}(OH)_8$	-8080	244.0
kaolinite	$Al_4Si_4O_{10}(OH)_8$	-7598	199.0
anortite	CaAl ₂ Si ₂ O ₈	-4220	100.8
diopside	CaMgSi ₂ O ₆	-3036	66.1
gehlenite	$Ca_2Al_2SiO_7$	-4007	90.2
albite	NaAlSi ₃ O ₈	-3900	100.7
orthoclase	KAlSi ₃ O ₈	-3950	108.7
kyanite	Al ₂ SiO ₅	-2441	44.1
corundum	Al ₂ O ₃	-1582	25.6
gibbsite	Al(OH) ₃	-1155	32.0
anhydrite	CaSO ₄	-1321	45.9
gypsum	CaSO ₄ * 2H ₂ O	-1797	74.7
calcite	CaCO ₃	-1129	36.9
quartz	SiO ₂	-911	22.7
water	H_2O	-237	18.1
CO,	CO,	-394	
Ca -ion	Ca^{2+}	-554	
Mg -ion	Mg^{2+}	-455	
Na -ion	Na ⁺	-262	
K -ion	K ⁺	-282	
H -ion	H ⁺	0.0	

structure resemble many natural materials. Degradation processes affect feldspars like anortite and orthoclase the most due to their high content of first and second group metal ions. Chloritization of biotite and kaolinization of muscovite are less important because their concentrations in bricks are low in comparison with other brick forming materials. Unfortunately, physico-chemical data for zeolites are not available, so there were no calculations for them. Nevertheless, the degradation reactions could be represented by the following equations:

Sericitization and kaolinization of minerals albite and anortite

$$3NaAlSi3O8 + 2H+ = albite = NaAl3Si3O10(OH)2 + 2Na+ + 6SiO2 sericite (8)$$

$$(\Delta G_{\text{reaction}} = -191 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -25.2 \text{ cm}^3 \text{ mol}^{-1})$$

$$4\text{NaAlSi}_3\text{O}_8 + 2\text{H}_2\text{O} + 4\text{H}^+ = \text{albite}$$

= $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 + 4\text{Na}^+ + 8\text{SiO}_2$ (9 kaolinite

$$(\Delta G_{\text{reaction}} = -146 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -22.2 \text{ cm}^3 \text{ mol}^{-1})$$

$$3\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{Na}^+ + 2\text{H}^+ =$$

anortite
= $2\text{NaAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 3\text{Ca}^{2+}$ (10)

$$(\Delta G_{\text{reaction}} = -278 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -21.0 \text{ cm}^3 \text{ mol}^{-1})$$

$$2CaAl_{2}Si_{2}O_{8} + 2H_{2}O + 4H^{+} =$$
anortite
$$= Al_{4}Si_{4}O_{10}(OH)_{8} + 2Ca^{2+}$$
(11)

$$(\Delta G_{\text{reaction}} = -208 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -18.6 \text{ cm}^3 \text{ mol}^{-1})$$

Sericitization and kaolinization of mineral orthoclase

$$3KAlSi_3O_8 + 2H^+ =$$

orthoclase
= $KAl_3Si_3O_{10}(OH)_2 + 6SiO_2 + 2K^+$ (12)

$$(\Delta G_{\text{reaction}} = -80 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -49.2 \text{ cm}^3 \text{ mol}^{-1})$$

$$4KAlSi_{3}O_{8} + 2H_{2}O + 4H^{+} =$$
orthoclase
$$= Al_{4}Si_{4}O_{10}(OH)_{8} + 8SiO_{2} + 4K^{+}$$
(13)

$$(\Delta G_{\text{reaction}} = -260 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -54.2 \text{ cm}^3 \text{ mol}^{-1})$$

Kaolinization of muscovite

$$4KAl_3Si_3O_{10}(OH)_2 + 4H^+ + 6H_2O =$$
muscovite
$$= 3Al_4Si_4O_{10}(OH)_8 + 4K^+$$
kaolinite
(14)

$$(\Delta G_{\text{reaction}} = -100 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = 34.2 \text{ cm}^3 \text{ mol}^{-1})$$

Chloritization of biotite

$$2K(Mg,Fe)_3AlSi_3O_8(OH)_2 + 5H_2O = biotite$$

= $(Mg,Fe)_6Si_4O_{10}(OH)_8 + 2K^+ + 2H^+ + SiO_2 + Al_2SiO_5$
chlorite (15)

$$(\Delta G_{\text{reaction}} = -1191 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -7.2 \text{ cm}^3 \text{ mol}^{-1})$$

Kaolinization of gehlenite

$$4Ca_2Al_2SiO_7 + 2H_2O + 16H^+ =$$

gehlenite
= $Al_4Si_4O_{10}(OH)_8 + 8Ca^{2+} + 4Al(OH)_3$ (16)

$$(\Delta G_{\text{reaction}} = -156 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -33.8 \text{ cm}^3 \text{ mol}^{-1})$$

Kaolinization of diopside

$$2CaMgSi2O6 + 4Al(OH)3 + 8H+ = diopside= Al4Si4O10(OH)8 + 2Ca2+ + 2Mg2+ + 6H2O (17)kaolinite$$

$$(\Delta G_{\text{reaction}} = -346 \text{ kJ mol}^{-1}, \Delta V_{\text{reaction}} = -61.2 \text{ cm}^3 \text{ mol}^{-1})$$

There is no contribution of gases or ions in the total volume change of these reactions since they were dissolved in water and carried away. Actually, the total volume change is only dependent on the volume difference between solid phases.

Appearance of two main sulphate bearing compounds (anhydrite and gypsum) causes volume change as well. The volume changes for the calcite to anhydrite and for anhydrite to gypsum transformations are positive (9.0 cm³ mol⁻¹ and 28.8 cm³ mol⁻¹ respectively):

$$Ca^{2+} + SO_4^{2-} = CaSO_4$$
 (18)

or

$$CaCO_3 + SO_4^{2} = CaSO_4 + CO_2$$

$$(\Delta V_{\text{reaction}} = 9.0 \text{ cm}^3 \text{ mol}^{-1}) \tag{19}$$

$$Ca^{2+} + SO_4^{2-} + 2H_5O = CaSO_4 2H_5O$$
 (20)

$$CaSO_4 + 2H_2O = CaSO_4 2H_2O$$

anhydrite gypsum

$$(\Delta V_{\text{reaction}} = 28.8 \text{ cm}^3 \text{ mol}^{-1}) \tag{21}$$

The pressure that the second reaction produces is about 110 MPa. The consequence of this chemical reaction is purely physical - the system expands. Since bricks and tiles are rigid, they usually crack. That was another example of chemically induced physical degradation.

Frost attack

However, so called physical degradation can take place apart from chemical degradation. Processes of physical degradation occur under the influence of climate, that is, under the influence of wet- and drayconditions during winter and summer periods. Obviously, microclimate conditions are important factors that determine intensity of aggression. Particularly important are: height with regard to sealevel, average winter and summer temperatures, average humidity of air, quantity of water precipitates, etc. Physical degradation process happens especially on facades of buildings and on the lower parts of facades. This kind of degradation proceeds during winters, when the absorbed water crystallizes. Frost attack is typical phenomenon that can occur without chemical changes on the system. It, also, can take place together with chemical reactions.

Porosity of building materials significantly contributes to frost attack. If pores and micro- crashes, which sizes are between 0.1 and 1 μ m [21, 22], are

filled with water crystals of ice can appear, but below the normal freezing point. Water present in the intercrystal space of aluminosilicates and water which is adsorbed as monomolecular layer on the silicate matrix does not cause physical degradation. Such water can not crystallize even at temperatures below 0 °C. Namely, water in pores of porous systems does not freeze easily. It was proved that porous media impose certain limitations, which do not allow a kind of reorganization of water molecules necessary for their crystallization [23]. This is a consequence of nonequilibrium conditions concerning metastable liquid phase inside the pores and solid phase (ice) out of pores. Obviously, there is a difference between partial pressures of H₂O above these two mentioned phases. The equilibrium can be reached at temperatures below -15 °C. It is very probable that adhesive forces between molecules of water and dissolved alkali- and earth- metals from matrix of bricks and tiles (that is between water and walls of pores) are far too intensive in comparison with cohesive forces among water molecules in the crystal of ice. Therefore crystallization starts when the forces become equal or when cohesive forces become greater, that happens at rather low temperatures. So, water inside the pores certainly can crystallize but kinetics and mechanisms of this phenomenon are not completely explained. Since ice has greater volume than the liquid phase (due to anomalous behaviour of water) it acts as an expanding medium causing severe inner destruction. Physical attack of ice is very powerful (for example, at -22 °C the expanding pressure of the ice crystals reaches 220 MPa). Once in the system appear smaller or greater cracks they are open to further water and frost activity. More water causes faster degradation processes which very probable lead to total destruction of a system.

BIODEGRADATION

Under the term: "biodegradation" one usually supposes an influence of low classes of plants (such as lichens and moss) as well as various types of microorganisms to building materials. These organisms frequently appear at wet spots and northern sides of buildings. Particularly facades are exposed to biodegradation. According to Krumbein [24] the microorganisms can penetrate 10 cm or even more into the building walls. This fact might be responsible for the detachment of external layers of buildings.

Actually, a survival of these organisms is affected by presence of moisture inside the pores of porous body more than by the presence of mineral materialsconstituents of bricks and tiles. While using water, these plant- organisms use mineral components of bricks and tiles as well. For example, Diatom Algae use silicium dioxide in their metabolism [25]. In this way they disturb equilibrium conditions for particular reactions that occur as a part of degradation processes. New, free ions appear which contribute to the progress of deterioration. Also, metabolic- products as well as products of their degradation in the presence of oxygen usually generate acid medium that stimulates degradation processes. For instance, Nitrobacteria produce the acid able to dissolve calcic compounds [26]. The same phenomenon was noticed by Ribas Silva [25] who investigated biodeterioration of concrete. He, also, noticed corrosion of micas, feldspars and quartz, very probable due to attack of Bacteria or Fungi.

There is no doubt that investigations of biodegradation of building materials are at a beginning. These investigations are complex due to the great number of various types of organisms, which can cause degradation, mostly dependent on microclimate. Each of them has its own metabolism that has to be known if one wants to determine corresponding mechanisms responsible for material degradation. So, tedious biological study has to precede investigations of the consequences of bioorganisms attack.

CONCLUSION

Considering previous analysis, it is obvious that most of durability problems are related to moisture and chemical transformations of the system. Negative influence of moisture was emphasized by many scientists, particularly by Fagerlund [27]. Water and chemical reactions take part in the destruction processes in many ways. The main degradation processes my be classified as follows: 1. chemical degradation, 2. chemically induced physical degradation, 3. physical degradation and biodegradation. The main steps during each of the degradation processes are defined as follows:

1. Chemical degradation

- la. Water (CO₂, O₂, SO₂,...) penetration into bricks and tiles and related change of physico- chemical conditions of the system.
- 1b. Water- solid phase interaction (hydration and dissolution of soluble species).
- lc. Chemical reactions (hydrolysis, oxidoreduction and other thermodynamically spontaneous reactions).
- ld. Recrystallization of high temperature minerals without water into low temperature minerals which contain water.
- le. Leaching of soluble species (the loss of alkali and earth- alkali metals, the loss of total mass).

2. Chemically induced degradation.

- 2a. Volume change of solid phase caused by chemical reactions (step 1c and 1d).
- 2b. Decrease of mechanical and other physical characteristics of bricks and tiles (loss of compressive strength, loss of flexural strength, etc.).
 - 2c. Possible increase of water content.

3. Physical degradation.

- 3a. Water penetration into bricks and tiles.
- 3b. Frost attack.
- 3c. Cracks due to induced stresses in buildings, which appear after decrease of bricks quality caused by the chemical degradation (step 2b).
 - 3d. Delamination of bricks and tiles.

4. Biodegradation.

- 4a. Water penetration into bricks and tiles.
- 4b. Arrival of algal and fungal seeds and spores.
- 4c. Development of algal or fungal colonies.
- 4d. Metabolic influence of these organisms on bricks and tiles.
- 4e. Change of physico- chemical conditions of the local environment that provoke chemical degradation.

Generally speaking, processes of degradation of building materials are opposite to the processes typical of their production. By sintering, one removes water from low- temperature minerals (obtained by natural degradation of rocks and stones). In this way, high-temperature, waterless compounds are formed as the main constituents of final products. On the other hand, during degradation of bricks and tiles, such processes occur which allow absorption of water and CO₂ from the environment as well as washing away of alkali- and earth- metals from matrix of product.

There is no doubt that future investigations of degradation mechanisms should provide better understanding of the degradation phenomena. This is necessary for production of better products as well as for finding ways for their preservation.

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