CZECH TECHNICAL UNIVERSITY IN PRAGUE
FACULTY OF CIVIL ENGINEERING
DEPARTMENT OF MATERIALS ENGINEERING AND CHEMISTRY

DEGRADATION OF BUILDING MATERIALS

Contents

- Degradation (corrosion) of non-metallic building materials
- Chemical degradation, physical degradation, physical-chemical degradation, bio-corrosion
- Causes of corrosion and degradation – temperature changes, moisture effects, atmospheric effects, mechanical effects
- Degradation due to the water-soluble salts, salts sources, classification of salt concentration, destructive principles of salt action
- Gypsum degradation + protection
- Degradation of calcium-carbonate binders
- Degradation of materials on magnesium basis
- Concrete degradation

Degradation of non-metallic building materials

degradation X corrosion

❑ the durability of structures is in clear relation with the resistivity and durability of inbuilt materials

❑ effect of agressive environment→ reaction with material constituents → damage (degradation)

❑ **chemical corrosion**

– processes where the chemical composition of material is changing, or some of its constituents reacts with ambient environment (contamination of atmosphere, metabolic products of live organisms, improper conservational adaptations, etc.)

- chemical corrosion usually results in color changes, volume changes and solubility changes of attacked components of building materials

☐ **physical corrosion**

- physical corrosion processes are related to action of different forces and pressures (inside and outside the porous structure of materials) that damage especially structure of materials
- rise of these forces and induced pressures is related most often to temperature changes, water and salt action, formation of new minerals, mechanical vibrations and surface abrasion

☐ **physical-chemical corrosion**

☐ **bio-corrosion**

- processes caused by live organisms action, their activity is performs as physical corrosion – (e.g. ingrowth of roots or sponge fibers into the substrate) or chemical corrosion (dissolution of substrate by means of live organism acids) – formation of pressures or chemical reaction with substrate materials

Corrosion causes I

❑ **effect of temperature changes**

- building material represents mainly heterogeneous system, where the particular constituents differ in properties

- one of the heterogeneous properties is just the volume change as response to temperature changes → given by the ability of particular material to absorb heat and by its thermal expansion (it can differ for specific types of materials in dependence on the direction of crystal axes)

- because of material surface heating, fire, etc.) the heat is transported into the inner structure of materials – **temperature differences between surface and inner space**

→ the differences in thermal expansion coefficient and temperature gradient between surface and inner layers lead to tension among particular particles, crystals→ **cracks formation**

Strength decrease, porosity rising, material surface rising – decrease of resistivity agains water action, salt solution action etc.

The volume changes due to the temperature are not fully reversible.

Corrosion causes II

❑ **effect of water**

- porous building materials contain always certain amount of water that is in equlibrium with moisture of their ambient environment

-**equlibrium moisture**– depends on material properties, temperature and moisture of environment

- **free water** (transport by gravity forces, capillary forces and diffusion)
- **bound water on surface of porous space** – lower moveability of water molecules (at temperatures lowe than 0°C is not forzen)

Mechanisms of degradation due to the water:

- **frost damage**– phase change of liquid water to its solid phase is acompanied by increase in volume (cca 9%) – damage by ice crystal pressures

- water represents danger for materials as transport medium for harmful substances (mainly salts)

Corrosion causes III

Mechanisms of degradation due to the water:

- the presence of water accelerates or directly effects chemical reactions on surface of pores and supports existence of live organisms (mosses, algaes, etc.)

- material dissolution – corrosion of hydrated binders consistency

- the biggest danger represent cyclic changes of moisture, especially for materials containing clay minerals and water-soluble salts

→ it can be generally conclude, the high moisture content is less harmful than its changes (it is valid even in the case of high moisture concentration)

Corrosion causes IV

Effect of atmosphere– composition, flow

- air contains except its main constituents also sulphur oxides, nitrogen oxides, hydrocarbon gases and other gases and solid particles like products of live organisms, volcanic eruption and activity, industrial processes and combustion processes, etc.

- highly important factor for degradation of building materials is amount of carbon dioxide (CO_2) – results of combustion of fossil fuels (production of cement 1t PC = 1t CO_2)

- locally also other types of gaseous products of chemical industry can be significant – chlorine, hydrogen, hydrogen suphide

- also the solid particles from the air takes part in corrosion process

Dry clean air in lower layeres of atmosphere (typically to the high of 20 km).

Gaseous constituent	chemical symbol	Amount of constituent		M_m	ρ_o
		volume	mass		
		%	%	kg/kmol	kg/m^3_n
nitrogen	N_2	78,09	75,5	28,016	1,251
oxigen	O_2	20,95	23,17	32,000	1,428
argon	Ar	0,93	1,286	39,944	1,783
carbon dioxide	CO_2	0,03	0,043	44,010	1,964
neon	Ne	$1,8.10^{-3}$	$1,2.10^{-3}$	20,183	0,901
helium	He	$5,24.10^{-5}$	$7,0.10^{-5}$	4,003	0,179
krypton	Kr	$1,0.10^{-4}$	3.10^{-4}	83,80	3,741
helium	H_2	$5,0.10^{-5}$		2,016	0,090
xenon	Xe	$8,0.10^{-6}$	$4,0.10^{-4}$	131,3	5,862
ozone	O_3	$1,0.10^{-6}$		48,000	2,143
air	-	100	100	28,97	1,293

Corrosion causes V

- solid particles and drops of liquids wafted by air are constituents of aerosol, whereas the time of their waftage depends on their dimension, mass and intensity of driftage (fog, dust)

- washing out of gaseous air pollutants by air, snow or fog→ diluted solutions of inorganic acids, partially are gases adsorbed on surface of solid particles of dust

- the acidy of rainfall water is increasing –pH decreases to values < 4

- from the chemical point of view is action of acid air pollutants reaction of inorganinc acids (<u>sulphuric acid, sulphurous acid, nitrogen acids and carbonic acid</u> with components of building materials – agressive effect on carbonates in natural limestones, calcareous marly limestones, lime plasters and mortars

- **corrosive products are more soluble and can be washed out from the material**

Degradation due to the water-soluble salts

- several failures of buildings and inbuilt materials that are usually assigned to the high moisture content would not arise in case of penetration of pure water

- water is transport medium for other pollutants that finally contribute to degradation of building material

- water transport– provides transport of water-soluble salts

- salt accumulation (drying – attainment of „saturation treshold“) – destruction – **crystal growing**, **recrystalization**

Salts sources

- salts primarily contained in materials

- salts transported by capillary action (elevation) from subsoil or other part of building

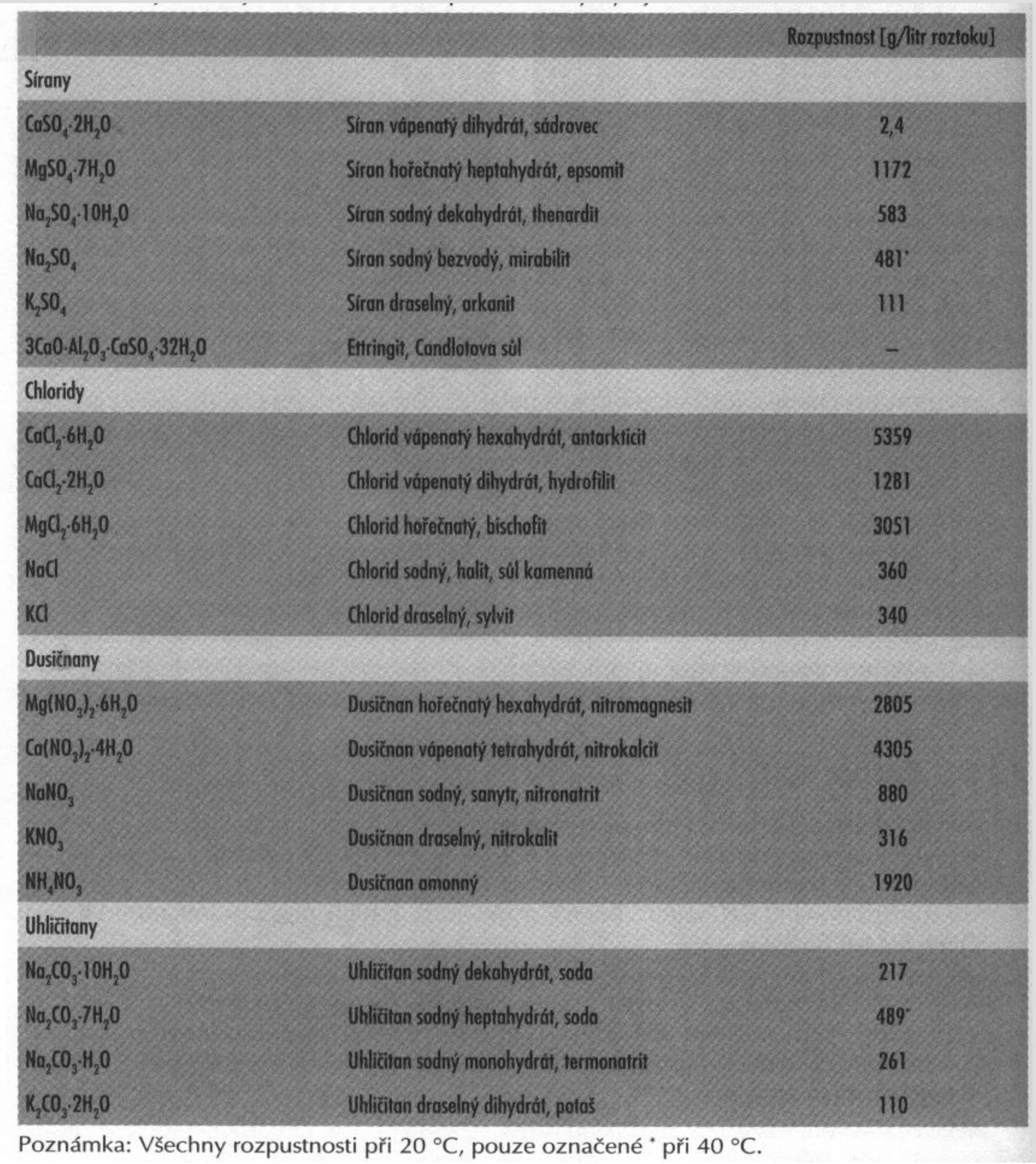
- salts originated from chemical reaction of materials due to the air pollutants (e.g. sulphates formed by reaction of carbonates with sulphur oxides)

- salts from biological sources (e.g. transformation of carbamide to nitrates)

- salts resulting as consequence of reconstruction and restoration treatments

- salts form winter maintence of roads and pavements

- salts in underground water



		Rozpustnost [g/litr roztoku]
Sírany		
$CaSO_4 \cdot 2H_2O$	Síran vápenatý dihydrát, sádrovec	2,4
$MgSO_4 \cdot 7H_2O$	Síran hořečnatý heptahydrát, epsomit	1172
$Na_2SO_4 \cdot 10H_2O$	Síran sodný dekahydrát, thenardit	583
Na_2SO_4	Síran sodný bezvodý, mirabilit	481*
K_2SO_4	Síran draselný, arkanit	111
$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O$	Ettringit, Candlotova sůl	–
Chloridy		
$CaCl_2 \cdot 6H_2O$	Chlorid vápenatý hexahydrát, antarkticit	5359
$CaCl_2 \cdot 2H_2O$	Chlorid vápenatý dihydrát, hydrofilit	1281
$MgCl_2 \cdot 6H_2O$	Chlorid hořečnatý, bischofit	3051
$NaCl$	Chlorid sodný, halit, sůl kamenná	360
KCl	Chlorid draselný, sylvit	340
Dusičnany		
$Mg(NO_3)_2 \cdot 6H_2O$	Dusičnan hořečnatý hexahydrát, nitromagnesit	2805
$Ca(NO_3)_2 \cdot 4H_2O$	Dusičnan vápenatý tetrahydrát, nitrokalcit	4305
$NaNO_3$	Dusičnan sodný, sanytr, nitronatrit	880
KNO_3	Dusičnan draselný, nitrokalit	316
NH_4NO_3	Dusičnan amonný	1920
Uhličitany		
$Na_2CO_3 \cdot 10H_2O$	Uhličitan sodný dekahydrát, soda	217
$Na_2CO_3 \cdot 7H_2O$	Uhličitan sodný heptahydrát, soda	489*
$Na_2CO_3 \cdot H_2O$	Uhličitan sodný monohydrát, termonatrit	261
$K_2CO_3 \cdot 2H_2O$	Uhličitan draselný dihydrát, potaš	110

Poznámka: Všechny rozpustnosti při 20 °C, pouze označené * při 40 °C.

Classification of salt concentration

- there is necessary to have information on salt content in building structures from the point of view of the reconstruction method
- incorporated in technical standards
- ČSN P 73 0610

Rate of salinity	Amount of salt in mg/g of the material sample and in the mass %					
	Chlorides		Nitrates		Sulphates	
	mg/g	mass %	mg/g	mass %	mg/g	mass %
low	< 0.75	< 0.075	< 1.0	< 0.1	< 5.0	< 0.5
Increased	0.75 – 2.0	0.075 – 0.20	1.0 – 2.5	0.1 – 0.25	5.0 - 20	0.5 – 0.2
High	2.0 – 5.0	0.20 – 0.50	2.5 – 5.0	0.25 – 0.50	20 - 50	2.0 – 5.0
extremely high	> 5.0	> 0.50	> 5.0	> 0.50	> 50	> 5.0

Classification of salt concentration

	Degree 0	Degree 1	Degree 2
Chlorides	0 – 0,01	0,01 – 0,03	0,03 – 0,09
Nitrates	0 – 0,01	0,01 – 0,05	0,05 – 0,15
Sulphates	0 – 0,02	0,02 – 0,08	0,08 – 0,24

	Degree 3	Degree 4
Chlorides	0,09 – 0,28	0,01 – 0,28
Nitrates	0,15 – 0,50	0,01 – 0,50
Sulphates	0,24 – 0,77	0,02 – 0,77

Classification of salt concentration in % of mass (according to EUREKA EU – 1270)

❑ **Degree 0** corresponds to low salt concentration. Only trace amount of salts is present in material and the failure of structure by means of salt action is excluded.

❑ **Degree 1** represents very low salt loading of building structures. Only at unfavourable conditions (e.g. massive wall with constant capillary moisture) the failure can be observed.

❑ **Degree 2** denotes middle salt loading, the durability of plaster and coatings is decreasing.

❑ **Degree 3** is considered as critical level regarding to the durability of plasters and coatings. In spite of active vertical water-proofing, the materials of structures remain wet because of hygroscopic properties of salts.

❑ **Degree 4** is extremely high salt concentration, the failures are observed in short time.

Classification of moisture content

Moisture content u [%]	Classification
$u < 3.0$	very low moisture content
$3.0 \leq u < 5.0$	low moisture content
$5.0 \leq u < 7.5$	increased moisture content
$7.5 \leq u < 10.0$	high moisture content
$10.0 < u$	very high moisture content

Classification of moisture content according to ČSN P 73 0610 (2000)

Mechanisms of salt action

- salt crystallization
- salt hydration
- hygroscopic water absorption
- efflorescence and salt leaching

Salt crystallization I

- physically-chemically degradation process

- salt solutions are transported into the materials, where within the water evaporation of solutions the salt concentration is increasing

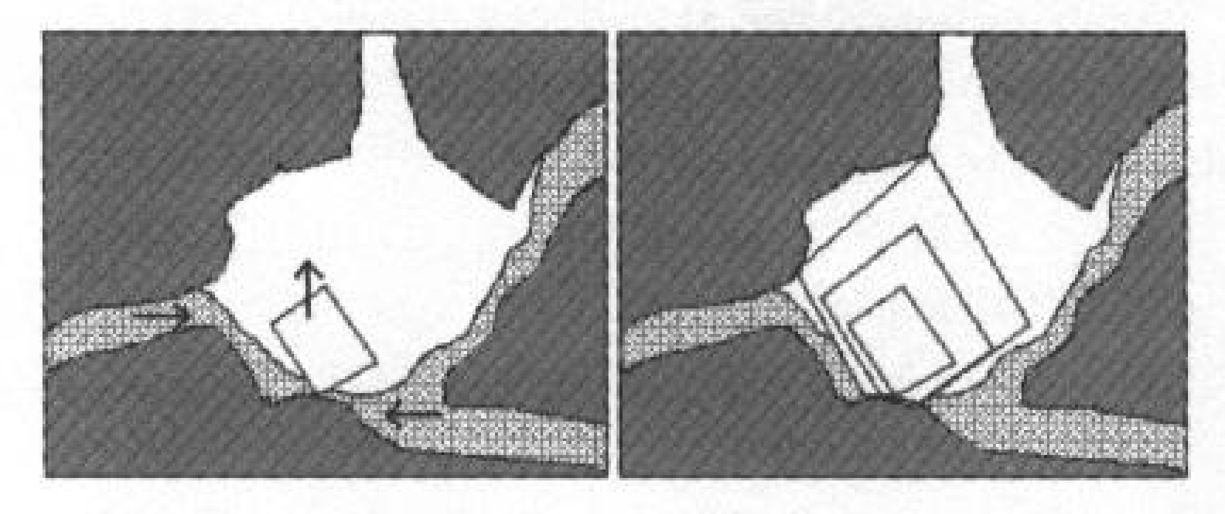
- there are formed saturated and oversaturated solutions, after over crossing of range of solubility, the crystals are growing

- exerting of crystallization pressures on walls of porous space → damage of porous structure of materials

- the degradation can be caused also by salt recrystallization, whereas the substances with higher number of molecules originate

- increase of temperature leads to acceleration of ion movement and to higher reaction velocity

Schematic illustration of crystal growing in porous space



Crystallization and recrystallization salt pressures

Compound	Crystallization pressure[MPa]
$CaSO_4 \cdot 2H_2O$	28,2
$MgSO_4 \cdot 2H_2O$	10,5
$Na_2SO_4 \cdot 10H_2O$	7,2
$Na_2CO_3 \cdot 10H_2O$	7,8
NaCl	55,4

Compound	Final product	Recrystallization pressure[MPa]
$CaSO_4 \cdot 0,5H_2O$	$CaSO_4 \cdot 2H_2O$	160
$MgSO_4 \cdot 6H_2O$	$MgSO_4 \cdot 7H_2O$	10
$Na_2CO_3 \cdot H_2O$	$Na_2CO_3 \cdot 7H_2O$	64

Salt crystallization II

- from the point of view of porosity, the most endanreged are materials having high amount of smaller pores

- crystal growing start in bigger pores, and the concentration of saturated salt solution is maintain by solutions in smaller pores

- after decrement in salt concentration, the formation of crystals is stopped

- the limiting factor for the salt crystal damage is not total porosity of material, but pores distribution

Salt hydratation I

❑ it is related to salts that are able to bond in their crystal lattice certain defined number of water molecules→ **formation of hydrates**

❑ transition from one hydrated form to another one is accompanied by loss of several water molecules, what is characteristic by volume changes

❑ by virtue of volume changes, hydration pressures are induced

❑ transition from one hydrated form to another one is given by stability of salt hydrated form at specific climatic conditions – dependent on temperature and relative humidity

❑ for building materials are the most dangerous salt changing their forms at standard climatic conditions – **sodium sulphate, sodium carbonate, calcium nitrate**

Salt hydratation II

$$\mathrm{Ca(NO_3)_2 \cdot 4H_2O} \xleftrightarrow[30\,^\circ\mathrm{C}]{} \mathrm{Ca(NO_3)_2 \cdot 3H_2O} \xleftrightarrow[100\,^\circ\mathrm{C}]{} \mathrm{Ca(NO_3)_2}$$

$$\mathrm{Na_2CO_3 \cdot 10H_2O} \xleftrightarrow[32\,^\circ\mathrm{C}]{} \mathrm{Na_2CO_3 \cdot 7H_2O} \xleftrightarrow[35{,}4\,^\circ\mathrm{C}]{} \mathrm{Na_2CO_3 \cdot H_2O}$$

Hygroscopic water absorption

- hygroscopic substances – capable to adsorb airy moisture– sorption moisture

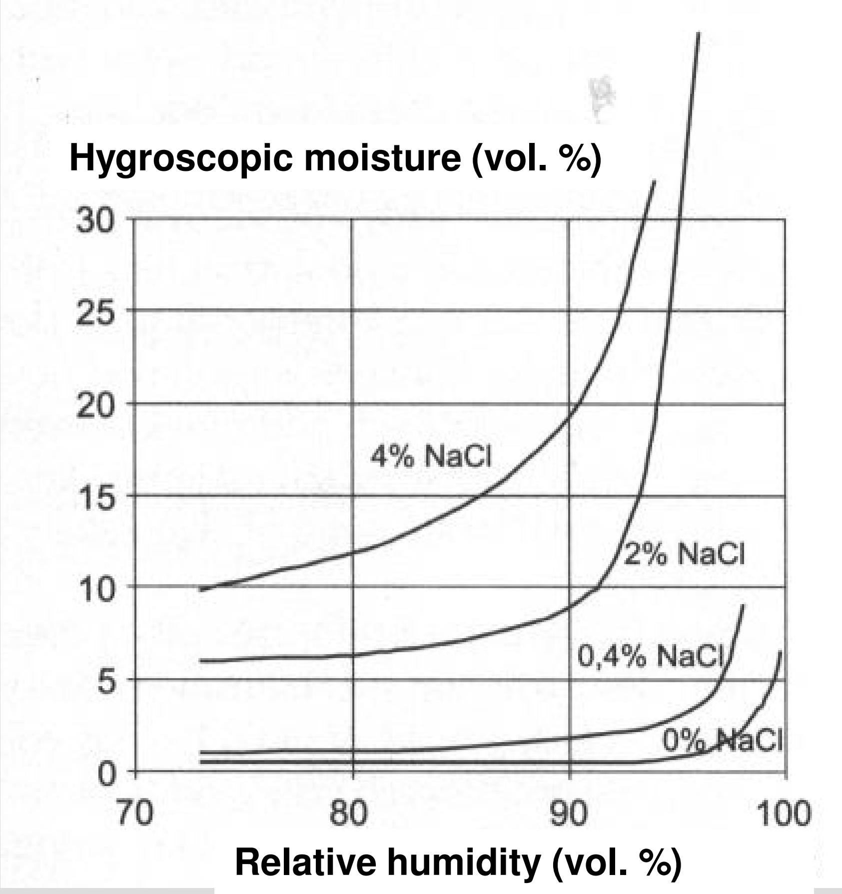
- physically adsorbed water (in this case the adsorbed water is not part of crystal lattice of material)

- the ability to adsorb moisture from water vapor at specific climatic conditions differ for specific type of salts – limited by relative airy moisture (relative humidity) and amount of water, that can be adsorbed by specific salt

- equlibrium relative humidity– corresponds to relative humidity value that steady in closed system above saturated salt solution at defined temperature (see section: measurement of sorption isotherms)

- at higher values of relative humidity the moisture is adsorbed (decrement of solution concentration)

- the salt concentration in material significantly effects its sorption properties (there is necessary to take into account the increase in sorption moisture with increase of salt concentration)



Soprtion isotherm of ceramic brick in dependence on NaCl concentration

Negative results of salt action

- from the point of view of degradation of building materials, there is necessary if the crystallization takes place on material surface or inside its porous structure

- within the slow drying of salt solution, the salts are transported to material surface – efflorescence – more or less estehtic problem or harmful for surface layers of structures, on the other hand finding the efflorescence can informa about crystalliation process in inner strcture of material

- more harmful is crystallization inside the pores - material destruction, loss of sstatical function

- the significant problem is also hygroscopicity that contributes to higher wetting of materials (often, in case of an ideal and proper water proofing, the structure remains wet)

- in dependence on changes of ambient environment (especially of its relative humidity) recrystallization can be observed

- corrosion of concrete reinforcement – failure of cocrete structures (e.g. chloride disrupts pasivation layer of concrete reinforcement (steel corrosion – increase of volume – failures of concrete cover

Efflorescence and leaches

❑ efflorescence and leaches are rising on surface of building materials and structures

❑ = salts in solid phase that were transported to surface layer by means of liquid water transport

❑ white or lightly colored coatings, particularly groups of crystals

❑leaches– tightly connected with substrate

❑ efflorescence – easy removeable

Leaches

-crystallic (eventually amorphous substances) having low solubility in water

- they are formed within the chemical reaction in water dissolved substance with other substance on material surface – e,g, calcite leach

$$\mathrm{Ca(OH)_2} + \mathrm{CO_2} \rightarrow \mathrm{CaCO_3} + H_2O$$

- calcite (limestone) rises on material surface (e.g. on concrete)
- calcite leaches can be observed in case the water is flowing through material on lime or cement basis

Efflorescence I

- salt crystals transported to the material surface

Potash efflorescence

- is created by reaction of already carbonated lime (after reaction of CO2) with binder of silicate color (contains small amount of potasium hydroxide)

$$\mathrm{Ca(HCO_3)_2} + \mathrm{4KOH} + 4H_2\mathrm{O} \rightarrow 2\underbrace{K_2\mathrm{CO_3}}_{\text{potash}} \cdot 6H_2O + Ca(OH)_2$$

-potash is bad soluble, non-hygroscopic→ it is not dangerous substance, after cleaning is usually not observed again

Efflorescence I II

Natrium efflorescence

- natrium hydroxide is part of natrium water-glass (alkaline activation, infusion solution for water proofing of building structures

- process of soda formation is very slow (several years)

- soda is highly hygroscopic

- it recrystallizes – highly negative consequences– decomposition of mortars and mortar joints, failures of walling materials

$$2NaOH + \mathrm{CO_2} + 6H_2O \rightarrow Na_2CO_3 \cdot 7H_2O$$

$$Na_2CO_3 \cdot 7H_2O + 3H_2O \rightarrow Na_2CO_3 \cdot 10H_2O$$

Gypsum degradation I

❑ hardened gypsum is partially soluble on water– 256 mg in100g of water at 20°C

❑ at permanent contact of gypsum based materials (gypsum plasters, blocks, plasterboards) the progressive dissolution of hardened gypsum binder will be observed in dependence on amount of moisture that comes into contact with material

❑ the dissolution will be more intensive in case the water at gyspum surface will be changed

❑ standing water dissolves such amount of gypsum, that corresponds to saturated solution

❑ in case of presence of calcium or sulphate ions the dissolution of gypsum is decreasing

❑ on the other hand, the solutions containing different ions or acids enhance gypsum dissolution (e.g. 100 g NaCl in 1 liter of water enhances the gypsum dissolution three times)

Gypsum degradation I

❑ in dependence on temperature and moisture content, gypsum changes its mechanical properties

❑ increase of moisture content in gypsum about 12% decreases the strength of gypsum cca about 50% → gypsum is not proper material for relative humidities higher than 60%

❑ gypsum degrade at higher temperatures- product of gypsum hydration ($CaSO_4 \cdot 2H_2O$) is stable to 40°C, then the water is lost and gypsum forms with lower amount of water are produced

❑ in final phase (at temperatures> 110°C) originates hemihydrate

❑ on this account gypsum can find use as material for protection of building strctures agains fire→ water contained in gypsum consumes part of heat necessary for burning, water is also transformed to water vapour (heat loss)

❑ products of gypsum temperature loading have lower strangth parameters

❑ gypsum is agressive for metals – in caseof gypsum higher moisture content (at RH > 60%) contains solution of $Ca_2(SO_4)$ – pH = 5, corrosion of iron and aluminum

Protection of gypsum against degradation

- for enhancement of gypsum resistivity against moisture, there is necessary to use hydrophobic admixtures
- hydrophobization can be performed in inner way – addition of hydrophobic additives to gypsum paste (zinc stearate) or can be performed on the gypsum surface by means of coatings

- properties of gypsum can be affected by its water/gypsum ratio and addition of plasticizers

- the resistivity of gypsum is possible also by addition of polymers

Degradation of calcium-carbonate based binders I

- ☐ among basic calcium-carbonate based binders belongs CaCO3 that is product of lime hydration

- ☐ solubility of $CaCO_3$ is at 20°C 1,4 mg in100g of water

1. action of agressive CO_2 from atmospheric water(rainfall water)

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^{2-}$$

- it is reversible reaction
- HCO_3 is higly soluble in water and can be washed out the material – loss of binder – exceeding of cohesive forces of material – material destruction

-this reaction takes place in nature in limestone and dolomitic moutains and represetns fundamental principle of karstic effects

Degradation of calcium-carbonate based binders II

2. action of SO_2

- With water creates sulphurous acid H_2SO_3
- It can also axidate to SO_3, from which the sulphuric acid oroginates H_2SO_4
- both above mentioned acids reacts with calcium carbonate

$$CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + CO_2 + H_2O$$

$$CaSO_3 + 1/2H_2O \rightarrow CaSO_3 \cdot 1/2H_2O$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

$$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

The final product (gypsum) has high molar volume and its crystalliation leads to material decomposition.

Degradation of calcium-carbonate based binders II

3. Action of nitrogen oxides NO_x

- contained also in atmosphere
- dioxide nitrogen NO easily oxides to NO_2 that forms with water mixture of nitrous acid and nitric acid

$$2NO + O_2 \rightarrow 2NO_2$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

Calcium nitrate is well soluble (127 g in 100g of water at 20°C) and has not binding properties – it can be washed out by rainfall water or can hydrate what is accompanied by increase of its molar volume.

Degradation of materials on magnesium binder basis I

- Magnesium mortar was developed in 1867 by Sorel – Sorel’s mortar, Sorel’s cement – two component material consisting of caustic magnesite and solution of magnesium chloride ($MgCl_2$) or magnesium sulphate $MgSO_4$
- caustic magnesite– magnesium oxide obtained by magnesite combustion ($MgCO_3$) at 700 – 800°C
- The second main component is magnesium chloride $MgCl_2$ (from carnallite)
- The final properties of hydrated product are dependent on ration of $MgO/MgCl_2$
- ratio range 2:1 – 8:1
- compressive strength of binder it self is after 28 days 60 – 100 MPa
- currently are materials on magnesium binder basis not very very often used in practise (historical lasters, presently část floors – xylolite) – lack of raw materials, more higher-quality binders

Degradation of materials on magnesium binder basis II

- Magnesium mortar has long durability and service life in case of proper treatment and curing

- It has low resistivity against moisture – dissolution of hydrated products, hydrolysis of hardened product → free $MgCl_2$ is dangerous for iron and steel structures– corrosion

- Durability of magnesium binder affects also temperature rising and accompanied water loosening – loss of cohesive forces (binder decomposition)

- degradation of binder due to the carbonation

$$3Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O + 2CO_2 \rightarrow Mg(OH)_2 \cdot 2MgCO_3 \cdot MgCl_2 \cdot 6H_2O + 2CO_2 + H_2O$$

→ carbonation leads to increase of molar volume – rising of tension in porous space – cracks formation