

6A. Degradation of inorganic building materials

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6A. „degradation“ - content

degradation (corrosion) agents

- temperature
- water
- atmosphere
- salts
- biodegradation

degradation of important building materials

- aggregates, building stone, mortar, gypsum...
 - concrete
-

Degradation of building materials

- ❑ **gradual, spontaneous**, slow process in which material loses own characteristic properties due to environment
 - ❑ **corrosion environment** – external agents taking effect on the material (water – ground, rain, surface; temperature, chemicals in soil and air)
 - ❑ degradation of material: loss of strength and cohesion, dissolution, appearance..
 - ❑ corrosion of construction: **lifetime of construction**, reparation costs, loss of material, costs due to forced outage
 - ❑ **prevention of corrosion**: selection of material (..concrete composition), protection of construction against aggressive environment
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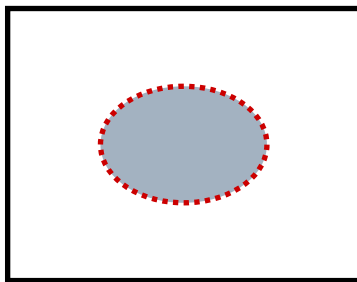
Corrosion actions

- ❑ **physical** caused by physical forces, no chemical reactions
(frost damage of concrete)
 - ❑ **chemical** chemical reactions of material with environments components causing degradation of material
(sulphate degradation of concrete)
 - ❑ **biocorrosion** material is damaged by action of animals, plants and microorganisms and their metabolic products; *(dry rot)*
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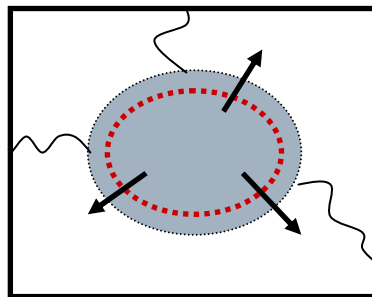
Degradation due to **temperature changes**

- **response of material to temperature changes:**
 - **very high temperature (fire):** thermal decomposition of the material
 - **„common temperature changes“** by cycling day-night, winter-summer and by sun shining (-20 to 40° C)

Thermal expansion: response of material to temperature changes → **tension** on binder+aggregates interface
→ **cracks**



winter



summer

**loss of strength and cohesion,
water attack to
construction**

Degradation due **to water action**

□ **water in building constructions**

- 1. water vapor:** component of atmosphere, everywhere
higher temperature = higher **possible** absolute air humidity
*warm air **may contain** more vapor than the cold one*
relative humidity = degree of saturation by vapor
*at **given temperature***
- 2. equilibrium dampness:** content of water in material
depends on: **air humidity**, temperature, type of material
is caused by vapor condensation in material
 - a) bonded water** – adsorbed on surface

non-moveable, not dangerous, does not freeze

Degradation due **to water action**

□ **water in building constructions**

2. equilibrium dampness: content of water in material

b) free water: liquid in porous system of material
origin: vapor condensation, ground water, rain

movement in pores: up – by **capillary action**

smaller pores = higher elevation

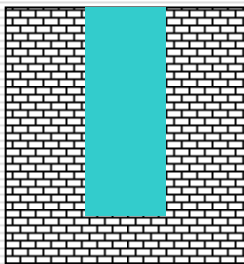
down – by **gravity**



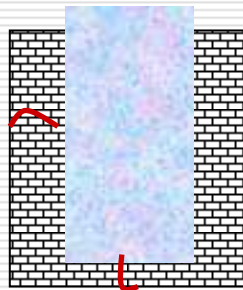
**equilibrium of gravity and capillary
elevation: cm to 2 meters above ground**

Degradation due **to water action**

- ❑ **freezing-thawing action:** ice - 10 % higher volume than liquid water
ice in pores expands and acts by **crystallization pressure** on the pore walls



10 °C



-10 °C

Degradation due **to water action**

- ❑ water is solvent and transport medium for other corrosion agents

1. anorganic and organic salts
2. components of atmosphere (CO_2 , NO_x , SO_x)
3. soluble components of material: $\text{Ca}(\text{OH})_2$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

→ **chemical corrosion**

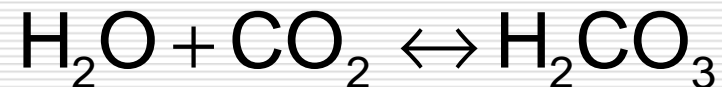
- ❑ water is necessary for life of bacteria, fungi and algae

→ **biocorrosion**

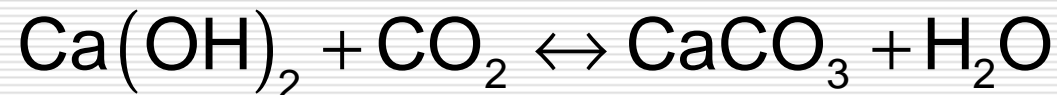
Degaradation by atmosphere

Corrosion agents in atmosphere

CO₂ natural occurence in atmosphere 0,03 %
carbonic acid – the weakest acid, salts carbonates



1. carbonation of lime mortars (+) and concrete (-)



mortar: + hardening

concrete: - reinforcement corrosion, disturbance of
equilibrium composition of cement binder

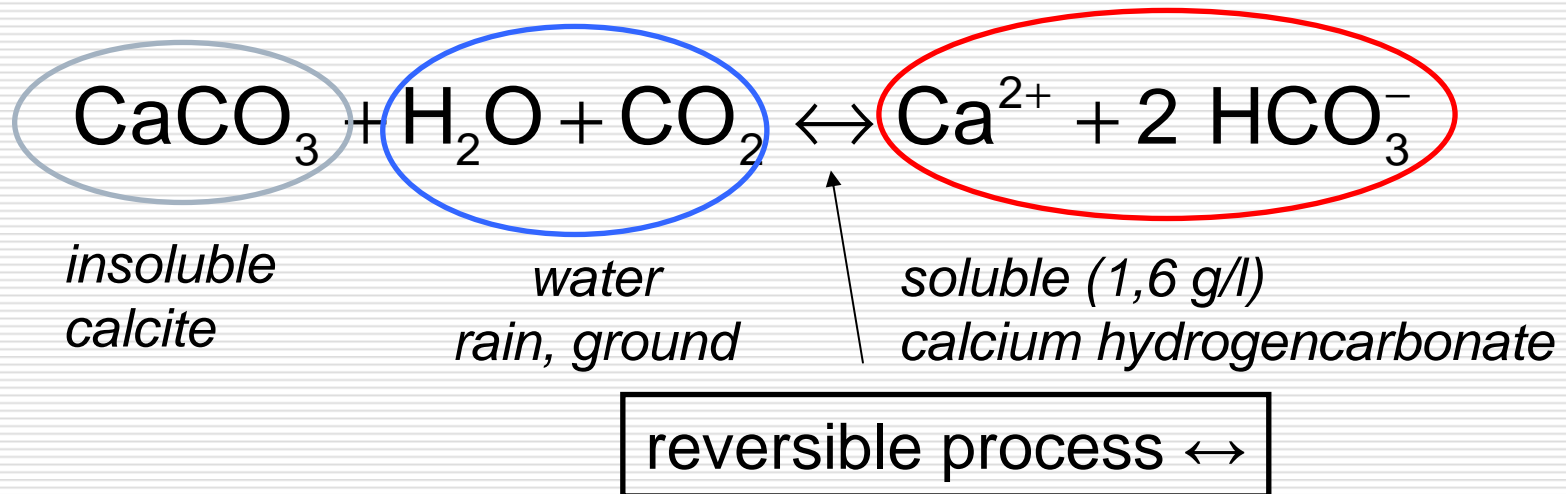
Degaradation by atmosphere

Corrosion agents in atmosphere

CO₂:

2. dissolution of carbonates

calcite CaCO₃: limestone, marble, marl, lime mortars



→ calcite dissolution (high CO₂ in water)

← calcite precipitation (low CO₂ in water, water evaporation)

Degaradation by atmosphere

Corrosion agents in atmosphere

Sulphur oxides SO_2 a SO_3

Nitrogen oxides NO_x (NO , NO_2 , N_2O_3)

origin: industry, transport, energy production

acid-forming oxides: forms acid with water (rain, aerosol)

(acid rain): H_2SO_3 , H_2SO_4 , HNO_2 , HNO_3

$\text{Ca}(\text{OH})_2$ in concrete and mortars– is neutralized to salts

carbonates CO_3^{2-} – salts of carbonic acid (the weakest acid)

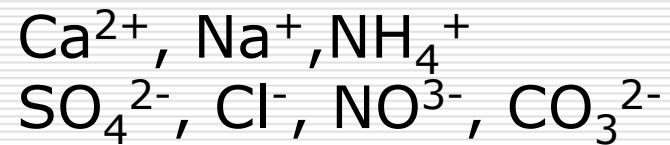
are dissolved by other acids:



loss of strength, dissolution of limestone and marl – statues, historical buildings

Degradation by soluble salts

Common ions in pore solution in building materials:



Origin of salts in buildings:

- materials component ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in gypsum)
 - dissolved in ground water which attacks constructions
 - products of corrosion by acid rains
 - metabolic products of microorganisms and animals
 - winter maintenance of roads and pavements
-

Degradation by soluble salts: **mechanism**

1. salt dissolves in water

unsaturated solution (*unsaturated = water can dissolve even more salt*)

2. the unsaturated solution is transported by pore system (capillary elevation)

3. formation of saturated solution

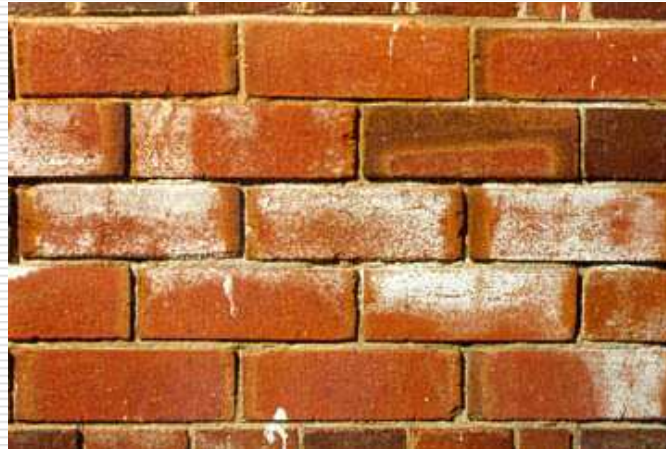
(*saturated – solution with the highest possible concentration of salt – e.g. NaCl 360 g/l*)

→saturation due to **water evaporation** (summer)

4. further evaporation → crystallization of salt from saturated solution

Degradation by soluble salts: **on surface**

- A) the saturated solution is formed on the surface of construction →
crystals are visible - **efflorescence**



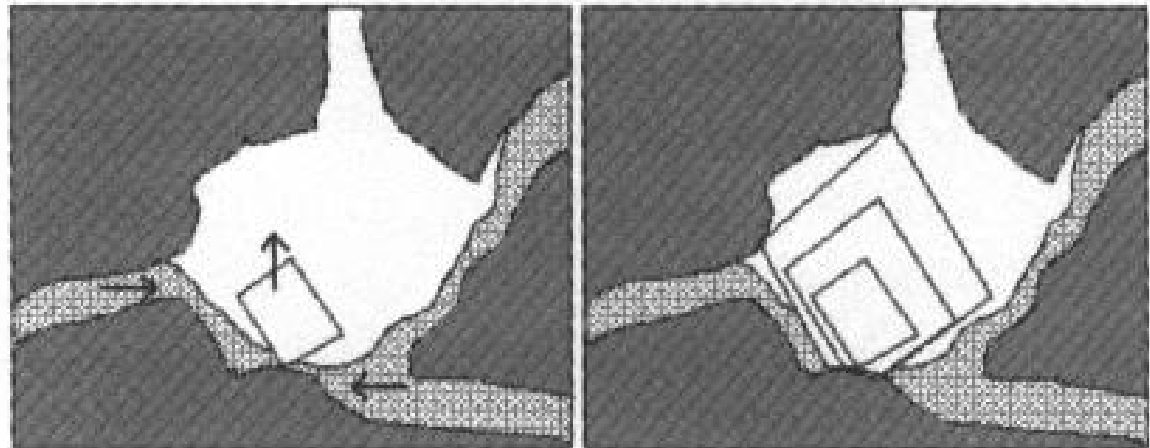
aesthetic problem – historical buildings, frescoes...
efflorescence does not damage the construction

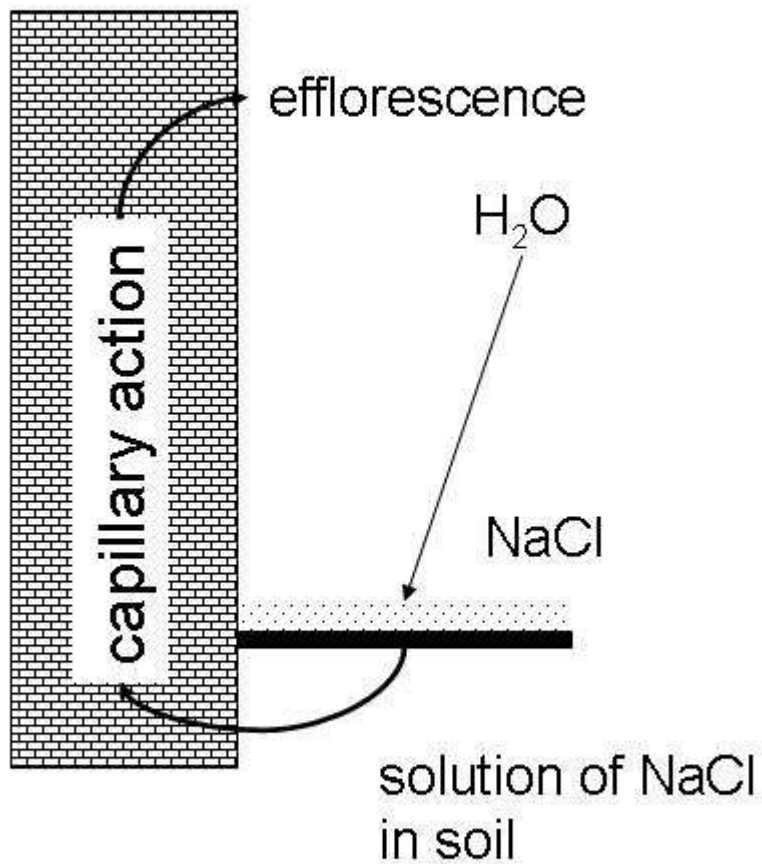
Degradation by soluble salts: crystallization in pore system

B) saturation is reached **in pores of material**
(close to surface) → **crystals are formed** in the pores
(subflorescence)

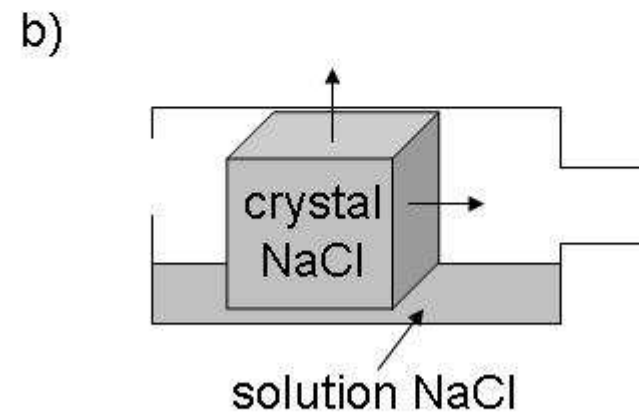
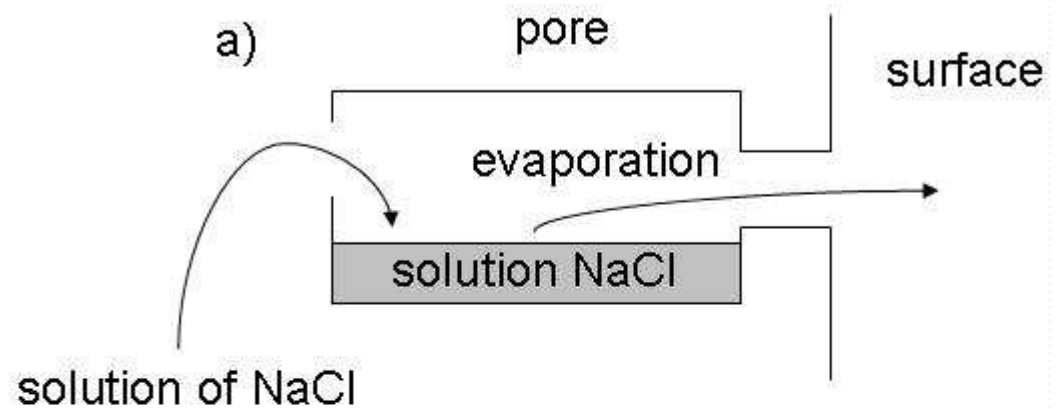
growing crystals generate **crystallization pressure** –
crystals press on the pore walls → up to 100 MPa –
higher than the material's strength →

→ **cracks in construction, flaking of plaster,
disintegration of construction**





Capillary elevation of salt solution in wall



Evaporation of salt solution in pore

Degradation by soluble salts: cyclic hydration and dehydration

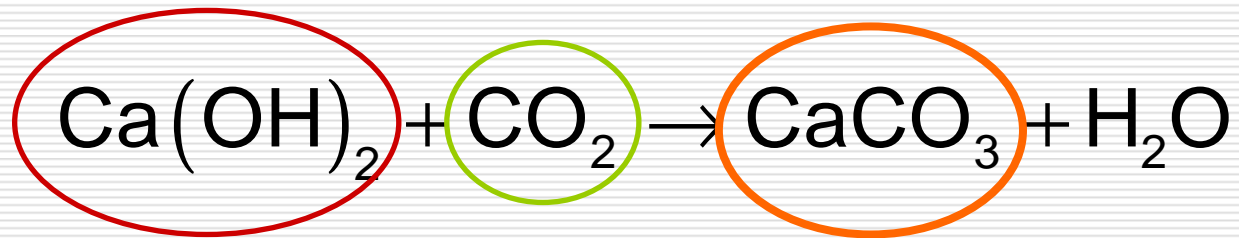
hydrates: crystals containing some molecules of water in structure

| | specific volume $\text{cm}^3 \text{g}^{-1}$ | expansion 1 g Na_2SO_4 crystals volume cm^3 |
|---|---|--|
| Na_2SO_4 | 0,373 | 0,373 (100 %) |
| $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | 0,683 | 1,549 (415 %) |

Hydration and dehydration depend on humidity of air:
in winter are stable hydrates, in summer crystals without
water. **Hydration pressure!**

Degradation by soluble salts: formation of insoluble salts

crystallization of **calcite** on the surface of concrete:



*solution of Ca(OH)_2
in pores of concrete*

from air

*insoluble calcite forms
crystals on surface of concrete*

Biodegradation

Biodegradation: **bacteria**

- ❑ unicellular microorganisms
- ❑ both auto and heterothrophic
- ❑ wide range of environments

sulphur and nitrifying bacteria:

are everywhere (water, soil, **cattle sheds**)
normal temperature, feed, neutral pH...
acquire energy by oxidation of S and N compounds
→ „**produce**“ **sulphates SO_4^{2-} and nitrates NO_3^-** →
source of soluble salts → **salt degradation**

prevention: cleanness, dry, light

Biodegradation: rot and fungi

- ❑ heterotrophic organisms → acquire energy by oxidation of organic substances: **wood, dust, fabric, paper**
 - ❑ environment: feed, damp, normal temperature
 - ❑ damages: sap rot – damage wooden constructions
 mycelium fibers grow in walls –
 mechanical damage
 metabolic production of organic acids
 → dissolve calcite
 - ❑ prevention: **fungicides**, dry, cleanness – no dust
-

Biodegradation: algae

- ❑ autotrophic organisms → production of **CO₂** → **support** dissolution of calcite CaCO₃ (limestone, mortars)
 - ❑ production of organic acid → dissolution of CaCO₃

 - ❑ form colour slimy coatings – water structures
 - ❑ algae growing in pores → expansion and mechanical damage
-

Biodegradation: plants and animals

- ❑ mechanical damage: growing roots, animals action in walls (insects, rats)
 - ❑ animals excrements: hosts bacteria → production of acids and salts → salt corrosion, dissolution of calcite
-

Biodegradation

- ❑ prevention of all kinds of biodegradation:
 - ❑ dry and light environment
 - ❑ cleanness
 - ❑ proper construction – insulation, water drainage
 - ❑ maintenance of building – reduction of ground water attack, rain in, presence of animals and plants...
-

Degradation of building materials

Degradation of building materials

- ❑ freezing-thawing and water action – affect all porous building materials
 - ❑ chemical degradation – depends on chemical composition of the material
 - ❑ biodegradation – wood is most sensitive, other materials are attacked by biodegradation in damp environment
-

Aggregates, stone-cutted products

- **aggregates made from magmatic rocks** (dominant in Czech Republic):

dense – no pores = no damage by ice and water
high chemical resistance

- **limestone aggregates**

calcite **CaCO₃**: attacked by acid rains and by
CO₂ dissolution

Aggregates, stone-cutted products

- aggregates with high content of amorphous SiO_2 (opal, chalcedony) → causes **Alkali-silica reaction - ASR**

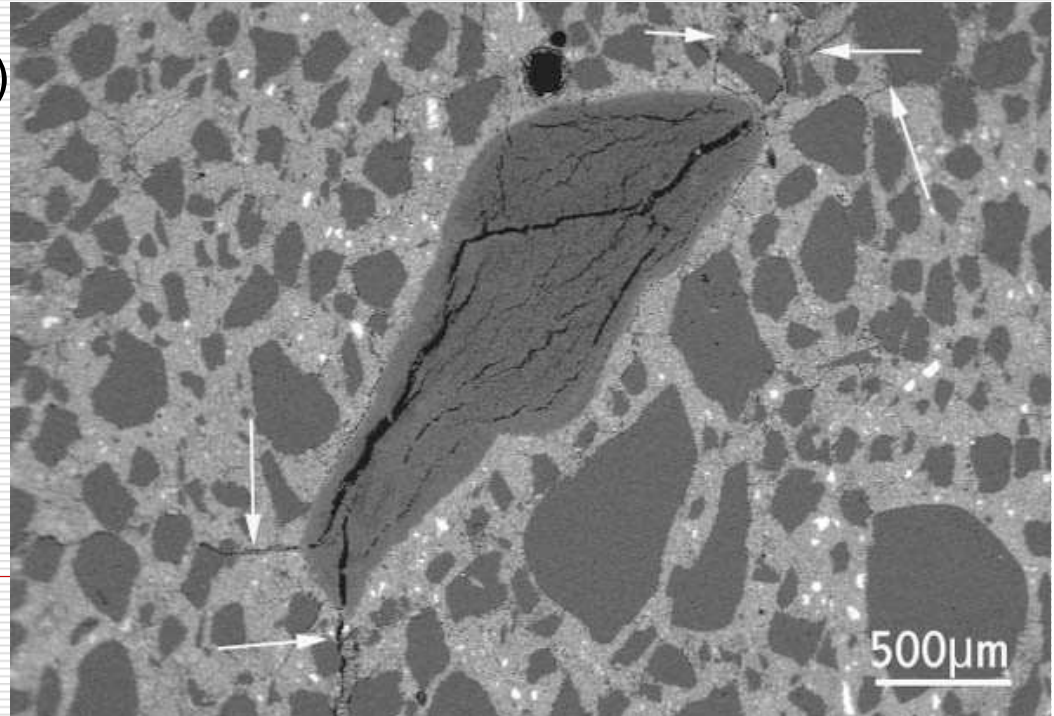
amorphous SiO_2 + NaOH (KOH)



gel of sodium silicate



absorbs water
→ **expansion**



Aggregates, stone-cutted products

- **prevention of alkali-silica reaction**
 - 1. no amorphous SiO_2 in aggregates**
 - maximum content – few percent
 - highest content in river sediments (USA, China)
 - 2. reduce alkali content (Na_2O , K_2O) in cement**



Aggregates, stone-cutted products

□ **sandstone**

porous – sensitive to freezing-thawing and water action

usually contains some calcite CaCO_3 – attacked by acid rains and biocorrosion

Degradation of concrete

Physical degradation of concrete

- ❑ mechanical damage: flowing water, plants..
 - ❑ freezing-thawing damage: depends on **porosity**
higher water/cement ratio → **higher porosity** → **higher freezing-thawing damage**

 - ❑ **thermal degradation of concrete:**
 1. decomposition of hydration products (CSH, CAH) (from 200 C)
 2. dehydration of $\text{Ca}(\text{OH})_2$ (from 500°C)
→ **loss of strength**
 - ❑ different thermal expansion of binder and aggregates:
cracks on interface between binder and aggregates
-

Chemical degradation of concrete

- 1. kind:** dissolution and leaching of binder
- 2. kind:** chemical reactions of binder with environment resulting to **non-binding products** (frequently followed by efflorescence)
- 3. kind:** chemical reactions with formation of **voluminous products** → **expansion**

All chemical corrosion processes cause loss of strength and cohesion

Extreme cases: disintegration of concrete

- 4. corrosion of steel reinforcement**
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Concrete: 1. kind dissolution and leaching

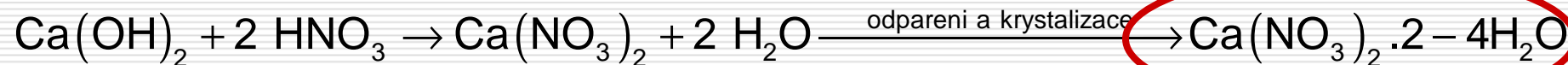
- dissolution of Ca(OH)_2 from cement binder in pore water and consequent **leaching out of Ca(OH)_2**
 - dangerous water: „hungry water“ (soft) – with low content of Ca^{2+} and other minerals (rain and river water)
 - leaching is dangerous for water and underground structures
 - prevention – proper waterproofing
-

Concrete: 1. kind dissolution and leaching

- **reduction of $\text{Ca}(\text{OH})_2$** concentration in concrete causes **disruption of equilibrium** between components of cement binder → results to **decomposition of CSH and CAH** hydrates → **decrease of strength**
 - **decrease of pH** due to lower $\text{Ca}(\text{OH})_2$ → damage of steel reinforcement
 - calcite efflorescence is formed on the surface
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Concrete: 2. kind non-binding products

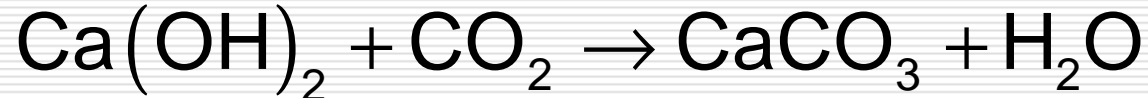
- **acid corrosion:** reaction of $\text{Ca}(\text{OH})_2$ from cement binder with acid components of environment: acids of sulphur and nitrogen (H_2SO_4 , H_2SO_3 , HNO_3) from acid rain and biocorrosion
 - Ca^{2+} salts are formed from $\text{Ca}(\text{OH})_2$ – **no binding ability**
 - decrease of $\text{Ca}(\text{OH})_2$ concentration results to disruption of equilibrium in cement binder and consequent decomposition of CSH and CAH binder
 - formed salt may be soluble → **efflorescence**



Concrete: 2. kind non-binding products

□ **carbonation of concrete:** reaction of $\text{Ca}(\text{OH})_2$ from binder with CO_2 from air or water (water structures)

- calcite CaCO_3 is formed

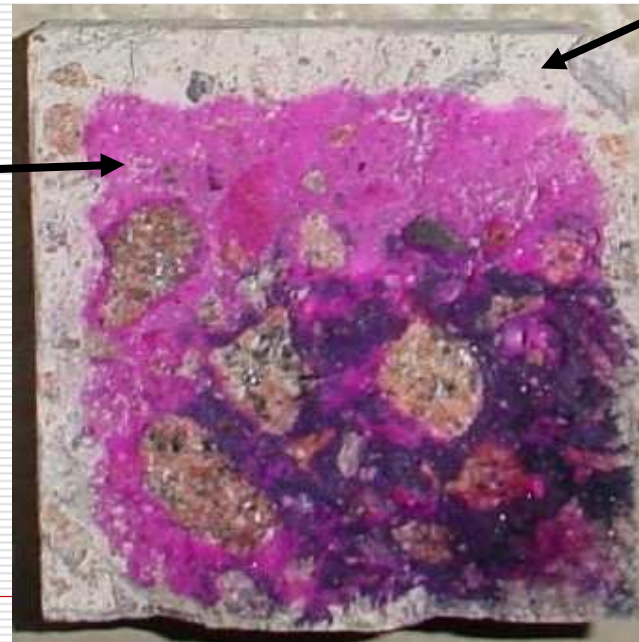


- decrease of $\text{Ca}(\text{OH})_2$ causes:
 - decrease of pH → **corrosion of steel reinforcement**
 - disruption of binder equilibrium
 - in extreme cases may start carbonation of CSH and CAH hydrates to SiO_2 , Al_2O_3 → decrease of strength
-

Concrete: 2. kind non-binding products

- observation of concrete carbonation by phenolphthalein: colour change at pH 8-10

violet:
pH > 10
high $\text{Ca}(\text{OH})_2$
OK

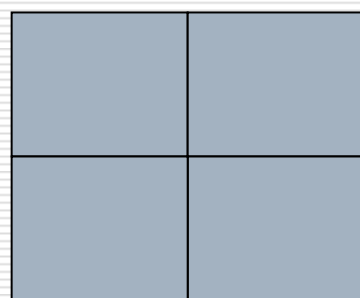


no colour:
pH \approx 8
carbonated concrete
no $\text{Ca}(\text{OH})_2$
**reinforcement
is damaged**

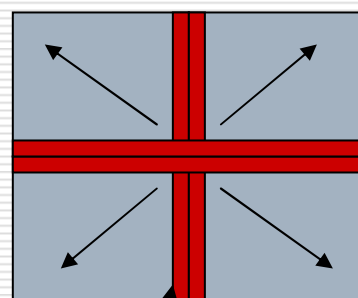
concrete cube

Concrete: 3. kind expansive products

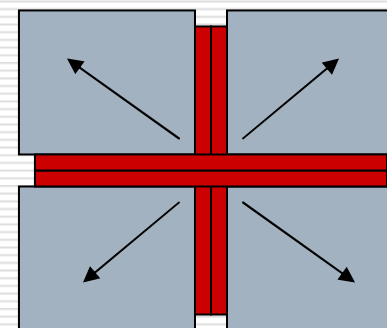
- chemical reactions having **voluminous products** → are formed and crystallized in concrete and generated crystallization pressure – products expansion damages structure of concrete: decrease of strength, disintegration



sulphate attack



*voluminous product
on grains boundaries*



expansion of binder

Concrete: 3. kind expansive products

□ sulphate expansion (gypsum expansion)

sulphate attack on concrete: ground water

sea water

sulphates from aggregates

sulphides: may be found in aggregates, are spontaneously oxidized to sulphates

test of aggregates on presence of sulphides and sulphates:

*1. **HCl** decomposes sulphides to H_2S (smells)*

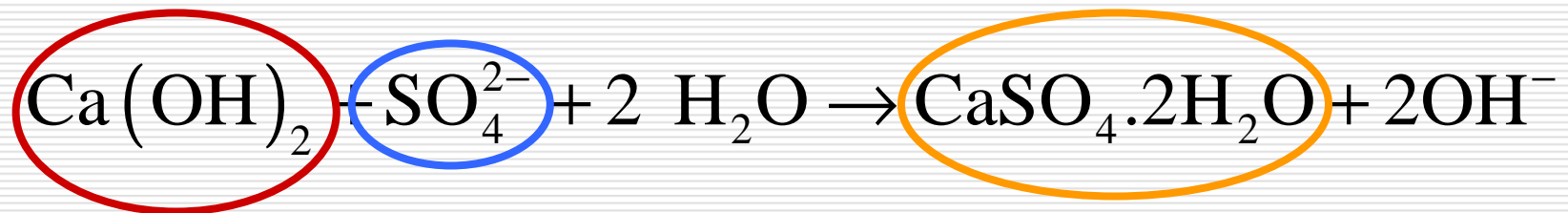
*2. sulphates are precipitated by **BaCl₂** as insoluble $BaSO_4$*

Concrete: 3. kind expansive products

□ sulphate expansion

■ mechanism:

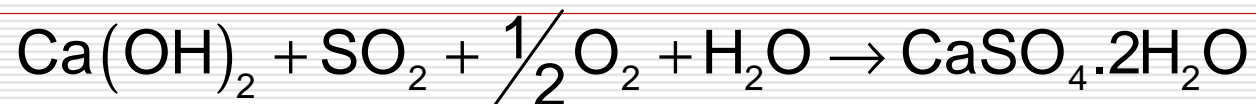
1. formation of gypsum



in concrete

**gypsum
volume + 17 %**

formation of gypsum from SO₂ from air:



Concrete: 3. kind expansive products

□ sulphate expansion

■ mechanism:

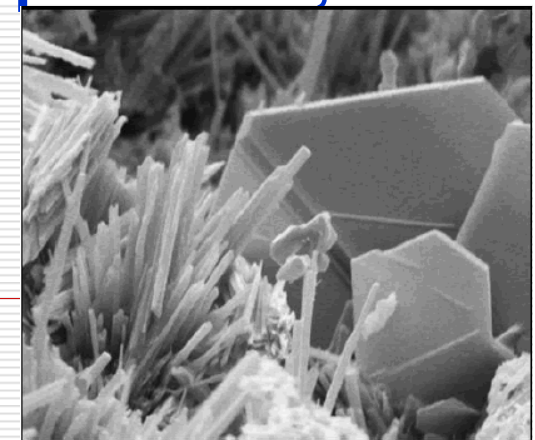
2. formation of ettringite



hydrate C_3AH_6
from concrete

gypsum

ettringite
expansion 2,65x



Concrete: 3. kind expansive products

□ **protection of concrete against sulphate expansion:**

- prevent from contact of concrete with high-sulphate water

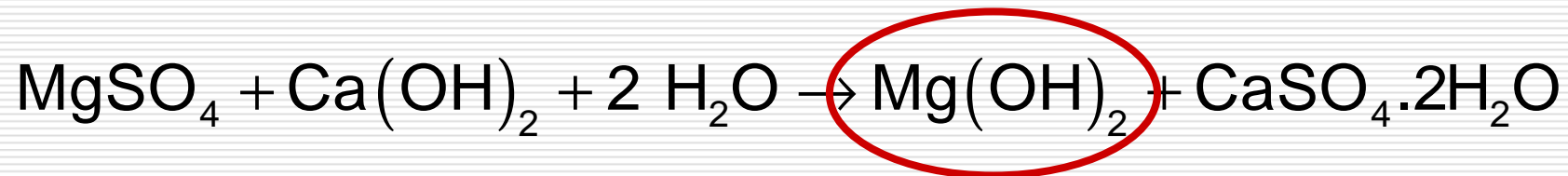
■ **sea structures:**

- cement with low C_3A (*to 5 %*)
 - low porosity of concrete (low w/c)
 - adding of pozzolana (slag) → it reacts with $Ca(OH)_2$ instead of gypsum formation
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Concrete: 3. kind expansive products

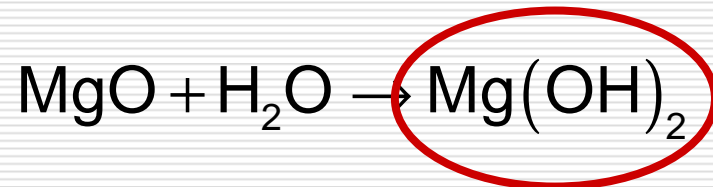
□ magnesium expansion

1. kind reaction of soluble Mg^{2+} salts (ground and sea water) with $\text{Ca}(\text{OH})_2$ in concrete



voluminous product

2. kind reaction of MgO (v cementu) with water:



slow process: takes place in settled concrete

Concrete: salt corrosion

□ chloride corrosion

origin of chlorides: winter maintenance salt, sea water

CAH hydrates react with chlorides (NaCl, CaCl₂) to

Friedel's salt $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$ (non-binding)

1. expansion of Friedel's salt

2. decrease of strength due to decrease of CAH concentration

□ salt corrosion: efflorescence and crystallization pressure

Concrete: salt corrosion

□ **sea water corrosion**

leaching out of $\text{Ca}(\text{OH})_2$ and decomposition of CSH and CAH hydrates

reaction of CAH to Friedel's salt

sulphate expansion

magnesium expansion

crystallization and cyclic hydration-dehydration of salts in pores of concrete

□ **prevention of salt corrosion of concrete**

low porosity (low w/c)

low C_3A in concrete

low $\text{Ca}(\text{OH})_2$ in concrete – use of blended cements with pozzolana content

Concrete: corrosion of steel reinforcement

- ❑ fresh concrete: very high pH (alkaline ≈ 12)
steel is **passivated** – layer of $\text{Fe}(\text{OH})_3$ protects steel against corrosion
- ❑ carbonated concrete: pH slowly decreases \rightarrow the passive layer is destroyed when pH decreases app. to 9,5 \rightarrow corrosion of reinforcement takes place
- ❑ **loss of contact between concrete and reinforcement**



Concrete: corrosion of steel reinforcement

□ **reinforcement protection**

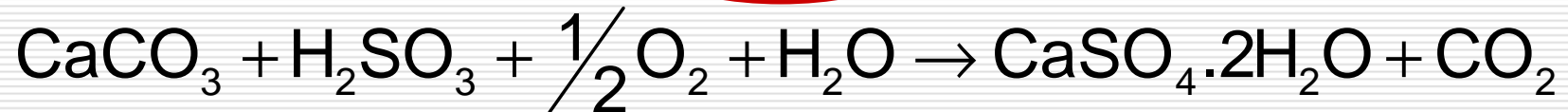
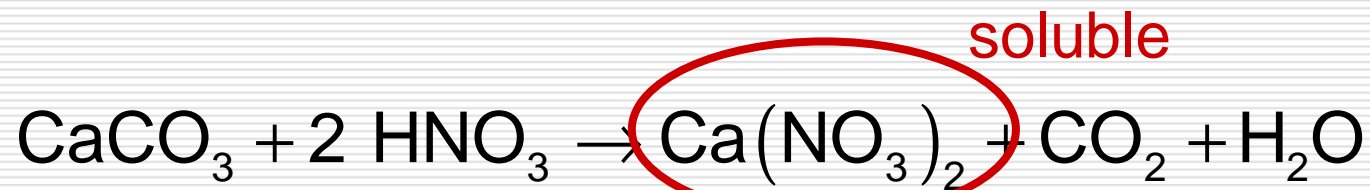
good concrete – no cracks – carbonation starts
in cracks

stainless steel reinforcement – expensive

cathodic protection of reinforcement

Degradation of materials based on calcium carbonate CaCO_3

- calcite CaCO_3 is dominant component of **lime mortars and plasters**, limestone, marlstone
- CaCO_3 is dissolved by all acids – both inorganic and organic (acid rains, biodegradation)



- **mortars with cement – higher corrosion resistance**
-

Degradation of gypsum

- ❑ gypsum = typical air binder
 - ❑ solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: **2,4 g/l**
 - ❑ dissolves mainly in **flowing water**
 - ❑ solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is **acid** → **steel corrosion**
gypsum can not be reinforced
 - ❑ gypsum in wet environment: **hydrofobization**
(hydrofobized gypsum repels water)
 - ❑ thermal stability of gypsum: **very low**
gypsum decomposes from 60 °C, from 120 °C
decomposes rapidly to hemihydrate $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$
-

Degradation of ceramics

- ❑ ceramics: high resistance to thermal and chemical action (dissolves only in HF)
 - ❑ physical corrosion: degradation by freezing-thawing action and by **salts**
 - ❑ resistance depends on granulometry of raw materials (Winkler diagram)
 - ❑ unfired bricks: sensitive to flood
-

Degradation of glass

- ❑ weak point - brittleness
 - ❑ chemical corrosion: glass dissolves in HF
 - ❑ and in **highly alkaline solutions**
(cheap or old glass in dishwasher)
 - ❑ increase of resistivity to alkalies:
boiling of glass in water or acid – surface layer
is enriched by SiO_2 – more resistant to alkalies
-

Wood degradation

- ❑ biodegradation – rot, insects
 - ❑ oscillation of temperature and humidity: causes contraction and swelling → cracks
 - ❑ chemical degradation: wood is attacked by oxidising agents, acids and bases → depolymeration and oxidation of cellulose, change of color and mechanical properties
 - ❑ wood of coniferous trees is more chemically stable than wood of deciduous
 - ❑ wood protection: fungicides, biocides, fire protection
-

Degradation of synthetic polymers

- depends on composition of the polymer
 - generally: high chemical stability
 - low thermal stability:** softening, melting, burning, thermal decomposition
 - UV radiation** (sun) causes **photochemical reactions** in polymer – decomposition of polymer chain (embrittlement)
 - biocorrosion of polymers: organic compounds serve as nutrient for fungi (rot) and bacteria
-

Goals

- describe principals of physical corrosion of building materials
 - degradation by water action
 - degradation by aggressive gasses
 - behaviour of salt in porous materials
 - biodegradation
 - chemical degradation of concrete
-

6B. Analytical chemistry

Analytical chemistry in civil engineering

□ **analysis of materials**

composition of cement, lime etc., content of sulphates in aggregates

□ **environmental analysis**

composition of **water**: drinking, mixing water for concrete, ground water – contains dangerous components for building materials

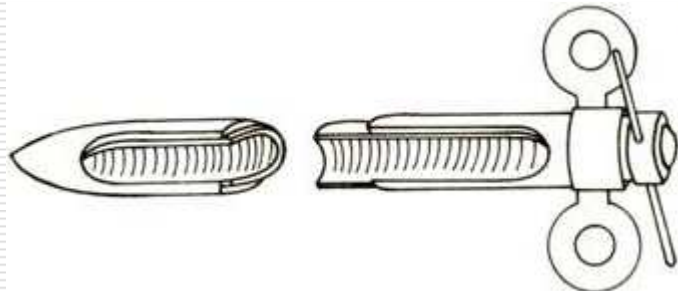
composition of **soil**: contamination by toxics

□ **waste analysis before landfilling**

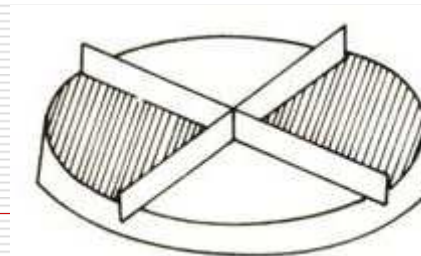
rubble composition, contaminated soils (oil, heavy metals Hg, Cu, Pb, Cd...)

Sampling

- ❑ **representative sample** contains all components of the material in the same ratio as are present in the sampled material
- ❑ sampling of liquids and gasses: usually homogeneity – no problem
- ❑ sampling of solids: the material is crushed, homogenized, quartered



sampler for solids and powders



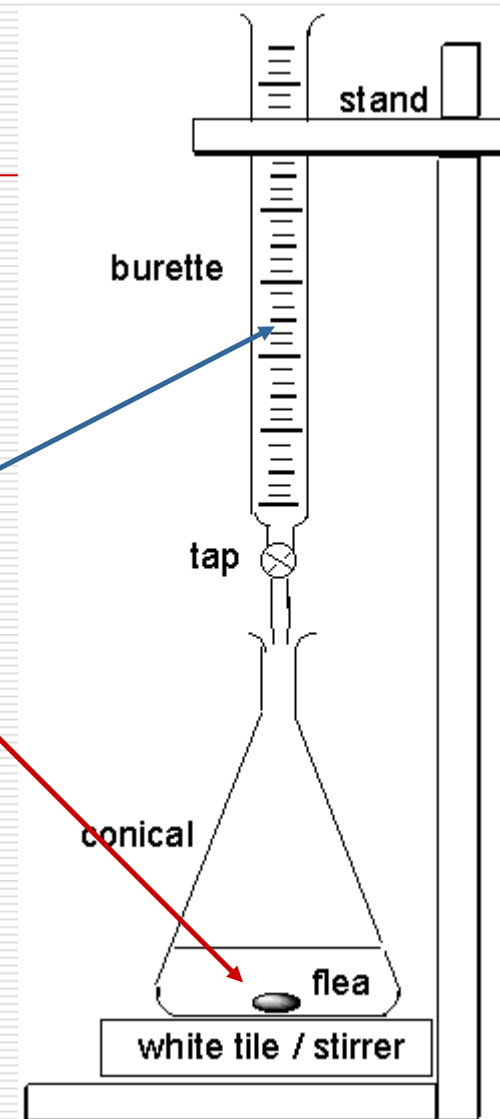
quartering

Chemical analysis

- ❑ qualitative: composition of sample (elements, ions, molecules)
 - ❑ quantitative: determination of concentration of components
 - ❑ conventional: **volumetry** and **gravimetry**
 - ❑ instrumental: by help of instruments
-

Volumetry - titration

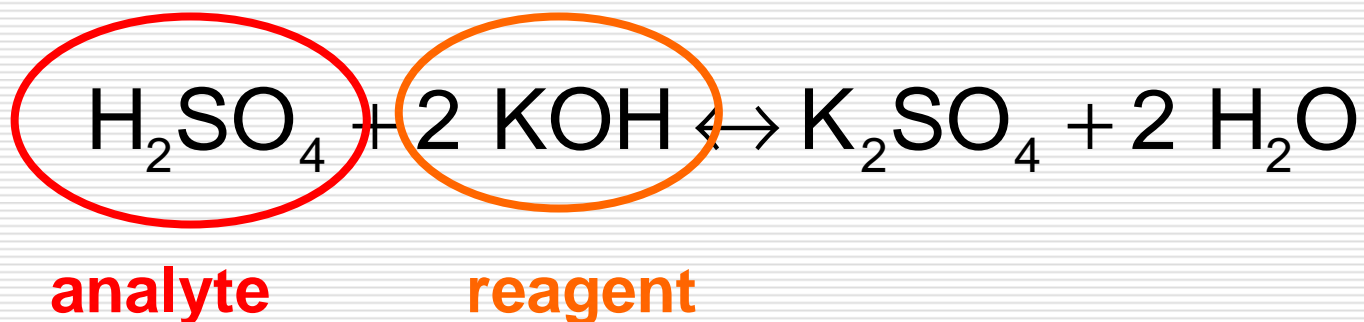
- for determination of concentration of a compound **in liquid solution**
- unknown solution = **analyte**
- **reagent** = standard solution of a compound (titrant)
- principle: analyte reacts with **equivalent** amount of reagent according known chemical reaction
- endpoint of titration – by visual **indicator** (point of equivalence)



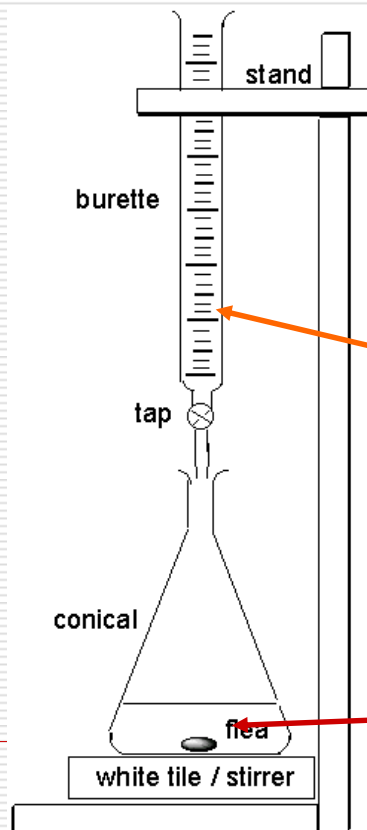
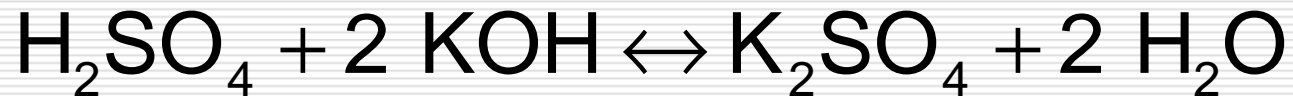
Volumetry - titration

□ acid-base titration:

- for determination of acid concentration by help of KOH reagent
- acid reacts with a base
- endpoint indicated by pH measurement (colour change of a chemical indicator, pH meter)



Volumetry - titration



$$\frac{n_{\text{ACID}}}{n_{\text{KOH}}} = \frac{1}{2}$$

$$n_{\text{ACID}} = \frac{1}{2} \cdot n_{\text{KOH}}$$

$$c_{\text{ACID}} \cdot V_{\text{ACID}} = \frac{1}{2} \cdot c_{\text{KOH}} \cdot V_{\text{KOH}}$$

$$c_{\text{ACID}} = \frac{\frac{1}{2} \cdot c_{\text{KOH}} \cdot V_{\text{KOH}}}{V_{\text{ACID}}}$$

Gravimetry

- analyte is **precipitated** by a chemical reaction in form of a **known and insoluble product**
- Fe^{3+} ions are precipitated in alkaline environment as **insoluble $\text{Fe}(\text{OH})_3$**



filtration, drying,
weighing

$$C_{\text{Fe}} = \frac{n_{\text{Fe}}}{V} = \frac{\frac{m_{\text{Fe}(\text{OH})_3}}{M_{\text{Fe}(\text{OH})_3}}}{V}$$

