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ÚJV Řež, a. s.

The role of pH in the Czech plug system and a summary of assumed pH influence in the Czech safety case

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pH - background and measurement

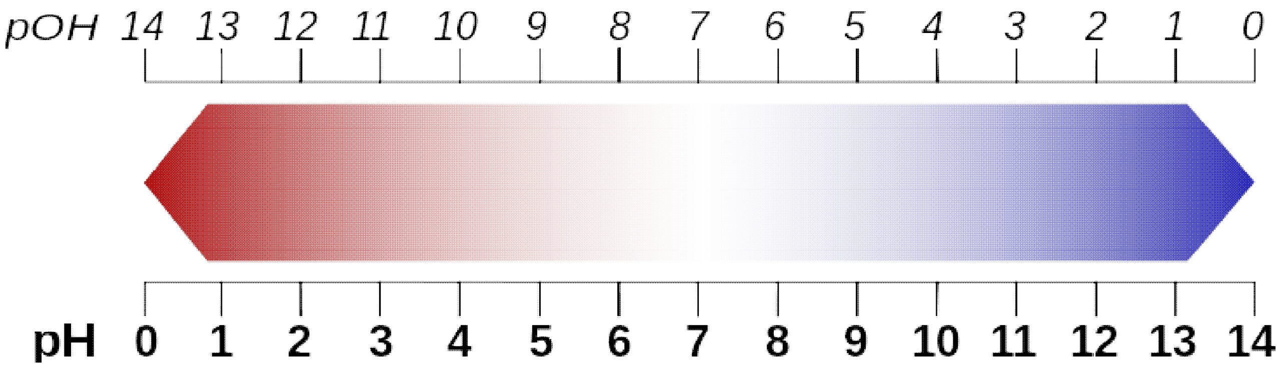
pH

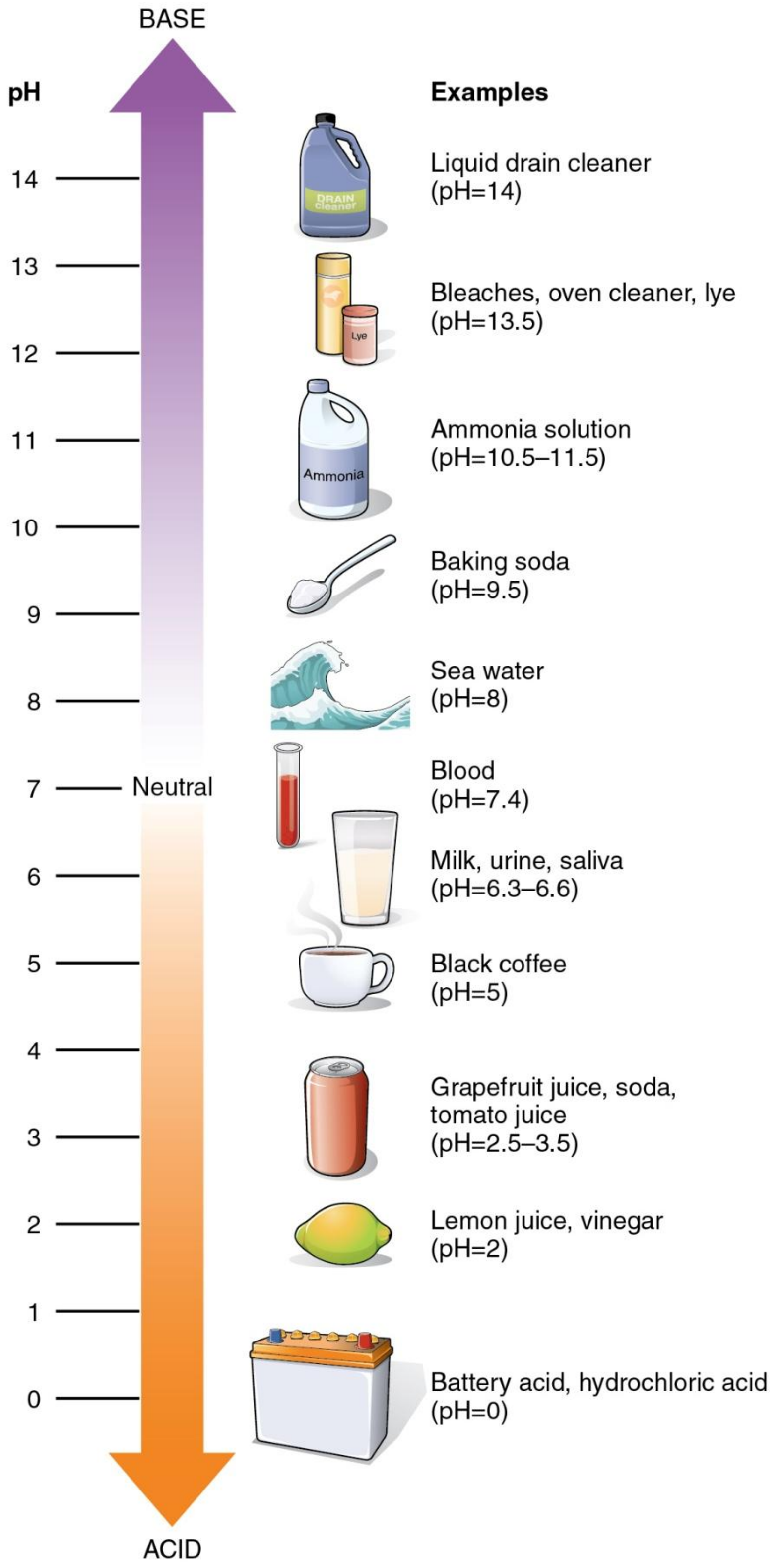
- numeric scale used to specify the acidity or alkalinity of an aqueous solution
- the negative of the logarithm to base 10 of the activity of the hydrogen ion

$$pH = -\log_{10}\left(a_{H^+}\right)$$

- values range: 0-14

  pH < 7- acidic, pH = 7 - neutral, pH > 7 - alkaline / basic




BASE
pH
Examples
14
13
12
11
10
9
8
7
Neutral
6
5
4
3
2
1
0
ACID
DRAIN cleaner
Lye
Ammonia
Liquid drain cleaner (pH=14)
Bleaches, oven cleaner, lye (pH=13.5)
Ammonia solution (pH=10.5–11.5)
Baking soda (pH=9.5)
Sea water (pH=8)
Blood (pH=7.4)
Milk, urine, saliva (pH=6.3–6.6)
Black coffee (pH=5)
Grapefruit juice, soda, tomato juice (pH=2.5–3.5)
Lemon juice, vinegar (pH=2)
Battery acid, hydrochloric acid (pH=0)

pH measurement

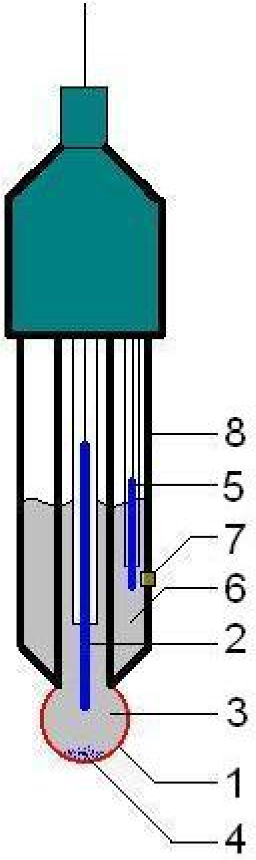
- an indicative – pH indicators

their color changes with pH

- precise – pH electrode

pH electrode

- combines the glass and reference electrodes into one body



1 - a sensing part of electrode, a bulb made from a specific glass

2 - internal electrode, usually silver chloride electrode or calomel electrode

3 - internal solution, usually a pH=7 buffered solution of 0.1 mol/L KCl

4 - when using the AgCl electrode, a small amount of AgCl can precipitate

5 - reference electrode, usually the same type as 2

6 - reference internal solution, usually 0.1 mol/L KCl

7 - junction with studied solution - frit usually made from ceramics

8 - body of electrode, made from non-conductive glass or plastics

pH meter

- consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading
- measuring of electric potential – transfer to pH values
- laboratory or field/in-situ devices

pH buffers

- for calibration
- available for all pH range
  - in laboratory: pH = 7, 9, 11 and 13

Cement and concrete
composition, behaviour, alkaline plume, pH

Cement

- **hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water forms a paste, which sets and hardens by means of hydration reactions and processes, and which retains its strength and stability even under water after hardening.**

(EN 197-1:2000)

Paste – is obtained by mixing cement and water.

Mortar – is obtained by mixing cement, water and sand.

Concrete – is obtained by mixing cement, water, sand, and coarser aggregates (and other components).

Cement and concrete composition, behaviour, alkaline plume, pH

- Can exist as natural product
- at Maqarin and Khuysham Matruk (Jordan) natural cements were produced in situ by combustion of a bituminous marl (an organic-rich clay, biomicrite) 10^5 to 10^6 years ago

- Man-made material
- in 1824 Joseph Aspdin took out a patent on Portland cement, a material he produced by burning powdered limestone and clay
- in 1845 Isaac Johnson made the first modern Portland cement by firing a blend of chalk and clay at high temperature (1400-1500°C), similar to those used today

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Cement and concrete
composition, behaviour, alkaline plume, pH

- **Production**

- **raw mix obtained by blending a calcareous material (limestone) with a small amount of an argillaceous one (clay or shale). These materials are crushed to a very fine powder (<200 μm) and then blended in the correct proportions.**

- **this blended raw material is heated in a rotary kiln where it reaches a temperature of about 1400-1500 °C. The material formed in the kiln is described as clinker.**

- **to produce Portland cement, the clinker is ground together with a small amount of gypsum to control the setting properties.**

Cement and concrete composition, behaviour, alkaline plume, pH

- 5 main cement types:

  CEM I – Portland cement

  CEM II – Portland-composite cement

  CEM III – Blastfurnace cement

  CEM IV – Pozzolanic cement

  CEM V – Composite cement

- Cement chemistry notation

C = CaO	S = SiO_2	A = Al_2O_3	Ŝ = SO_3	F = Fe_2O_3
H = H_2O	M = MgO	T = TiO_2	K = K_2O	N = Na_2O

Cement and concrete
composition, behaviour, alkaline plume, pH

27 products in the family of common cements (EN 197-1:2000)

Main types	Notation of the 27 products (types of common cement)		Composition (percentage by mass [a])										
			Main constituents										Minor additional constituents
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						natural	natural calcined	siliceous	calca-reous				
			K	S	D [b]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	–	–	–	–	–	–	–	–	–	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	–	–	–	–	–	–	–	–	0-5
		CEM II/B-S	65-79	21-35	–	–	–	–	–	–	–	–	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	–	6-10	–	–	–	–	–	–	–	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	–	–	6-20	–	–	–	–	–	–	0-5
		CEM II/B-P	65-79	–	–	21-35	–	–	–	–	–	–	0-5
		CEM II/A-Q	80-94	–	–	–	6-20	–	–	–	–	–	0-5
		CEM II/B-Q	65-79	–	–	–	21-35	–	–	–	–	–	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	–	–	–	–	6-20	–	–	–	–	0-5
		CEM II/B-V	65-79	–	–	–	–	21-35	–	–	–	–	0-5
		CEM II/A-W	80-94	–	–	–	–	–	6-20	–	–	–	0-5
		CEM II/B-W	65-79	–	–	–	–	–	21-35	–	–	–	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	–	–	–	–	–	–	6-20	–	–	0-5
		CEM II/B-T	65-79	–	–	–	–	–	–	21-35	–	–	0-5
	Portland-limestone cement	CEM II/A-L	80-94	–	–	–	–	–	–	–	6-20	–	0-5
		CEM II/B-L	65-79	–	–	–	–	–	–	–	21-35	–	0-5
		CEM II/A-LL	80-94	–	–	–	–	–	–	–	–	6-20	0-5
		CEM II/B-LL	65-79	–	–	–	–	–	–	–	–	21-35	0-5
	Portland-composite cement [c]	CEM II/A-M	80-94	<---------- 6-20 ---------->									0-5
		CEM II/B-M	65-79	<---------- 21-35 ---------->									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	–	–	–	–	–	–	–	–	0-5
		CEM III/B	20-34	66-80	–	–	–	–	–	–	–	–	0-5
		CEM III/C	5-19	81-95	–	–	–	–	–	–	–	–	0-5
CEM IV	Pozzolanic cement [c]	CEM IV/A	65-89	–	<-------- 11-35 -------->					–	–	–	0-5
		CEM IV/B	45-64	–	<-------- 36-55 -------->					–	–	–	0-5
CEM V	Composite cement [c]	CEM V/A	40-64	18-30	–	<---- 18-30 ---->			–	–	–	–	0-5
		CEM V/B	20-38	31-50	–	<---- 31-50 ---->			–	–	–	–	0-5

a The values in the table refer to the sum of the main and minor additional constituents.
b The proportion of silica fume is limited to 10 %.
c In Portland-composite cements CEM II/A-M and CEM II/B-M, in pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).

Cement and concrete composition, behaviour, alkaline plume, pH

- hydration of C_3S and C_2S

calcium silicates + water → calcium silicate hydrate + portlandite

Dissolution:

$Ca_3SiO_5 + 3\,H_2O \rightarrow 3\,Ca^{2+} + H_2SiO_4^{2-} + 4\,OH^-$

$Ca_2SiO_4 + 2\,H_2O \rightarrow 2\,Ca^{2+} + H_2SiO_4^{2-} + 2\,OH^-$

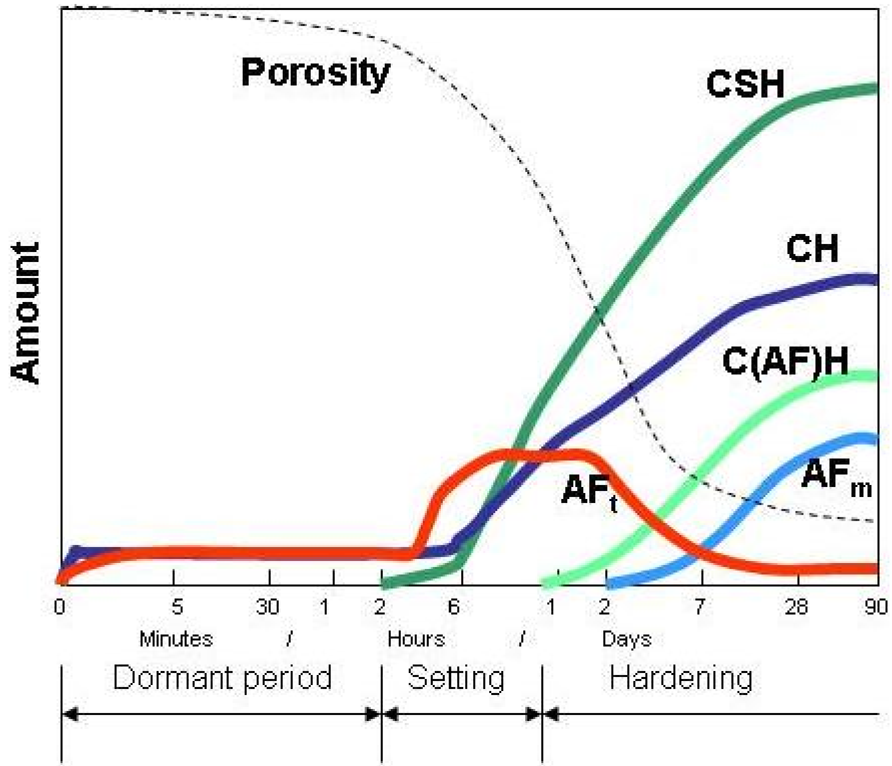
Precipitation:

$x\,Ca^{2+} + H_2SiO_4^{2-} + 2(x-1)\,OH^- \rightarrow (CaO)_x(SiO_2)(H_2O)_y$

$Ca^{2+} + 2\,OH^- \rightarrow Ca(OH)_2$

To sum up:

$C_3S, C_2S + H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2$



Source: ITC School (2008), Eurajoki, Finland © Posiva & CAU DIT COUMES C.: Basics of cement chemistry

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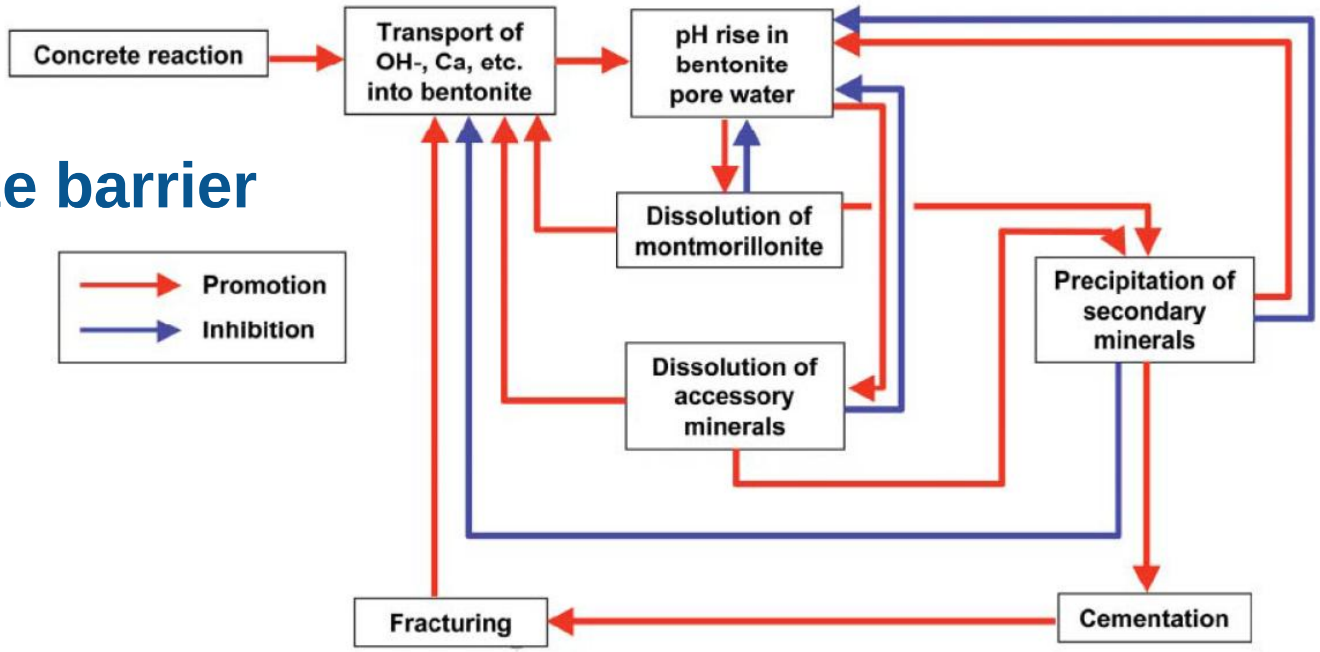
Cement and concrete composition, behaviour, alkaline plume, pH

- **Cement water composition**
  - highly basic (pH = 12.5-13.5)
  - main components:

    OH^-, Ca^{2+}, K^+, Na^+, SiO_3^{2-}, SO_4^{2-}

- **Alkaline plume**
  - can influence bentonite barrier
  - some of the important processes involved in bentonite alteration



ITC School (2008), Eurajoki, Finland © Posiva:
R. Alexander: Applications and long-term safety and performance aspects II: a new natural analogue of bentonite alteration by low alkali cement leachates

Influence of alkaline plume on bentonite properties

- **Effect of alkaline plume**
  - Effect of pH – influencing stability fields of various mineral phases
  - Effect of chemical composition – degradation products of concrete (especially alkaline waters rich in Na, K, Ca)

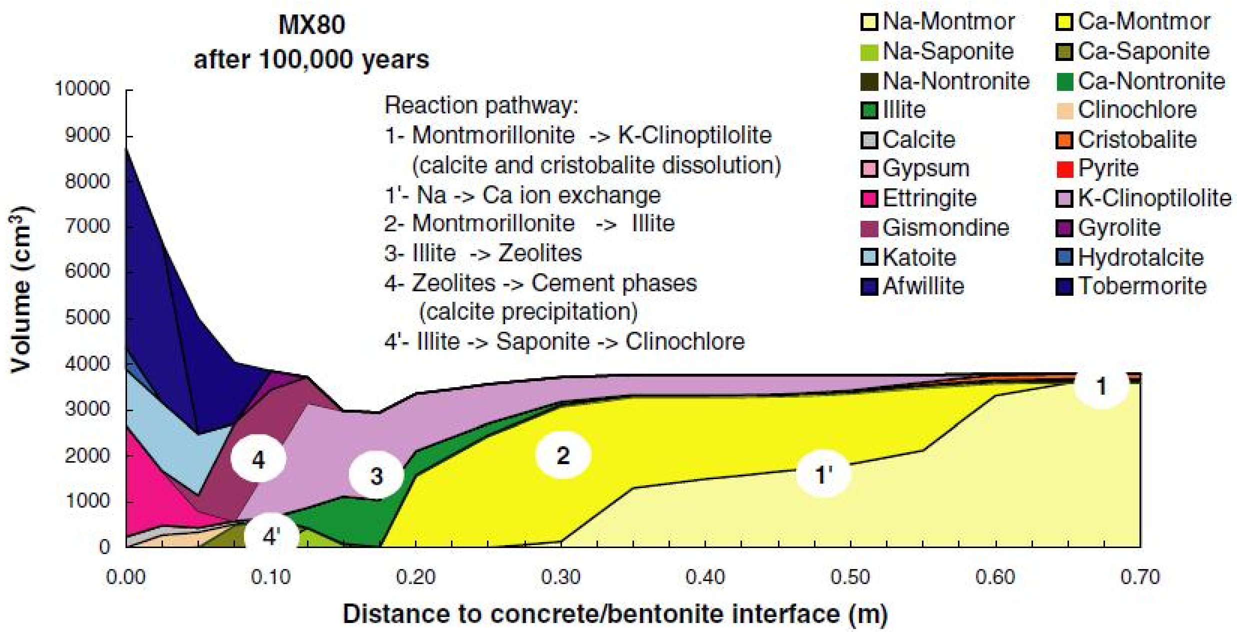
⬇

  - Change in composition of bentonite porewater
  - Accessory minerals dissolution
  - New mineral phases formation and mineral transformation (both as a result of concrete degradation and bentonite alteration)
  - Clogging of bentonite pore space by the newly-formed minerals

Influence of alkaline plume on bentonite properties

Effect of alkaline plume

- Long term processes – reaction paths and products depend on the concrete type, bentonite ionic form and accessory minerals presence
- Important factors – temperature, time, volume of materials in the interaction, diffusion coefficients of species in bentonite
- Modeling of long-term alteration and its spatial range in bentonite – important for the prediction of spatial range and alteration rate



Example of modeling – Composition of a clay barrier after 100,000 years of interaction with an effective diffusion coefficient of 10^{-11} $m^2.s^{-1}$ (from Gaucher and Blanc, 2006)

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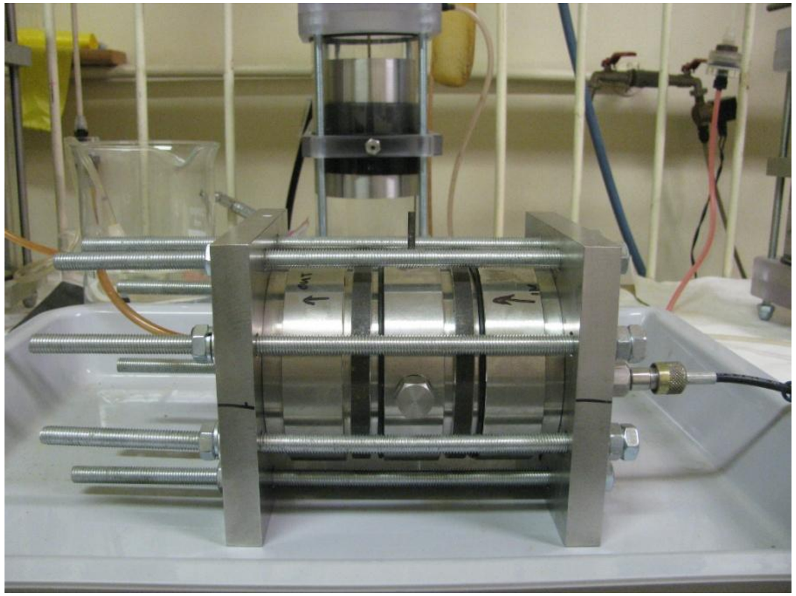
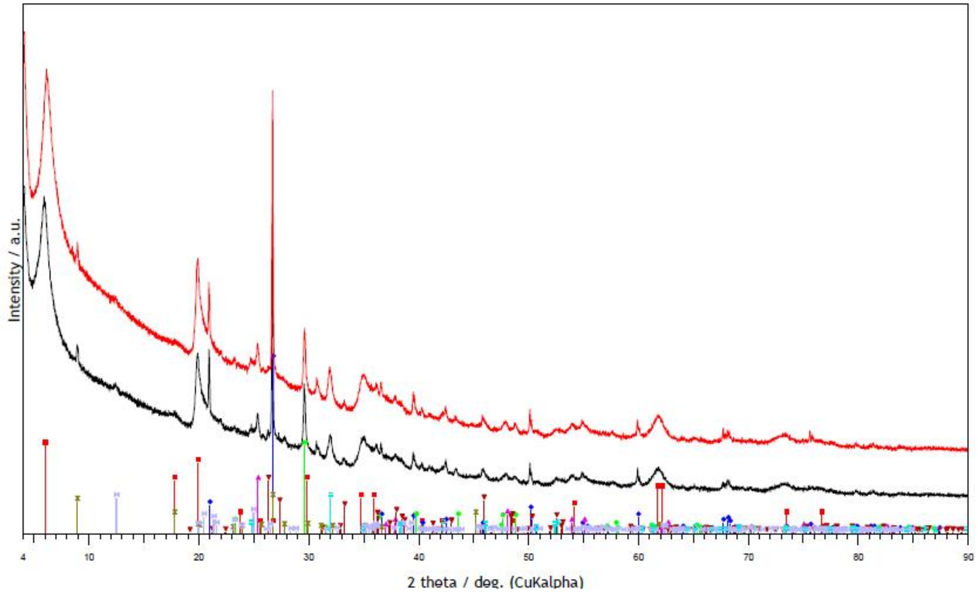
Influence of alkaline plume on bentonite properties

Small scale laboratory and physical models

- Spatial range depends on concrete type, used bentonite and time
- Laboratory conditions often far from the repository conditions (high-pH solutions (e.g. NaOH), high temperature, low amount of bentonite ® to obtain alteration products)
- Physical models and URL experiments close to real conditions are very time-consuming, amount of alteration products may be very low



Physical Interaction Model of the EPSP plug (project DOPAS)



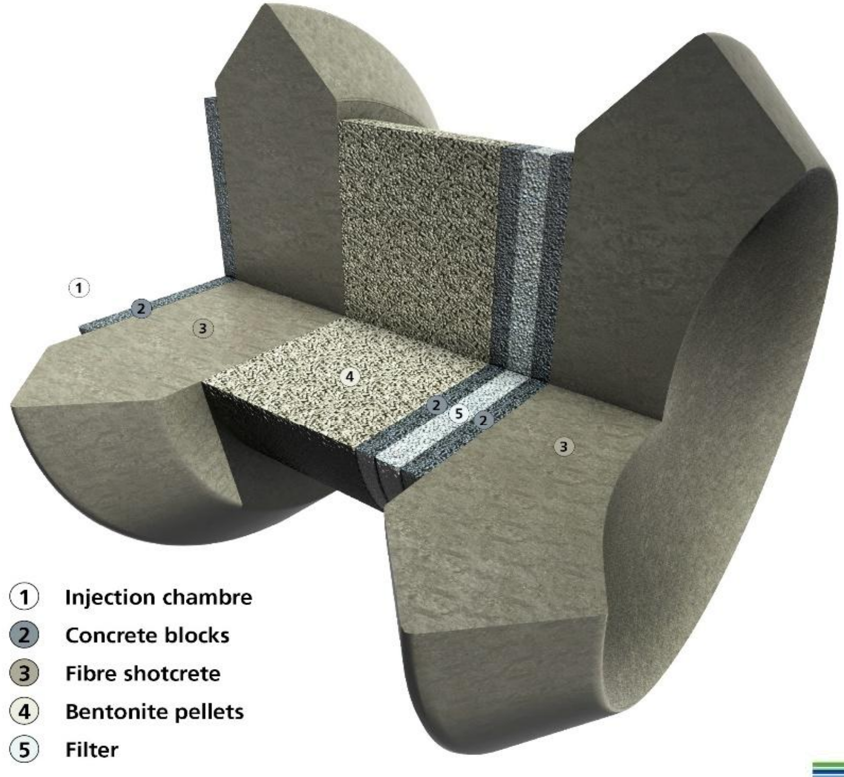
Bentonite RTG diffraction patterns after 20 months (red line) and after 26 months (black line) of bentonite 75 interaction with OPC in underground laboratory Josef conditions (from project FR-TI1/362)

Concrete mixtures for EPSP

- Concrete plugs in EPSP are constructed of sprayed fibre concrete
- Low-pH concrete mixtures were developed in cooperation on the experimental basis of ÚJV and subcontractor
- Two mixtures were tested in experimental niche in URL Josef

- Composition:
  - cement CEM II/B-M,
  - micro silica,
  - aggregates 0-4 & 4-8,
  - glass fibres,
  - plasticiser,
  - retardant and accelerator.

Exact recipe of the mixture is the internal know-how of the subcontracting company



3D model of EPSP (DOPAS Project)

Concrete mixtures for EPSP

- Material properties of concrete plug were projected to fulfill following limits (with norms or procedures of testing):

  - leachate pH < 11.7 (Alonso et al. (2012) - SKB R-12-02)
  - compressibility strength > 30 MPa (ČSN EN 12390-3)
  - flexural strengths > 3 MPa (ČSN EN 14488-3)
  - hydraulic conductivity < 10^{-8} m/s (ČSN CEN ISO/TS 17892-11)
  - fibre content > 3 kg/m^3 (ČSN EN 14488-7)

- Control measurements have confirmed fulfillment of limits and conditions

pH of the leachate = 11.4-11.5

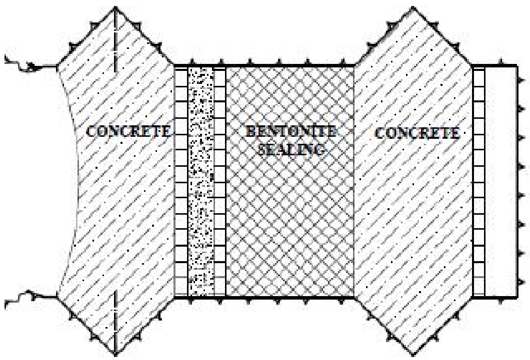
compression strength: 44.4 MPa

flexural strengths: 5.8 MPa

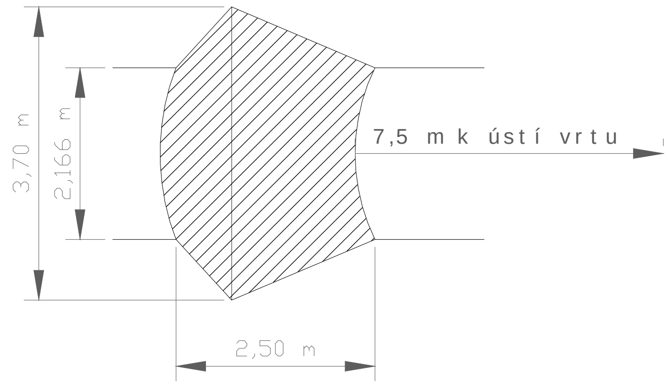
Role of the plug in the Czech DGR concept

- **Concrete plugs of disposal boreholes (horizontal disposal concept)**
  - Simple mechanical plug, main role is to seal the disposal borehole

- **Concrete plugs of galleries (both concepts)**
  - Combined mechanical/hydraulic plug
  - Prototype plug for Czech deep geological repository



Prototype of combined pressure sealing plug, realized as EPSP in Josef underground laboratory (DOPAS Project)



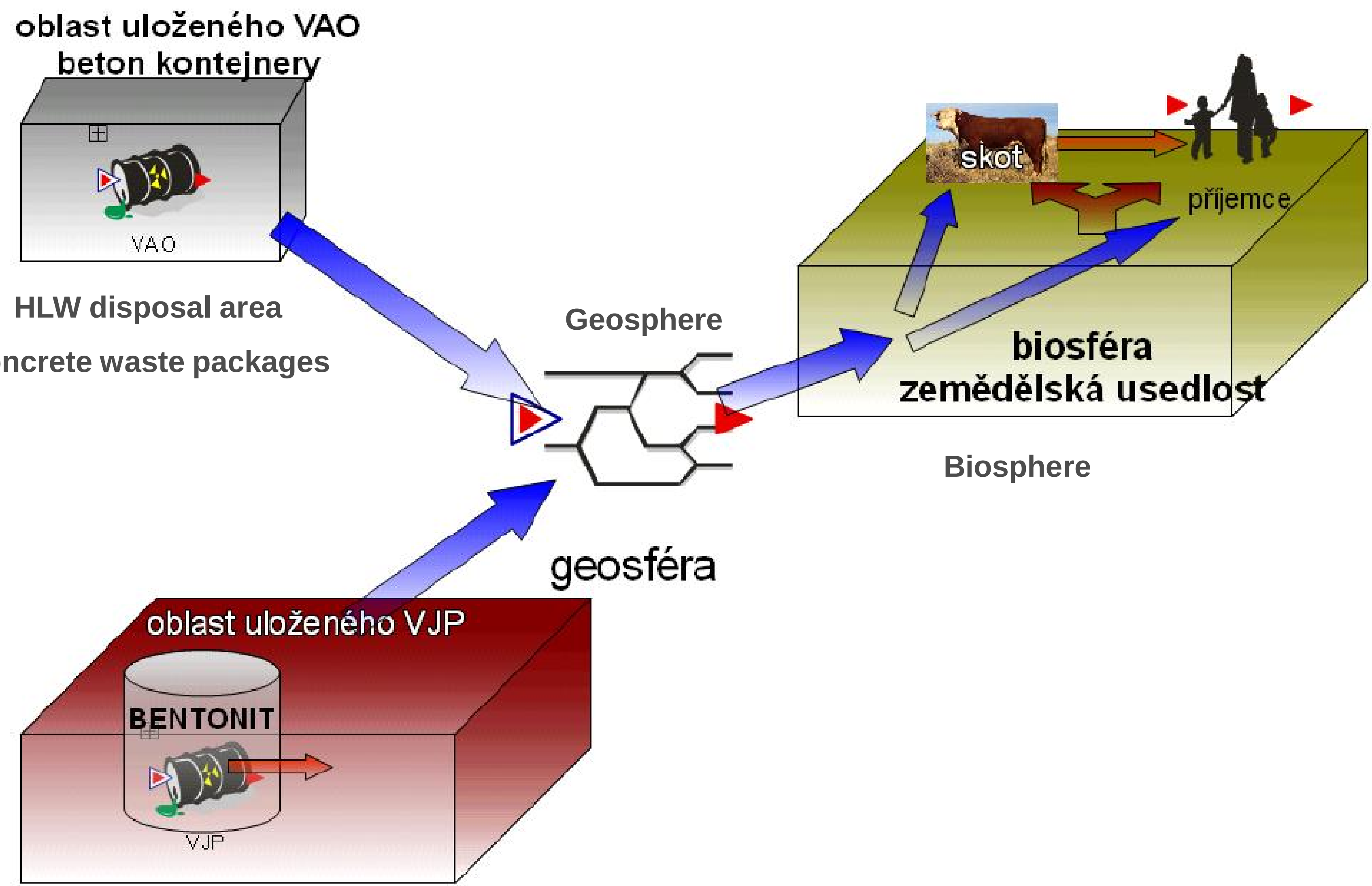
Reinforced concrete plug for the disposal borehole sealing (from Update of Czech Reference Programme, 2012)

- **Main role of plugs – closure of filled boreholes or galleries, mechanical function**

Role of other concrete materials in the Czech DGR concept

- **Concrete waste package for HLW**
  - Waste isolation, main waste package for HLW disposal in the repository
- **Concrete filling of HLW caverns**
  - Filling of empty space in HLW caverns after waste packages disposal , final sealing of the caverns
- **Concrete groutings**
  - Usage when necessary
- **Concrete plugs for deep boreholes**
  - Usage when necessary
- **Concrete obstruction plug (whole repository closure)**

HLW disposal
Concrete containers in separate compartment



HLW disposal area

concrete waste packages

Biosphere

SNF disposal area

Concept model from Update of Czech Reference Programme (2012)

R&D on the topic of radionuclide behaviour under cement matrix conditions

- **Scientific support of safety assessment of Czech deep geological repository (DGR) project (2014-2018)**
  - Behaviour of cement matrixes being used for solidification in ÚJV (for institutional waste), in Bratrství and Richard ILW repositories (pH, leaching stability, strength properties)
  - Radionuclide solubility and migration through the material under leachate conditions

- **CEBAMA Euratom H2020 Project (2015-2019)**
  - Long term interaction with bentonite
  - Change of migration properties due to interaction

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- ČSN EN 14488-3: Testing sprayed concrete - Part 3: Flexural strength (first peak, ultimate and residual) of fibre reinforced beam specimens
- ČSN CEN ISO/TS 17892-11: Geotechnical investigation and testing - Laboratory testing of soil - Part 11: Determination of permeability by constant and falling head
- ČSN EN 14488-7: Testing sprayed concrete - Part 7: Fibre content of fibre reinforced concrete

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