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Long-term chemical evolution of wasteforms predicted by geochemical modelling

PAUL SCHERRER INSTITUT PSI

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EUROSAFE 2019

Low- and intermediate-level radioactive waste (L/ILW)

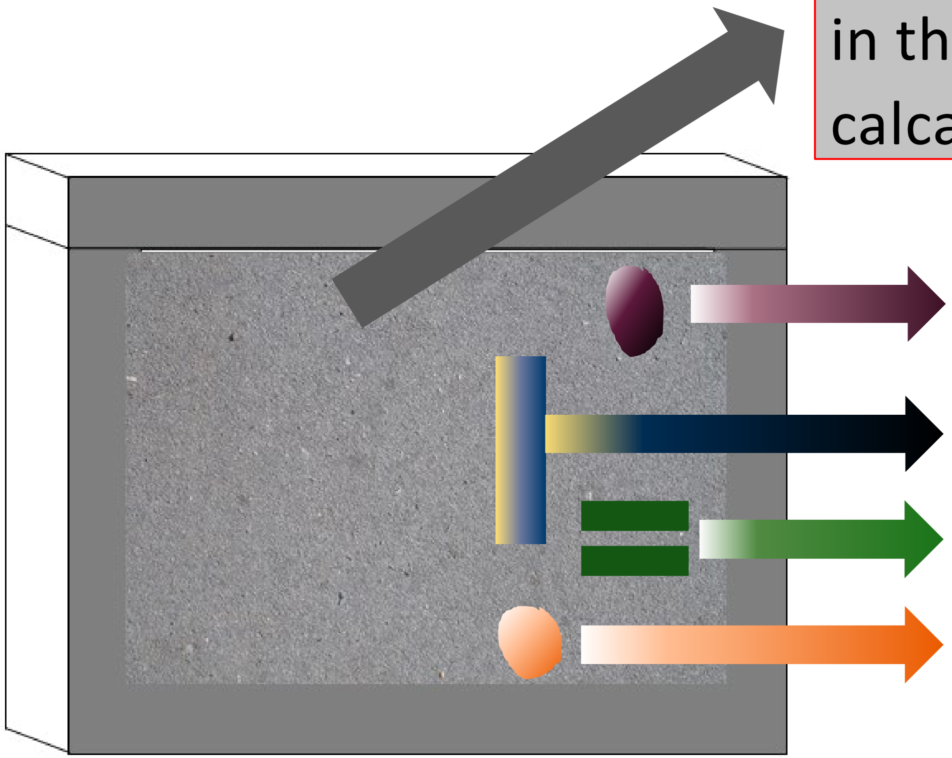
Source: NPP Leibstadt / Nagra

Source: ENSI / PSI

Layout

- Introduction
- Information on wasteform and processes
  - Inventory of potential decommissioning waste package
  - Stoichiometry and kinetics of chemical degradation processes
- Results
  - Initial conditions of the potential decommissioning wasteform
  - Temporal evolution of the chemical conditions of the potential decommissioning wasteform containing siliceous or calcareous aggregates
- Conclusions

Modelling the evolution of L/ILW



Thermodynamic modelling of the initial conditions in the cementitious matrix containing siliceous or calcareous aggregates

1) Dissolution of siliceous aggregate (quartz)
2) Equilibrium with calcareous aggregate (limestone)

Corrosion of metals

Degradation of organic matter

Carbonation of cementitious matrix

Key questions:

What chemical processes influence the system evolution?

What is the effect of the type of aggregates on the system evolution?

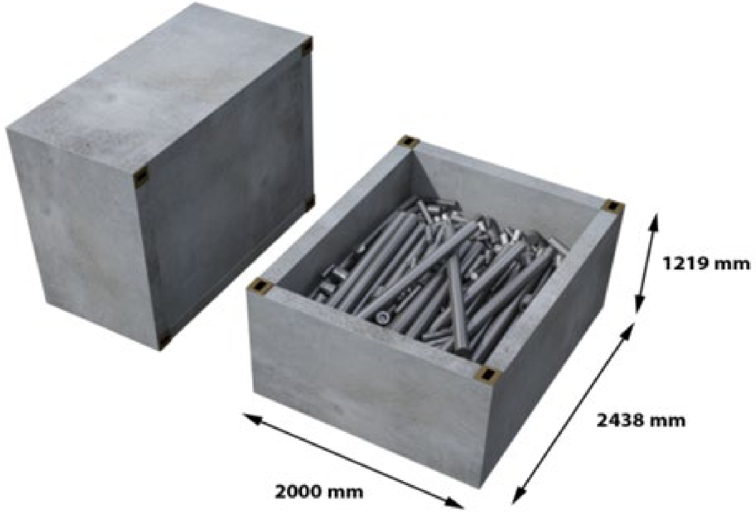
Geochemical modelling of the evolution of wasteforms

- Inventory according to MIRAM 14 (Nagra Report NTB 14-04)
- Development of the stoichiometry/kinetics of the relevant degradation processes for the waste materials:
  - Degradation of organic materials
  - Corrosion of metals (iron/steel, aluminium, zinc, brass)
  - Dissolution of sand/gravel ("quartz")
- Modelling initial conditions of the solidifying cementitious matrix
  - GEM-Selektor code in combination with established thermodynamic databases
- Modelling the evolution of the in situ chemical conditions of the wasteform
  - Implementing the degradation kinetics for the waste materials in GEM-Selektor code

Basic assumption: „ Mixing tank" approach holds at the waste package level

Inventory of wasteform

Studied wasteform: Potential decommissioning waste in large concrete containers (5.95 m^3)



- Moderate water content (w/c ~ 0.5)
- Large inventory of metals
- Small amount of readily (LMW, urea) and slowly degradable (PVC) organics
- Large amount of aggregate
- Addition of large amounts of SCMs during fabrication of the solidifying cementitious matrix

Material	Mass (kg)
Low molecular weight (LMW) organics	12.92
Polyvinylchloride (PVC)	0.752
Aluminium	3.17
Brass	124
Copper	139
Iron (cast)	210
Steel	5930
Zinc	0.557
Aggregate (limestone, quartz sand)	1950
Cement	1250
Silica fume («Micropoz»)	375
Clinoptilolite	187
Urea	4.49
Water	757

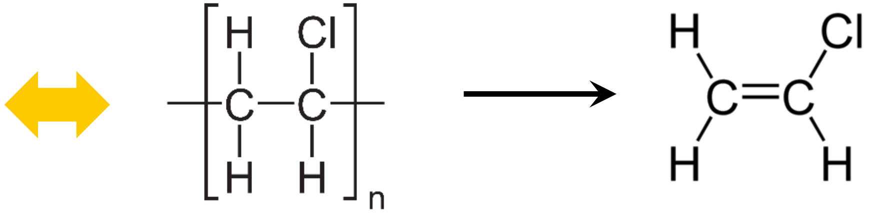
Nagra Technical Report NTB 14-04

Degradation of organics

- Stoichiometry of degradation reactions

Basic process: Methanogenesis: $2\ \{CH_2O\} \rightarrow CO_2 + CH_4$

Polyvinyl chloride (PVC):



$$4\ C_2H_3Cl + 6\ H_2O = 3\ CO_2 + 5\ CH_4 + 4\ HCl$$

LMW organics: Acetic acid (CH_3COOH) as model compound

$$C_2H_4O_2 = CO_2 + CH_4$$

PVC: $CO_2:CH_4 = 3:5$ **LMW organics:** $CO_2:CH_4 = 1:1$

Wieland (2010), PSI Internal Report AN 44-10-07
Cloet et al. (2014), Nagra Work Report NAB 14-52 rev.1

Degradation kinetics of organics

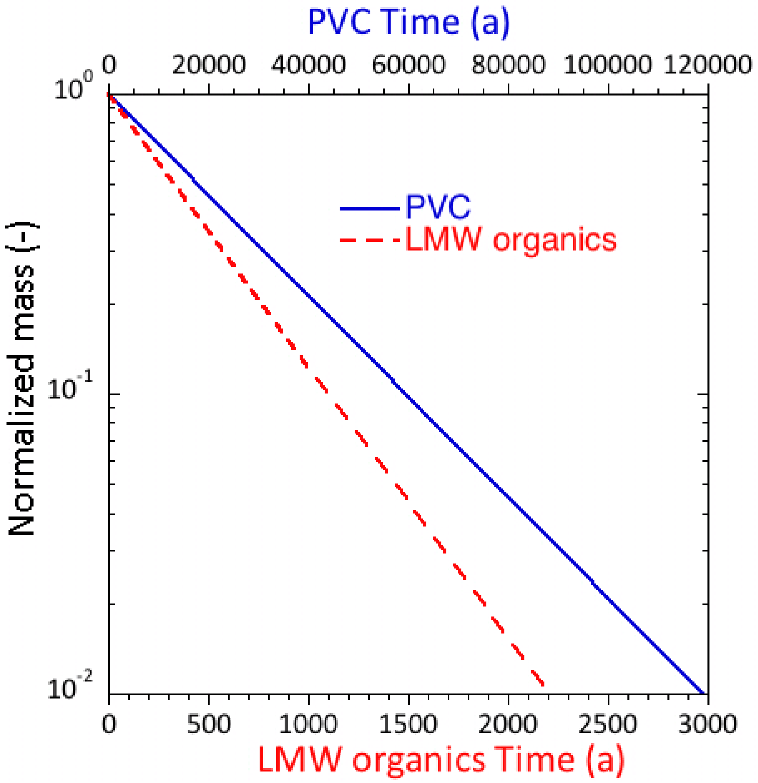
- Anaerobic degradation rates

Gas production rates

	Rate (mole gas kg^{-1} a^{-1}) reference
Category 1 (fast degradation)	0.07
Category 2 (slow degradation)	0.005

Cloet et al. (2014), Nagra Work Report NAB 14-52 rev.1

Degradation rates of organics



First order kinetics of degradation: $m(t) = m(0) \cdot e^{-k_D t}$ (mol)

	LMW organics	PVC
k_D (a^{-1})	2.10×10^{-3}	3.91×10^{-5}
$T_{1/2}$ (= $\ln 2/\lambda$) (a)	330	17728
$m(t)/m(0) = 0.01$	2193	117’780

Wieland et al. (2018), Nagra Work Report NAB 18-05

Fast degradation: Cellulose, **LMW organics**
Slow degradation: Acrylic glass, **PVC**, polystyrene, plastic materials, rubber

Degradation of organics and effect on cementitious materials

- Carbonation
  - CO_2 produced by the degradation of organics
  - Reaction of CO_2 with cement phases: Fast reaction!

Main cement phases reacting with CO_2:

- Portlandite ($Ca(OH)_2$)
- Calcium silicate hydrate (C-S-H) phases with varying Ca/Si ratio (typically 0.8 – 1.6)


http://www.understanding-cement.com

$$Ca(OH)_2(s) + CO_2(aq) \Leftrightarrow CaCO_3(s) + H_2O$$

$$(CaO)_{1.667}\cdot SiO_2\cdot(H_2O)_{2.1}(s) + 1.667\ CO_2(aq) \Leftrightarrow 1.667\ CaCO_3(s) + SiO_2(s) + 2.1\ H_2O$$

$$(CaO)_{0.833}\cdot SiO_2\cdot(H_2O)_{1.33}(s) + 0.833\ CO_2(aq) \Leftrightarrow 0.833\ CaCO_3(s) + SiO_2(s) + 1.33\ H_2O$$

Corrosion of metals

- Reactions - anoxic

Iron/carbon steel:

$3\ Fe(s) + 4\ H_2O(l) \rightarrow Fe_3O_4 + 4\ H_2(g)$

Aluminium:

$Al(s) + 3\ H_2O(l) \rightarrow Al(OH)_3(s) + 1.5\ H_2(g)$

Zinc/brass:

$Zn(s) + 2\ H_2O(l) \rightarrow Zn(OH)_2(s) + H_2(g)$

$CuZn(s) + 4\ H_2O(l) \rightarrow Zn(OH)_2(s) + Cu(OH)_2(s) + 2\ H_2(g)$


Steel corrosion

- Rates

Diomidis (2014), Nagra Work Report NAB 14-21

Diomidis et al (2016), Nagra Technical Report NTB 16-03

Conditions	$^*R_{corr}$ Fe(0) ($m\ a^{-1}$)	$^*R_{corr}$ Al(0) ($m\ a^{-1}$)	$^*R_{corr}$ Zn(0), CuZn(0) ($m\ a^{-1}$)
pH < 10.5	$2 \cdot 10^{-6}$	10^{-5}	10^{-4}
pH ≥ 10.5	$2 \cdot 10^{-8}$	10^{-5}	10^{-4}

* GEMS implementation: Rates are corrected according to the actual surface area of the metalic wastes reported in MIRAM 14

Internal degradation of concrete by dissolution of silica source

source: www.fhwa.dot.gov

- Reactions

Reaction of portlandite with silica to form calcium silicate hydrates (C-S-H):

$0.833\ Ca(OH)_2(s) + SiO_2(aq) + 0.447\ H_2O(l) \Leftrightarrow (CaO)_{0.833}\cdot SiO_2\cdot(H_2O)_{1.33}(s)$

Reaction of C-S-H phases with silica to form C-S-H with lower Ca/Si ratio:

$0.5\ (CaO)_{1.667}\cdot SiO_2\cdot(H_2O)_{2.10}\ (s) + 0.5\ SiO_2(aq) \Leftrightarrow (CaO)_{0.833}\cdot SiO_2\cdot(H_2O)_{1.05}(s)$

- Rate – quartz dissolution

Stoichiometry

$SiO_2(cr) + H_2O(l) \Leftrightarrow H_4SiO_4(aq)$

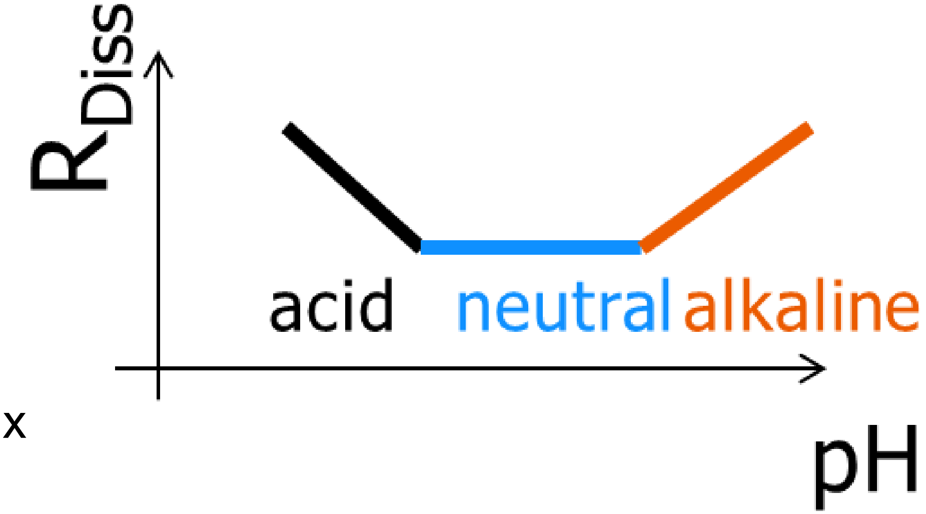
$$R_{diss} = \frac{dm}{dt} = A\cdot(k_1(1-\Omega) + k_2\cdot a_{H^+}^{-0.5}(1-\Omega))$$

Surface area

Kinetic constant

Activity of protons

Saturation index



A: Surface area according to the grain size of sand and gravel in the wasteform

Palandri and Kharaka (2004), Open File Report, USGS

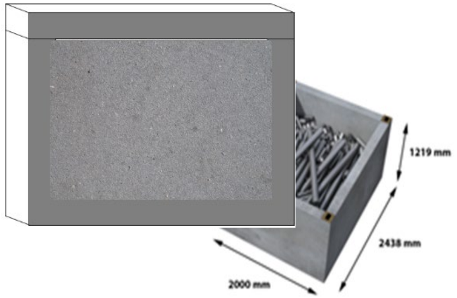
Thermodynamic data and models

- ☐ GEM-Selektor v3.3 code *(Kulik et al. 2013)*
- ☐ Nagra/PSI thermodynamic database *(Hummel et al. 2002, Thoenen et al. 2014)*
  CEMDATA 14.01 database *(Lothenbach et al. 2012)*
  Zeolites: Thermoddem database *(Blanc et al. 2015)*
  Zn and Cu species: SUPCRT database *(Helgeson et al. 1978)*
  Chloride-containing minerals: SUPCRT database (halite, sylvite) and from *Robin and Hemingway (1995)* (chloromagnesite, hydrophilite, laurencite)
- ☐ Alkali uptake by C-S-H phases:
  ideal solid solution model between jennite, tobermorite
  $[(KOH)_{2.5}SiO_2H_2O]_{0.2}$ and $[(NaOH)_{2.5}SiO_2H_2O]_{0.2}$
  Kulik et al. (2007), Lothenbach (2011), Lothenbach et al. (2012)

Previous applications

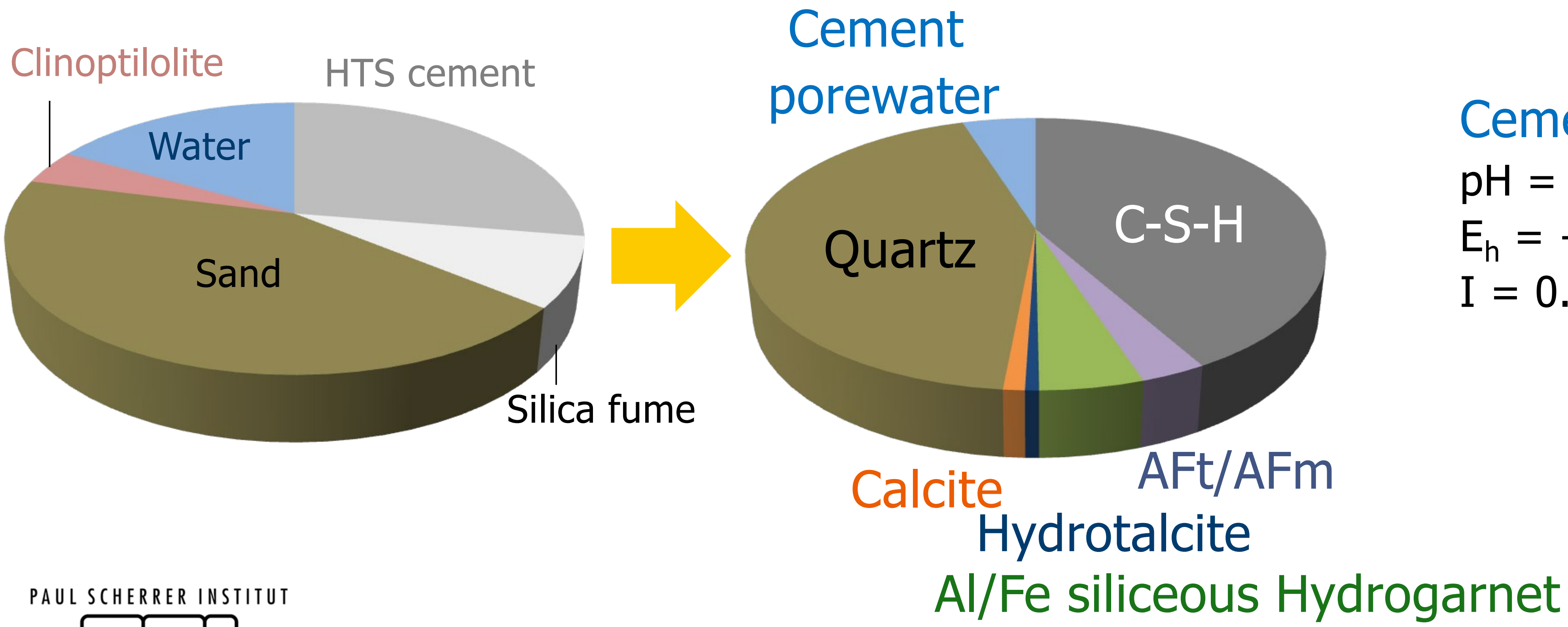
- ☐ Hydration of ordinary Portland cement (OPC):
  e.g. Lothenbach & Winnefeld (2006), Lothenbach & Wieland (2006)
- ☐ Hydration of blended cements («low-pH» cements):
  e.g Lothenbach et al. (2012), Lothenbach et al. (2014)
- ☐ *Clay-cement interaction:*
  e.g. Berner et al. (2013), Kosakowski & Berner (2013)

Modelling of the initial conditions in the cementitious matrix



- Solidifying cementitious matrix with siliceous aggregate

Composition of initial mix → Thermodynamic modelling → Composition of cementitious matrix



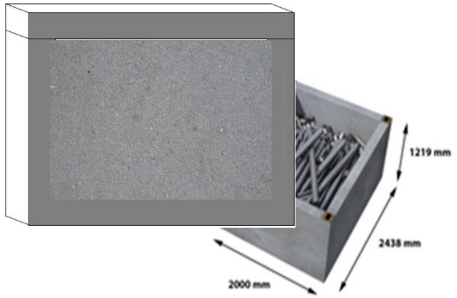
Cement porewater:

pH = 12.68

E_h = + 0.45 V

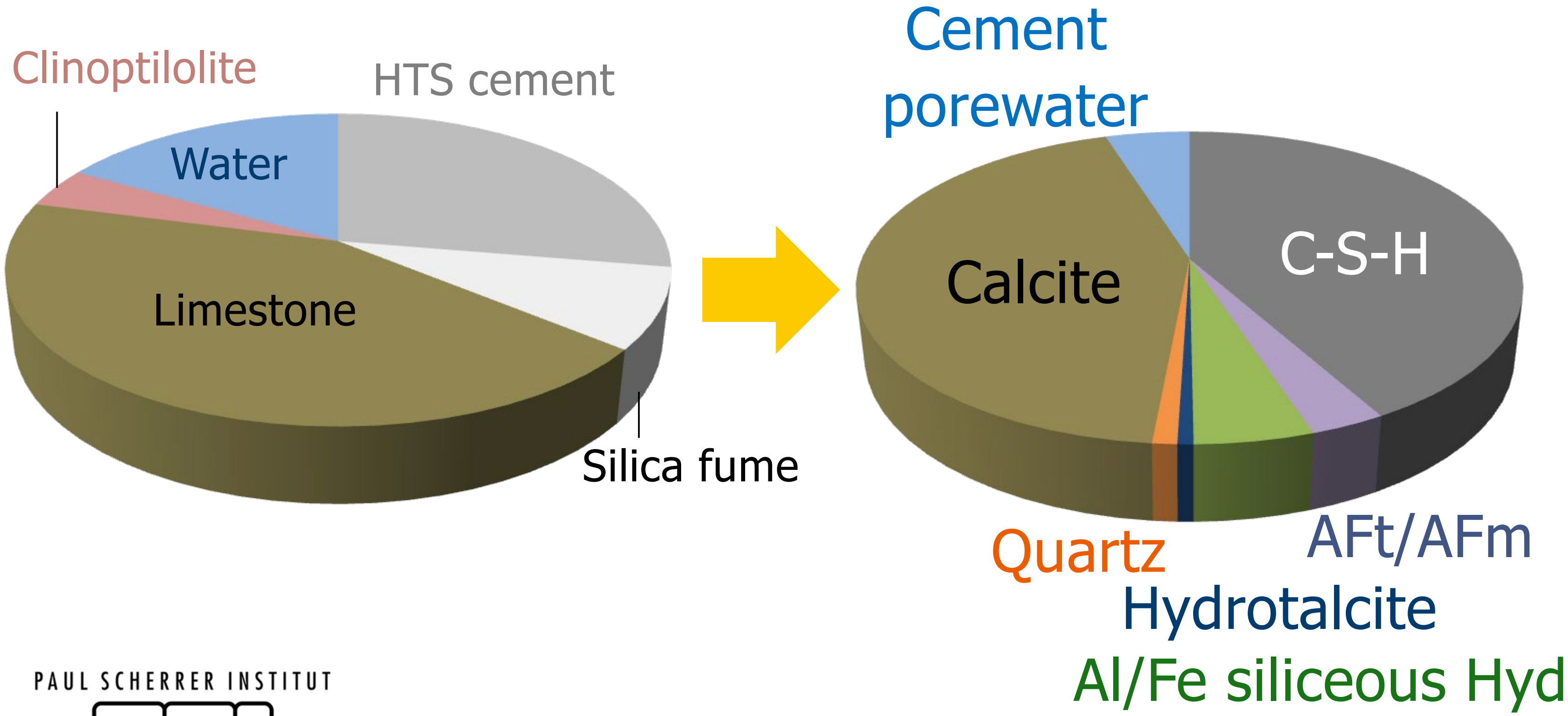
I = 0.17 mol kg^{-1}

Modelling of the initial conditions in the cementitious matrix



- Solidifying cementitious matrix with calcareous aggregate

Composition of initial mix → Thermodynamic modelling → Composition of cementitious matrix



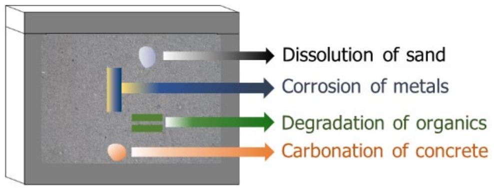
Cement porewater:

pH = 12.68

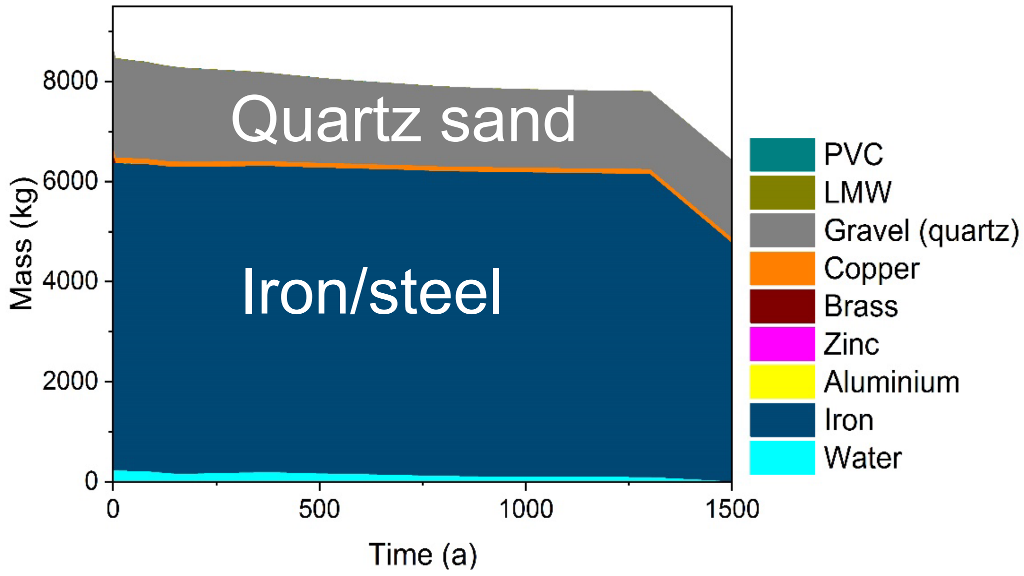
E_h = + 0.45 V

I = 0.17 mol kg^{-1}

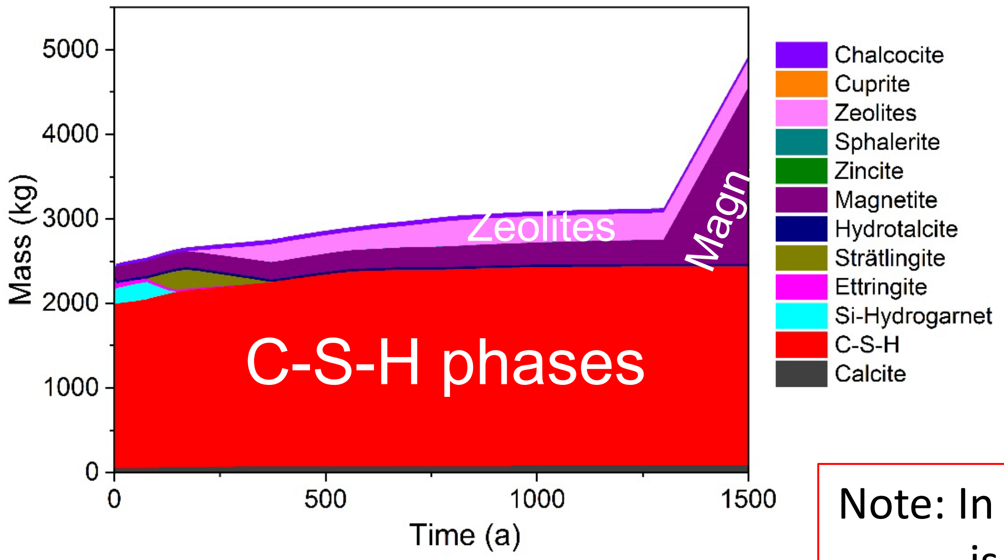
Temporal evolution of wasteform with siliceous aggregate



- Closed system (limited water): siliceous aggregate & zeolites



- Organic materials degrade continuously with time
- Iron/steel corrosion is accelerated after ~ 1300 years
- Water consumed within 1500 years

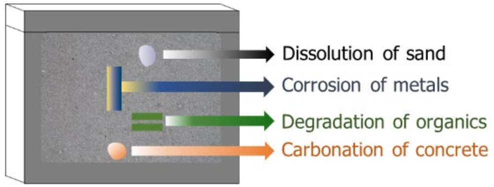


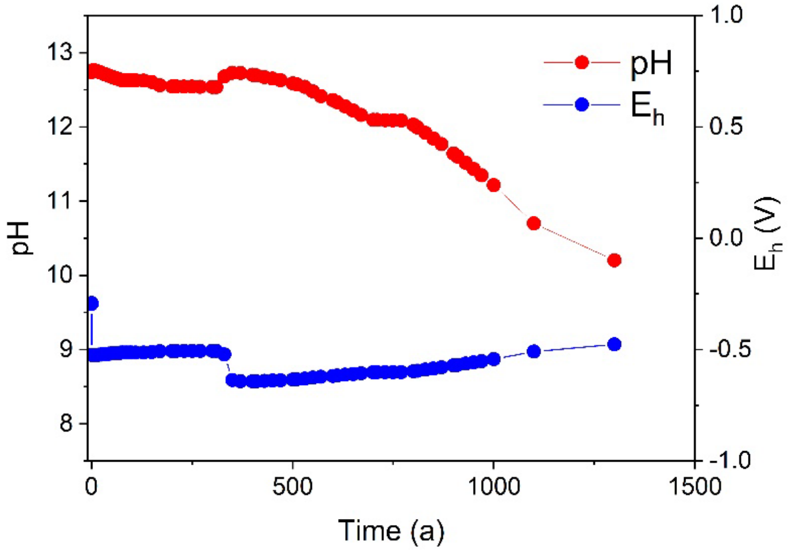
- Matrix is degraded due to conversion of C-S-H with high C/S (1.01) into C-S-H with low C/S (0.75)
- Formation of zeolites at pH < 12.5
- Carbonation has little impact due to the low inventory of PVC and LMW organics

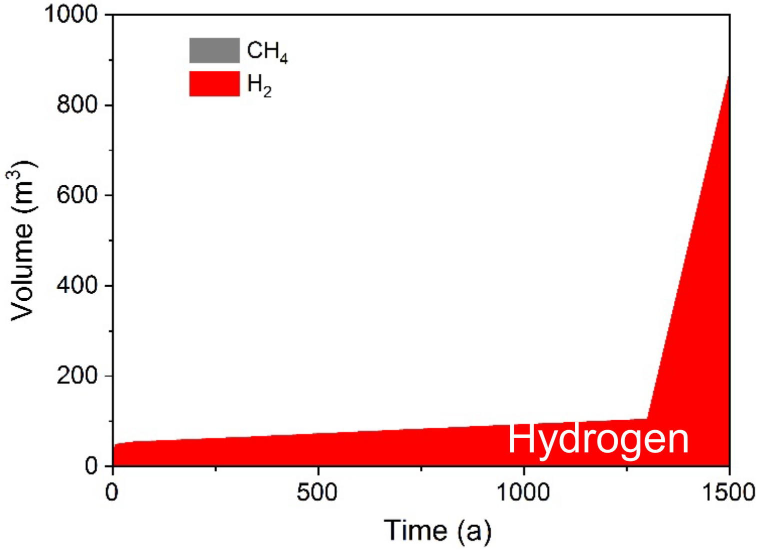
Note: In the real system, the time scale is affected by transport processes

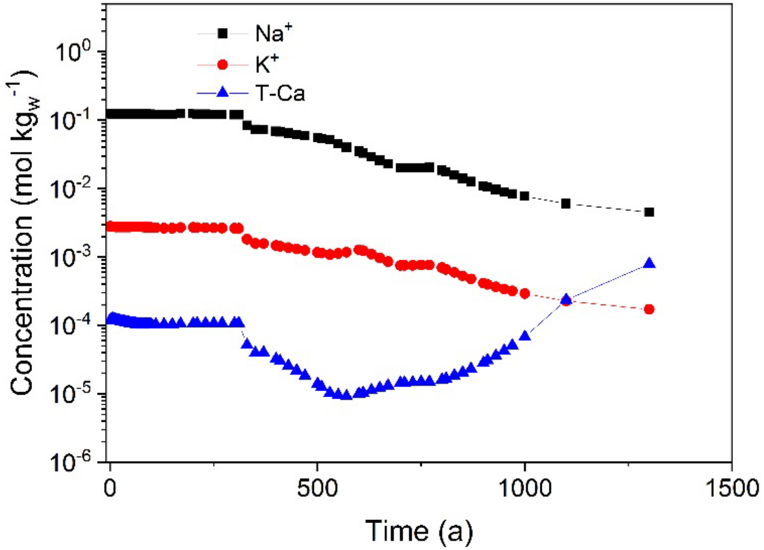
Temporal evolution of wasteform with siliceous aggregate

- Closed system (limited water): siliceous aggregate & zeolites









- pH drops < 12.5 at ~ 250 years → formation of zeolites
- pH drops < 10.5 at ~ 1300 years → accelerated iron/steel corrosion
- Reducing conditions at all times

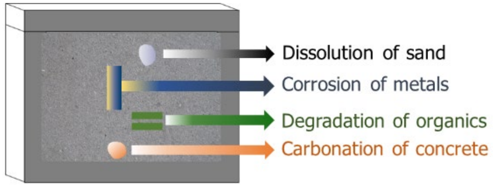
- H_2 production accelerated after ~ 1300 years due to pH drop below 10.5
- CH_4 production very small due to low inventory of organics
- CO_2 bound by C-S-H (carbonation)

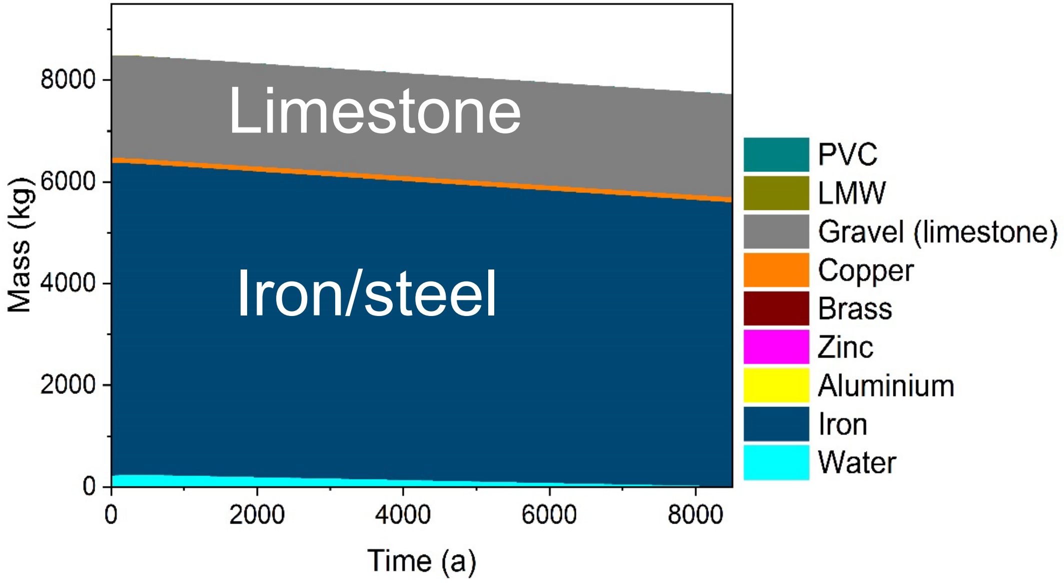
- Continuous decrease in the alkali concentration after ~ 250 years due to uptake by zeolites and C-S-H phases

Note: In the real system, the time scale is affected by transport processes

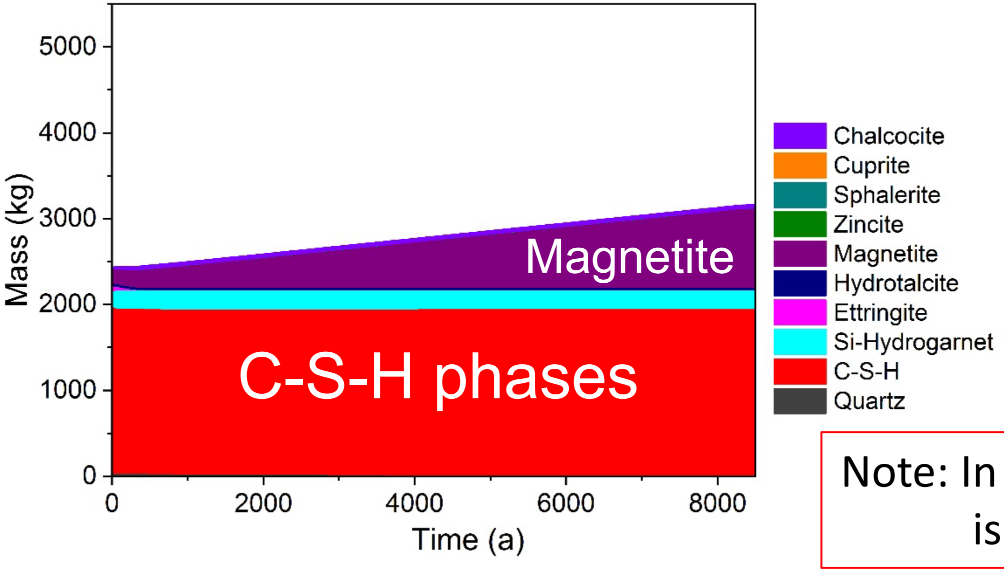
Temporal evolution of wasteform with calcareous aggregate

- Closed system (limited water): calcareous aggregate & zeolites





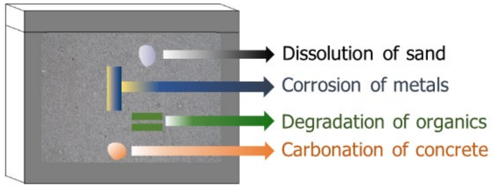
- Organic materials degrade continuously with time
- Slow corrosion of iron/steel
  → no acceleration caused by pH drop
- Water consumed within 8500 years



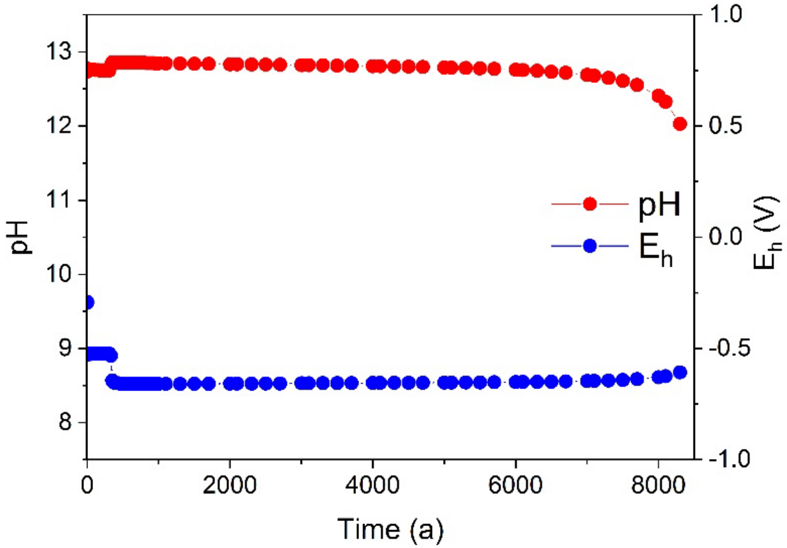
- No degradation of cementitious matrix - C-S-H is almost constant (1.01 to 0.96)
- Carbonation has little impact due to the low inventory of PVC and LMW organics

Note: In the real system, the time scale is affected by transport processes

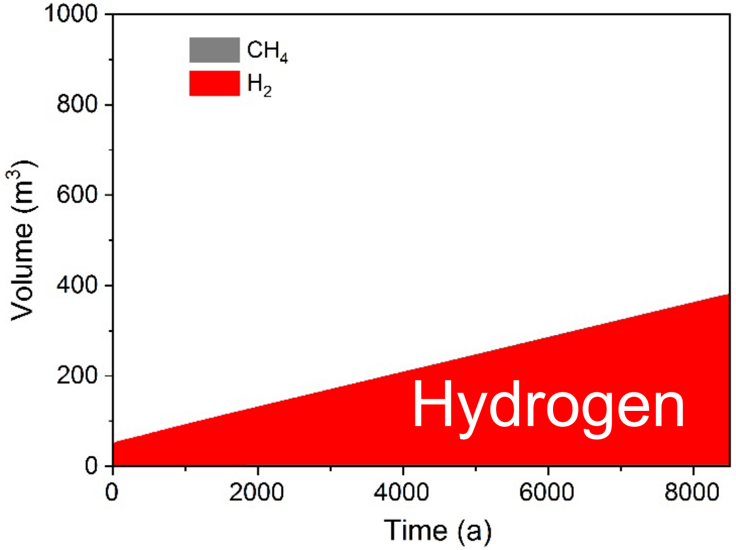
Temporal evolution of wasteform with calcareous aggregate



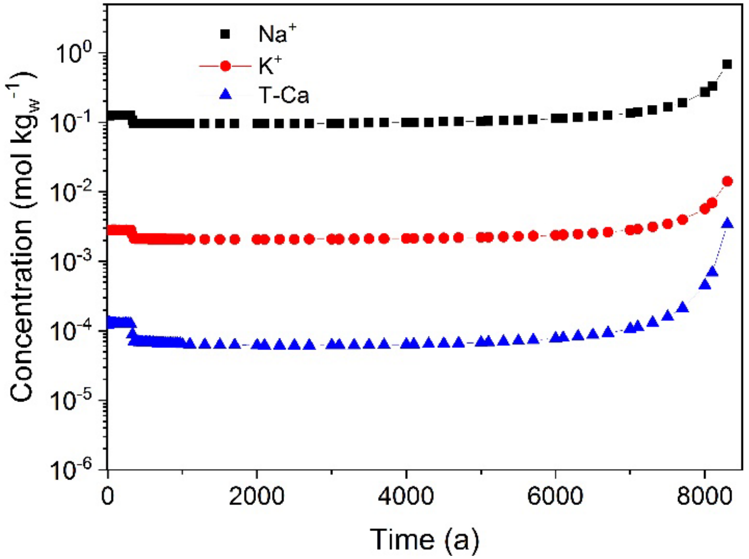
- Closed system (limited water): calcareous aggregate & zeolites



- pH stays ≥ 12.5 until the end of reactivity of the wasteform
  → no zeolite formation
- Reducing conditions at all times



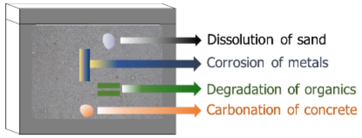
- Continuous H_2 production until the end of reactivity of the wastform
  → no accelerated iron/steel corrosion
- CH_4 production very small due to low inventory of organics
- CO_2 bound by C-S-H (carbonation)



- High alkali concentration maintained

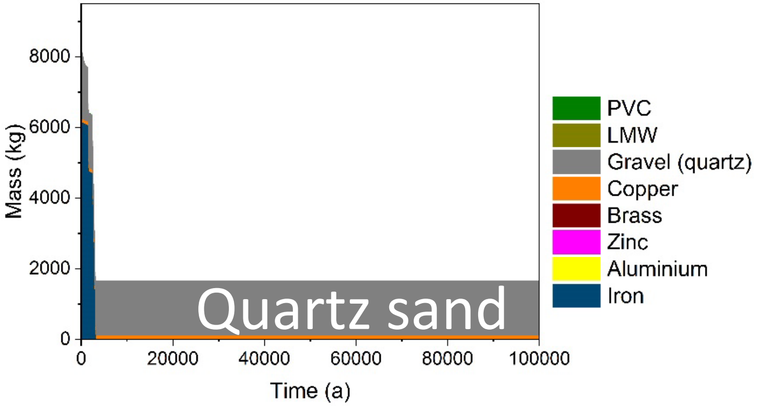
Note: In the real system, the time scale is affected by transport processes

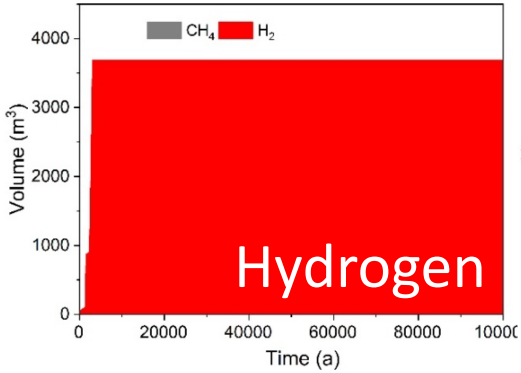
Temporal evolution of wasteform

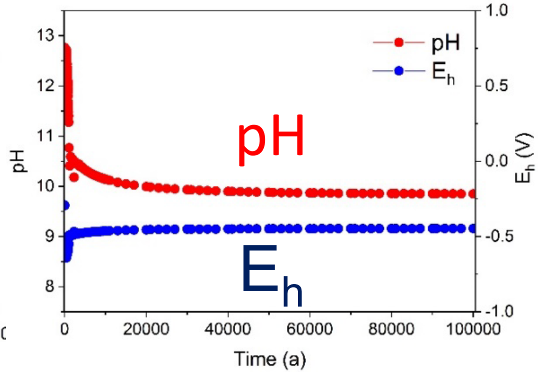


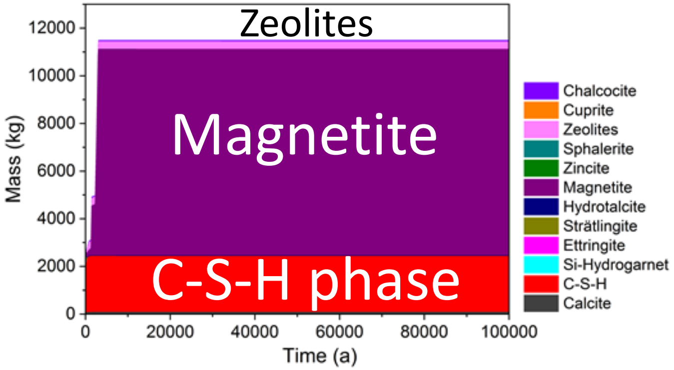
- Semi-open system (unlimited water): Evolution over 10^5 years – presence of zeolites

Siliceous aggregate

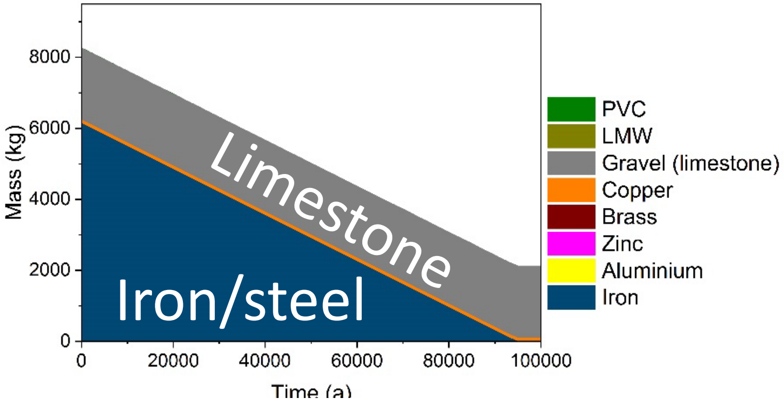


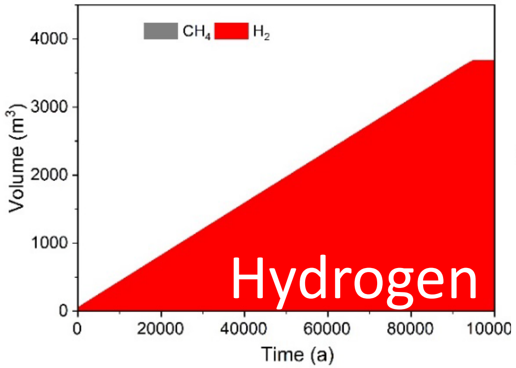


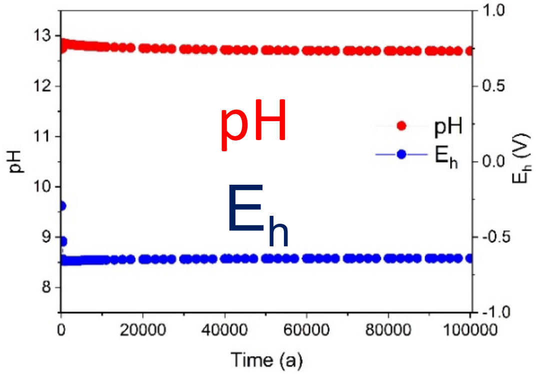


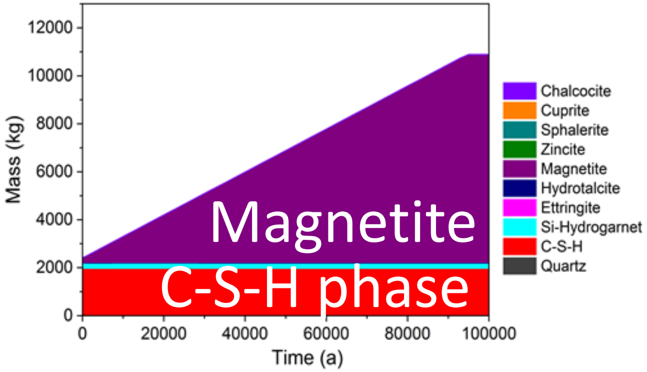


Calcareous aggregate









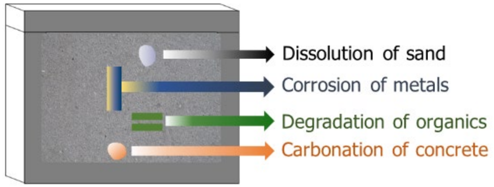
Waste materials and aggregates

Gas

pH

Minerals

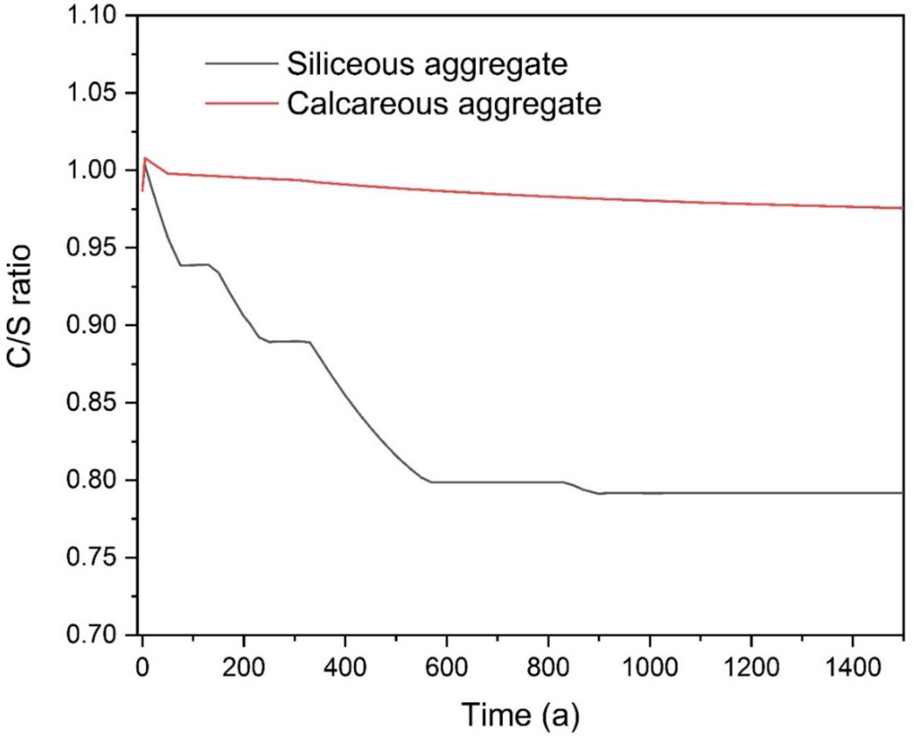
Sinks for alkalis



- Effect of siliceous and calcareous aggregates on pH evolution
  - C-S-H phases: Decrease in Ca/Si (C/S) ratio in the presence of siliceous aggregate – no change in the C/S ratio in the presence of calcareous aggregates

    Alkali binding by C-S-H phases improves with decreasing Ca/Si ratio

    (Hong and Glasser, Cem. Concr. Res. 29, 1999)



  - Zeolites:

Ca-Phillipsite	$Ca_3Al_6Si_{10}O_{32}\cdot 12H_2O$
K-Phillipsite	$K_6Al_6Si_{10}O_{32}\cdot 12H_2O$
Na-Phillipsite	$Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$

Note: Alkali binding by zeolites and C-S-H phases reduces pH with time

Conclusions

- Long-term evolution of wasteforms predicted by coupling kinetic processes and thermodynamic equilibrium - GEM-Selektor code and thermodynamic data
- Important parameters/processes controlling the chemical evolution of wasteforms:
  - Inventory of organics - degradation kinetics of organics - carbonation - effect on pH
  - Water availability - water consuming reactions – determines the period of reactivity
  - pH dependence of iron/steel corrosion - significantly accelerated corrosion at pH < 10.5 - H_2 production
  - Alkali binding by C-S-H phases with low C/S ratios and zeolites - effect on pH
- Effect on chemical evolution of wasteforms by replacing siliceous by calcareous aggregates for fabrication of the cementitious matrix - high pH conditions maintained
- Geochemical modelling supports the assessment of the relevance of degradation processes and the development of design options while it is of limited use for predictions of «realistic» time scales of the evolution of wasteforms as transport process are ignored («mixing tank») – transport of water may determine time scale

Acknowledgement

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Disclaimer

The views, opinions and conclusions of the author herein do not necessarily state or reflect those of Nagra. The kinetic parameters, materials and inventories used in this study are not necessarily those of the reference concept of Nagra and future license applications.

Thank you for your attention