Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

Laboratory for Waste Management (LES)

Sergey V. Churakov

Kompetenzen und Highlights LES

18 March 2015

- LES Mission

- Status of the Swiss Waste Disposal Program

- LES contribution to Swiss Waste Disposal Program

- Research Highlights

- Facts and figures

LES Mission

The aim is to provide realistic model concepts, reliable expert knowledge and robust data for Performance Assessment which are supported by the broad scientific community.

- LES carries out the experimental program on geochemical retention and transport of trace elements in the field of radioactive waste disposal.

- LES develops holistic descriptions of transport and sorption processes, in situ conditions and up-scaling.

- Together with the laboratory of Mineralogy at the University of Bern, LES focuses on basic and applied research in the physical chemistry of high surface area materials and their technological applications.

LES's main contributions are in the areas of:
- **Chemistry at solid/liquid interfaces**
- **Repository in situ geochemistry**
- **Mass transport mechanisms**

Status of Swiss Waste Disposal Program

Stage 1 of the sectoral plan has ended in November 2011

Stage 2 of the sectoral plan (current phase):

Narrowing the number of siting regions to at least 2 for each repository type (HLW and L/ILW) and selection of sites for surface infrastructure

Swiss Federal Ministry of Energy News Letter April 2014

Safety has the highest priority !

Status of Swiss Waste Disposal Program

Geological siting regions

- HLW (overlap with L/ILW)
- L/ILW
- Placed in reserve
- Siting areas for the surface facility

Südranden (SH)

Zürich Nordost (ZH, TG)

Jura Ost (AG)

Nördlich Lägern (ZH, AG)

Jura-Südfuss (SO, AG)

Wellenberg (NW, OW)
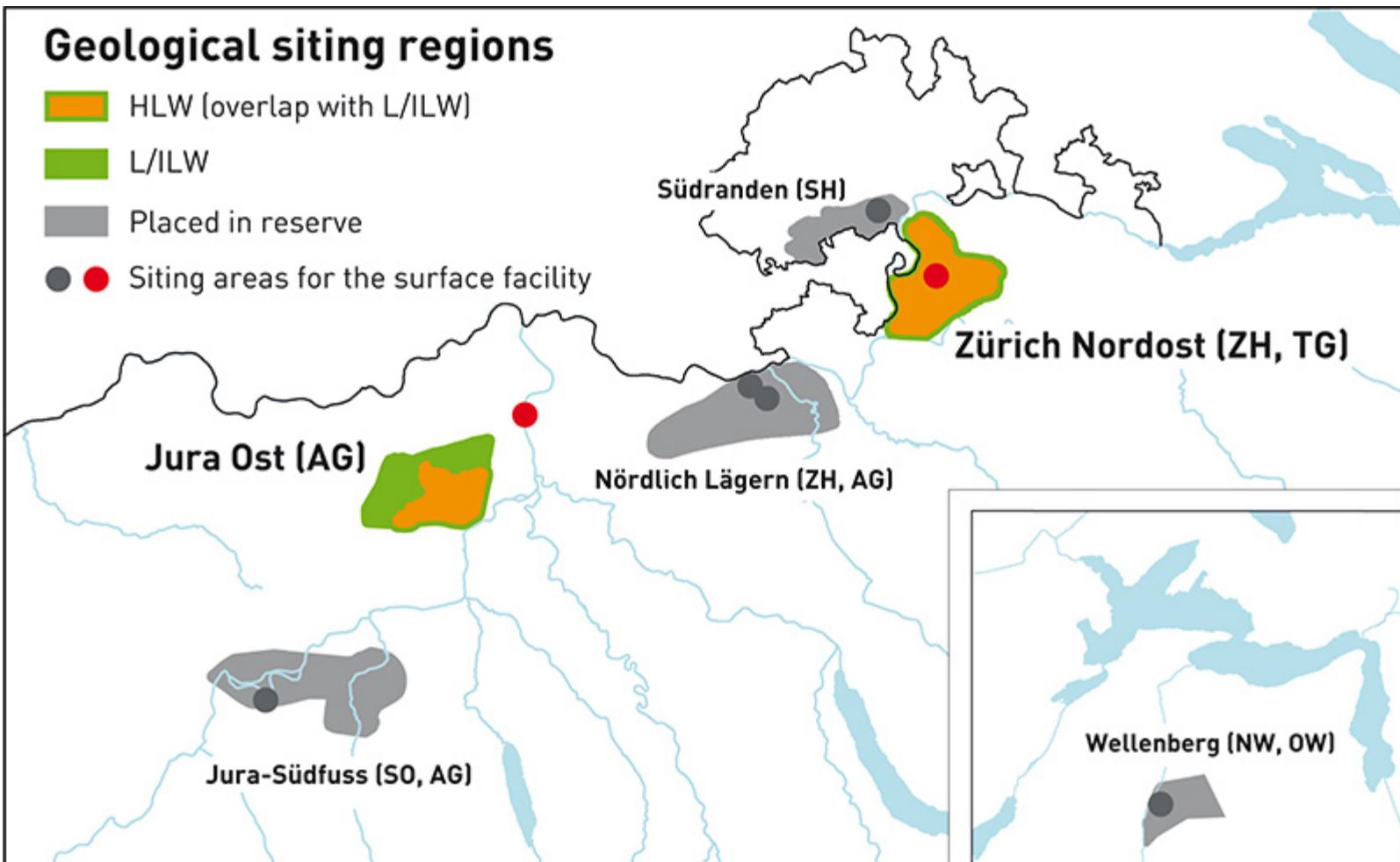
Nagra, 30.01.2015

Nagra Reports:

8 Nagra Technical Reports

3 Nagra Work Reports

Key reports:

- G. Kosakowski, U. Berner, E. Wieland, M. Glaus, C. Degueldre (2014)
  Geochemical evolution of the L/ILW near field. NTB 14-11.

- M.H. Bradbury, U. Berner, E. Curti, W. Hummel, G. Kosakowski, T. Thoenen (2014) The Long Term Evolution of the Near field of the HLW Repository. NTB 12-01.

Kosakowski et al., 2015
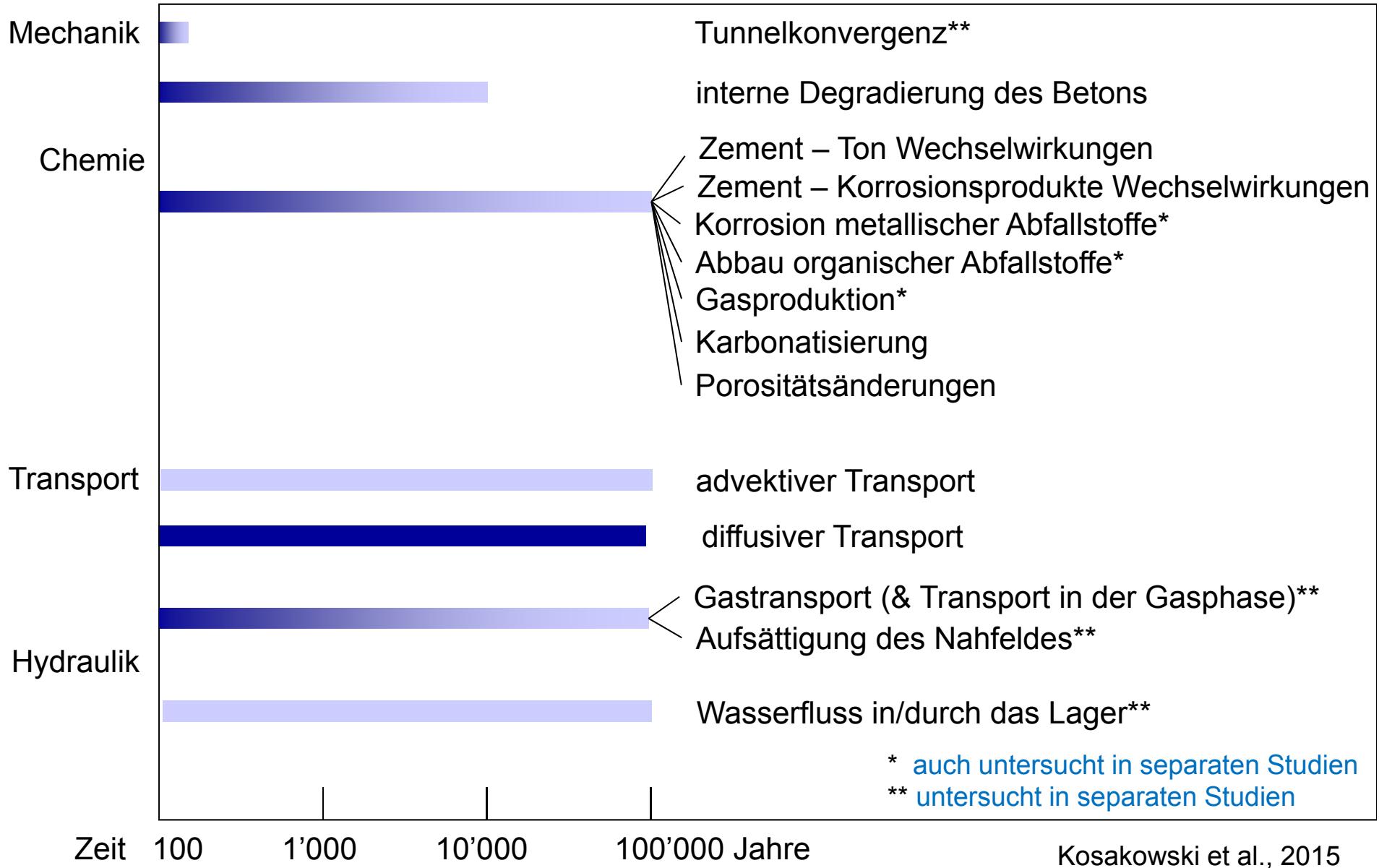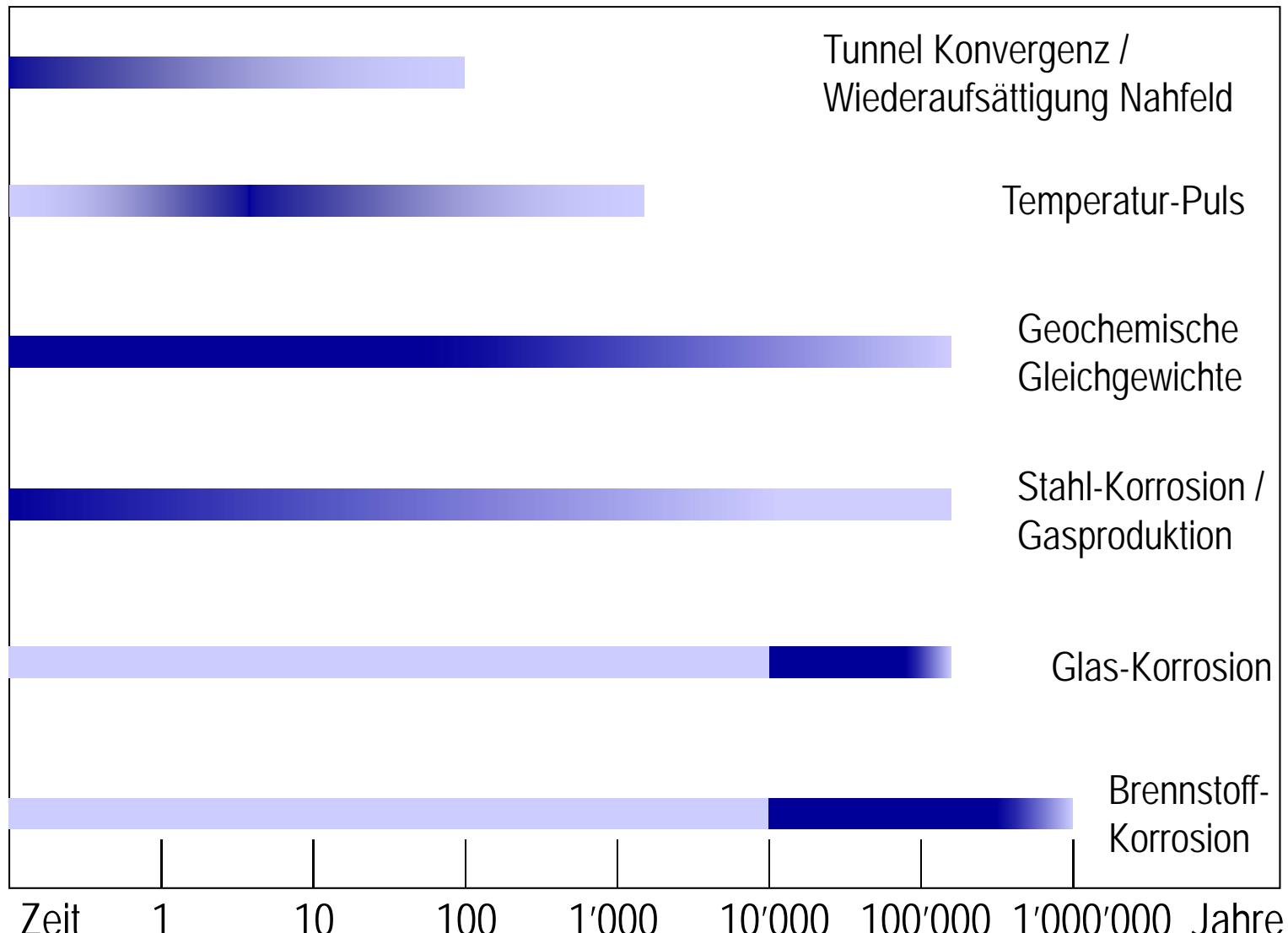
Berner et al., 2015

Understanding processes and predicting long-term repository behavior

Experiments

- **Mont Terri**
- **Diffusion Experiments**
- **XRF/XRD**
- **Scanning electron microscopy**
- **Computer-tomography**
- **Optical - Microscopy**

Theory / Concepts

- **Diffusion/advection equation**
- **Sorption models**
- **Boltzmann equation**
- **Thermodynamics**
- **Dissolution/ precipitation**
- **Mineral growth**
- **Gibbs energy**

$$\frac{\partial SC_i}{\partial t} = \nabla(SvC_i) + \nabla(SD_i\nabla C_i) + Q$$

$$\frac{\partial SC_i}{\partial t} = \Gamma_i(C_1....C_m)$$

Simulations

- **Reactive transport simulation**
- **OpenGeoSys-GEMS**
- **MCOTAC**
- **Lattice Boltzmann**
- **Random walk**
- **Gibbs energy minimization**

Platform for simulations of coupled phenomena

Experimental data and experimental reactive transport benchmarks

GEM-Selektor: thermodynamic modelling of aquatic (geo)chemical systems by Gibbs Energy Minimization
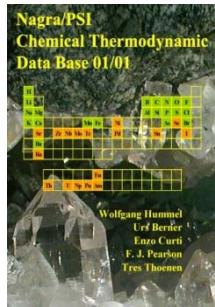
Thermodynamic databases: PSI/Nagra TDB-12/07(release 2014), CEMDATA, SUPCRT92, HERACLES databases, etc.
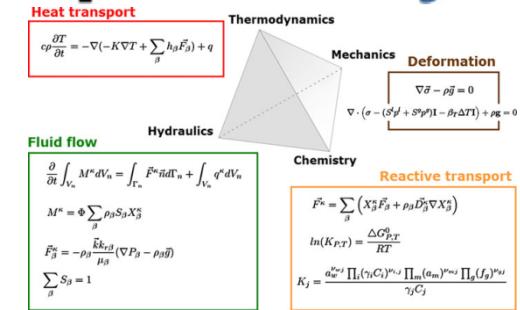
modeling platform for coupled phenomena in porous and fractured media

OpenGeoSys-GEM

- **Fully and partially saturated fluid flow (H) in fractured and porous media**
- **Multi-species solute transport (T)**
- **Heat transport (T)**
- **Chemical thermodynamic and kinetics (C)**

-> coupled T-T-H-C phenomena

Cooperative development and application platform

GEMS TM:

Gibbs **E**nergy
Minimization
Software for
Thermodynamic
Modelling

Modular Package

(Win, Mac, Linux; > 2500 downloads)

GEMS ELEKTOR

Phase Model Code Libraries

TSolMod: Mixing

TKinMet: Kinetics

TSorpMod: Sorption

Graphical User Interface (**GUI**)

Chemical System Definition Tools

GEM IPM 3 Minimizer Kernel Code (**GEMS3K**)

Help and Reference Data Base, I/O Tools

TDB & Project Data Bases & Tools

Process and Reactive Transport Simulations

Kulik et al. (2004, 2013); Wagner et al. (2012); Berner et al. (2013)

Thermod. **D**ata **B**ases / Applications in:

PSI-Nagra / (Rad)waste geochemistry

Hummel et al. (2002); Thoenen (2013)

Cemdata / Cement chemistry (EMPA)

Lothenbach & Matschei (2007)

HERACLES / Nuclear materials (NES)

Shcherbina (2012); Orlov et al. (2012)

SUPCRT / Hydrothermal geochemistry

Shock et al. (1997)

Attracted many externally-funded projects at LES

Perspectives, Innovation, & Needs

GEMSFIT2: GEM Input Parameter Fitting

**GEMSPHAD**: Phase Diagrams Generator

Chemistry and transport coupling

The project focuses on improving stability and robustness of geochemical solvers (e.g. **GEMS**) with an overarching aim to speed up the reactive transport simulation used for the assessment of the in situ conditions in the repository.

- Robustness: Simplified interface for use with a multitude of numerical transport solvers

- Access to >25 models of mixing in phases, collection of kinetic rate models, sorption phase models. Thermodynamic models and databases.

- Faster numerical methods for geochemical modeling.

- Coupling with lattice Boltzmann codes for reactive pore-scale fluid flow modeling.
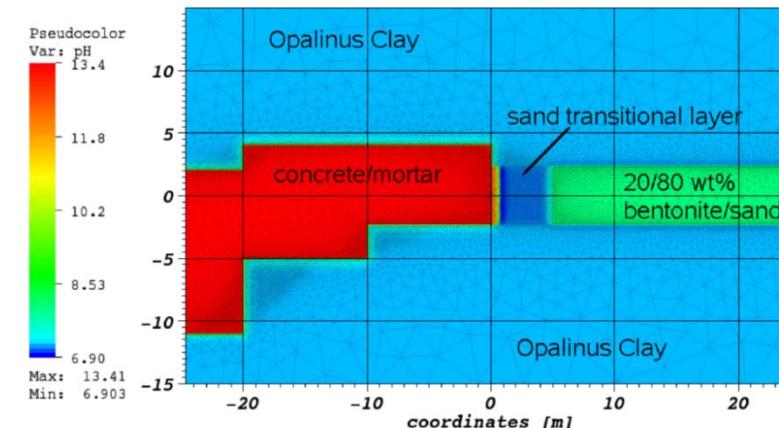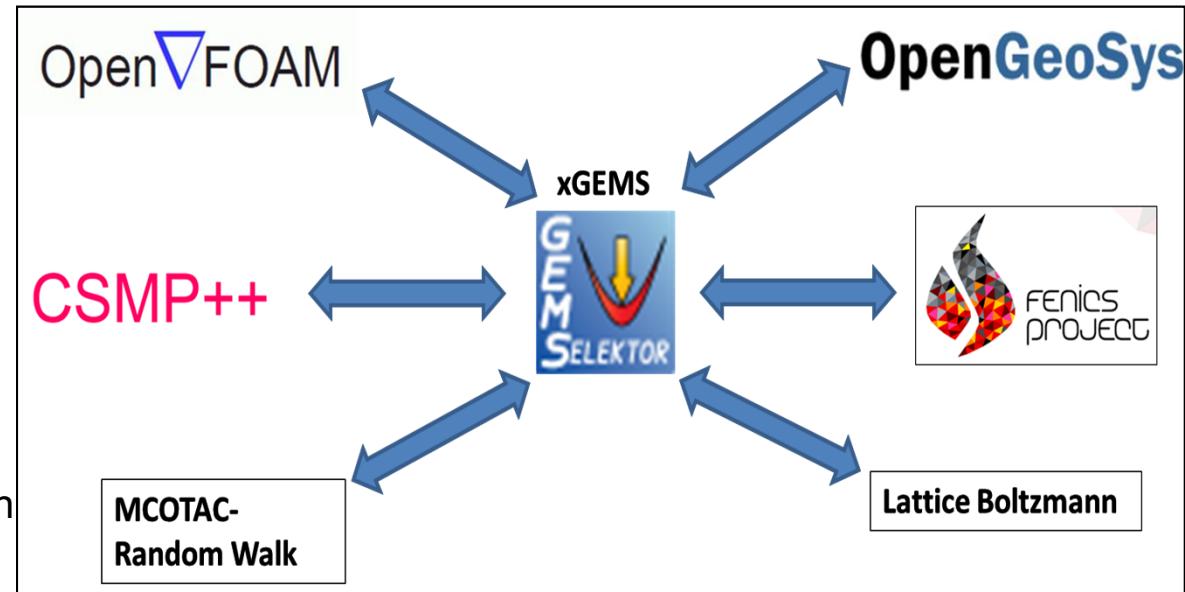
Speed-up of reactive transport simulations
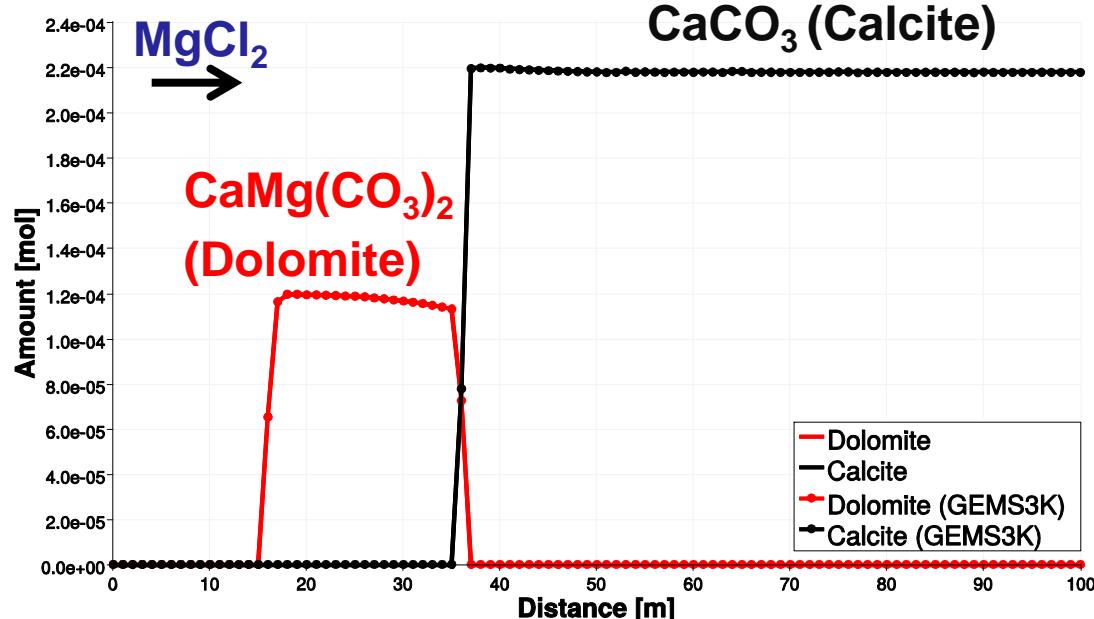
- Comparing transport results between GEMS3K and new libraries.

- Results match very well.

- Both solvers identify correctly the stable minerals and have the same sharp interface.
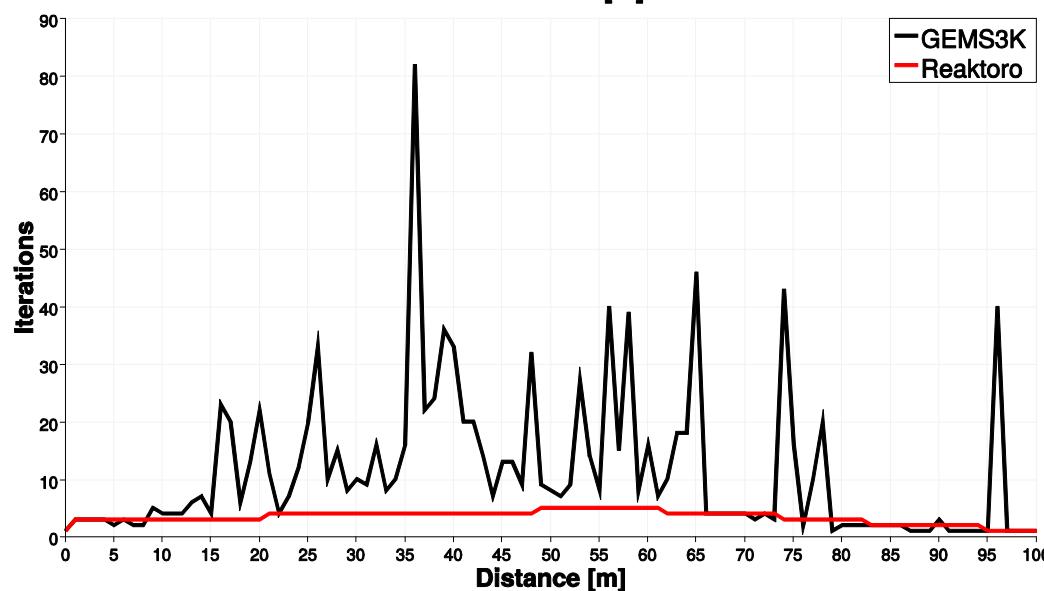
- **More than 3 times** faster than GEMS3K for this particular problem.

Thermodynamic data are essential for modelling the release, migration and retardation of radionuclides in the nearfield of a deep underground radioactive waste repository

LES has developed an extensive chemical thermodynamic database to support the safety analyses of Nagra in the framework of the Sectoral Plan
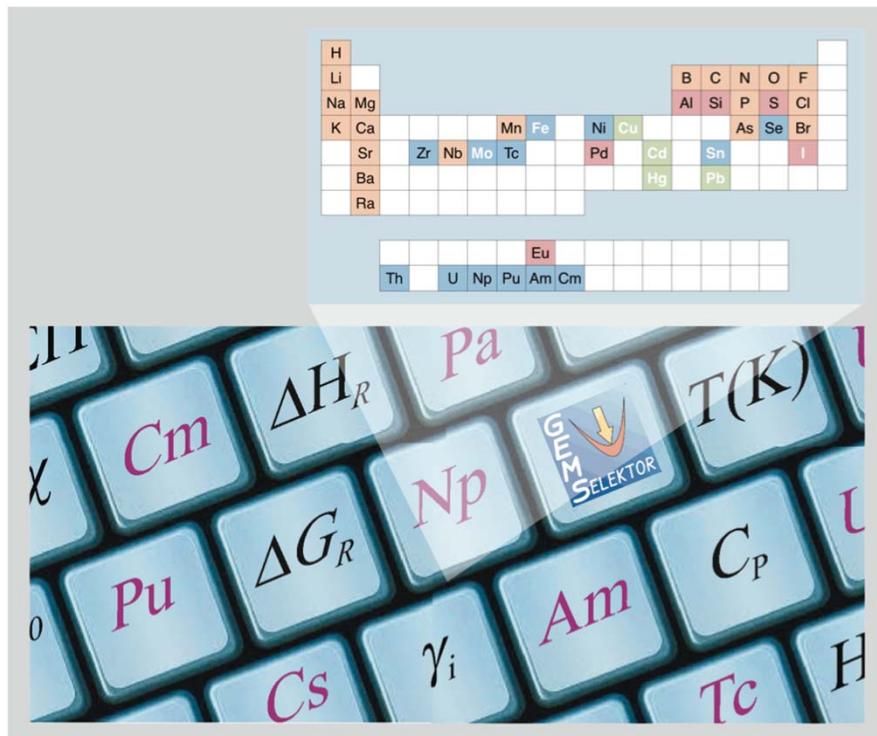

The database has been successfully applied for the

- Calculation of porewater compositions of hostrocks and bentonite

- Calculation of the solubility limits of radionuclides in porewaters

- Development of sorption databases for the sorption of radionuclides on the hostrocks and bentonite

- Reactive transport modelling of the geochemical evolution of the nearfield

PSI/Nagra Chemical Thermodynamic Database 12/07
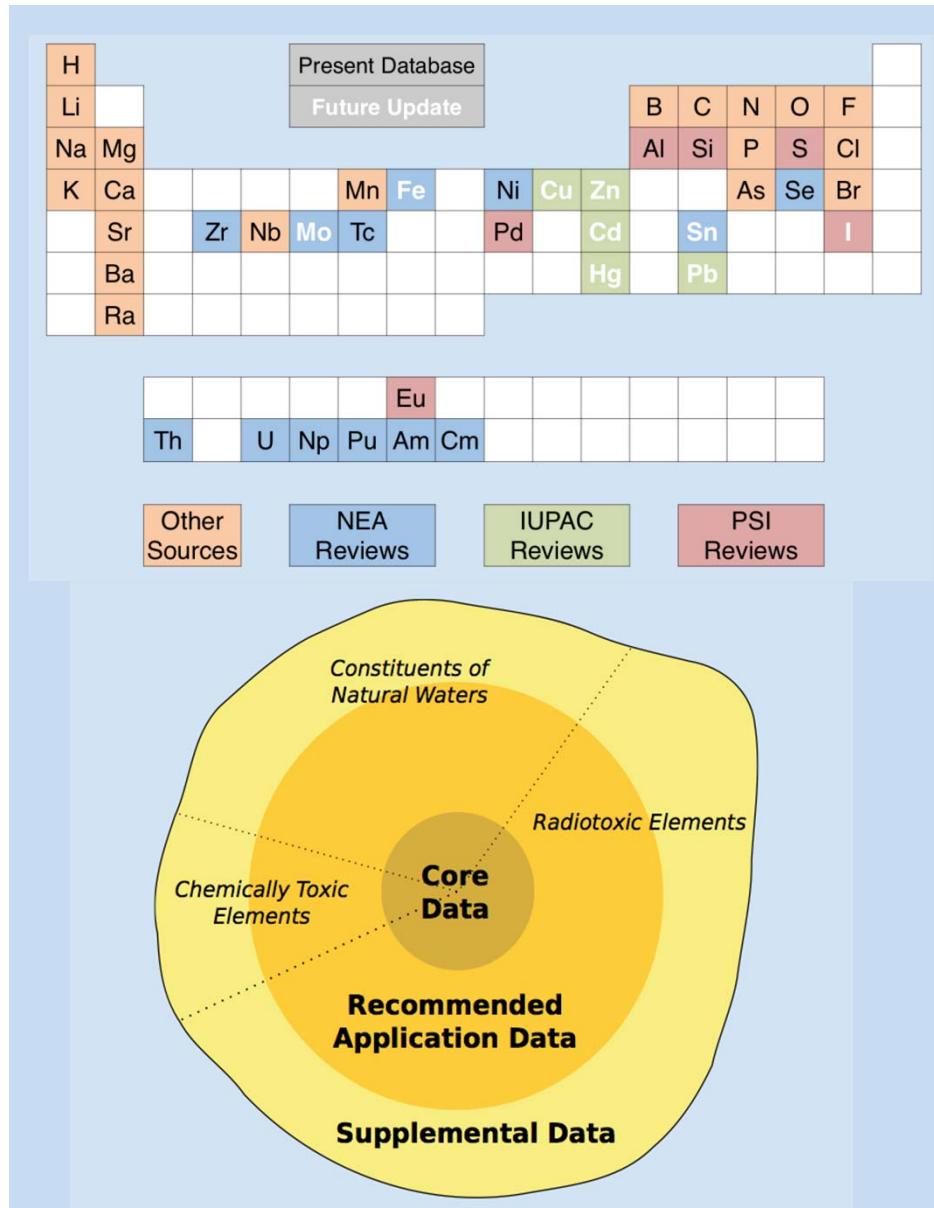
Database contains thermodynamic data for

- Main constituents of pore- and groundwaters
- Safety relevant radiotoxic and chemotoxic elements
- Solids and gases fixing the composition of pore- and groundwaters or limiting the solubility of radiotoxic and chemotoxic elements

Three types of data

- **Core data**: Widely accepted data of high quality that are not expected to change
- **Recommended application data**: High quality data in active research fields that may be revised over time
- **Supplemental data**: Data of lesser quality whose omission would lead to clearly erroneous results

Database distributed with our geochemical modelling code GEMS: gems.web.psi.ch
Documentation: www.psi.ch/les/database

Cement-Clay interactions studies

Diffusion cell

5mm
5mm 5mm
Cement Clay
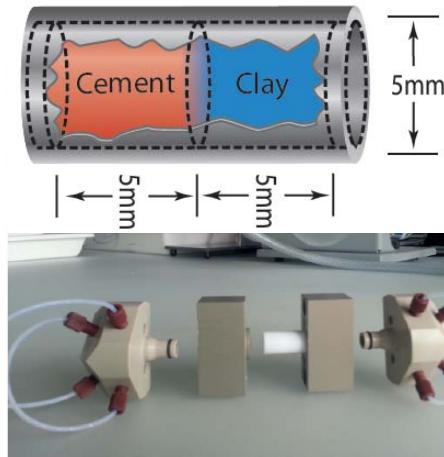
Radiography measurements

sample cell   dry cement   wet cement

empty cell   dry clay   cement/clay wet
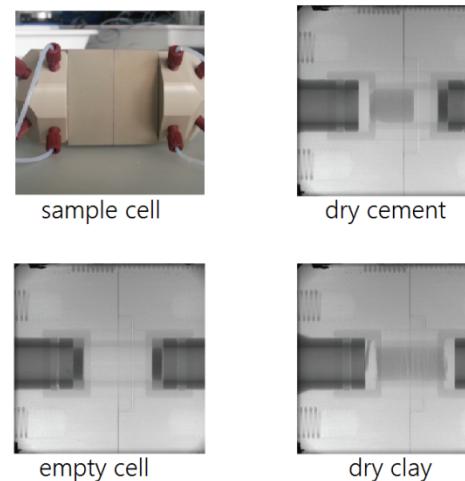
Extracted water content

64 days
85 days
104 days
113 days
162 days (dashed)
176 days (dashed)

ICON-NIAG/NUM/PSI

FOV

Clay
Fresh Interface
Cement
D_2O

Clay
Aged Interface
Cement
D_2O

$t = t_{ref} + 20$ min $t = t_{ref} + 6$ h $t = t_{ref} + 12$ h
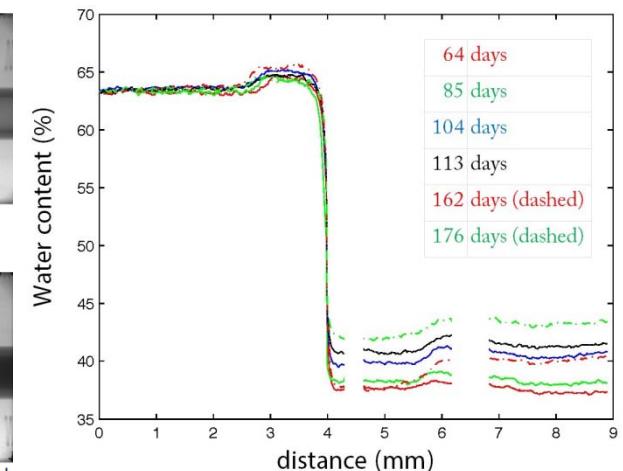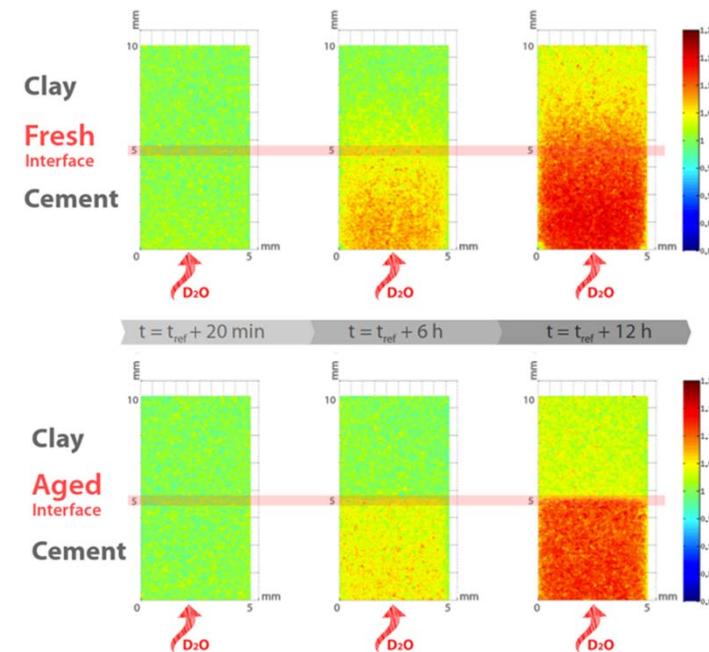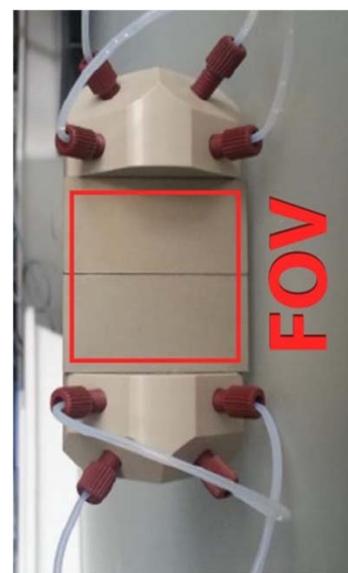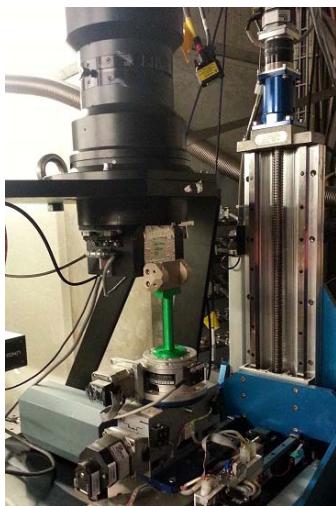
C-14 Project: Release of ^{14}C from activated steel under the conditions relevant to the cementitious near field

Financing: Swissnuclear, EU project «CAST» (CArbon Source Term), Nagra

Host rock

Unsaturated backfill

Saturated backfill

Cement

C-14

Metallic waste material

$^{14}C_xH_yO_z$

Key processes

Transport/stability/ sorption in the host rock

Air-water exchange

Decomposition

Transport in pore water

Sorption on cement

C-14 release by anoxic corrosion

Examples: x=1, y=4, z=0: $^{14}CH_4$ = methane
x =1, y=2, z=2: $H^{14}COOH$ = formic acid
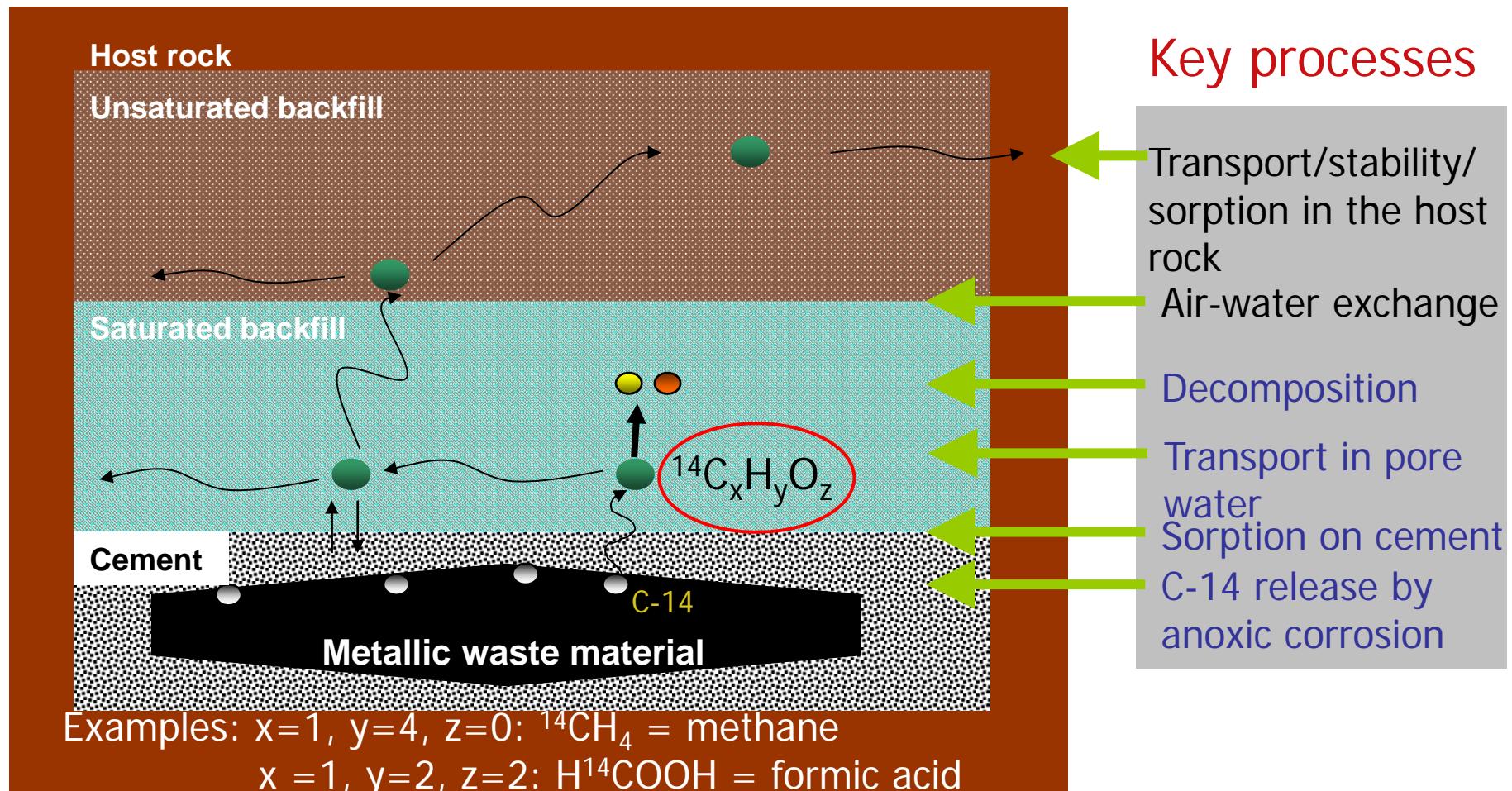
□ **Project:** *Identification and quantification of ^{14}C labelled chemical species formed during anoxic corrosion of activated steel under the conditions relevant to a cement-based repository (Partially financed by Swissnuclear and Nagra; Cooperation with University of Bern)*

□ **Motivation:** - Corrosion experiment with activated steel nuts from KKG
- Determination of the type of ^{14}C-containing organic compounds formed
- Challenge: Extremely low concentrations of the compounds due to the very low ^{14}C inventory in activated steel (~ 0.1 µg ^{14}C/g), the very low corrosion rate of steel in alkaline media (≤ 50 nm/year) and low amount of activated steel (~ 1 g ^{14}C/g; dose rate: 10 mSv/h) that can be used (use of hot cells in PSI hotlaboratory not possible)

□ **Development of the reactor (autoclave) for corrosion studies**
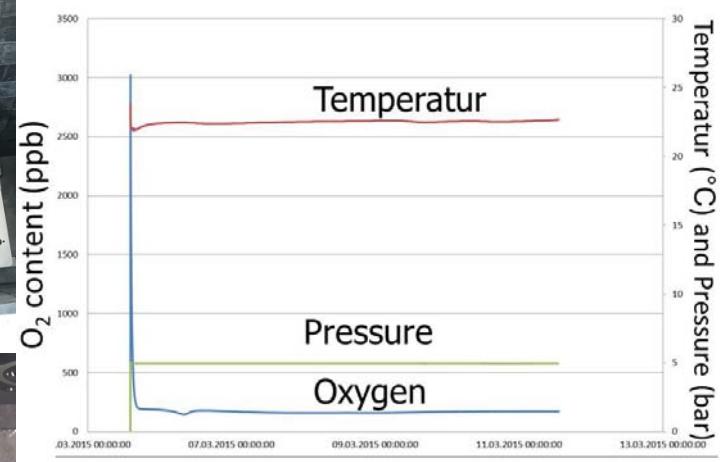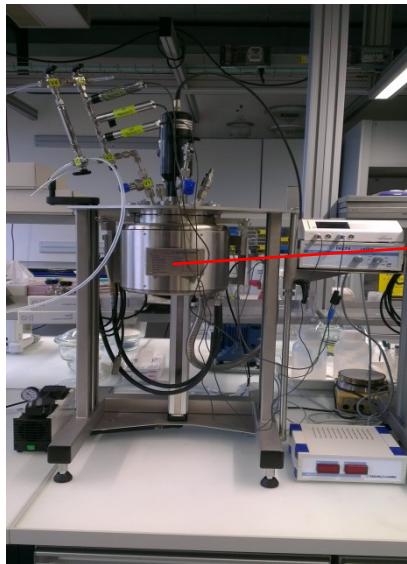
□ Development of a compound-specific ^{14}C AMS analytical method for determining ^{14}C-containing organic compounds (dissolved, gas phase) at extremely low concentrations

## Analysis of aqueous compounds

Ion chromatography (IC)

Analysis of gaseous compounds

$$1\ F^{14}C = {}^{14}C/({}^{12}C \times 10^{-12})$$
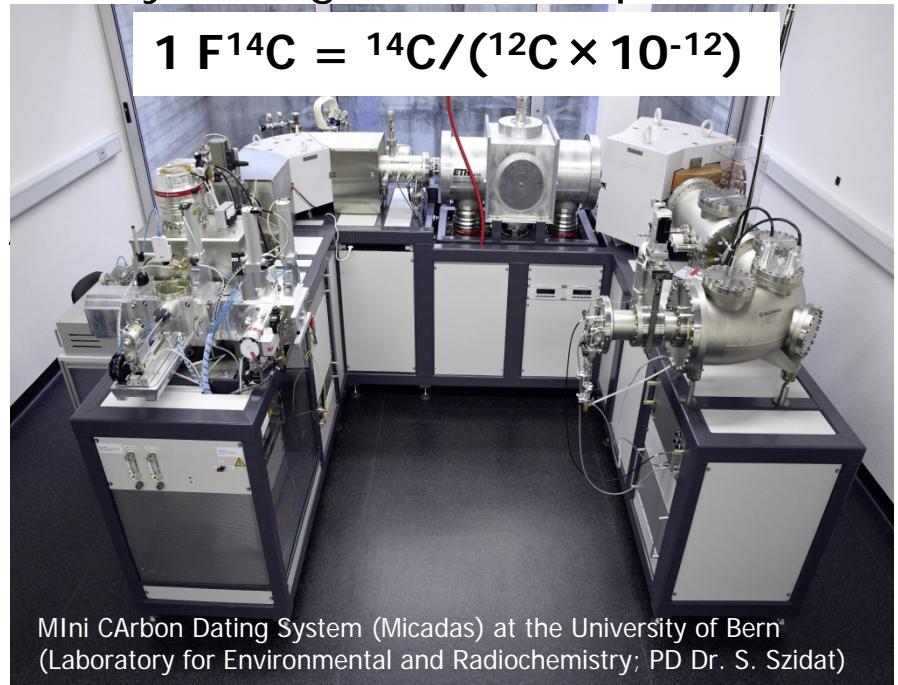
MIni CArbon Dating System (Micadas) at the University of Bern (Laboratory for Environmental and Radiochemistry; PD Dr. S. Szidat)

Results

Background (Milli-Q water percolated through IC): ~ 0.06 F^{14}C

Dynamic range of AMS: ~ 0.06 - ~ 50 F^{14}C

Conclusion

The proposed analytical approach is feasible as the amount of ^{14}C produced in the reactor per day is expected to be significantly higher than the ^{14}C background.

**(1) Preparation of SNF micro-samples for microXAS (< 100 LA**

1.circular grinding => 2. SF particles
3. "fingerprint" on Kapton => 4. sub-sampling

total activity: 70 LA
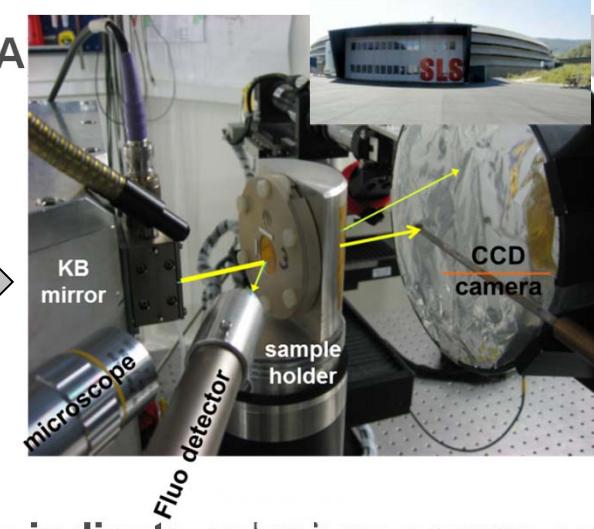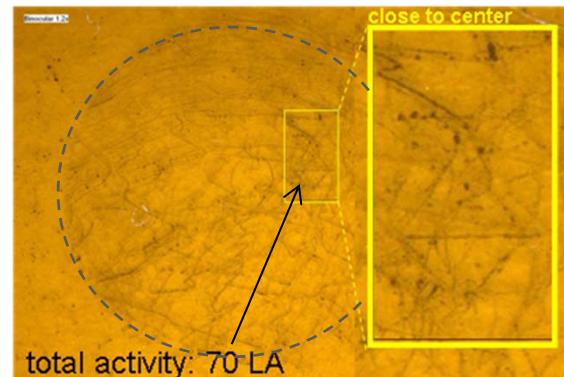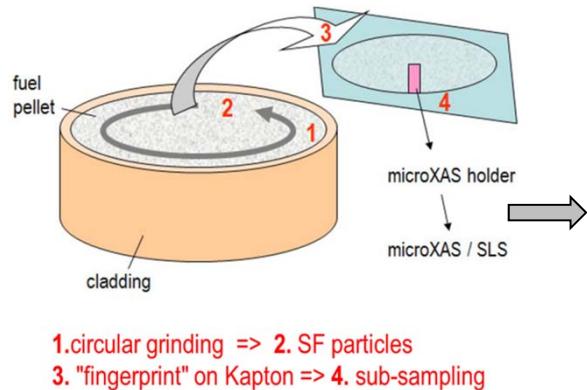
(2) Elemental mapping (Se) of SF particles from Leibstadt with microfocused X-ray beam
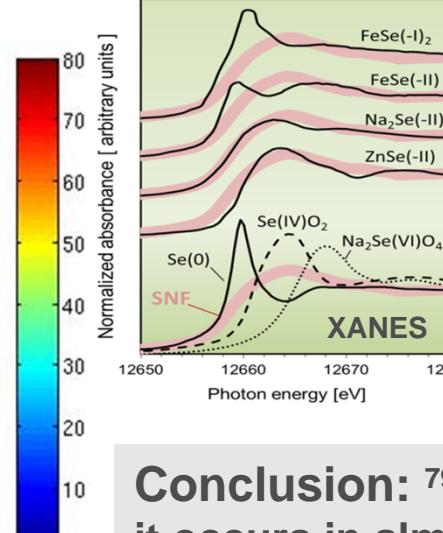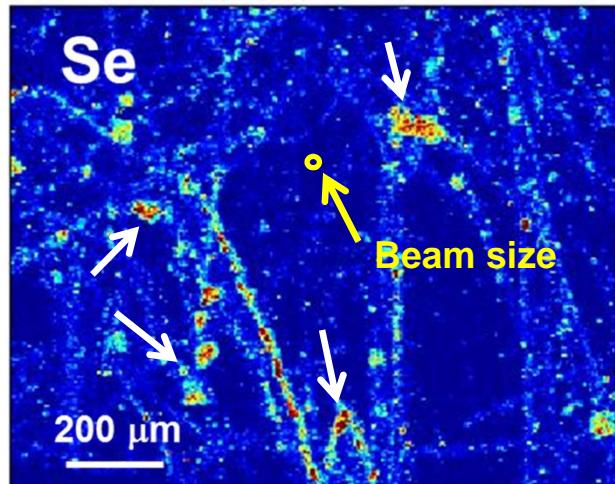
(3) EXAFS/XANES data indicate selenium occurs as tightly bond Se^{-II} in UO$_2$ lattice
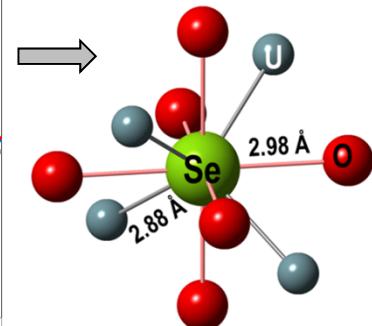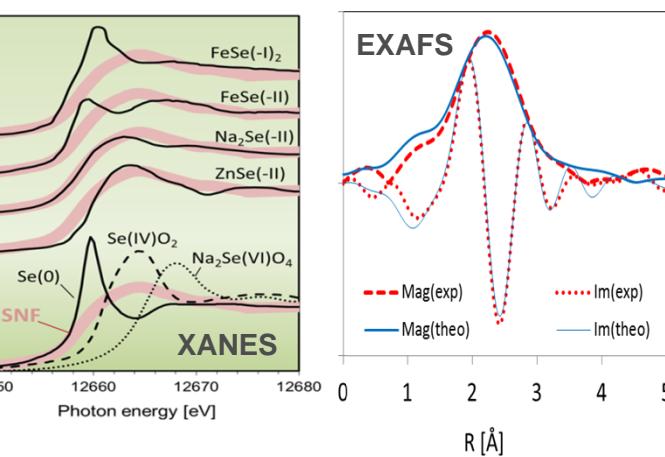
Conclusion: ^{79}Se probably not an IRF nuclide, since it occurs in almost insoluble form in UO$_2$ SF

Important infrastructure

Hot Laboratory (PSI)

SLS (PSI)

CSCS

SINQ (PSI)

Mineralogy

u^b PAUL SCHERRER INSTITUT PSI

UNIVERSITÄT BERN

Geological Disposal Systems

Modeling Platform

GEMS SELEKTOR
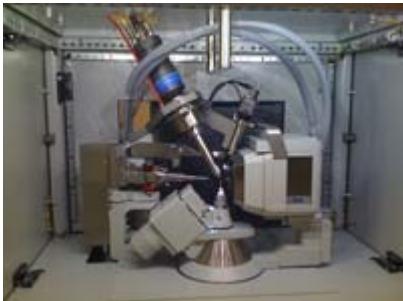
MCOTAC

B&B

OpenGeoSys

**XRD-Lab (UniBe)**

Mont Terri and Grimsel URLs

Education platform

1913

LES Publications

ACS NANO, Anal. Chem., Appl. Clay Sci., Appl. Geochem., Cem. Concr. Res., Chem. Geol., Comput. Geosci., Environ. Sci. Technol., Geochim. Cosmochim. Acta., J. Mat. Chem., J. Phys. Chem. C, Macro Lett., Radiochim. Acta., . …….
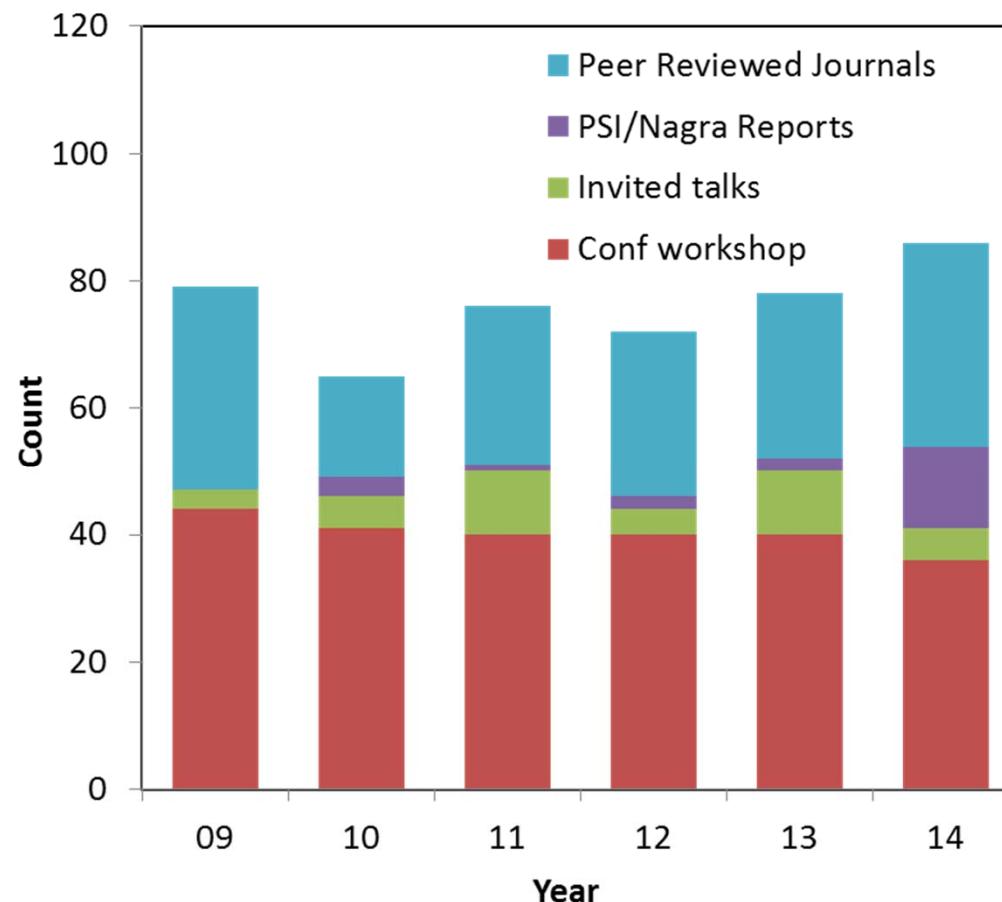
2014: 32 Journal articles; 13 Reports (8 NTB, 3 NAB, 2 PSI); 2 Proceedings

Education

New PhD/Postdocs

- **Allan Leal (Postdoc) 1 year contract September 2014/15**
- **Annamaria Keri (SNF-PhD) started January 2015**

Master students/Training

- **Shao Meng (ETHZ/CH)**
- **Annamaria Keri (BUTE/HU)**
- **Albert Riera (International Industrial Master, UBC, Spain)**
- **Delia Folghera (Training as laboratory assistant)**
- **Livia Knecht   (Training as laboratory assistant)**

Successful PhD defences in 2014

> **Daniela Soltermann (ETHZ)**
>
> **Martina Bestel (UBern, LES co-supervision)**
>
> **Emilie L'Hopital (EMPA/EPFL, LES co-supervision)**

www.psi.ch/les

LES

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EDUCATION & JOBS   EVENTS

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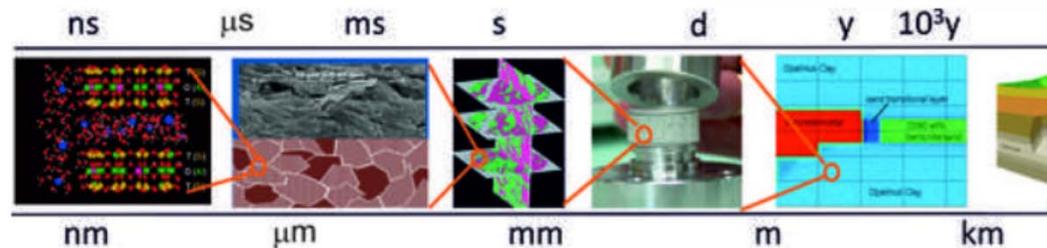
Laboratory for Waste Management (LES)

LES is the Swiss competence center for geochemistry and multi scale radionuclide and mass transport in argillaceous rocks and cement and their applications to deep geological systems and Swiss radioactive waste repositories.
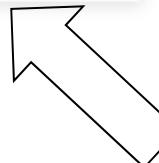
Thank you for your attention