CArbon-14 Source Term
CAST

^{14}C behaviour under repository conditions – application to geo-chemical based long-term safety analysis for a underground disposal system

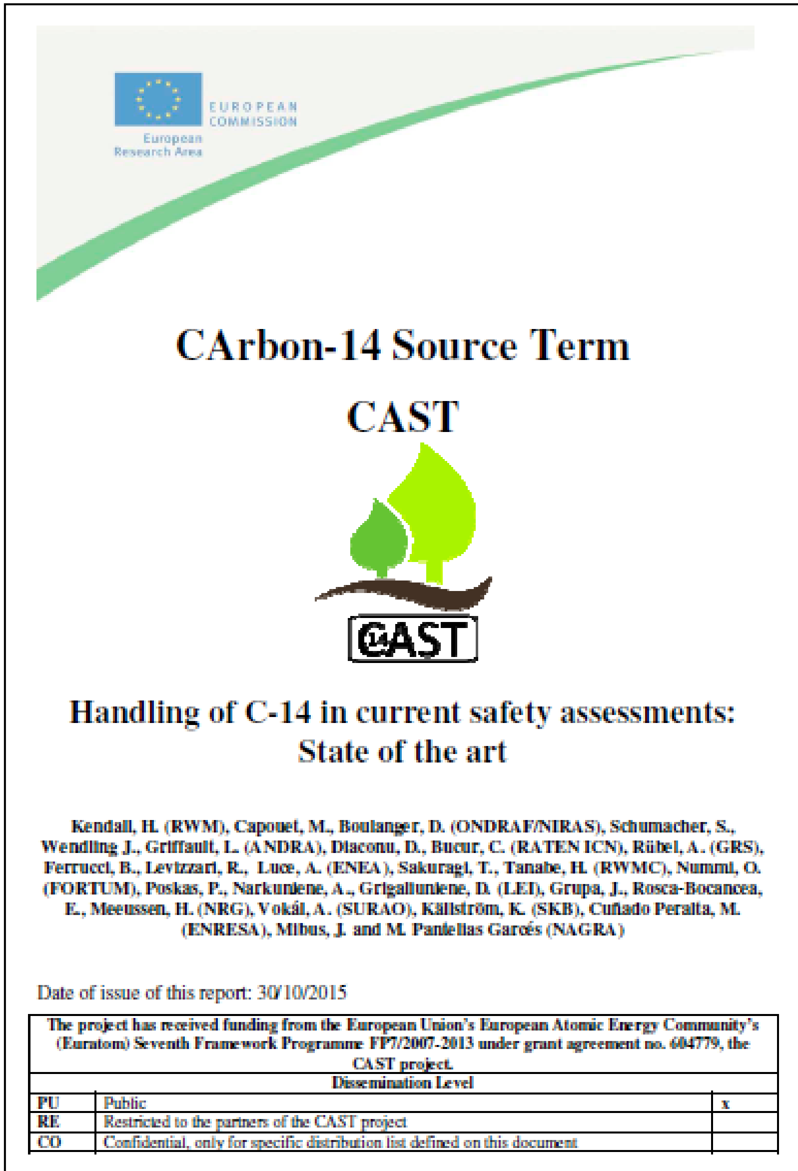
Volker Metz, KIT-INE

The project has received funding from the European Union’s Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project.

Kendall, H. (RWM), Capouet, M., Boulanger, D. (ONDRAF/NIRAS), Schumacher, S., Wendling J., Griffault, L. (ANDRA), Diaconu, D., Bucur, C. (RATEN ICN), Rübel, A. (GRS), Ferrucci, B., Levizzari, R., Luce, A. (ENEA), Sakuragi, T., Tanabe, H. (RWMC), Nummi, O.(FORTUM), Poskas, P., Narkuniene, A., Grigaliuniene, D. (LEI), Grupa, J., Rosca-Bocancea, E., Meeussen, H. (NRG), Vokál, A. (SURAO), Källström, K. (SKB), Cuñado Peralta, M. (ENRESA), Mibus, J. and M. Pantelias Garcés (NAGRA)

Handling of C-14 in current safety assessments: State of the art.

CArbon-14 Source Term report CAST-2015-D6.1



EUROPEAN COMMISSION
European Research Area

CArbon-14 Source Term

CAST

Handling of C-14 in current safety assessments: State of the art

Kendall, H. (RWM), Capouet, M., Boulanger, D. (ONDRAF/NIRAS), Schumacher, S., Wendling J., Griffault, L. (ANDRA), Diaconu, D., Bucur, C. (RATEN ICN), Rübel, A. (GRS), Ferrucci, B., Levizzari, R., Luce, A. (ENEA), Sakuragi, T., Tanabe, H. (RWMC), Nummi, O. (FORTUM), Poskas, P., Narkuniene, A., Grigaliuniene, D. (LEI), Grupa, J., Rosca-Bocancea, E., Meeussen, H. (NRG), Vokál, A. (SURAO), Källström, K. (SKB), Cuñado Peralta, M. (ENRESA), Mibus, J. and M. Pantelias Garcés (NAGRA)

Date of issue of this report: 30/10/2015

The project has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

Dissemination Level		
PU	Public	x
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

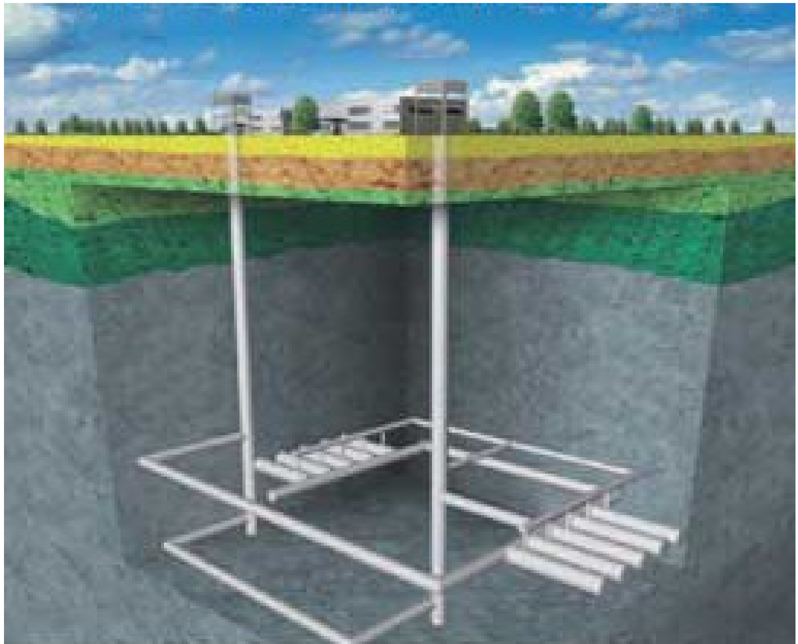
containment and isolation of radioactive waste

→ deep geological multi-barrier systems

European Council Directive 2011/70/EURATOM of 19 July 2011 establishing a Community framework for the responsible and safe management of spent fuel and radioactive waste:

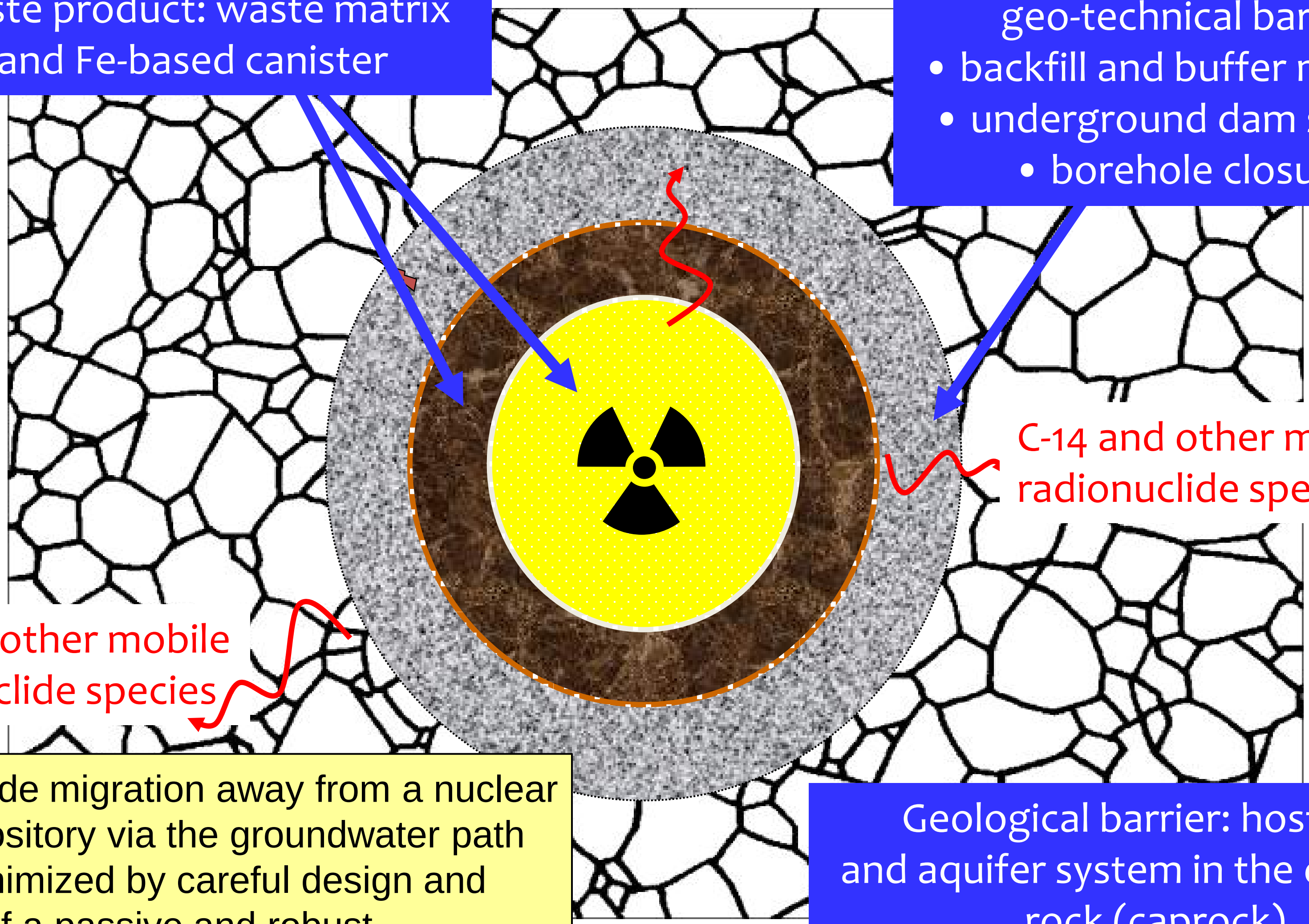
"Radioactive waste, including spent fuel considered as waste, requires containment and isolation from humans and the living environment over the long term. Its specific nature, namely that it contains radionuclides, requires arrangements to protect human health and the environment against dangers arising from ionising radiation, including disposal in appropriate facilities as the end location point. The storage of radioactive waste, including long-term storage, is an interim solution, but not an alternative to disposal. (…)"

There is still no alternative to final disposal in deep multi-barrier systems for the safe management of high-level radioactive waste. Isolating radioactive waste from the biosphere in a geologically stable environment over periods of several hundreds of thousands of years offers maximum safety, which cannot be guaranteed at present by other concepts



source: Official Journal of the European Union (ABl. L 199, 2. Aug. 2011, p. 48f), http://eur-lex.europa.eu/LexUriServ

Basic concept of multi-barrier disposal systems



Engineered / technical barrier
waste product: waste matrix
and Fe-based canister

Geo-engineered
geo-technical barrier:
- backfill and buffer materials
- underground dam systems
- borehole closures

C-14 and other mobile
radionuclide species

C-14 and other mobile
radionuclide species

Radionuclide migration away from a nuclear waste repository via the groundwater path can be minimized by careful design and selection of a passive and robust <u>multi-barrier system</u>.

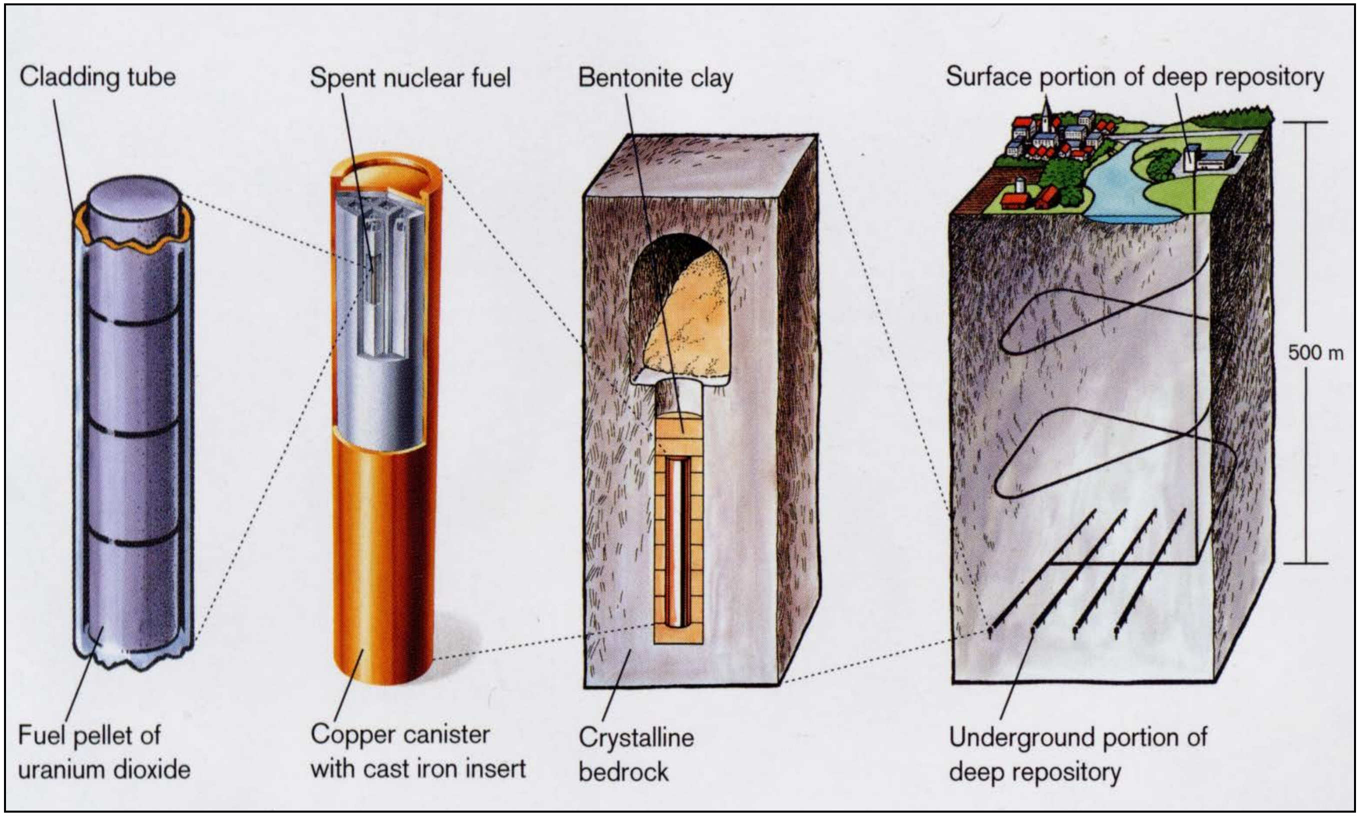
Geological barrier: host rock
and aquifer system in the overlying
rock (caprock)

Example : Swedish multi-barrier concept (KBS-3)

Engineered Barrier
- Spent fuel
- HLW-glass
- Container

Geoengineered Barrier
- Drift backfill
- Underground dam systems
- Shaft and borehole seals

Geological Barrier
- Host rock (crystalline rock)
- Aquifer system in the overlying sediments



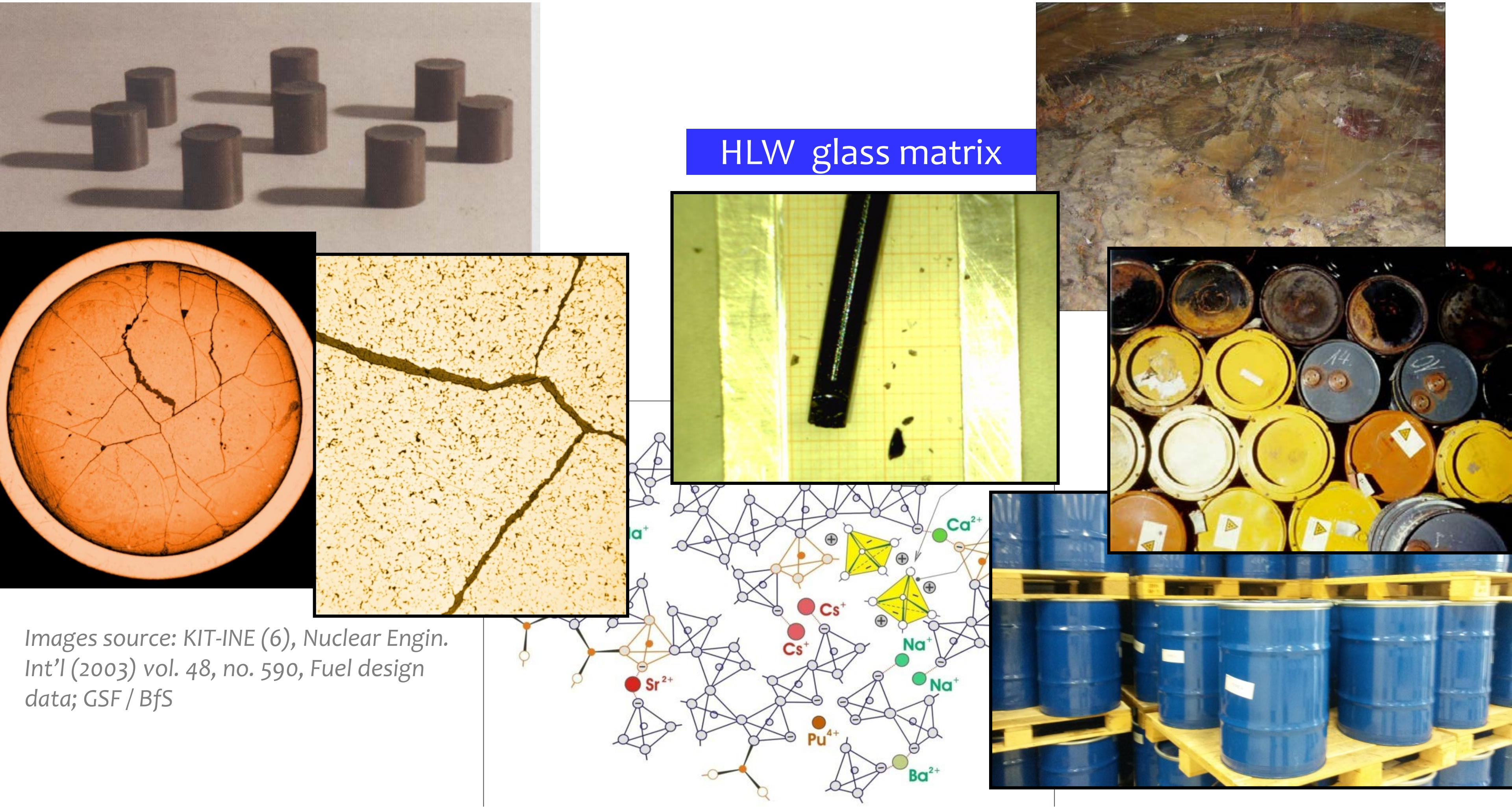
sources: SKB (2006) Long-Term Safety for KBS-3 Repositories at Forsmark and Laxemar – A First Evaluation, Main Report of the SR-Can project, SKB TR 06-09, Swedish Nuclear Fuel and Waste Management Co., Stockholm; Hedin et al. (2007) NEA-RWM report, NEA No. 6362, Nuclear Energy Agency, Paris, pp 45-56

Technical barrier: UO_x / HLW glass / cement matrix

UO_x matrix of spent nuclear fuel (SNF)

HLW glass matrix

cement matrix of LLW/ILW



Images source: KIT-INE (6), Nuclear Engin. Int'l (2003) vol. 48, no. 590, Fuel design data; GSF / BfS

Engineered barriers: containers for spent nuclear fuel / HLW glass

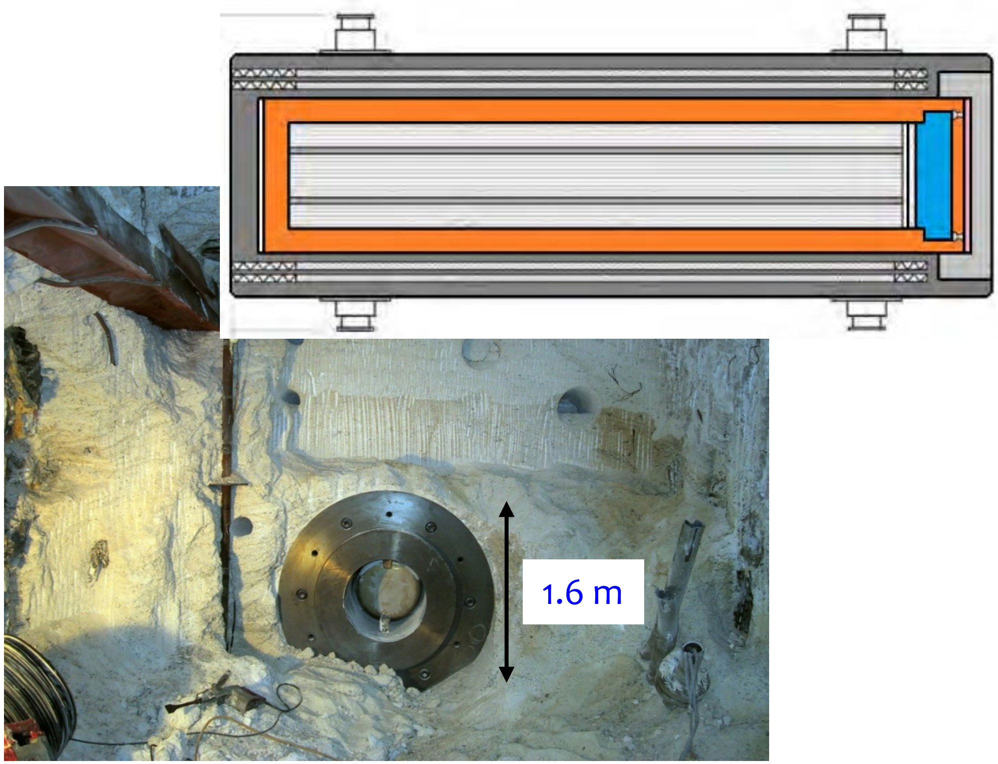
Thin walled iron “CU1”containers for spent MOX fuel elements and iron “C-overpacks” for HLW coquilles for disposal in claystone (France)

Source: ANDRA 269 VA (Dec 2006): Dossier 2005 Argile, Phenomenological evolution of a geological repository (Dezember 2005), Report Series ; T. Hassel et al. (2014) Behälterdossier, ENTRIA, Leibniz Universität Hannover, Version 0.2

Engineered barriers: containers for spent nuclear fuel / HLW glass

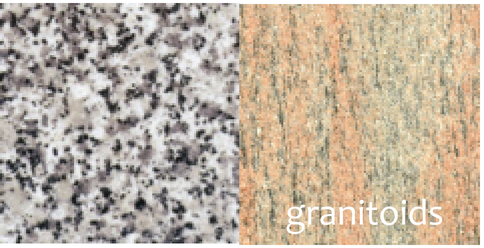
Thick walled cast iron container with inner steel container for spent nuclear fuel elements and HLW coquilles for disposal in rock salt (for example Germany)

Nodular iron (a kind of cast iron) container with 5 cm thick copper liner as chemical barrier against corrosion for disposal in crystalline rock (for example Sweden and Finland)



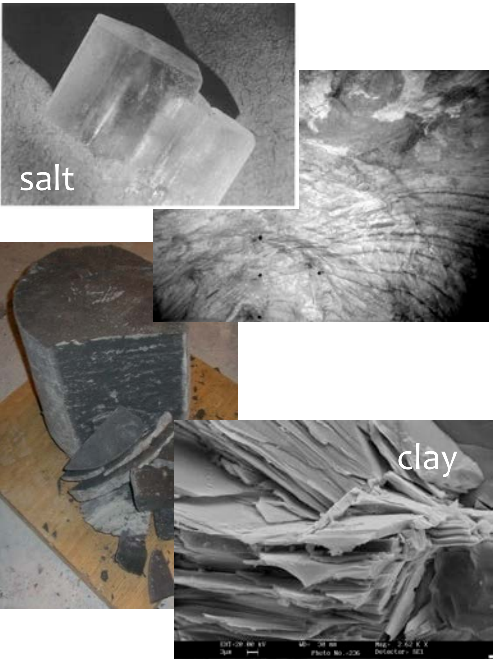
Sources: GRS, Endlagerung wärmeentwickelnder Abfälle in Deutschland, GRS-247, 2008; 9. Projektstatusgespräch BMBF/BMWI-geförderter FE-Vorhaben zu Entsorgung gefährlicher Abfälle in tiefen geol. Formationen, 2010; SKB, Technical Report, TR-01-03, December 2000

International concepts for final disposal of radioactive waste



short-lived LLW - shallow land disposal

- at sites with *clay-rich aquicludes* for reasonable protection of groundwater (Czechia, France, Finland, Japan, Sweden, Spain, United Kingdom, USA …)



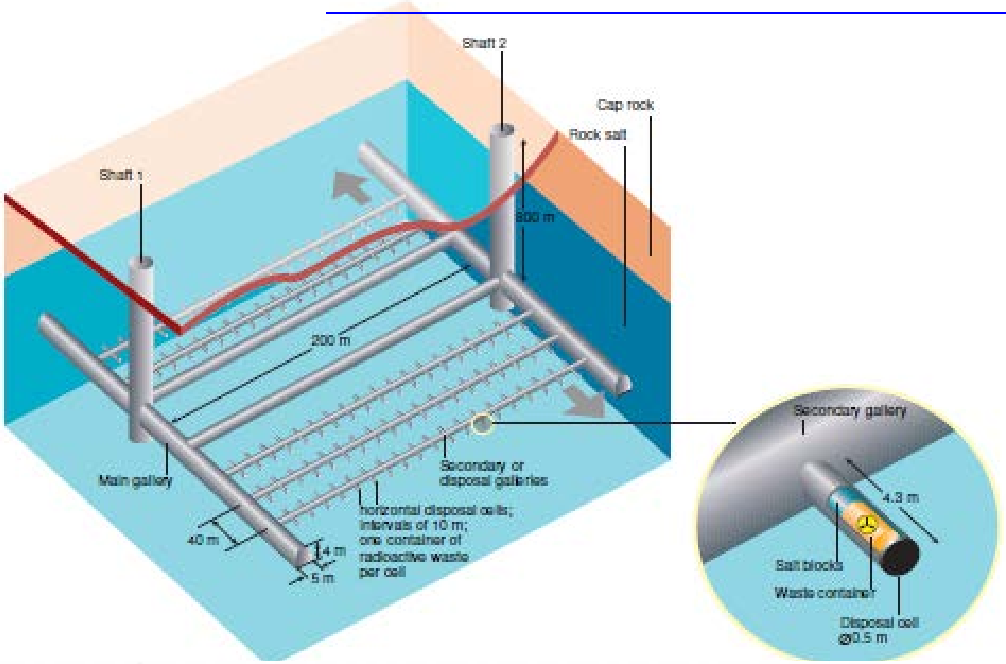
LLW / ILW – final disposal in deep geological formations

- *rocks with argillaceous overburden* (Canada, Germany)
- *granite* (Hungary)
- *bedded salt formations* (USA)
- *salt diapirs* (Germany)
- *clay rock* or *marl* (Switzerland)

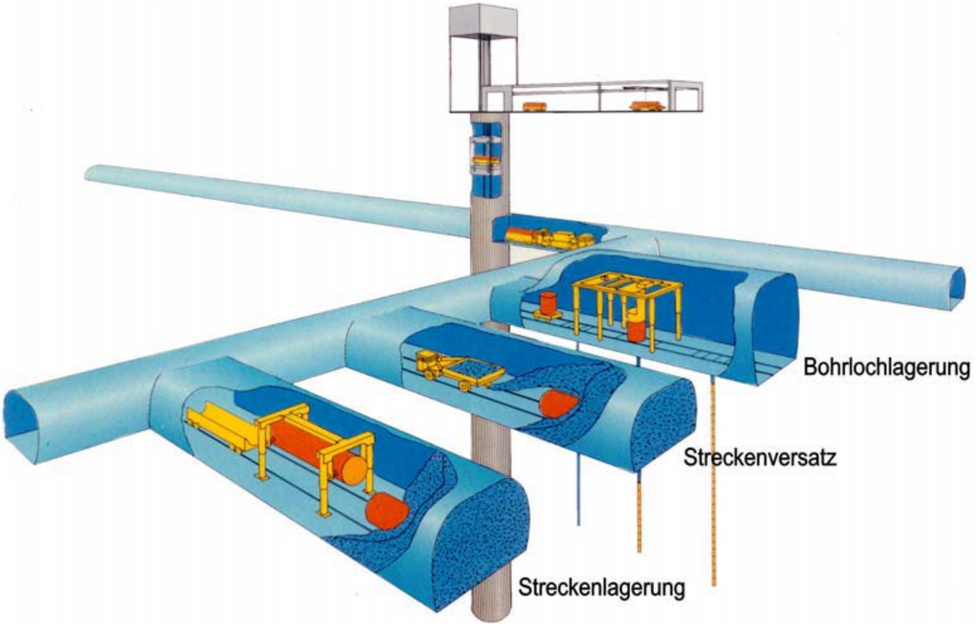
HLW – final disposal in deep geological formations

- *granite / granitoides* (Finland, Sweden, Spain and Argentina, China, Czechia, Hungary, India, Japan, Korea, Lithuania, Russia, Slovakia, South Africa, United Kingdom)
- *salt* (Germany, Lithuania, Netherlands, Romania, Russia, USA)
- *clay rock*, plastic (Belgium , Netherlands)
- *clay rock*, solidified (Argentina, Bulgaria, France, Germany, Hungary, Italy, Japan, Lithuania, Switzerland, Slovenia, Spain, United Kingdom

SNF and HLW-glass disposal in rock salt (Germany, Netherlands)



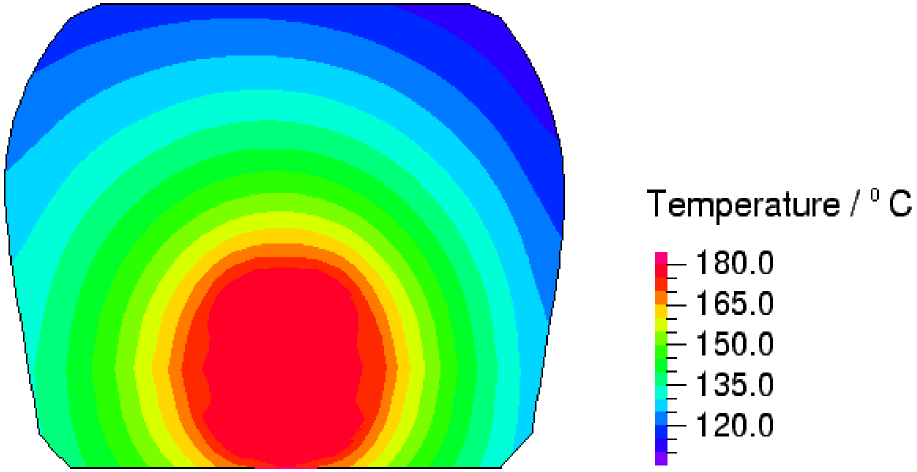
- disposal in depth of 500 to 800 m
- very high plasticity →
  "complete isolation" possible
- host rock posses extremely low permeability (except anhydrite zones)
- thick-walled cask iron / steel container
- back-filling with crushed rock salt
- reference case: no water access
- less probable scenarios: water access due to failure of shaft sealing etc.



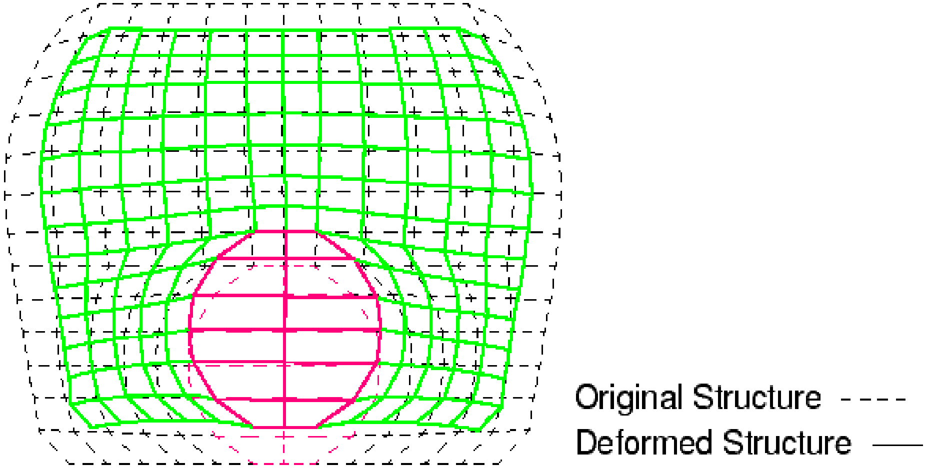
Sources: J. Grupa, E. Rosca-Bocancea & H. Meeussen (2015) NRG contribution to D6.1 in Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term (CAST). Thermal Simulation of Drift Emplacement (TSDE) 1990 – 2000, Asse II, 800 m level; Bollingerfehr, W. et al. (2011) EUGENIA, DBE-Technology, BGR; FKZ 02 E 10346

Rock salt : heat conductivity and convergence

start

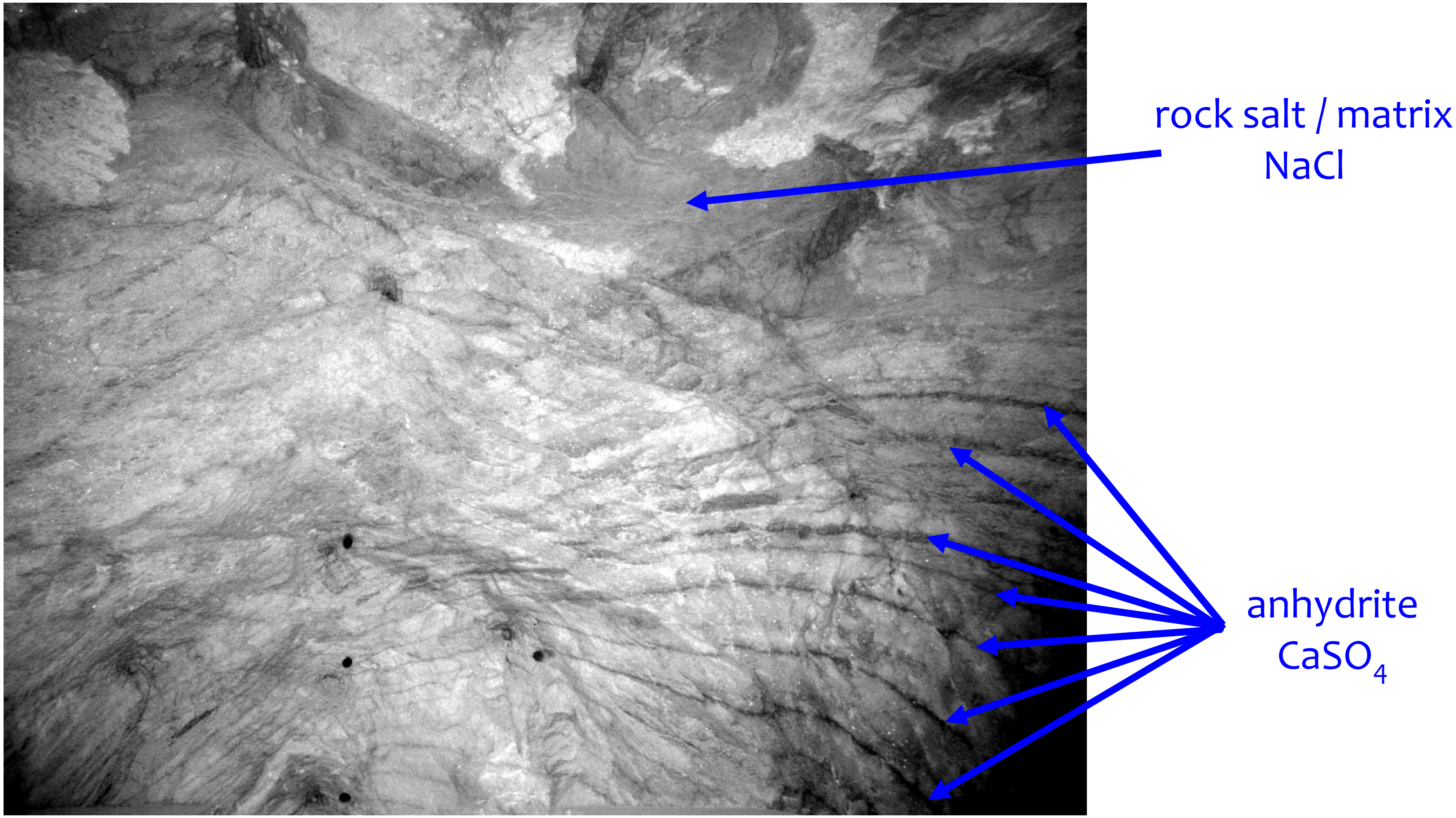


11 years



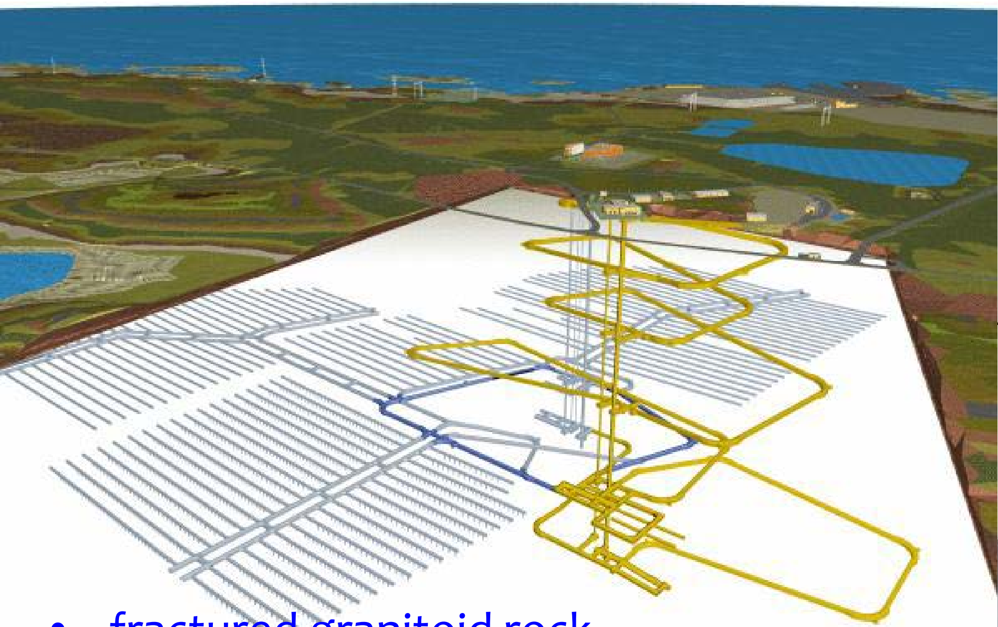
Source: Thermal Simulation of Drift Emplacement (TSDE) 1990 – 2000, Asse II, 800 m level

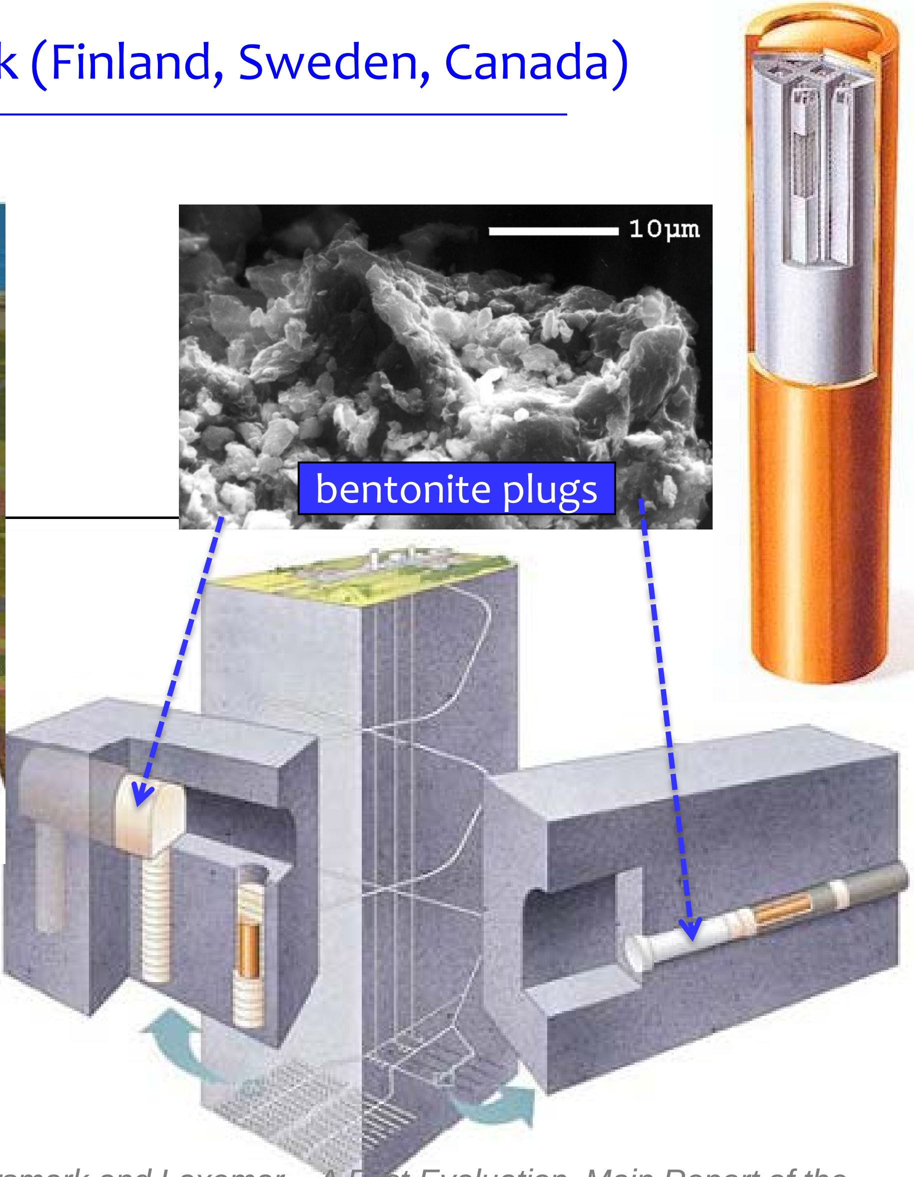
Potential migration paths in rock salt : anhydrite bands



rock salt (Na3) with anhydrite bands,
Schachtanlage Asse II

SNF disposal in crystalline rock (Finland, Sweden, Canada)



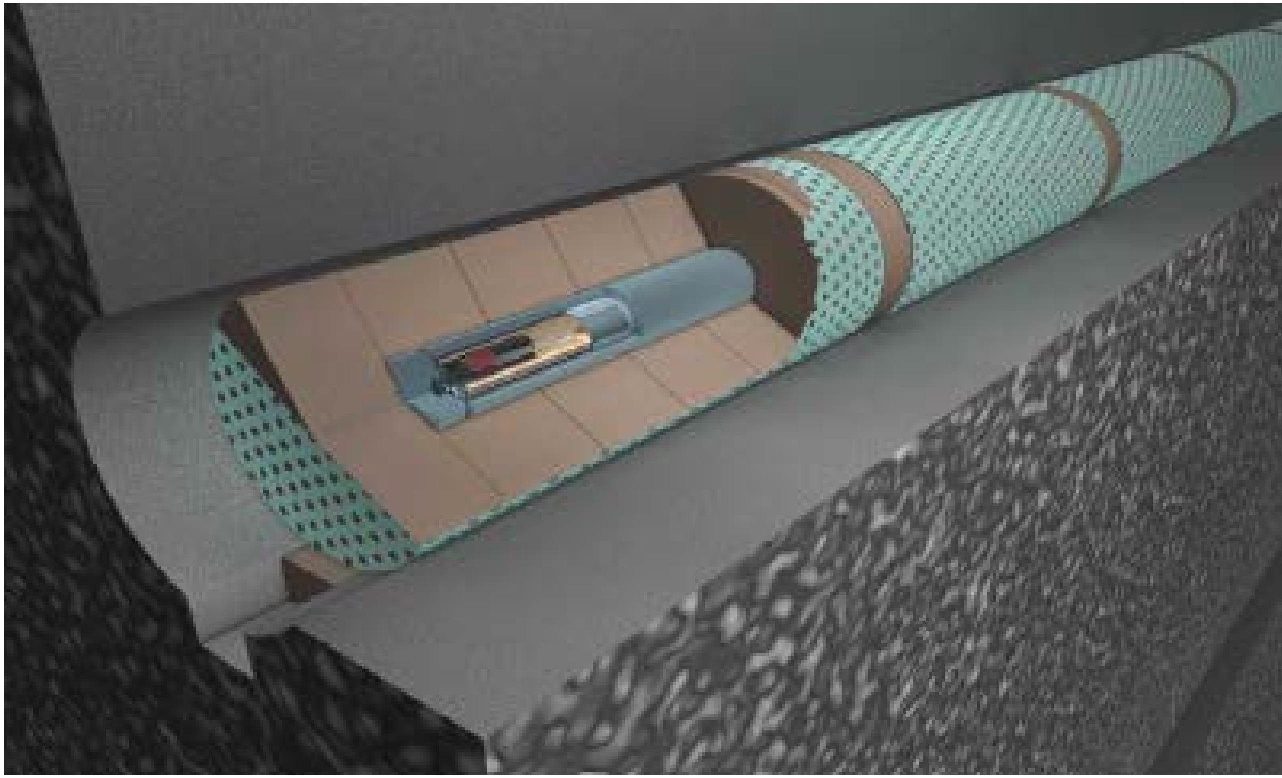


- fractured granitoid rock
- advective water transport → bentonite as barrier against water access and radionuclide migration
- nodular iron with 5 cm thick Cu liner as chemical barrier against corrosion

sources: SKB (2006) Long-Term Safety for KBS-3 Repositories at Forsmark and Laxemar – A First Evaluation, Main Report of the SR-Can project, SKB TR 06-09, Swedish Nuclear Fuel and Waste Management Co., Stockholm; Hedin et al. (2007) NEA-RWM report, NEA No. 6362, Nuclear Energy Agency, Paris, pp 45-56; Pastina, B. & Hellä, P.: Expected evolution of a spent fuel repository in Olkiluoto, Posiva 2006-05, December 2006

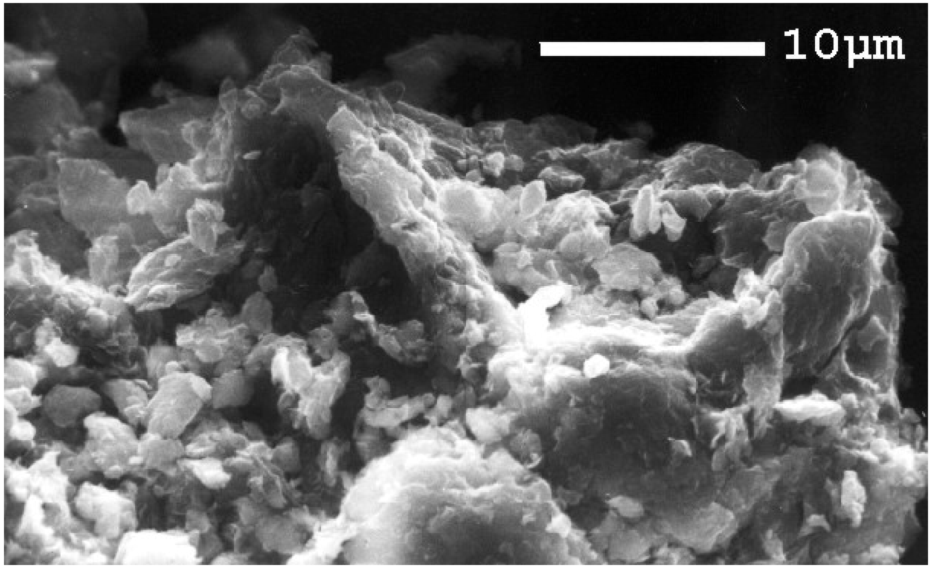
SNF disposal in crystalline rock (Czech Republic)

- fractured granitoid rock with advective water transport → bentonite as barrier against water access and radionuclide migration
- canister consists of an outer layer of carbon steel (which will corrode very slowly under anaerobic conditions) and a second inner layer of stainless steel (which will corrode at an almost negligible general corrosion rate and exhibit a low tendency to local corrosion under anaerobic conditions)



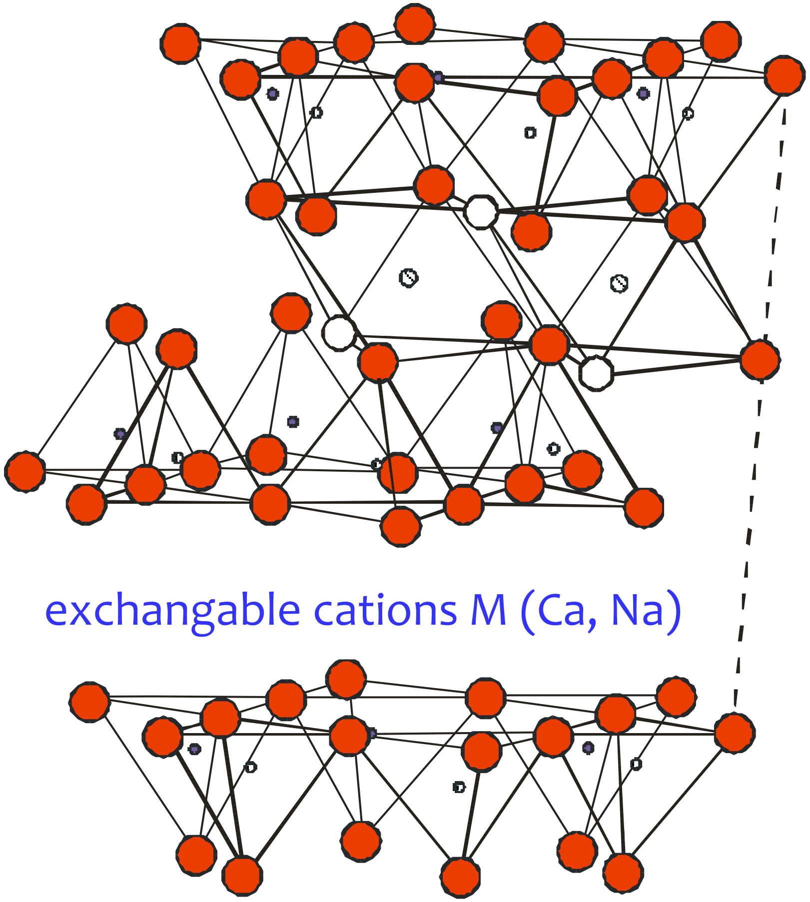
source: Antonín Vokál (2015) SURAO contribution to D6.1 in Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term (CAST)

Montmorillonitic smectite: main constituent of claystone / bentonite



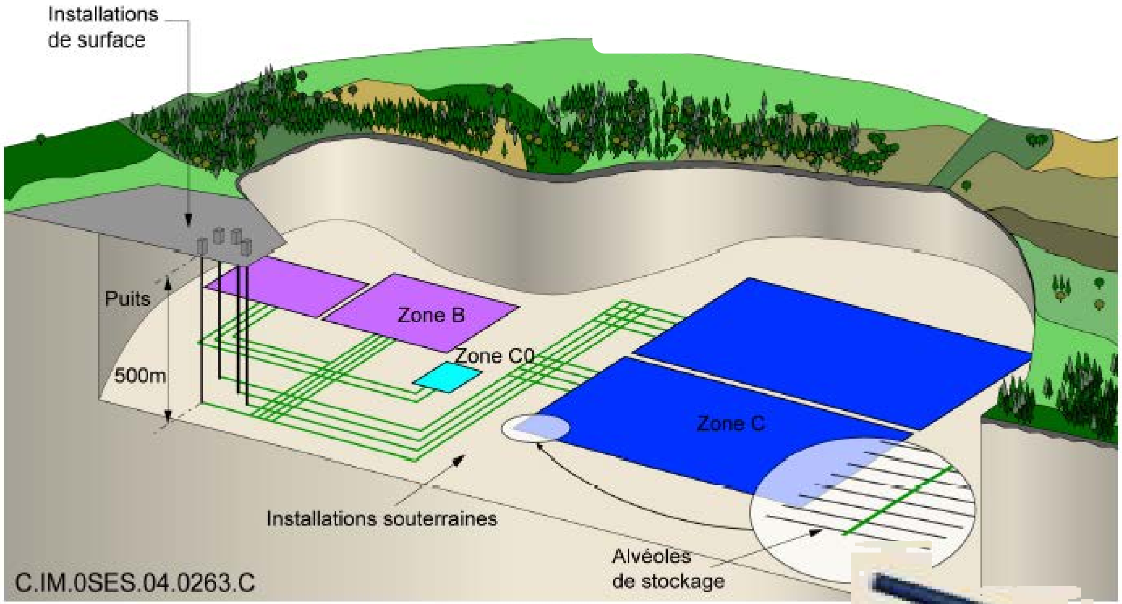
chemical analysis (wt %)	
SiO2	61
Al2O3	20
TiO2	<1
Fe(III) as Fe2O3	3
MnO	<1
MgO	3
CaO	1
Na2O	2
K2O	<1
loss on ignition	11
total	100

$M_{0.66}[Mg_{0.66}Al_{3.34}][Si_8]O_{20}(OH)_4 \cdot (H_2O)_n$

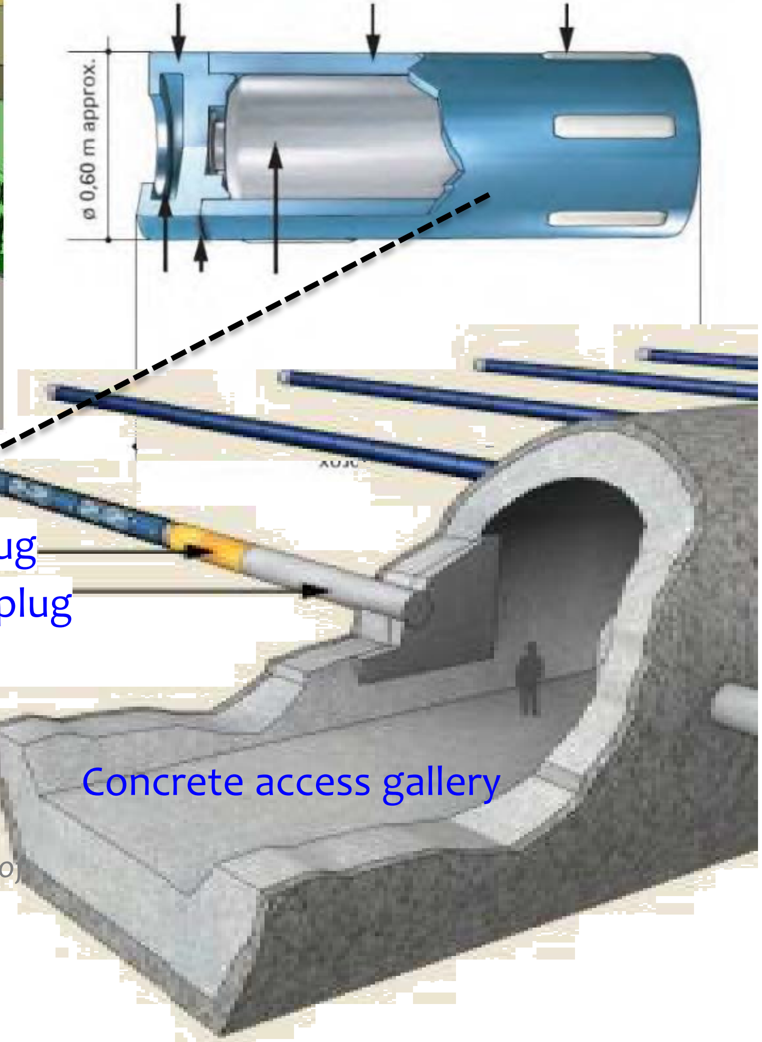


exchangable cations M (Ca, Na)

SNF/HLW and LLW/ILW in Callovo-Oxfordian clay rock (France)



Nanoporous solidified clay rock characterized by high plasticity; only diffusive water transport



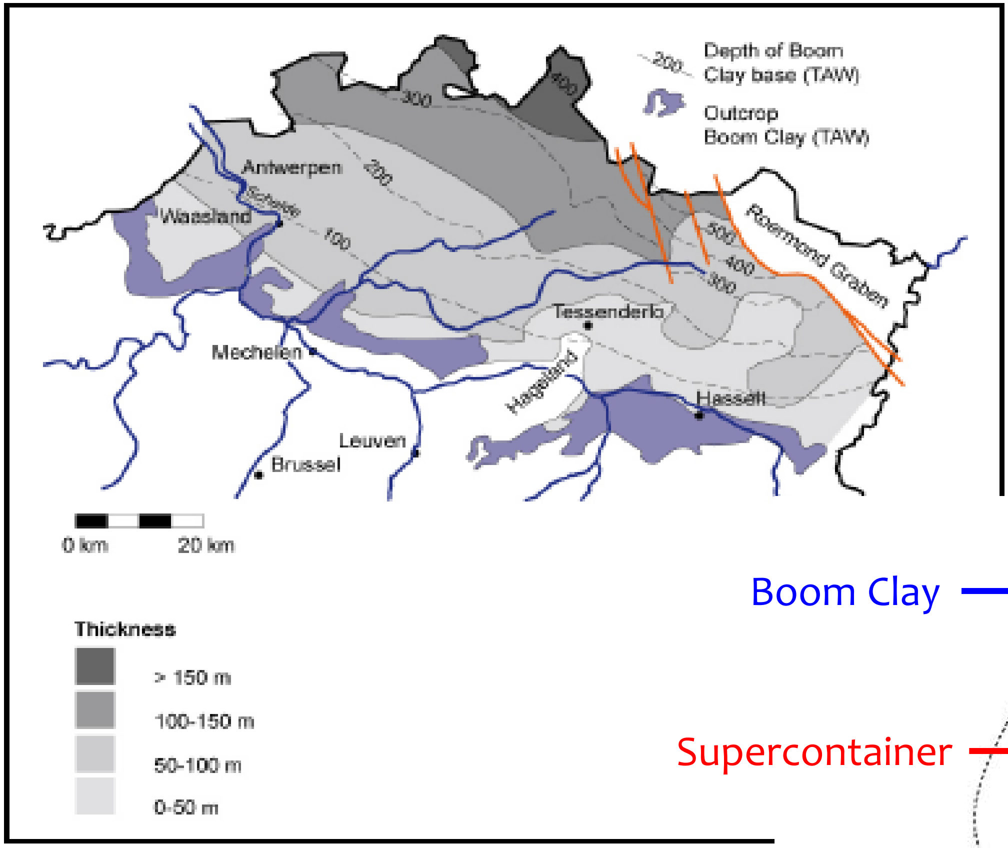
Clay mineral plug

Concrete plug

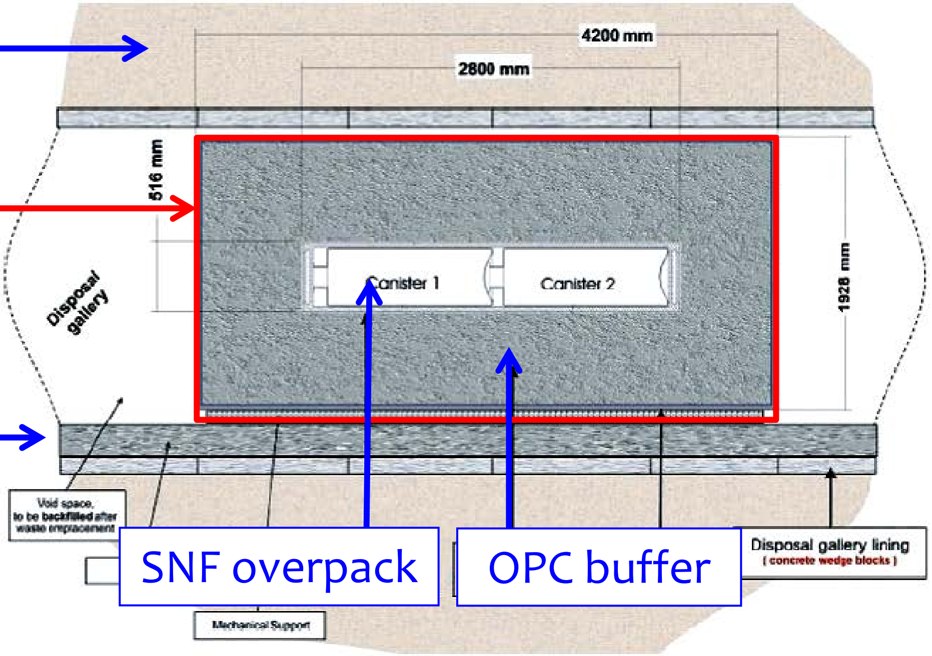
Concrete access gallery

Sources: ANDRA 269 VA (Dec 2006): Dossier 2005 Argile, Phenomenological evolution of a geological repository; Tome: Architecture and management of a geological (Dezember 2005); Haverkate et al. (2006) Review of the Horizontal Emplacement Technique concerning Retrievability Disposal Cell Concept, Petten

SNF disposal in Boom Clay (Belgium, Netherlands)



- plastic clay rock
- only diffusive water transport
- *Supercontainer* concept: carbon-steel overpack with SNF within Ordinary Portland Cement (OPC) buffer



Boom Clay

Supercontainer

Concrete access gallery liner

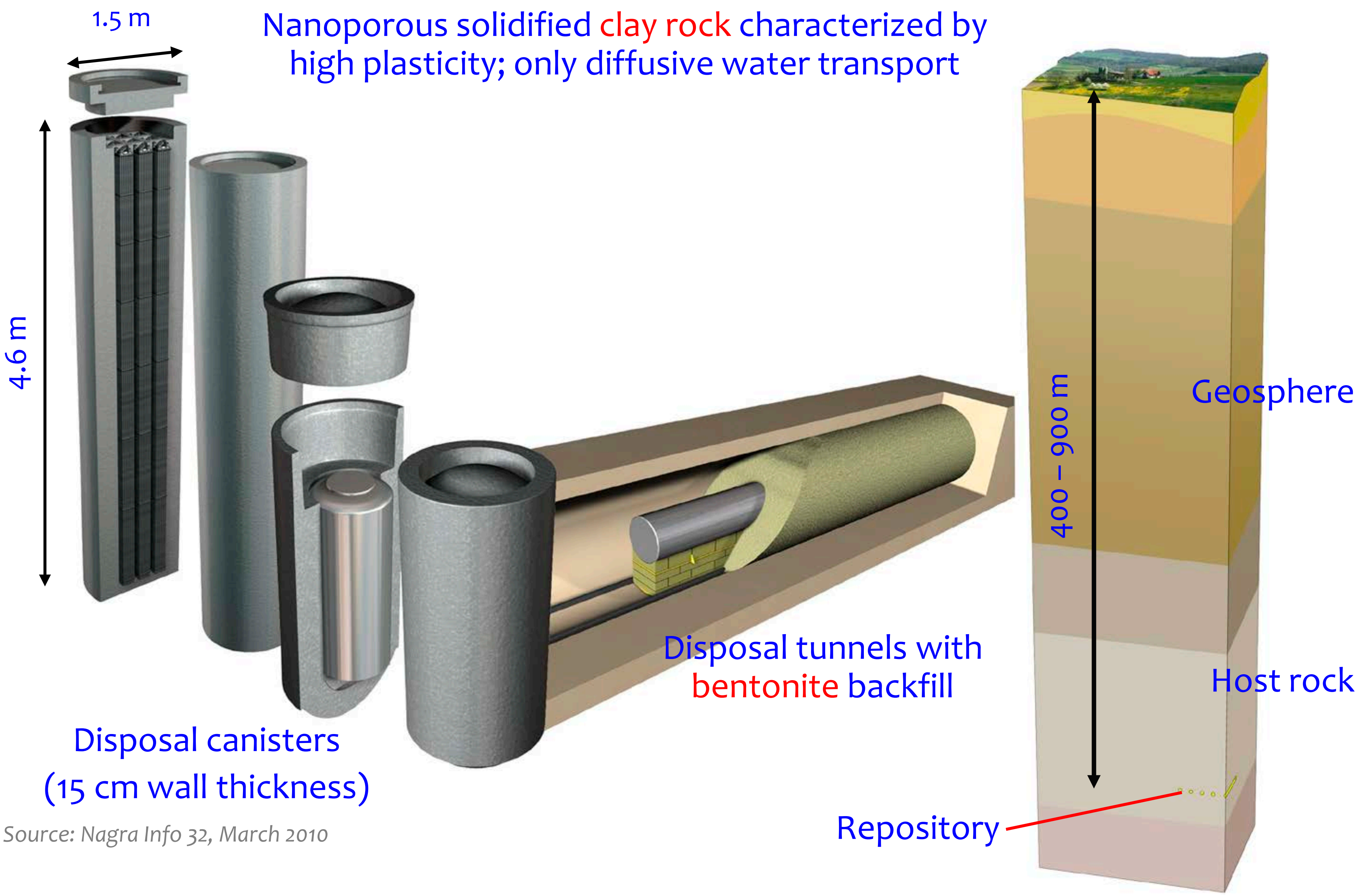
SNF overpack

OPC buffer

Source: Poyet, J. Phys. IV, France 136 (2006) 167

SNF and HLW-glass disposal in Opalinus clay (Switzerland)

Nanoporous solidified clay rock characterized by high plasticity; only diffusive water transport



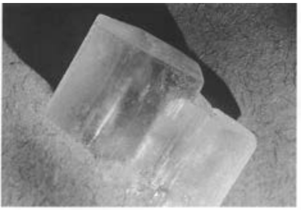
Disposal tunnels with bentonite backfill

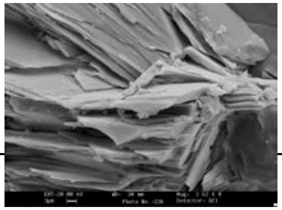
Repository

Disposal canisters
(15 cm wall thickness)

Source: Nagra Info 32, March 2010

Properties of rock types





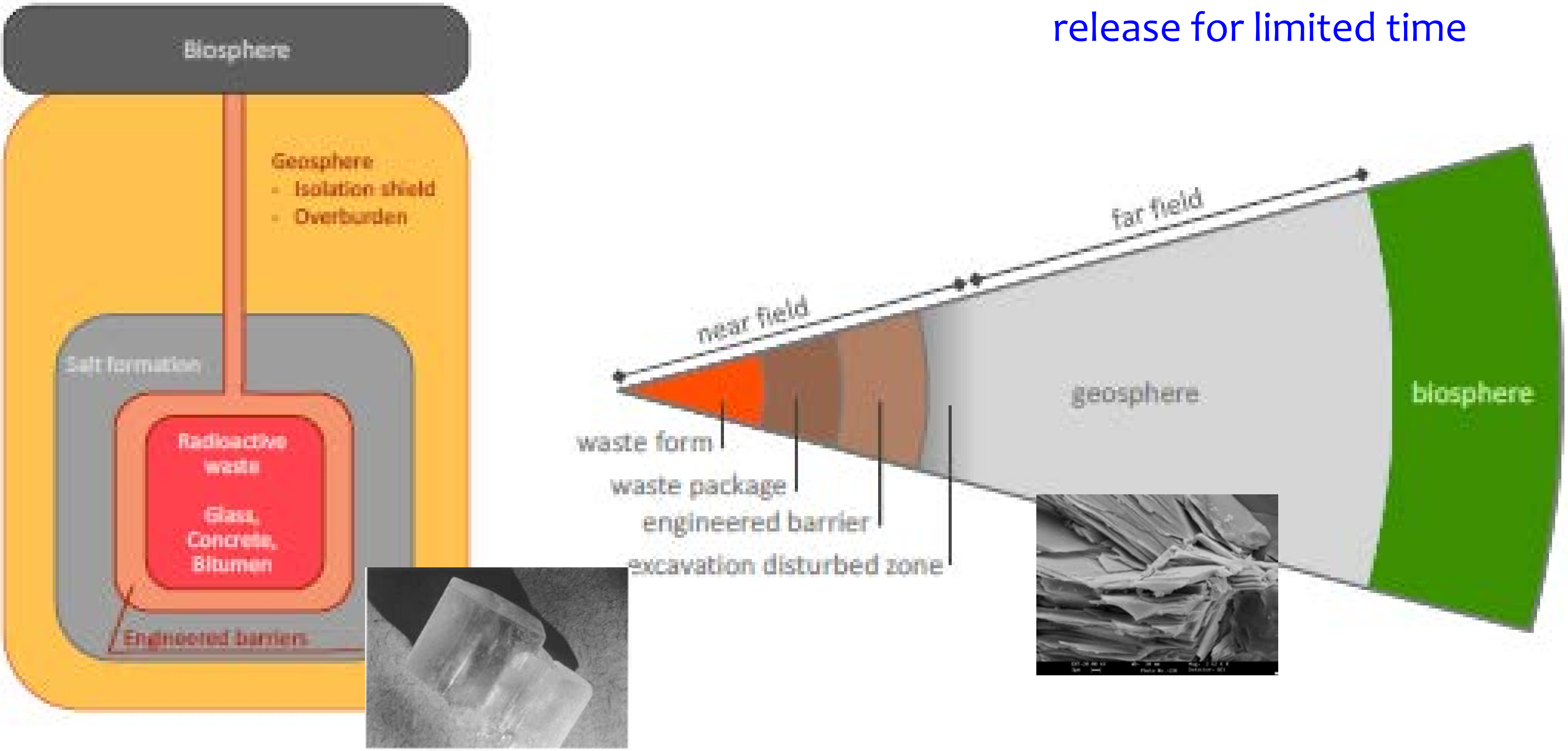
Properties	**rock salt**	**clay / clay rock**	**crystalline rock**
heat conductivity *	high	**low**	**medium**
temperature load *	high	**low**	high
permeability **	impermeable	very low	**permeable**
sorption capacity **	**very low**	very high	**medium**
solubility **	**high**	very low	very low
mechanic stability *	**medium**	**medium**	high
plastic behavior *	viscose	**plastic**	**brittle**
excavation stability *	convergence	**very low**	**low (fractured)**

Source: Table after BGR (2007) „Untersuchung und Bewertung von Regionen mit potenziell geeigneten Wirtsgesteinsformationen“ Hannover / Berlin

Primary safety functions assigned to engineered anthropogenic and natural geogenic parts of the repository system

Rock salt contains waste + canister
retains / delays release for limited time

Clay retains / delays radionuclide
release + canister retains / delays
release for limited time



source: J. Grupa, E. Rosca-Bocancea & H. Meeussen (2015) NRG contribution to D6.1 in Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term (CAST)

Long-term safety analysis as component of safety case

IAEA / OECD-NEA definitions

IAEA
International Atomic Energy Agency

AEN NEA Agence pour l'énergie nucléaire
Nuclear Energy Agency

The safety case is an integration (a synthesis) of evidences, analyses and arguments that describe, quantify and substantiate the safety, and the level of confidence in the safety, of the geological disposal facility

Safety assessment is a crucial part of the safety case. It is the process of systematically analyzing the hazards associated with the facility and the ability of the site and designs to provide the safety functions and meet technical requirements

Safety Analysis Model Chain:

- Container and waste degradation → radionuclide release (leaching, dissolution of waste)
- Near-field source term → including radionuclide retention by engineered barriers
- Transport and retardation in the geosphere
- Biosphere modelling (e.g. dilution in near-surface waters and aquifers, up-take through food chain, exposure) → Annual individual dose mSv/a

Transport processes under repository conditions (near-field)

After breaching of the container, radionuclides may be released from the waste after contact with water

⇩

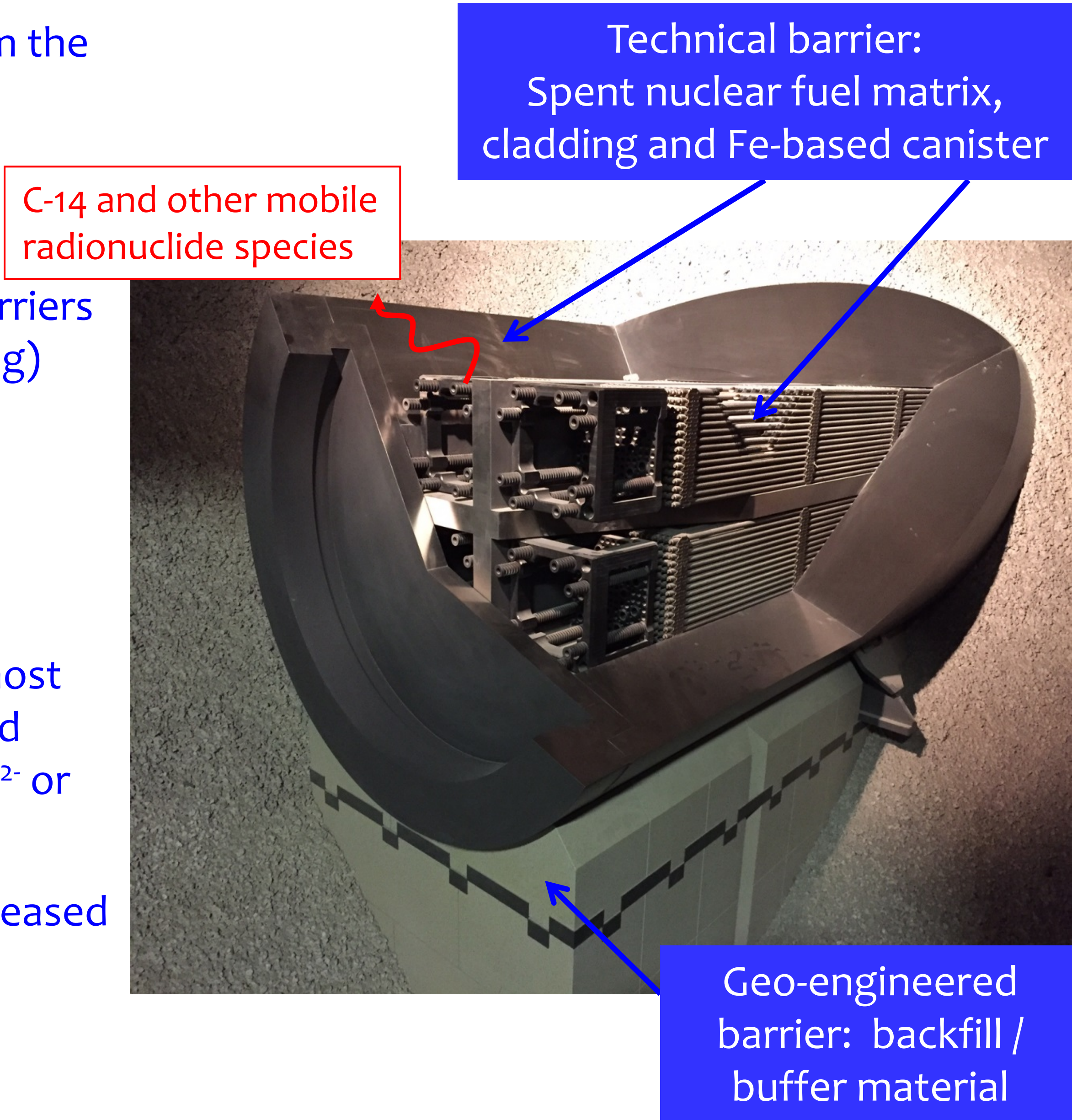
Transport and retardation of radionuclides in the engineered barriers (i.e. corroded container + backfilling)

⇩

Release into geosphere

Radionuclide transport occurs in most cases in aqueous solution (pore and ground water) e.g. dissolved $^{14}CO3^{2-}$ or $^{14}CH_3COO^-$

In some cases radionuclides are released as gases e.g. $^{14}CH4$



Technical barrier:
Spent nuclear fuel matrix,
cladding and Fe-based canister

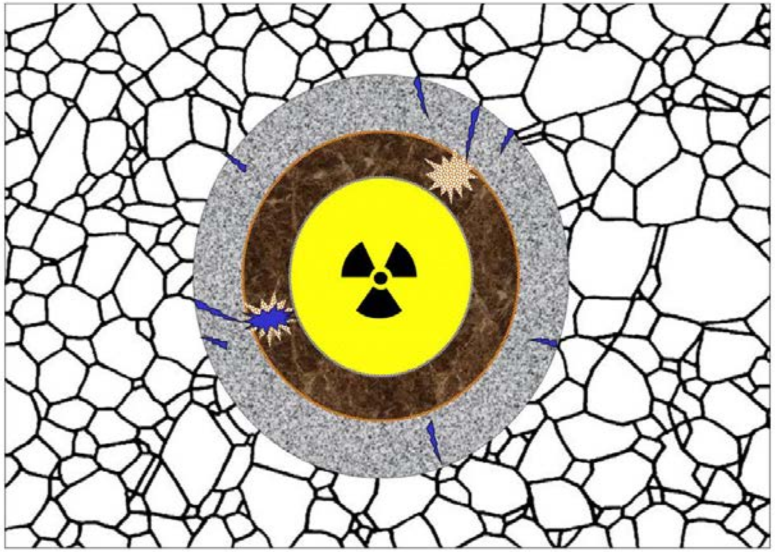
C-14 and other mobile radionuclide species

Geo-engineered barrier: backfill / buffer material

Relevance of ^{14}C in long-term safety analyses

^{14}C is relatively fast released from spent nuclear fuel (^{14}C belongs to Instant Release Fraction) as well as fast released from metallic parts of fuel assemblies

Retention of ^{14}C by container material, geoengineered depends both on chemical speciation of ^{14}C and on geochemical milieu in repository system (i.e. pH, eH, fluid composition, properties of barrier materials)



^{14}C is expected to migrate through multi-barrier system as dissolved species (e.g. $^{14}CO3^{2-}$ or $^{14}CH_3COO^-$) or as gases (e.g. $^{14}CH4$)

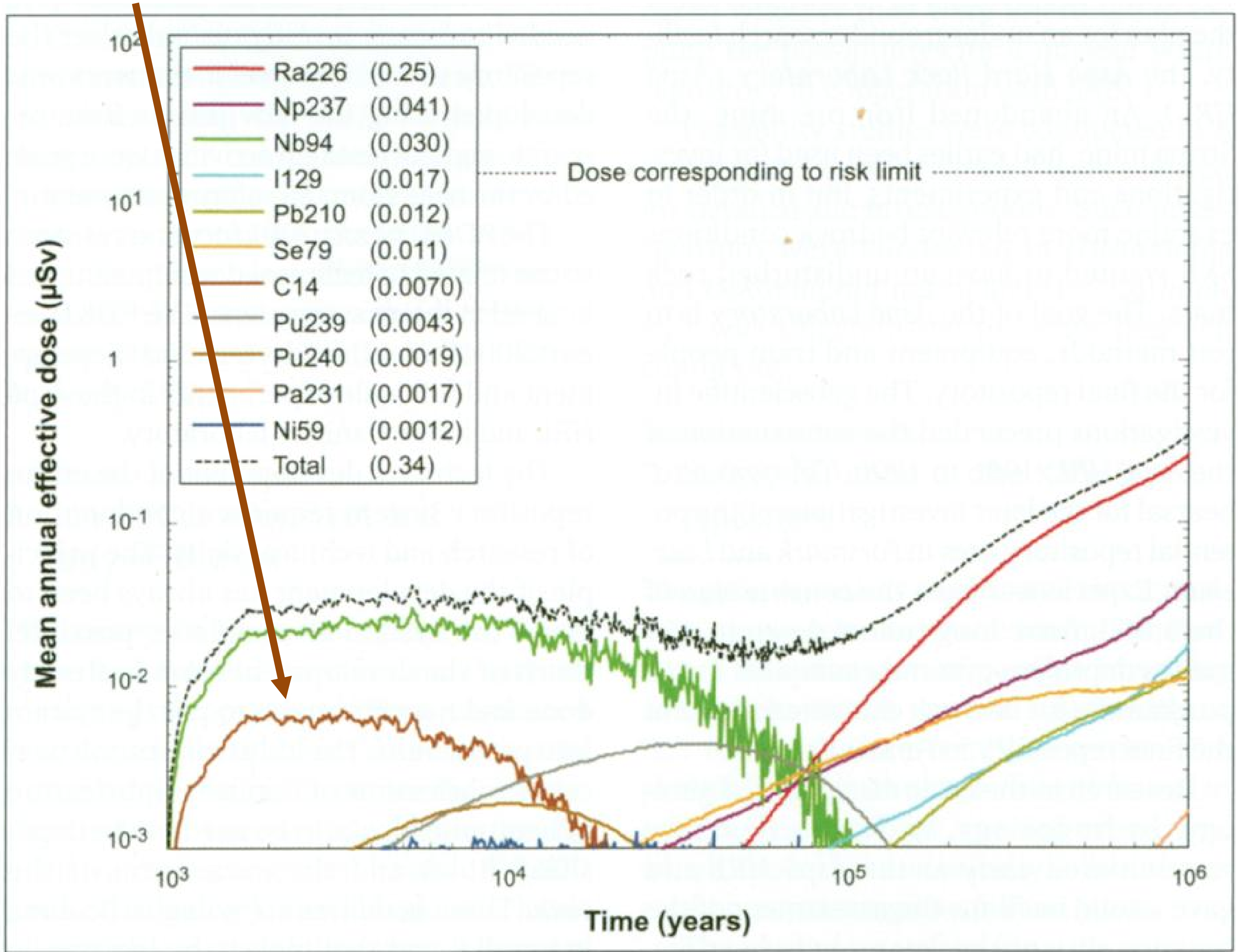
Since knowledge on chemical speciation of ^{14}C and reliable knowledge on retention mechanisms is rather **poor**, a significant ^{14}C release and negligible ^{14}C retention is assumed in most safety assessments →
^{14}C is one of the radionuclides that produces the highest releases from the near field to the geosphere, especially in the first thousands years, according to long-term safety analyses for repositories in clay / clay stone and crystalline rocks

source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of SKB (Sweden)

Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in a SNF repository in granite → calculated dose dominated by long-lived fission, activation and decay products (C-14, Cl-36, I-129, Nb-94, Pb-210, Ra-226, Se-79) and to less extent by actinides

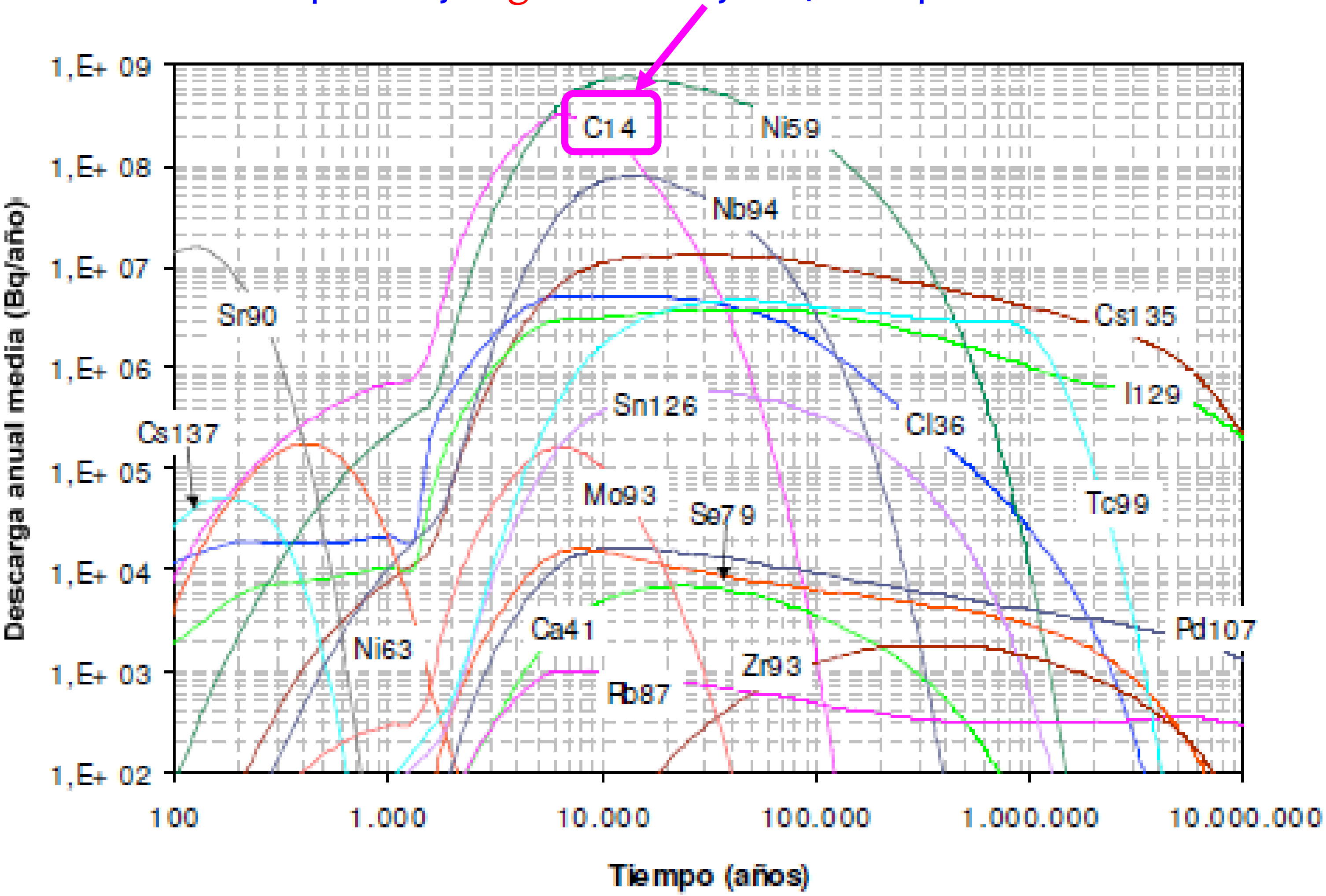
Mean annual effective dose (µSv), i.e. mean effective dose rate (µSv/year)



source: Wikberg (2012) ATW Int'l Journal Nucl Power 57, 102-105

Example: Long-term safety analysis of ENRESA (Spain)

Mean release rates from the near field in probabilistic calculations for a normal evolution scenario in a SNF repository in granite. Only C-14 transport as solute is considered.

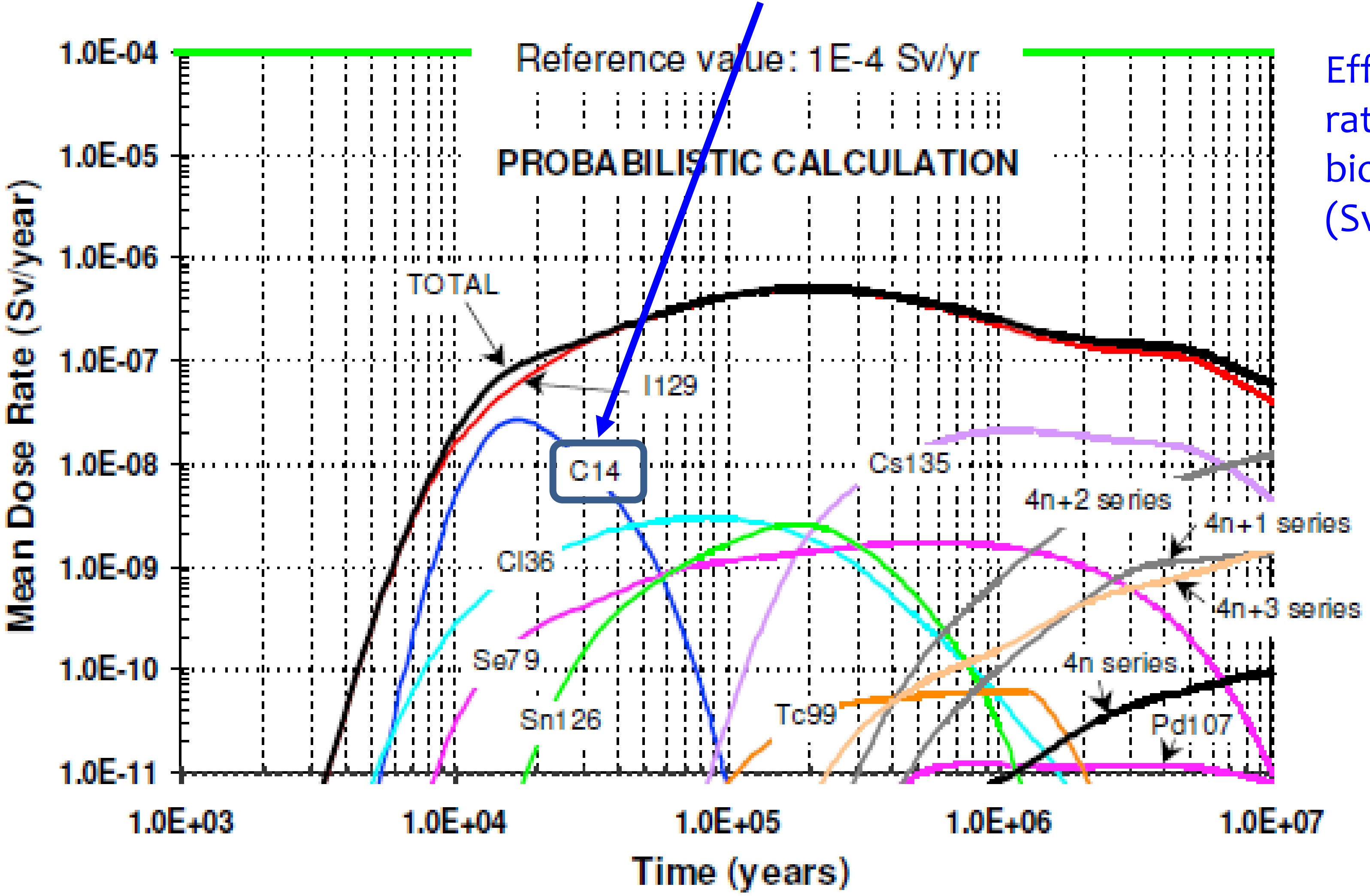


Released activity flux to biosphere (Bq/year)

source: Miguel Cuñado Peralta (2015) ENRESA contribution to D6.1. Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of ENRESA (Spain)

Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in SNF repository in clay stone. Only C-14 transport as solute is considered.

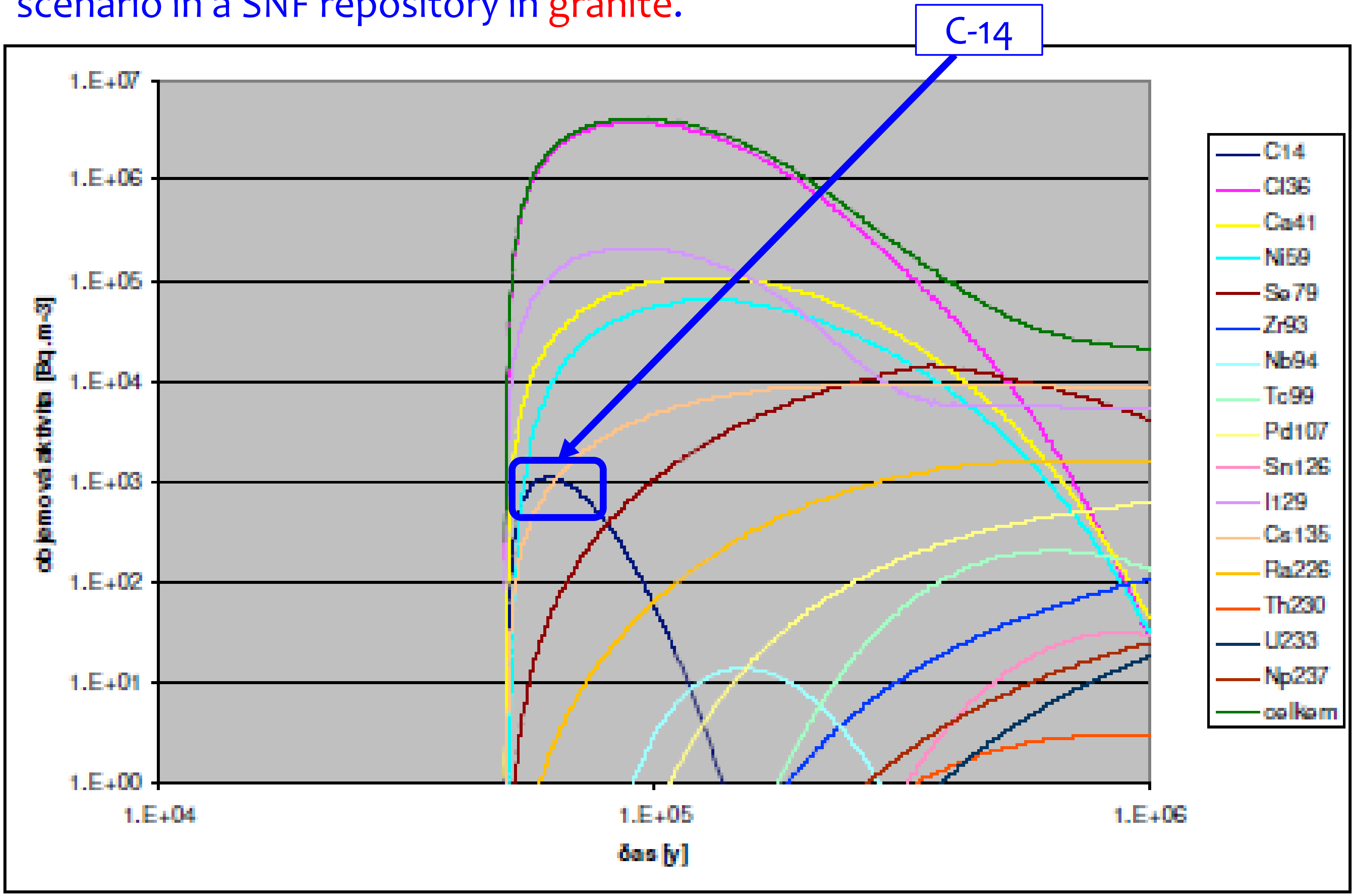


Effective dose rate in biosphere (Sv/year)

source: Miguel Cuñado Peralta (2015) ENRESA contribution to D6.1. Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of SURAO (Czech Republic)

Mean release rates from the near field in probabilistic calculations for a normal evolution scenario in a SNF repository in granite.



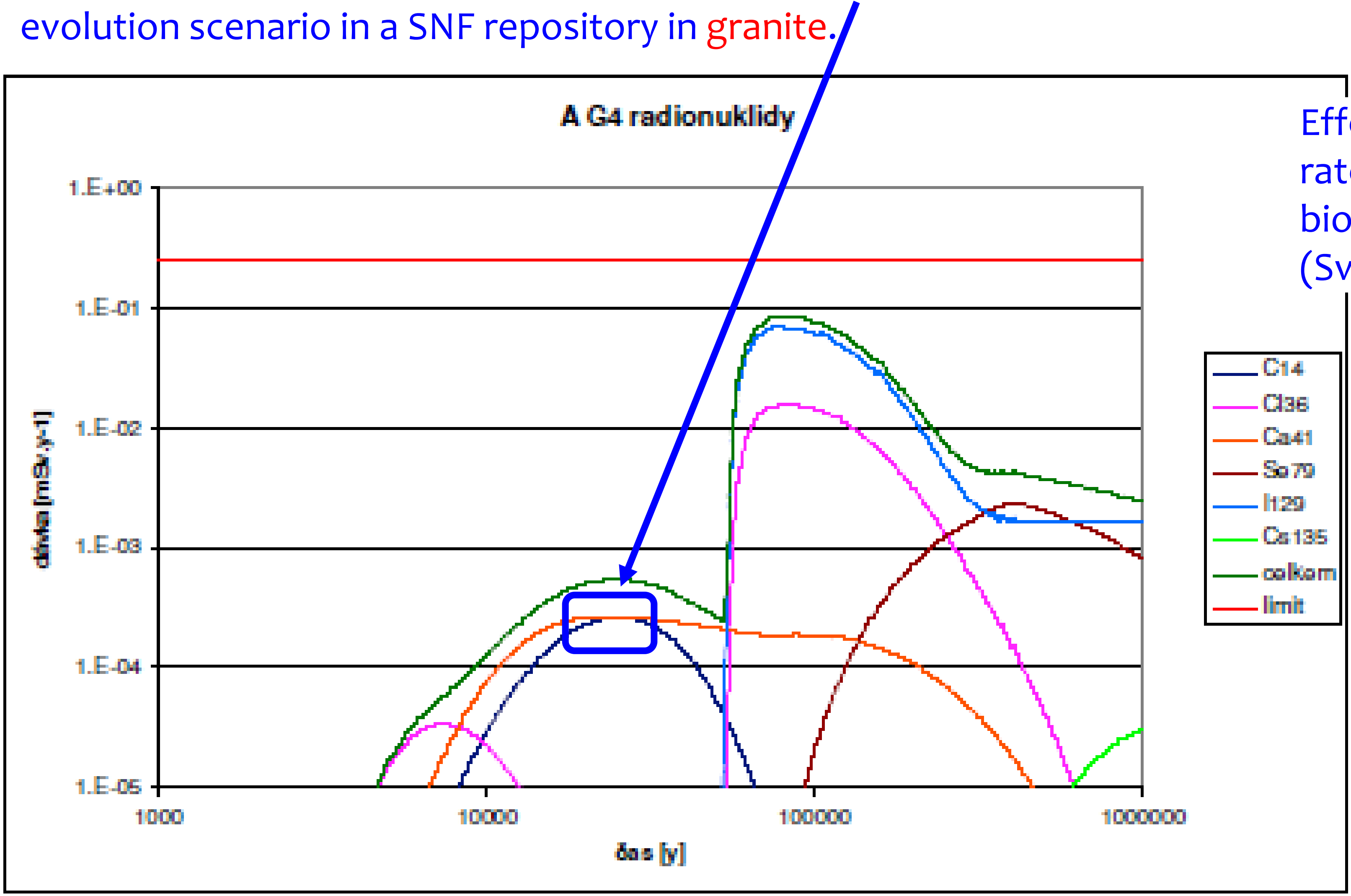
C-14

Released activity to biosphere (Bq/m^3)

source: Antonín Vokál (2015) SURAO contribution to D6.1. in Kendall et al., Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of SURAO (Czech Republic)

Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in a SNF repository in granite.

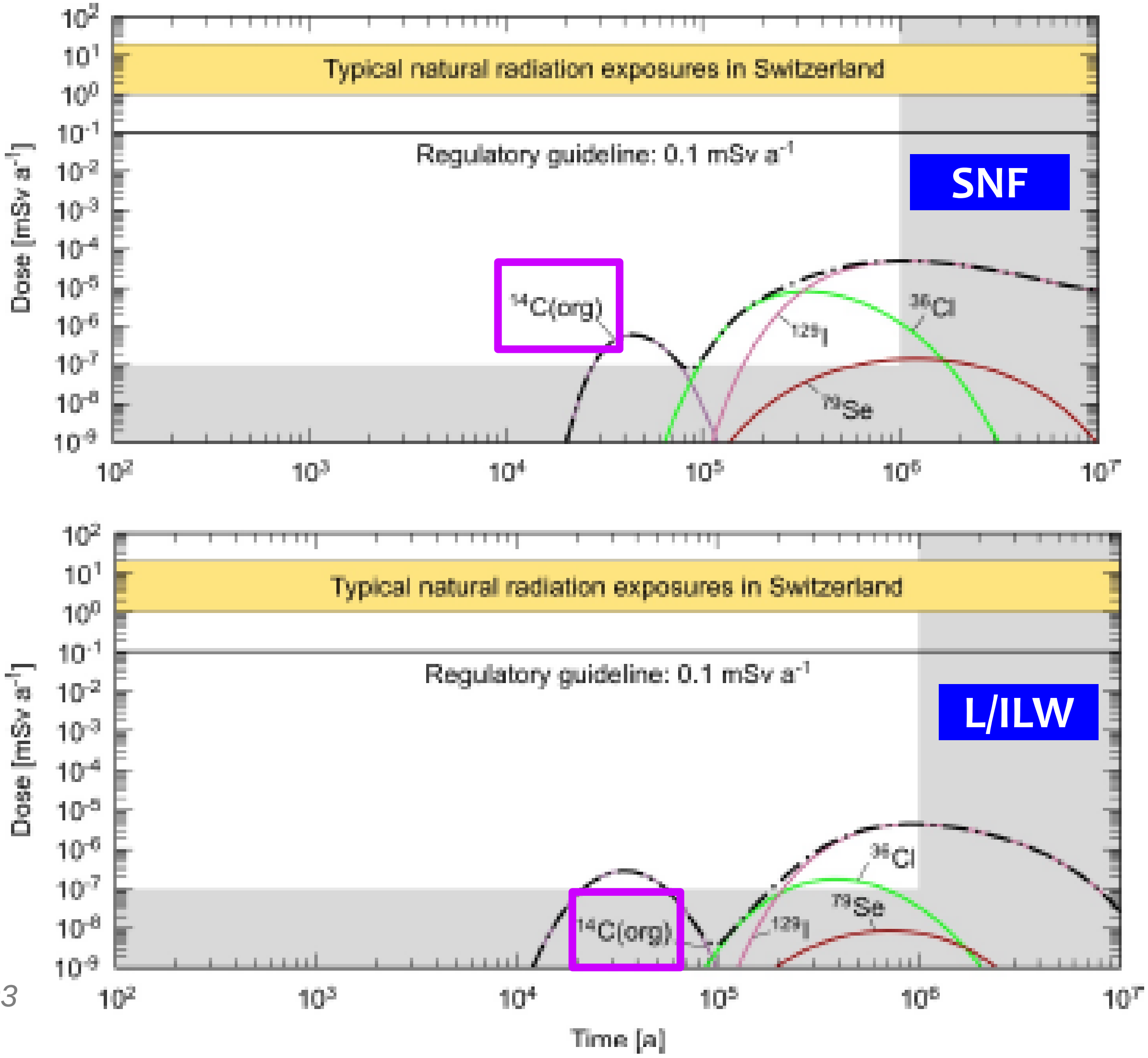


Effective dose rate in biosphere (Sv/year)

source: Antonín Vokál (2015) SURAO contribution to D6.1. in Kendall et al., Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Example: Long-term safety analysis of NAGRA (Switzerland)

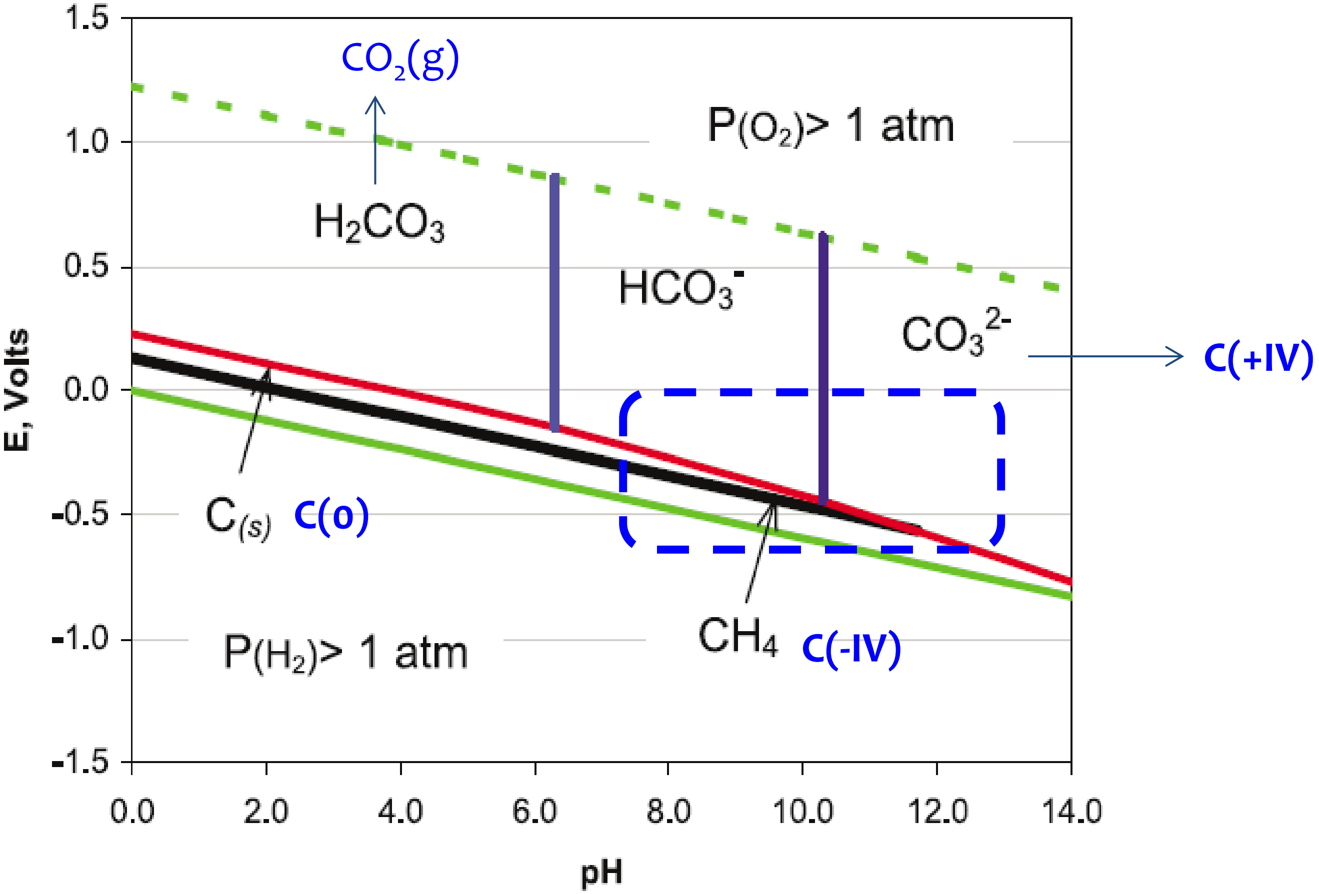
Estimate of effective doses with contribution of C-14 in probabilistic calculations for a normal evolution scenario in a spent nuclear fuel (SNF) repository and low-/intermediate level waste (L/ILW) repository in clay stone.



Effective dose rate in biosphere (Sv/year)

source: Johnson et al. (2004) NAGRA NTB 04-03

Simplified thermodynamic stability fields of ^{14}C compounds at 25°C



$^{14}CO_3^{2-}$, $H^{14}CO_3^-$, $^{14}CH_4$, $^{14}CO_2$

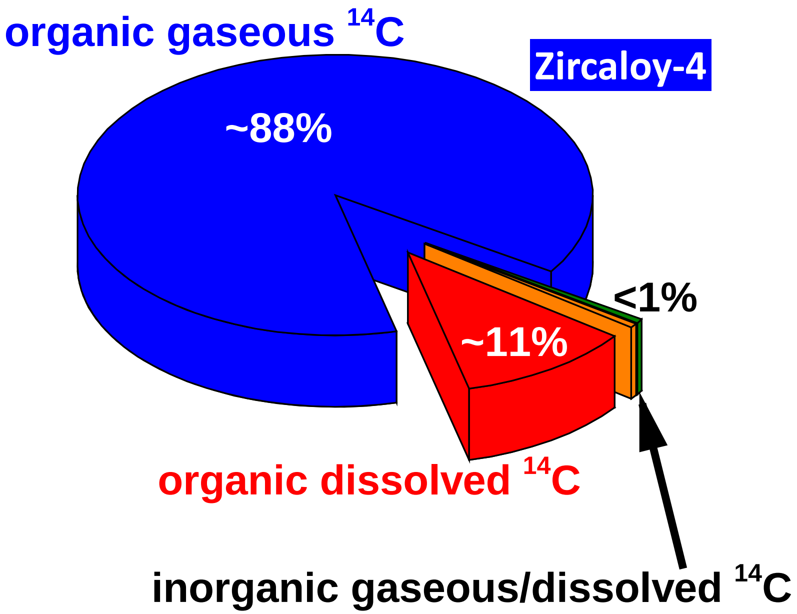
however other organics species are not included (mixed oxidation states)

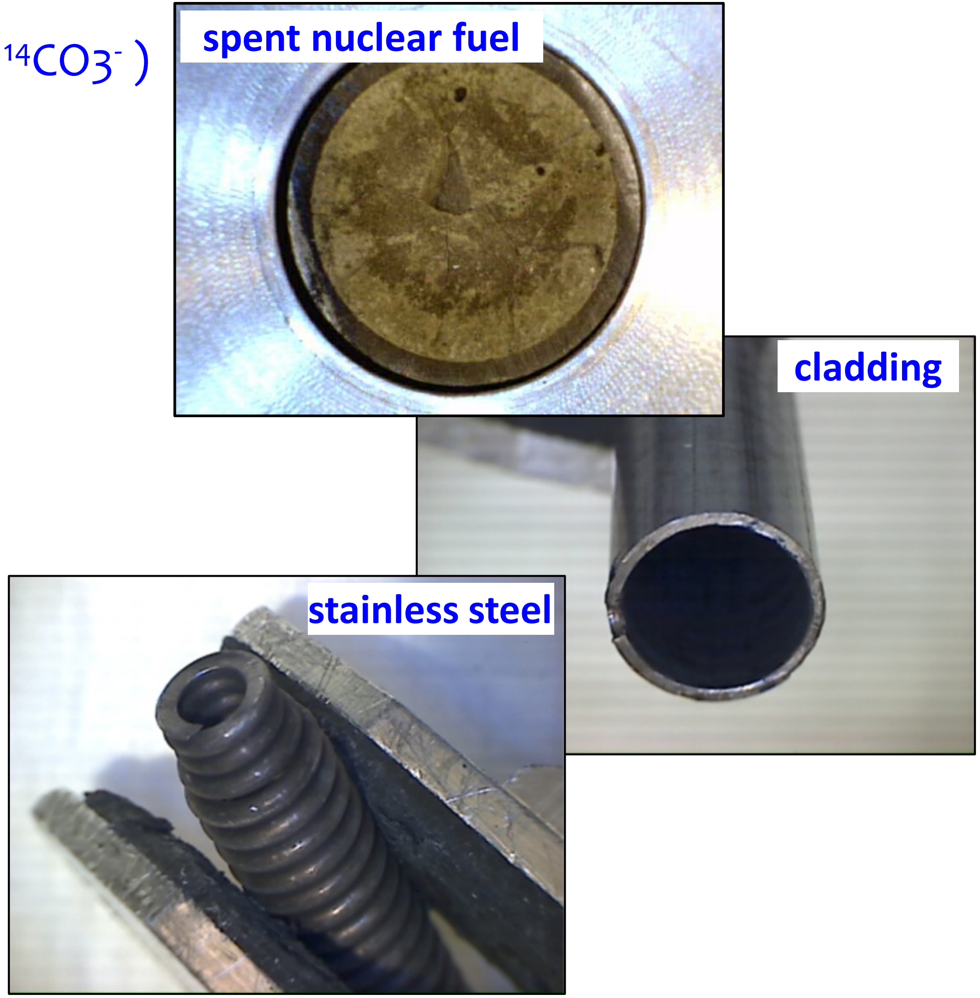
Chemical speciation of released C-14

Under repository conditions, ^{14}C is released from spent nuclear fuel, cladding (Zircaloy) and other metallic parts of fuel assemblies as

- organic solutes (e.g. methanol, ethanol, formaldehyde, acetaldehyde, formate, acetate)
- aqueous inorganic species (e.g. $^{14}CO_3^{2-}$, $H^{14}CO_3^{-}$)
- organic gases (e.g. $^{14}CH_4$)
- inorganic gases (e.g. $^{14}CO_2$)

→ defining the ^{14}C source term





Transport / retardation processes under repository conditions

After breaching of the container, radionuclides may be released from the waste after contact with water

Transport and retardation of radionuclides in the engineered barriers

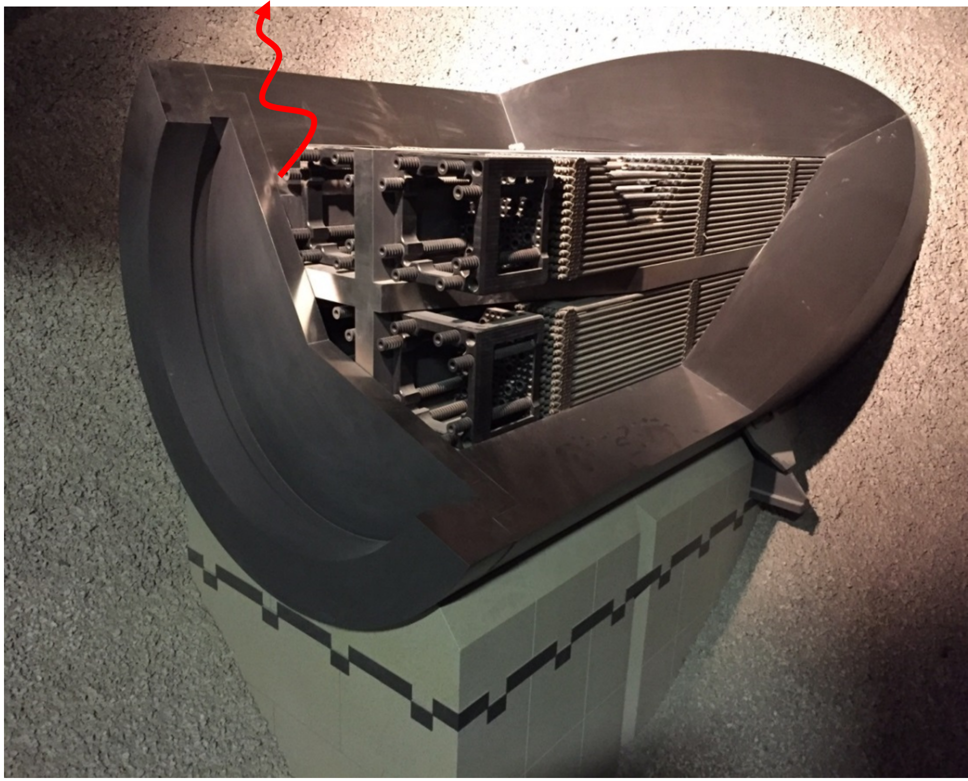
= chemical interactions with ground-water / porewater (e.g. $Ca^{2+} + {}^{14}CO_3^{2-} \rightarrow$ precipitation of calcite) ruled by solubility phenomena

and biotransformation of organic species into $^{14}CH_4$, $^{14}CO_2$

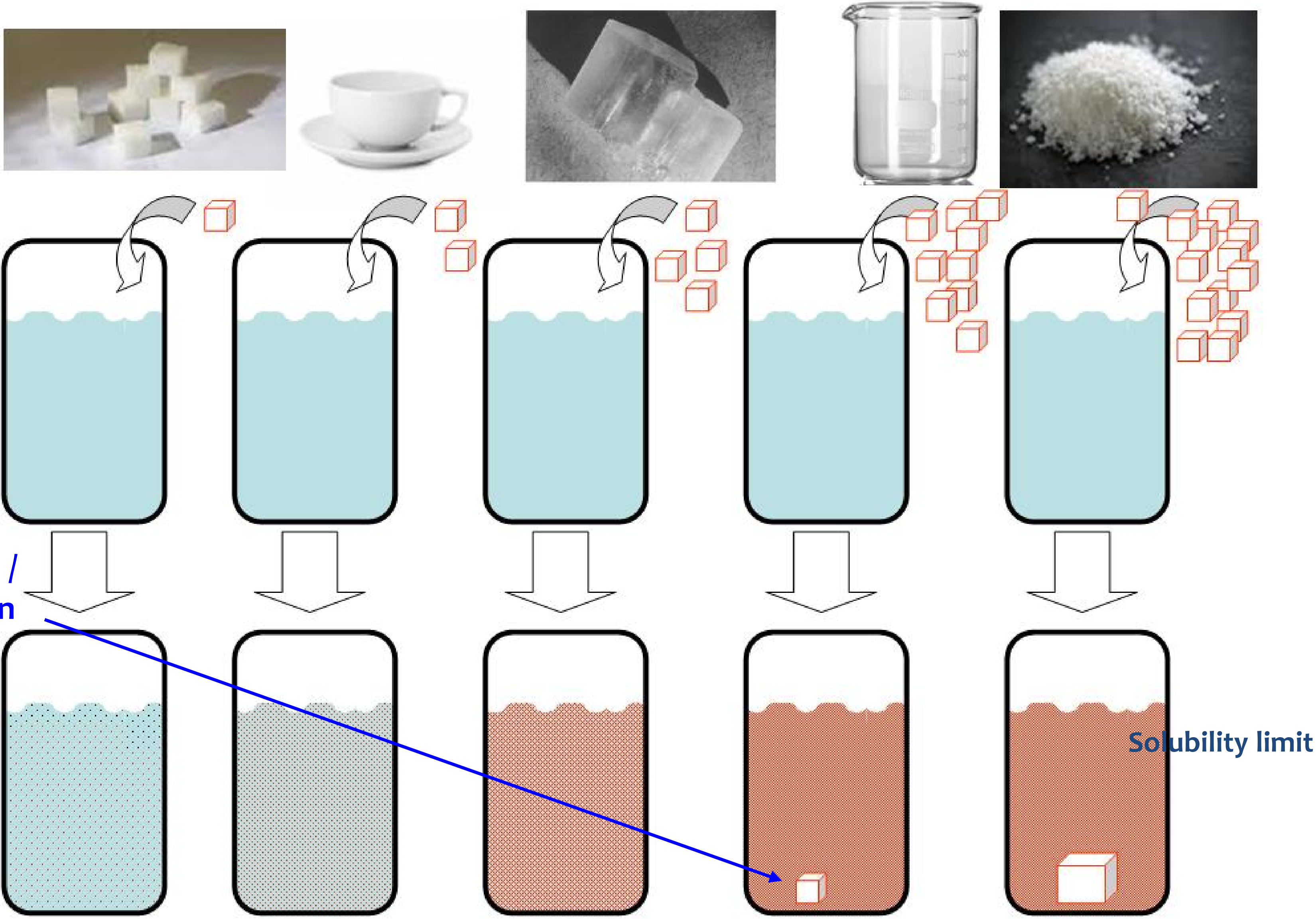
and chemical interactions with solid phases (corroded metal, bentonite, concrete, host rock)

- isotopic dilution,e.g. $Ca^{12}CO_3 \rightarrow Ca^{14}CO_3$
- sorption, surface precipitation, solid solution formation, incorporation

C-14 and other mobile radionuclide species



Basic concept for concentration limitation due to solubility phenomena



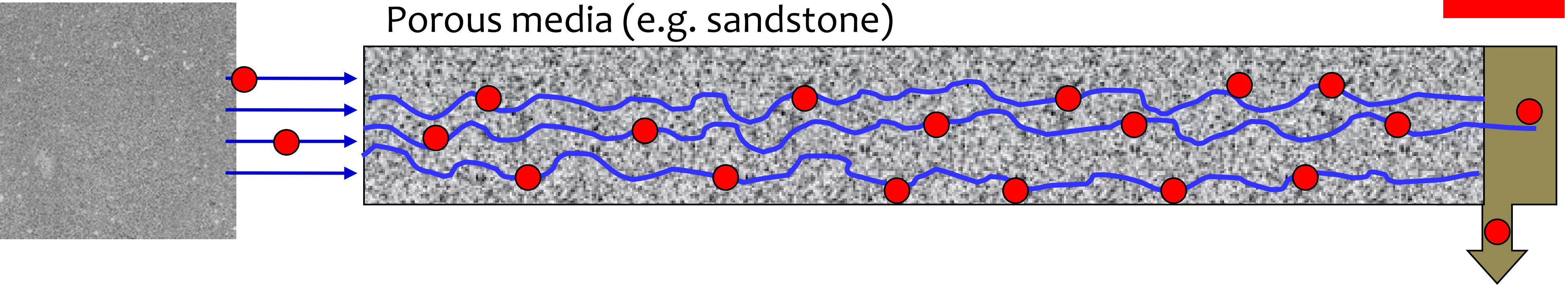
Precipitation / crystallisation

Solubility limit

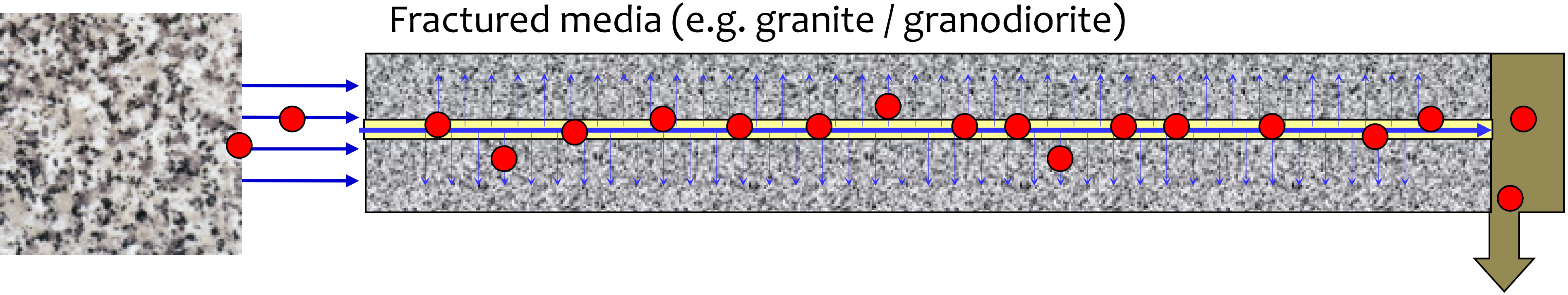
Basic concept for migration and retention in geo-engineered / geological barriers

^{14}C

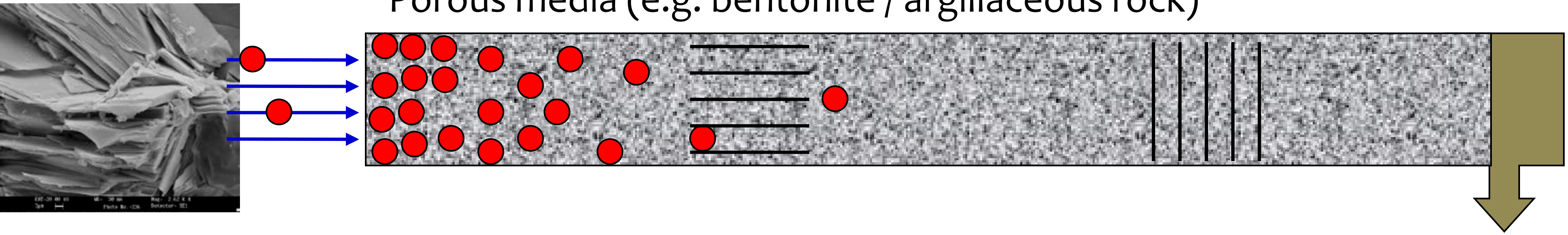
Porous media (e.g. sandstone)



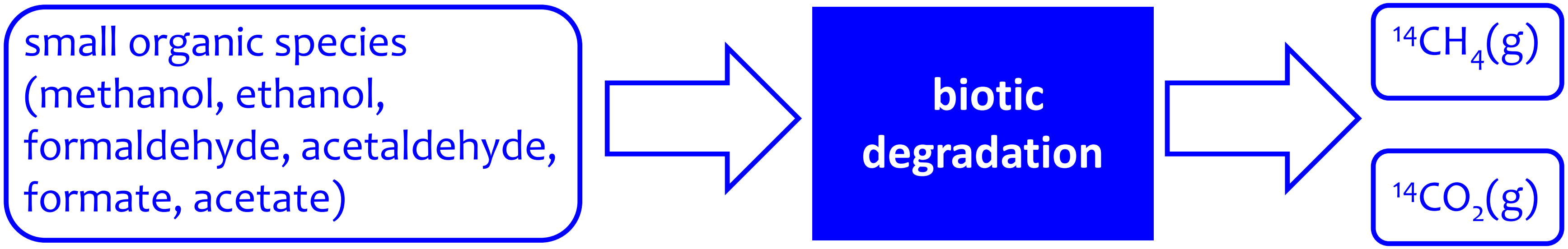
Fractured media (e.g. granite / granodiorite)



Porous media (e.g. bentonite / argillaceous rock)



biotic degradation of organic ^{14}C compounds into $^{14}CH_4$ and $^{14}CO_2$



small organic species (methanol, ethanol, formaldehyde, acetaldehyde, formate, acetate)

biotic degradation

$^{14}CH_4(g)$

$^{14}CO_2(g)$

$^{14}CO3^{2-}$, $H^{14}CO3^{-}$ (aq)

$^{14}CH_4(g)$

$^{14}CO_2(g)$

aqueous inorganic species partly retained; small organic species sorbed to some extent

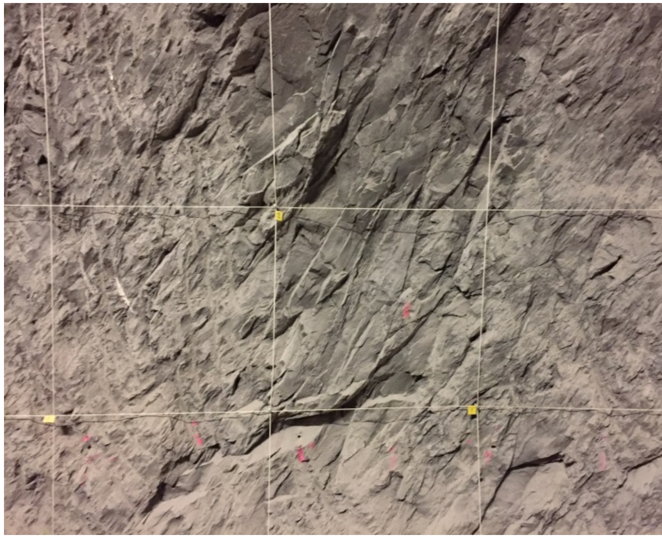
$^{14}CH_4(g)$ is highly mobile (hardly any retention in multi-barrier system); $^{14}CO_2(g)$ retained to some extent under alkaline conditions

- aerobe respiration $CH_2O + O_2 = CO_2 + H_2O$
- denitrification $CH_2O + 4/5\ H^+ + 4/5\ NO_3^- = CO_2 + 2/5\ N_2 + 7/5\ H_2O$
- Fe^{3+} reduction $CH_2O + 8\ H^+ + 4\ Fe(OH)_3 = CO_2 + 4\ Fe^{2+} + 11\ H_2O$
- SO_4^{2-} reduction $CH_2O + {}^1/_2\ H^+ + {}^1/_2\ SO_4^{2-} = CO_2 + {}^1/_2\ HS^- + H_2O$
- methanogenesis $C_6H_{10}O_5 + H_2O = 3\ CO_2 + 3\ CH_4$

^{14}C behaviour under repository conditions – application to long-term safety analyses for SNF / HLW repositories in clay / claystone (BE, CH, NL)

Conservative approaches to simulate ^{14}C behaviour:

- ^{14}C released from SNF is assumed to be in organic form; transport in Opalinus Clay and Boom Clay is dominated by diffusion, whereas advective flow and gas transport are considered negligible
- no sorption is considered for organic forms of ^{14}C (NAGRA)
- ^{14}C is assumed to be not retarded at all (ONDRAF-NIRAS)
- Still, since diffusion rate is very slow and migration path from deep underground repository to biosphere is rather long, virtually all ^{14}C will decay in Boom Clay host rock (NRG)

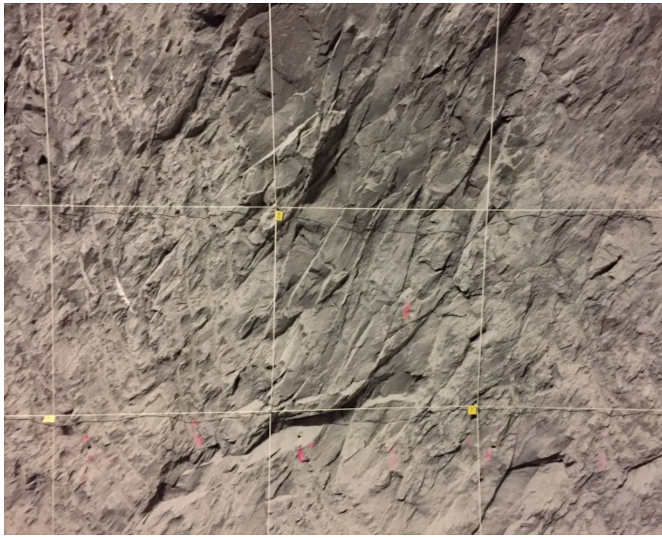


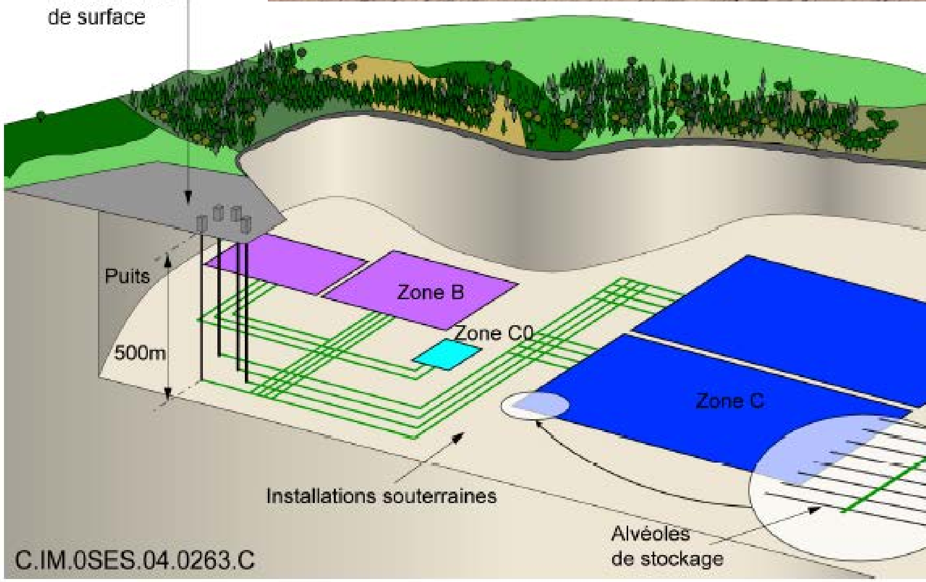
source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

^{14}C behaviour under repository conditions – application to long-term safety analyses for HLW repository in clay stone (FR)

Conservative approach to simulate ^{14}C behaviour:
Migration of complete ^{14}C inventory as gas without any retention; conservative approach chosen by ANDRA due to lack of knowledge on chemical ^{14}C behaviour under repository conditions

Alternative approach to simulate ^{14}C behaviour (ANDRA):
Taking into account migration of complete ^{14}C inventory as dissolved inorganic species; considering migration by diffusion, advection and dispersion and sorption of inorganic ^{14}C species in bentonite, concrete and claystone





source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

14C behaviour under repository conditions – application to long-term safety analyses in crystalline rock (SF, CZ)

Diffusion through bentonite backfilling and advective transport of dissolved species in crystalline bedrock considered

14C speciation may change due to reactions either inside the repository or while migrating along the bedrock fractures

Due to related uncertainties, 14C is conservatively assumed to be released in organic gaseous form in alternative scenario (FORTUM)

Diffusion coefficients for bentonite as well as sorption coefficients for bentonite and granite are estimated (SURAO)

source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Complete isolation in "normal evolution scenarios" of long-term safety analyses for repositories in rock salt (DE, NL)

"In the case of disposal in rock salt, the waste is completely enclosed by several hundred meters of dry rock salt. Consequently, ***all C-14 will decay in the facility****. The displacement of air from the mine (potentially including C-14), caused by the convergence of the rock salt has not yet been taken into account."* (NRG)

"Crushed salt backfill is expected to be compacted over time by convergence of the host rock to achieve a sufficiently high hydraulic resistance to avoid inflow of brines into the repository. Plugs and seals ***must*** *provide their sealing function during the early post closure phase, until the compaction of the backfill is adequate and the permeability of the backfill is sufficient low. (…) According to the regulations, the waste containers (…)* ***must*** *be designed to avoid the release of radioactive aerosols for a period of 500 years.* ***No dissolved radionuclides are released from the isolating rock zone*** *during the whole reference period."* (GRS)

Different results for less probable scenarios: water access due to failure of shaft sealing etc.

source:
Kendall et al. (2015) Handling of C-14 in current safety assessments: State of the art. CArbon-14 Source Term. CAST-2015-D6.1

Summary

- ^{14}C is relatively fast released from spent nuclear fuel as well as fast released from metallic parts of fuel assemblies

- Retention of ^{14}C by container material, geo-engineered barriers and geological barriers depends both on chemical speciation of ^{14}C and on geochemical milieu in repository system

- ^{14}C is expected to migrate through multi-barrier system as dissolved species or as gases

- Since knowledge on chemical speciation of ^{14}C and reliable knowledge on retention mechanisms is rather poor, a significant ^{14}C release and negligible ^{14}C retention is assumed in safety assessments for repositories in clay / clay stone and crystalline rock → ^{14}C is one of the radionuclides that produces the highest releases

- With respect to "normal evolution scenarios", no 14C release is expected from the near-field of a SNF / HLW repository in rock salt