Nuclear waste disposal in France : 35 years of corrosion studies

M. Helie

DE LA RECHERCHE À L'INDUSTRIE

NUCLEAR WASTE DISPOSAL IN FRANCE

—

35 YEARS OF CORROSION STUDIES

M. HÉLIE

TYPES OF WASTE TO BE DISPOSED OF

- They are mainly of two types, Intermediate Level Waste and High Level Waste, both containing long-lived radionuclides

Spent Fuel Reprocessing

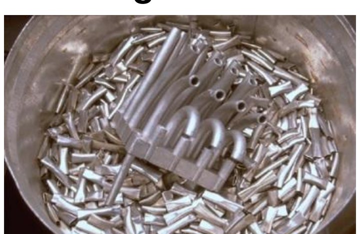
Fuel Cladding sections and end-fittings

Spent Fuel

ILW container (Compacted Waste)

HLW container (Vitrified Waste)

Fuel Cladding sections and end-fittings before compacting



Sample of Vitrified Waste

SCHEMATIC OF THE STUDIES

- ❑ **Pre select candidate materials for containers overpacks**

- ❑ **Carry preliminary corrosion studies in conditions representative of storage and disposal**

- ❑ **Select a candidate material from the results**

- ❑ **Carry advanced corrosion studies in parallel with disposal concept evolution**

1980 – 1985 : EXPLORING CONCEPTS AND MATERIALS

❑ Candidate Overpack Materials and Concepts

Two overpack concepts were considered :

- **"Corrosion resistant" overpack (nickel base or titanium alloy), whose behavior could be controlled by the conditions imposed by the buffering material**

- **"Corrosion allowance" overpack (mild steel) possibly in direct contact with the host formation**

With a prior emphasis on the corrosion resistant concept

1980 – 1985 : CANDIDATE AQUEOUS ENVIRONMENTS

- **Studies mainly performed in the framework of European Communities Commission programs**

Tests carried out in various environments representative of Belgian, British, German, and French candidate host formations such as :

- **Argillaceous (1.4 $g.L^{-1}$ $NaHCO_3$ + minor elements)**
- **Granitic (3 $g.L^{-1}$ NaCl + minor elements)**
- **Salt dome (250 $g.L^{-1}$ $MgCl_2$ + minor elements)**

1980 – 1985 : CORROSION RESISTANT CONCEPT

- For "corrosion resistant" alloys, general corrosion can be considered as very low (< 0.1 µm.y^{-1})

The tests carried out addressed the following forms of localized corrosion :

- **Pitting Corrosion**
- **Crevice Corrosion**
- **Stress Corrosion Cracking (SCC)**
- **Hydrogen Embrittlement**

1980 – 1985 : CREVICE AND PITTING CORROSION

- Tests carried out on alloys 625, C 276, C 4, and Ti-0.2%Pd at 90°C

Pitting corrosion in granitic solutions :
Ti-0.2%Pd > C 276 and C 4 > 625

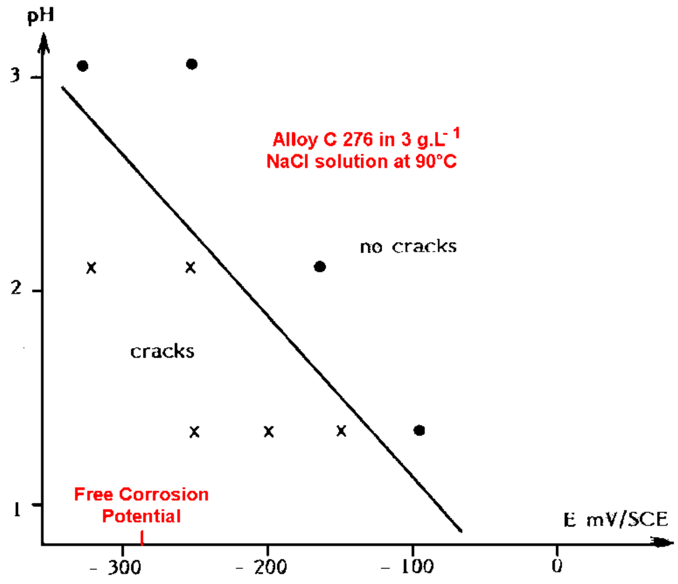
Crevice corrosion in granitic solutions :
Ti-0.2%Pd > C 276 and C 4 > 625

Pitting and crevice corrosion possible on all "corrosion resistant" alloys

Ti-0.2%Pd alloy has a much better resistance than nickel base alloys

1980 – 1985 : SCC AND HYDROGEN EMBRITTLEMENT

- Tests carried out on alloys 625, C 276, C 4, and Ti-0.2%Pd at 90 and 170°C



M. Hélie and G. Plante, MRS 1985, Stockholm

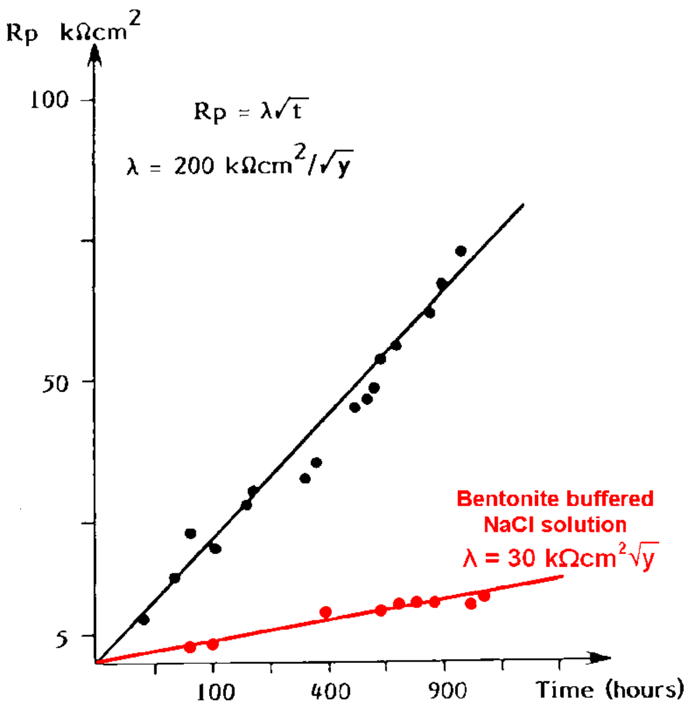
SCC likely to occur in granitic solutions on nickel base alloys provided local pH be sufficiently low (<3 as in a pit) and a sufficient stress level be applied (such as by the host rock after recovery of the geological formation)

As expected, Ti-0.2Pd alloy was prone to hydrogen embrittlement provided a high rate of atomic hydrogen production (possible with water radiolysis?)

Once again, Ti-0.2%Pd was the best candidate material for the "corrosion resistant" concept

1980 – 1985 : CORROSION ALLOWANCE CONCEPT GENERALIZED CORROSION

❑ Polarization resistance measurements on mild steel in aerated 3 g.L^{-1} NaCl solutions at 90°C



M. Hélie and G. Plante, EFC Workshop, Arnhem, 1985 and MRS 1985, Stockholm

❑ **Polarization resistances follow a parabolic law, which allows deriving the corroded thickness "e" with time**

NaCl solution $e\ (\mu m) = 5\ t^{1/2}$

Bentonite buffered $e\ (\mu m) = 0.75\ t^{1/2}$

$e_{(1000\ yr)}$ = 150 µm (or 20 mm *)

$e_{(1000\ yr)}$ = 25 µm (or 3 mm *)

* : if complete oxide scaling every month (duration of the tests)

Further studies were thus focused on the corrosion allowance concept

1991 : CHOOSING A POLICY

- **A law was voted in 1991 defining three main lines of action for Long Lived Waste management:**
  - **Transmutation of actinides in FBRs**
  - **Long term storage of HLW for a maximum period of about 300 years. CEA is in charge of the definition of the storage concept**
  - **Geological disposal of HLW (at the end of the storage period) and of ILW. ANDRA is in charge of the definition of the disposal concept**
  - **CEA performs the R&D for a thick low alloy steel or cast iron "corrosion allowance" HLW container that will suit :**
    - **The long term storage concepts developed by CEA**
    - **The disposal concept developed by ANDRA**

Scientific evaluation to be delivered by 2006

1991 – 2006 : LONG TERM STORAGE ➡ DISPOSAL

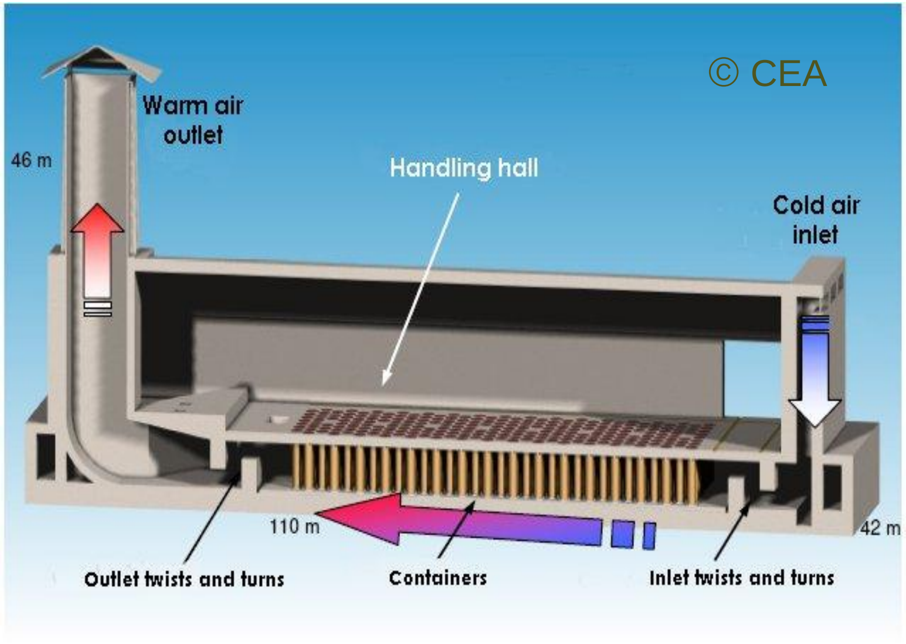
- ❑ Definition of Long Term Storage facilities
- ❑ Evolution of Disposal concept

⬇

- ❑ Assessment of the corrosion of a low alloy steel or cast iron overpack in long term storage
- ❑ Corrosion of a low alloyed steel or cast iron overpack in new disposal concepts conditions

1991 – 2006 : LONG TERM STORAGE FACILITY

- **Passive concept which relies on thermodynamics (no forced venting)**

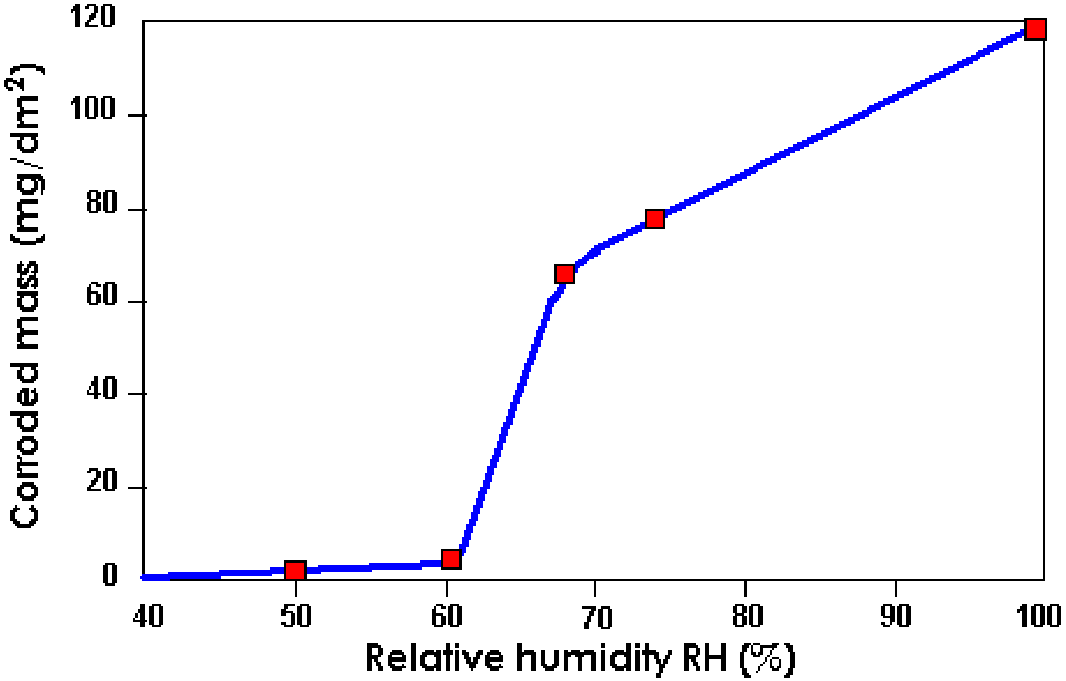


- **Associated forms of corrosion:**
  - **Dry corrosion**
  - **Atmospheric corrosion**

Depending on overpacks surface temperature

1991 – 2006 : CORROSION DURING STORAGE

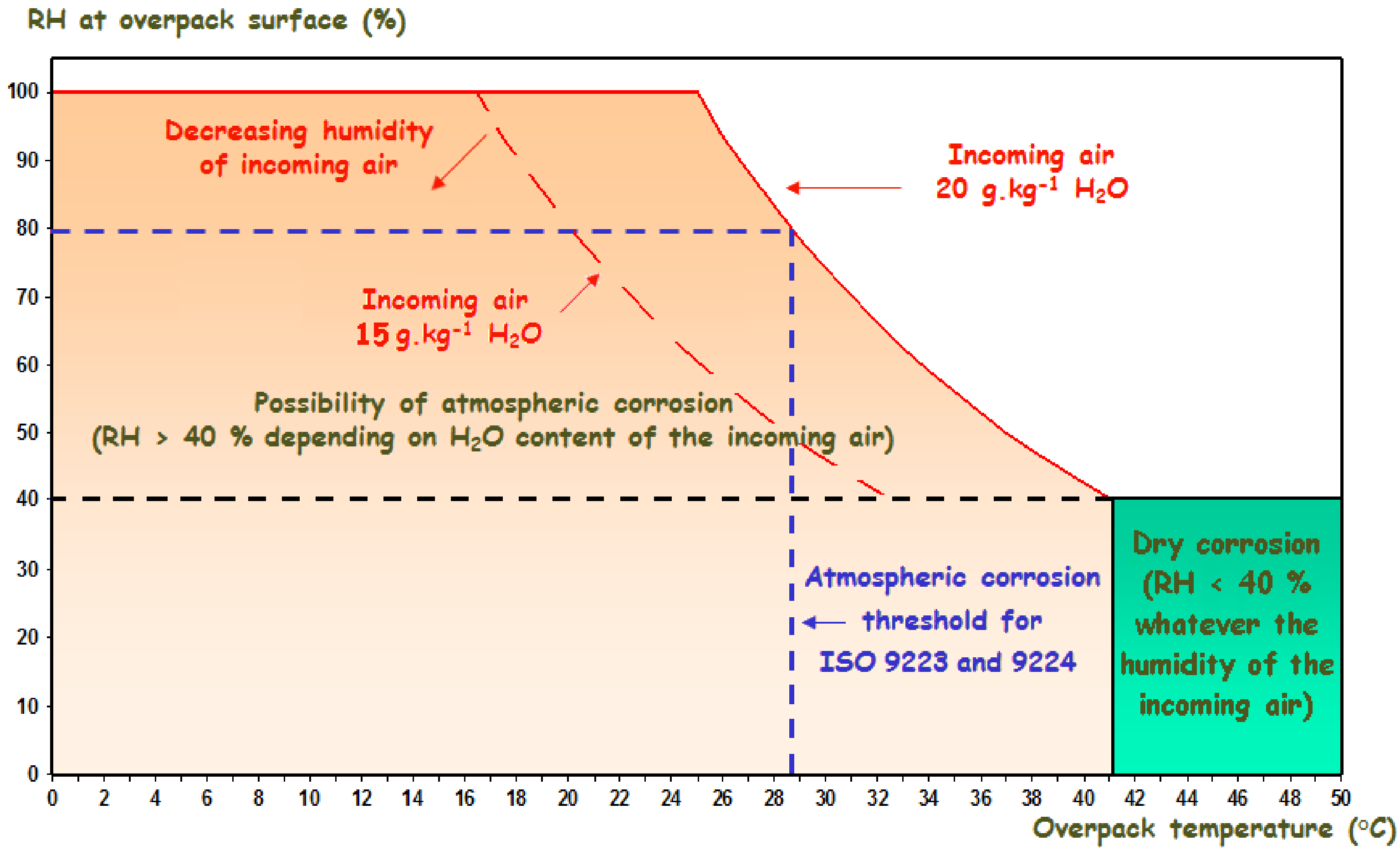
- **In a conservative approach, it was considered that atmospheric corrosion could not occur only if the relative humidity (RH) at the containers surface was lower than or equal to 40%**



Mass of corroded steel as a function of RH, 55 day tests, air with 0.01% SO_2 pollution (after W.H. Vernon)

1991 – 2006 : DRY AND ATMOSPHERIC CORROSION CONDITIONS IN STORAGE

❑ Dry and atmospheric corrosion domains



Relative humidity RH at the overpack surface vs temperature for a humidity of the incoming air between 0 and 20 g.kg^{-1} H_2O (highest humidity measured in 1996)

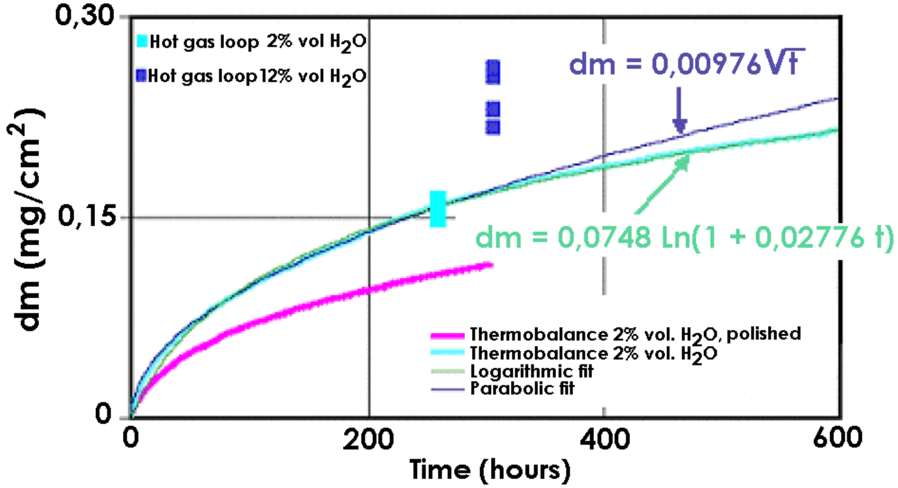
1991 – 2006 : DRY CORROSION TESTS AND MODELING

- Very little data in the literature for temperatures below 300°C

- **Modeling of short term laboratory tests**

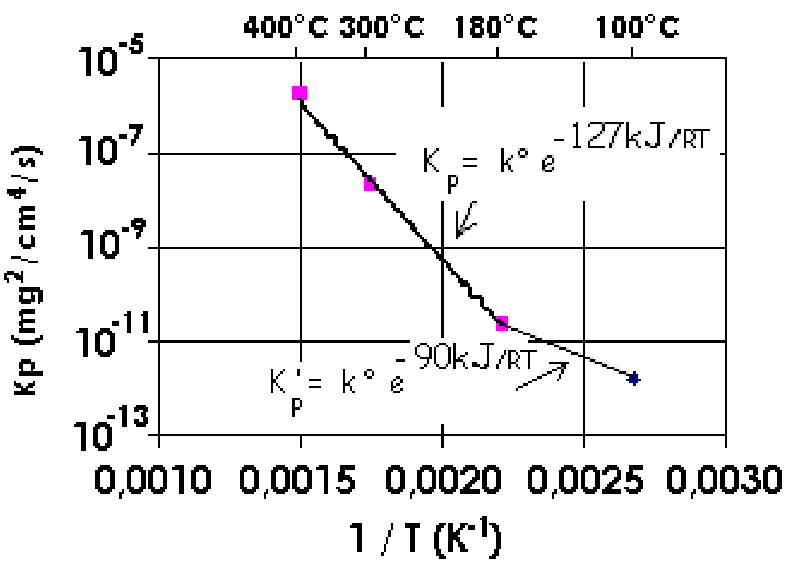
- **Comprehension of the mechanisms for a reliable extrapolation of lab test results**

1991 – 2006 : DRY CORROSION EXPERIMENTAL RESULTS



Parabolic fit more conservative

$$dm^2 = Kp\ t$$



Study of Kp as a function of temperature

$$Kp = Ko\ e^{-E/RT}$$

T > 180°C : E = 127 kJ

T < 180°C : E = 90 kJ

1991 – 2006 : DRY CORROSION : EXTRAPOLATION OF EXPERIMENTAL RESULTS

- **In a conservative approach, the parabolic fit was retained for extrapolation purposes, as well as the data obtained at 300°C**
- **The mass gain "w" corresponds to the oxygen captured to form the Fe_3O_4 oxide. With a ratio "λ" (voluminal fraction of metal in the oxide) between the mass gain "w" and the corroded thickness of metal "e", we obtain after a time "t" at temperature "T":**

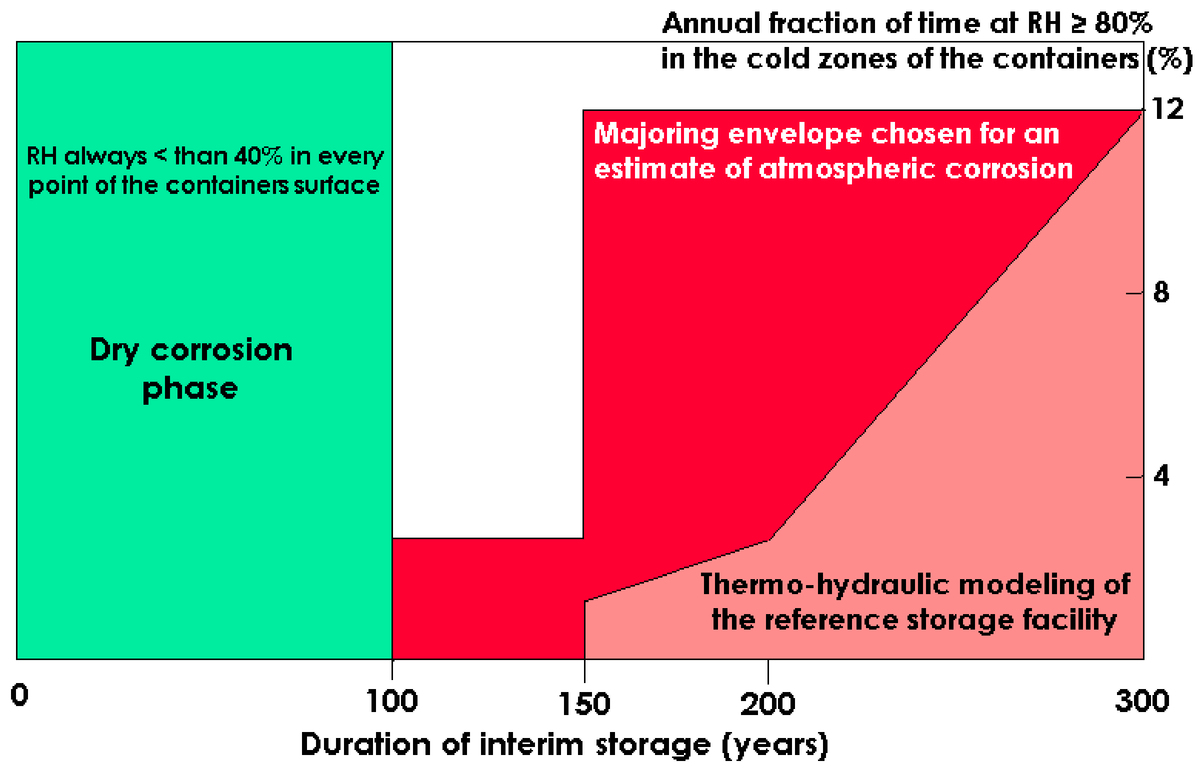
$$e = 1/\lambda \left(K_0\, e^{-127\,10^3/RT}\, t\right)^{1/2}$$

- **Considering a dry corrosion phase of a duration of 100 years at a majoring temperature of 300°C this leads to a value of approximately 30 µm for the total thickness of corroded metal**
- **Taking into account a possible periodic scaling of the oxide layer leads to a thickness of corroded metal lower than 100 µm after 100 years of dry corrosion in interim storage conditions**

1991 – 2006 : ATMOSPHERIC CORROSION : BASIC DATA

- **A great number of experimental data are available in the open literature**
- **These data have been used to develop ISO standards 9023 and 9024, based in particular on the time of wetness $\tau 80$, annual fraction of time at RH > 80%**
- **They are outdoor results relative to samples exposed to various atmospheres, and in thermal equilibrium with their environment**
- **Thermo-hydraulic modeling of a reference storage facility was carried out to determine the evolution of RH at the overpacks surface**

1991 – 2006 : ATMOSPHERIC CORROSION : NORMATIVE APPROACH



- In a conservative approach, two phases of atmospheric corrosion were considered to apply ISO standards 9223 and 9224
- For each phase, the time of wetness τ80 considered was the maximum one of the next phase as determined by the thermo-hydraulic modeling of the reference storage facility

1991 – 2006 : ATMOSPHERIC CORROSION : NORMATIVE APPROACH

❑ A conservative approach gives the following:

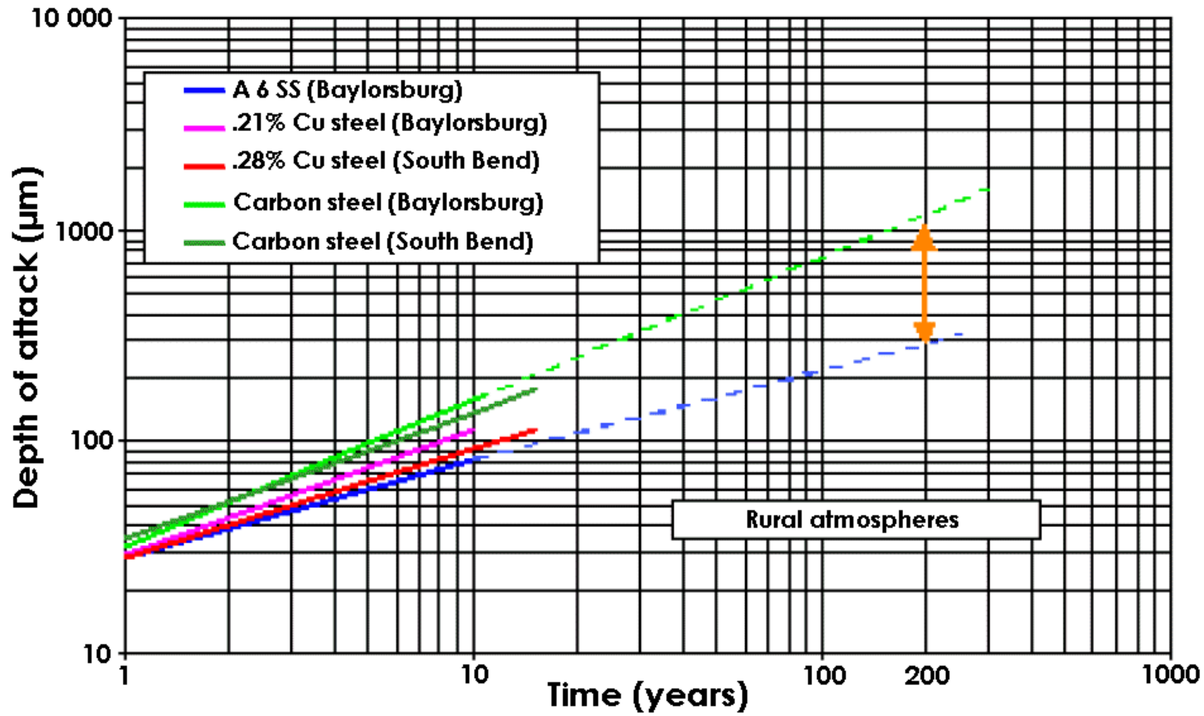
- ❑ **From 100 to 150 years: frequency of RH > 80% lower than or equal to 3% of time**
- ❑ **From 150 to 300 years: frequency of RH > 80% lower than or equal to 12% of time**

Application of ISO 9223 and 9224 gives then for the corroded thickness of metal after 200 years of atmospheric corrosion:

- ❑ **250 µm for a non significant Cl^- or SO_2 pollution**
- ❑ **900 µm for significant Cl^- and SO_2 pollution**

These results are in good agreement with observations made on indoor archaeological analogues

1991 – 2006 : ATMOSPHERIC CORROSION : PHENOMENOLOGICAL APPROACH



- **Results from coupons exposed to outdoor atmosphere do not describe the behavior of overpacks in an indoor storage facility**
- **There is uncertainty in extrapolating them over a 200 year period**

1991 – 2006 : ATMOSPHERIC CORROSION : PHENOMENOLOGICAL APPROACH

- Based on the data from the literature, on ISO 9023 τ_{80} and on the thermo-hydraulic modeling of a reference storage

- Literature data can be modeled using a power law:

$$P = K\, t^{n}$$

- Replace the total exposure time "t" with the time at RH > 80% in outdoor experiments "$\tau_{80\ outdoor}$ t":

$$P = Ko\, \tau^{n}_{80\ outdoor}\, t^{n}$$

- Use this new relation with $\tau_{80\ storage}$ derived from the thermo-hydraulic modeling of a reference storage facility

1991 – 2006 : ATMOSPHERIC CORROSION : PHENOMENOLOGICAL APPROACH

Experimental : $P = Ko\ \tau^n_{80\ outdoor}\ t^n$ — $28.5\ t^{0.456}$ **(USA Rural)**

$\tau_{80\ outdoor}$ **(local climatic data)** — 0.41

$\tau_{80\ storage}$ **(modeling of reference storage)** — 0.12

Storage : $P = Ko\ \tau^n_{80\ storage}\ t^n$ — $16.28\ t^{0.456}$

P after 200 years of atmospheric corrosion in storage ≈ 180 µm

This model contains fitting parameters "n" and "Ko" which render its extrapolation over a long period of time hazardous.

⇒ Use of the more conservative normative approach

1991 – 2006 : CORROSION IN STORAGE : CONCLUSION

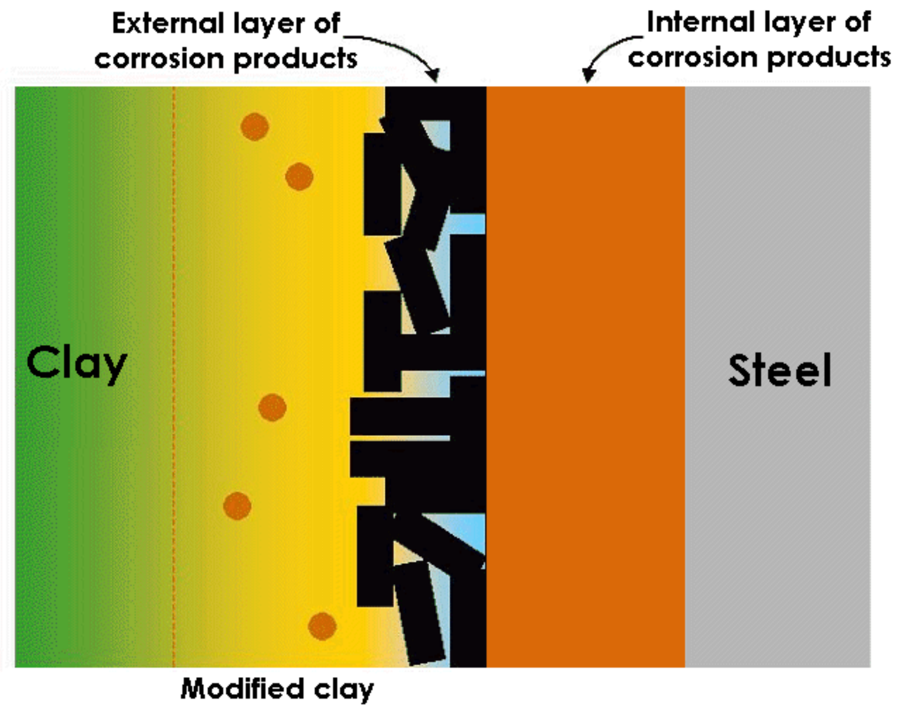
- **Current experimental laws and laboratory results can give a relatively good estimate of HLW overpacks behavior during interim storage**

- **This estimate leads to a maximum of 1 mm of corroded metal after 300 years of storage (100 µm during the dry corrosion phase and between 250 and 900 µm during the atmospheric corrosion phase), hence of about only 2% of the overpack wall thickness of 45 mm**

- **There is however an uncertainty in extrapolating experimental results over long periods of time**

1991 – 2006 : CORROSION IN DISPOSAL CONDITIONS

- **The first disposal concept included direct contact of the overpacks with the filling material of the disposal tunnels (bentonite clay)**



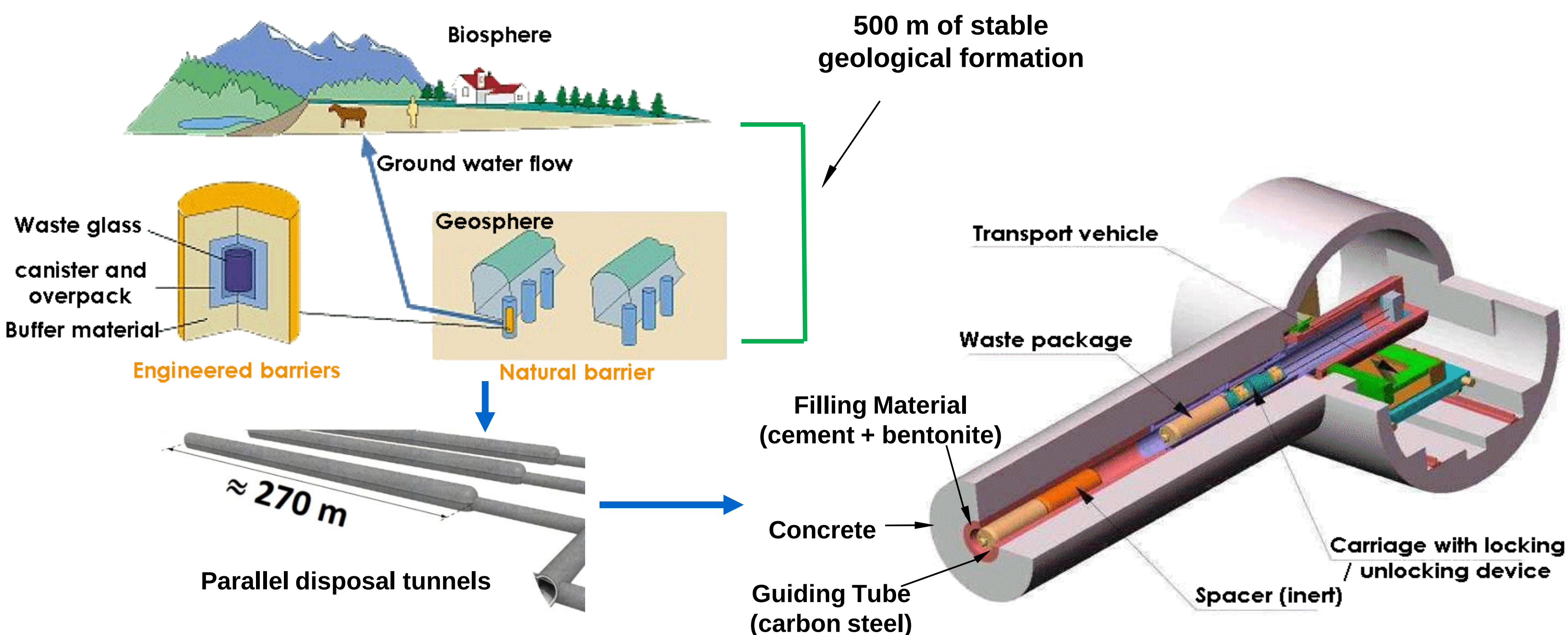
- **Diffusion and transport in the clay and corrosion products layers**
- **Interface reactions**

↓

Corrosion rate

CURRENT GEOLOGICAL DISPOSAL CONCEPT (ANDRA)

- Due to the small volume of waste produced and to reduce handling operations, the intermediate storage for HAVL waste was abandoned



© ANDRA

Studies focused on the corrosion of the guiding tube and overpacks by the water coming from the filling material

THANK YOU FOR YOUR ATTENTION

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 54 83 | F. +33 (0)1 69 08 15 86

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

Direction de l'énergie nucléaire
Département de physico-chimie
Service de la corrosion et du comportement des matériaux dans leur environnement
Laboratoire d'étude de la corrosion aqueuse