

Corrosion in nuclear waste geological storages how to predict corrosion for millenniums?

D. Feron

► To cite this version:

D. Feron. Corrosion in nuclear waste geological storages how to predict corrosion for millenniums?. Cycle de conferences donnees sur invitation de l'IMR CAS, Nov 2016, Shenyang, China. cea-02437059

HAL Id: cea-02437059 https://cea.hal.science/cea-02437059

Submitted on 13 Jan2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



CORROSION IN NUCLEAR WASTE GEOLOGICAL STORAGES: HOW TO PREDICT CORROSION OVER MILLENNIUMS?

Institut of Metal Research, Chinese Academy of Sciences Shenyang November 15, 2016

Damien Féron

Service de la corrosion et du comportement des matériaux dans leur environnement Commissariat à l'énergie atomique et aux énergies alternatives French atomic energy and alternatives energies Commission Saclay, France



Content

Overviews of nuclear waste disposal in France

How to predict corrosion over millennia?

- Laboratory tests
- Modeling
- Archeological artefacts
- Integrated experiments



ceaden

I OVERVIEWS I LONG TERM CORROSION

NUCLEAR WASTE

VITRIFIED WASTE CONTAINERS



Illustration of planned container for vitrified High Level Radioactive Waste for long term interim storage and clay disposal





6 Stainless steel canisters on two levels

3 Carbon steel spacers

The containers are made of six stainless steel canisters containing the vitrified waste and placed into an overpack made of cast iron, with carbon steel spacers

Cast iron overpack





I OVERVIEWS I LONG TERM CORROSION

UNDERGROUND DISPOSAL

Background of the French nuclear waste disposal



1991: The French government decided to plan research for nuclear waste management
2006: Choice of a clay environment for deep geological experimental laboratory
2016: Licensing authorization (start of the process)





Berkeley April 2015



UNDERGROUND DISPOSAL

S periods: unsaturated and aerated conditions (over decadesexploitation phase), mixed period (over decades), and saturated & anoxic period (over milleniums)

&The corrosion resistance of the container material over centuries (long term interim storages) and millenniums (geological waste disposal) is one of the greatest scientific and technical challenges

&The reliability and the viability of integrity predictions in HLNW storages and disposals are of paramount importance for public acceptance

- ♦ Local Committees
- ♦ National Commissions
- ♦ International organisations OCDE/NEA, IAEA





Is function of the container thickness

With corrosion allowance materials (copper or carbon steel), the overparck will be quite thick

UNDERGROUND REPOSITIRY

HOW TO PREDICT CORROSION FOR MILLENNIA ?

OVERVIEWS I LONG TERM CORROSION

How to predict corrosion over millennia ?



ceaden



<u>ceaden</u>

I OVERVIEWS I LONG TERM CORROSION

LABORATORY TESTS

Long term behaviour of passive Ni alloys Anodic segregation of sulphur at the alloy interface



P. Marcus & Co., Corrosion Science 24(1984)259, 29(1989)455, 31 (1990) 377



LABORATORY TESTS

Anodic segregation of sulphur at the Ni alloy/passive film interface leading to passivity breakdown



D. Féron

Ceaden

VIEWS I LONG TERM CORROSION

LABORATORY TESTS

Evaluation of uniform corrosion rates of carbon steel under anaerobic conditions at 80°C-85°C with various water chemistries



Carbon steel (micrography) in clay environment







LABORATORY TESTS



CEA results, Référentiel Matériaux, ANDRA, 2005

Pitting observed on carbon steel after 8 months in saturated clay

P = Pitting factor = D/X

D = maximum pit depth at t X = Mean uniform corrosion depth at t

D. Féron

page 15

Berkeley April 2015

UNDERGROUND REPOSITIRY

HOW TO PREDICT CORROSION FOR MILLENNIA ?

MODELLING



MODELLING

> Empiricism (semi-empirical models)

- (Semi-)empirical modelling is based on experimental data or service life data
- It is used for obtaining initial estimates
- It has the disadvantage of having to know the answer "in advance"
- > Determinism (mechanistically based models)
 - ✓ it is based on physics, requires viable physical model
 - the greatest challenge is to decide what processes should be included
- continuously improved via the knowledge evolution
 Stochastic taking into account the stochastic nature of corrosion phenomena

 In complementary, rather than supplementary manner
 The validation of these models is an absolute necessity: archaeological analogues

D. Féron	page 17 Berkeley April 2015				
	I OVERVIEWS I LONG TERM CORROSION				
Ceaden	MODELLING - 1				





Uniform corrosion rate of carbon steel in clay (anaerobic conditions) limited by the water flux or by the interface reaction



MODELLING - 2

Thermodynamics / Critical crevice potential

LONG TERM CORROSION



<u>ceaden</u>

MODELLING - 3





MODELLING - 4

The Point Defect Model is applied and describes:

- the evolution of oxide films on carbon steel in clay and concrete environments
- ✓ the growth and breakdown of passive films of high alloyed materials in saturated brine



Ceaden

D. Féron

LONG TERM CORROSION

MODELLING - 4



Corrosion modeling of an iron based alloy in passive conditions

C. Bataillon & al. , Elect. Acta 55 (2010) 4451-4467

- Corrosion modeling based on Fick and Poisson equations with moving interfaces (Diffusion Poisson Coupling Model - DPCM)
- Electrochemical experiments for data acquisition and verification
- Coupling with geochemical models
- Clay and concrete



MODELLING - 4









C. Bataillon & al. , J. Comput. Physics 231 (2012) 6213-6231

This model is under implantation in the nuclear waste simulations codes



UNDERGROUND REPOSITIRY

HOW TO PREDICT CORROSION FOR MILLENNIA ?

ARCHEOLOGICAL ARTIFACTS / ANALOGUES

- corrosion rates
- influence of the environment
- influence of the metal
- corrosion mechanisms
- modeling validation

<u>ceaden</u>

I OVERVIEWS I LONG TERM CORROSION

ARCHEOLOGICAL ARTIFACTS



- > Use of archaeological analogues
 - ✓ to demonstrate
 - ✓ to provide a database
- > Sufficient care has to be taken
 - many old metallic materials have corroded away
 - differences between old and new materials
 - v poor knowledge of exposure conditions
- > Illustrations:
 - Corrosion rates (but take care!)
 - Importance of the corrosion product layer (and not only the corrosion rate)

Roman nail found at the Adrian Wall (1900 years old, 35 cm long), *from Miller W &Co. 1994*

Ceaden

ARCHEOLOGICAL ANALOGUES - 1

Uniform corrosion

Evaluation of long term evolution of the average corrosion depth of carbon steel in contact with bentonite under anaerobic conditions based on experimental data and a comparison with lifetime assessment and with natural analogue data



LONG TERM CORROSION

D. Féron

Ceaden

page 27

Berkeley April 2015





Mean corrosion rates observed on artifacts exposed more than a century in various environments (from P. Dillmann)





- Without oxygen, corrosion rates are lower than 10 µm/year (and often lower than 1µm/year)
- In aerated conditions, large variations of the corrosion rates are observed (from few µm to several hundreds µm)

Ceaden



MILD STEEL

Monnier J. & al. Anal. At. Spectrom., 2011, 26, 885

Ceaden





I OVERVIEWS I LONG TERM CORROSION

ARCHEOLOGICAL ANALOGUES - 4

Mechanisms

Localization of the cathodic reaction in aerated conditions (oxygen reduction) : use of tracers ¹⁸O et ²H



Corrosion mechanisms: localization of the cathodic reaction

Use of ${}^{18}O_2$ during reexposure of the specimen to atmospheric corrosion Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA)



Isolating layer (goethite): reaction at the interface metal/oxide

E. Burger & al. , J. Mater. Res., Vol. 26, No. 24, Dec 28, 2011 D. Féron page 33



Conductive oxide layer: external interface

Berkeley April 2015

Ceaden

Ceaden

I OVERVIEWS I LONG TERM CORROSION

ARCHEOLOGICAL ANALOGUES - 4

Localization of the cathodic reaction in anoxic conditions

Use of D_2O during re-exposure of an artefact from the Glinet site to aqueous corrosion Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA)



Deuterium in the oxide layer, near the interface metal/oxide



M. Saheb & al., JNM, 423 (2012) 61-66



Ceaden

From A. Michelin & al., JAAS, 2012

Equivalent thicknesses of the different phases obtained from the fit of the extracted spectra.



Support for modelling

- Corrosion products of a 450 year old archaeological iron nail in anoxic environment were investigated at the nanometer level using STXM
- > Interfacial layer of about 100 nm at the interface metal/oxide
- Support the hypothesis of a nanolayer controlling the corrosion process (Point Defect Model and associated models)

page 35

D. Féron

Ceaden

I OVERVIEWS I LONG TERM CORROSION

ARCHEOLOGICAL ANALOGUES - 6

In many archeological sites, SRBs are found and/or corrosion products with S⁻⁻ are observed in the corrosion product layer



7 Schematic representation of influence of SRB on corrosion system formed by archaeological nails in anoxic soils (TM, transformed medium; DPL, dense products layer)

C. Remazeilles & al., CEST, 2010 VOL 45 NO 5, 388-394

Roman ingot (2000 years old)



C. Rémazeilles et al. , Corrosion Science 51 (2009) 2932-2941

Berkeley April 2015

Even with SRBs, low corrosion rates are observed



(Nydam site in Denmark – anoxic conditions with sulphides)



H. Matthiesen, Proceedings of the Second International workshop, Nice, 2004 – published by ANDRA (ISBN 2-95101108-6-9, p.114

	Min.	Max.	Mean	95% CI of Mean	
рН	5.99	7.02	6.50	6.47 to 6.54	140
Sulphate (mg SO₄/ L)	<10	200	21	16 to 27	101
Sulphide (mg S(-II)/L)	<0.03	2.22	0.18	0.12 to 0.23	116



Measurements on 151 lances have demonstrated corrosion depths as low as 50 μ m (average of 20 measurements on a lance). With 1700 years of age this corresponds to an average corrosion rate of 0.03 μ m/year (or even lower,

Even with sulphur environments and bacteria, very low corrosion rates

D. Féron

page 37

Berkeley April 2015

UNDERGROUND REPOSITIRY

HOW TO PREDICT CORROSION FOR MILLENNIA ?

INTEGRATED EXPERIMENTS



OVERVIEWS I LONG TERM CORROSION

INTEGRATED EXPERIMENTS

Six years in bentonite





Nothing on stainless steels & titanium alloys 0.1 μ m/year on mild steels 0.7-0.8 μ m/year on copper alloys



Fig. 4 Sensor in block of ber

V. Madina & Co., Corrosion of several components of the *in situ* test performed in a deep geological granite disposal site, Proceedings of the Second International workshop, Nice, 2004 – published by ANDRA (ISBN 2-95101108-6-9, p.61)

D. Féron

page 39

But on one sensor ...

Berkeley April 2015



I OVERVIEWS I LONG TERM CORROSION

INTEGRATED EXPERIMENTS



In addition, simultaneous presence of SRB and aerobic bacteria leads to the worse conditions for passive alloys, as seen for seawater applications

V. Madina & Co., Corrosion of several components of the *in situ* test performed in a deep geological granite disposal site, Proceedings of the Second International workshop, Nice, 2004 - published by ANDRA (ISBN 2-95101108-6-9), p.61

CORROSION AND THE FRENCH CONCEPT OF THE UNDERGROUND DISPOSAL FOR HIGH RADIOACTIVE NUCLEAR WASTES

FINAL COMMENTS

Ceaden

I OVERVIEWS I LONG TERM CORROSION

FINAL COMMENTS

Life time prediction over millenna



http://www.cigeo.com/

Damien Féron Centre de Saclay | Bâtiment 458 – PC50 Tel : 33 1 69082065 Email: damien.feron@cea.fr

Commissariat à l'énergie atomique et aux énergies alternatives Centre de Saclay | 91191 Gif-sur-Yvette Cedex

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

Direction de l'Energie Nucléaire Département de physico-Chimie Service de la corrosion et du comportement des matériaux dans leur environnement



SUPPLEMENTARY OVERHEADS







Ni-21Cr-8Fe at.% with 0,009 at.% of S

Chromium strongly counteracts the detrimental effect of sulphur

D. Féron page 45 Berkeley April 2015



a) Equisolubility

Berkeley April 2015

immunity



CELLULAR AUTOMATA

Bases of the modeling: probabilities of reactions



1 Simple scheme of forming layer with clusters and solution representation of reactions (1) and (2)



2 Definition of λ and ϵ : λ defines extension of top region where probability of corrosion is $p\epsilon$; in remaining bottom area, probability of corrosion is $p(1-\epsilon)$

D. Féron

page 47

Berkeley April 2015