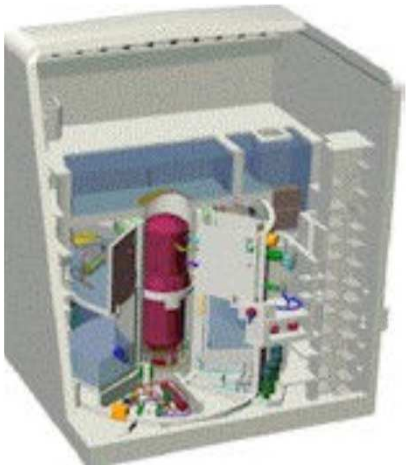
energie atomique • energies altern

Colis métallique contenant
plusieurs galettes de déchets MA-VL

Conteneur de stockage MA-VL

Overview of the radiolysis topic in the nuclear fuel cycle



C. Lamouroux*
And DEN departments involved in radiolysis
*CEA Saclay/DEN/DANS/DPC
CEA Saclay/DEN-DANS/DRSN
CEA Marcoule/DEN/DRCP
CEA Marcoule/DEN/DTCD
CEA Cadarache/DEN/DSN

Outline

- **Radiolysis**
  - > **Basic**
  - > **Why ?**
  - > **Where ?**
  - > **How ?**
    - Nature of radiation
    - Targets diversity
- **Water radiolysis**
  - > ***State of knowledge***
  - > ***PWR***
  - > ***Fuel storage***
  - > ***Highly concentrated media***
- **Gaz radiolysis**
- **Organic molecules**
- **Exemple of an operationnal approach : case of the radiolysis of waste packages.**

Radiolysis - Basic

- **G-values**

  G = # Molecules Produced per 100 eV absorbed energy

  Dependent on Incidental Radiation (α, β, γ, n)

$$G(X) = \frac{N(X)x100}{Dose(eV)}$$

- **Forward (Radiolytic) vs. Back Reactions**
  - > **Gi Primary steps (at very short time ps)**
  - > **G_{app} Stable compounds in solution after recombination**

Emitters

α , β, γ, X, n,…

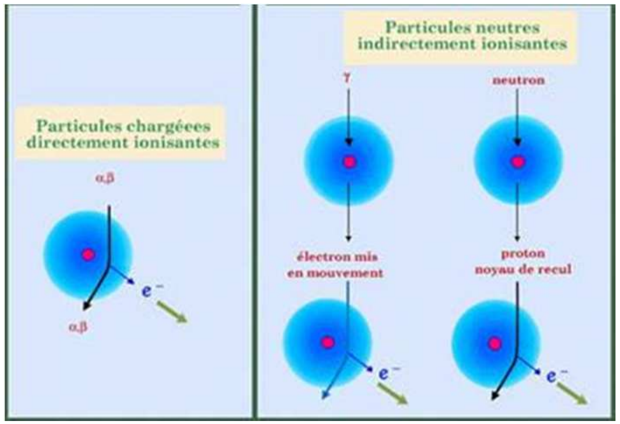
Radical formation

H_2O - - - - - - - -> $H^\bullet$, $OH^\bullet$,,,- - - - - -> H_2, H_2O_2, e^-_{aq}, H, OH, HO_2, H_3O^+

Breaking of molecular bonds

Chemical recombination

- **LET Linear energy transfer** is a measure of the energy transferred to material as an ionizing particle travels through it
  - > *for α and β : direct energy deposition*
  - > *for γ and n : indirect energy deposition*



Radiolysis study : Why?

- **All conditions are met to promote radiolysis in the nuclear fuel cycle – difficult to prevent, we have to**
  Anticipate - Evaluate - Manage ⇨ The impact of the phenomenon

Modifications	Type of species	Consequences
Gaz production	H_2 CH_4, CO, CO_2 H2S,	Safety Depressure - Overpressure Inflammability Toxicity
Corrosive species production	$OH^{\bullet}$ $H_2 0_2$ F^- ; Cl^- ; ClO^-	Aging – Life time Corrosion Solution chemistry equilibrium ⇔ speciation
Molecules degradation	Extractants TBP, diamides, …⇨ breakdown sequences	Process reliability and robustness Loss of extraction capacities
Materials degradation	Polymers ⇨ scission; crosslinking; oxydation Ion exchange resins degradation	Aging – Life time Loss of mechanical properties Loss of exchange capacity
Complexant molecule production	Formation of small oxydised molecules : carboxylic acids, ketons, aldehydes, alcohols	Environmental impact Complexing properties Migration of radionuclides

Radiolysis in the nuclear fuel cycle : where ?

Long term waste behaviour
- wastes (polymers, precipitates, cellulose,…)
- matrices (bitumen, cement, sand, glass)

⇨ gaz release G(X)
⇨ complexant molecules

SAFETY / ENVIRONMENTAL IMPACT

Recycling
- Stability of the reprocessing solvent

⇨ G(-L)
⇨ degradation products

- Highly concentrated PF solutions

⇨ New species formation

SAFETY /PROCESS RELIABILITY

Fuel fabrication
- Radiolysis of sorbed water

⇨ G(H2)

SAFETY

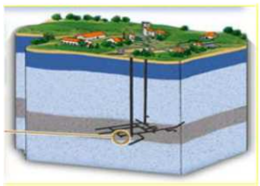
Reactor operations
- water radiolysis

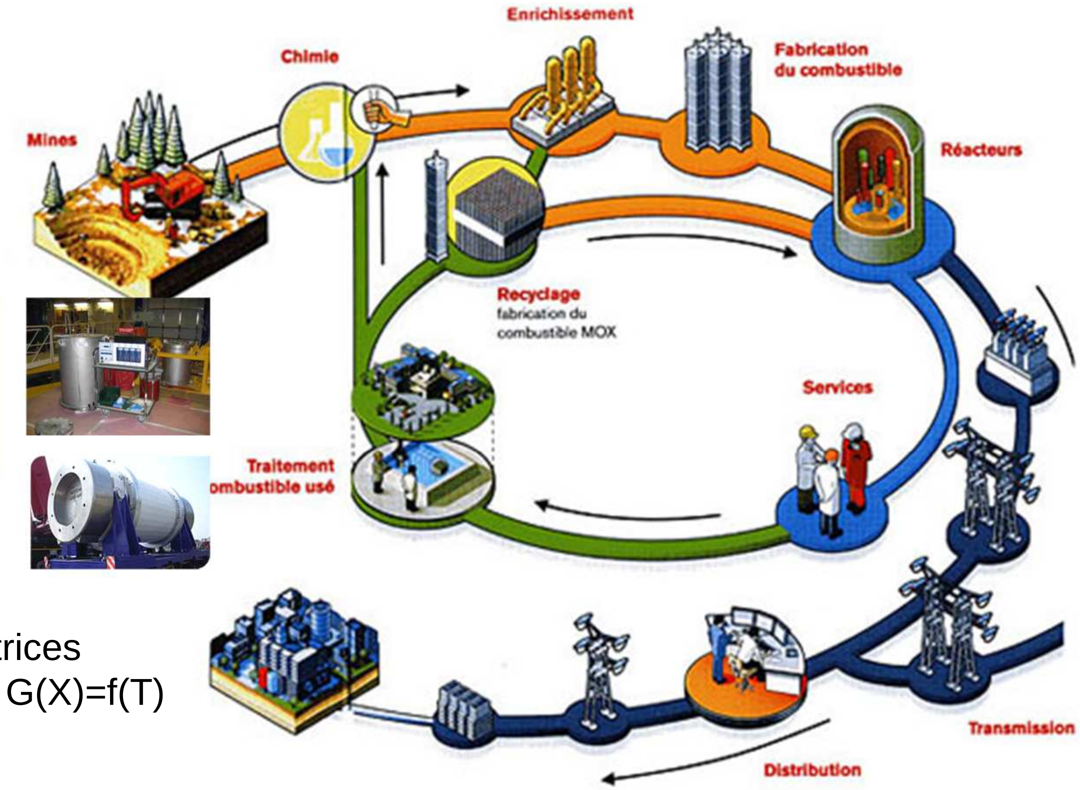
⇨ Gaz production
⇨ Corrosive species production

- materials aging (polymers)

⇨ Loss of mechanical properties (cables, …)

SAFETY / AGING – LIFE TIME





Fuel storage
- water radiolysis

⇨ Gaz

SAFETY

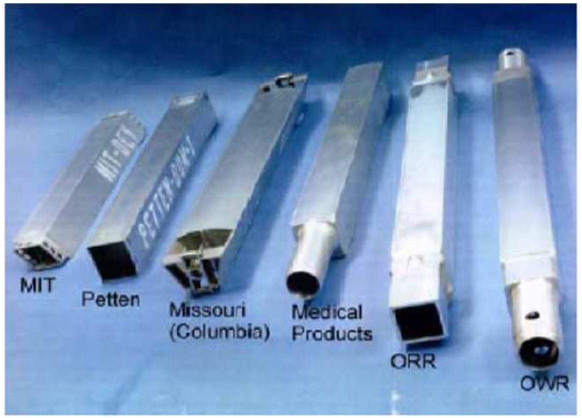
Transport :
- various matrices

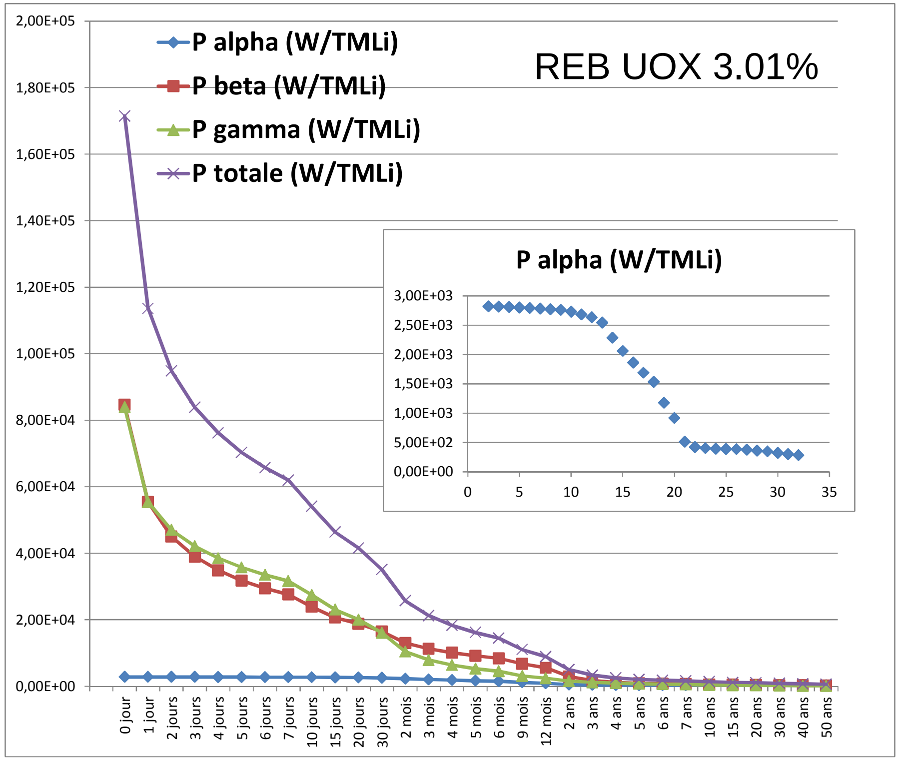
⇨ Evolution G(X)=f(T)
SAFETY

Document AREVA www.areva.com

How ? Radiation sources

- **Requirement**
  - > ***Nature of emitters* (α, β, γ)***
    - - *Fuel Type (Uox, Mox, UNGG,…)*
    - - *% Enrichment*
  - > ***Power***
    - - *Burn-up*
    - - *Cooling time*





**There are few pure Alpha or Beta emitters, Gamma emission is concomitant*

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  - ***Highly concentrated media***
- **Gaz radiolysis**
- **Organic molecules**
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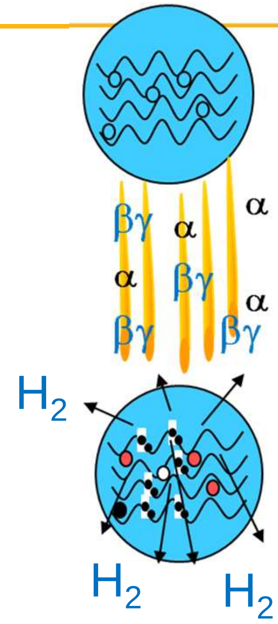
Water radiolysis

- **Dependent on**
  - > **Type of radiation**
  - > **Atmosphere (aerated or not)**
  - > **Temperature and Pression (typically for reactor)**
  - > **Purity of water (fuel storage pool)**
  - > **Concentrate solution (nitric acid solution)**



Emitters

α , β, γ, X, n,…

Radical formation

H_2O - - - - - - - -> **$H^{\bullet}$, $OH^{\bullet}$,,,** - - - - - -> **H_2, H_2O_2, e^{-}_{aq}, H, OH, HO_2, H_3O^{+}**

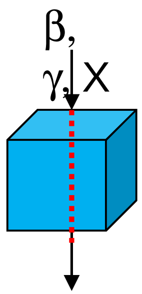
Breaking of molecular bonds

Chemical recombination

- **Products of water radiolysis**
  - > **oxydizing species :** $OH^{\bullet}$, $O_2^{\bullet -}$, H_2O_2, O_2
  - > **reducing species :** $H^{\bullet}$, e_{aqu}, H_2
  - > **gaz species : H_2**

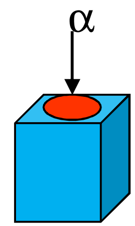
Radiolysis of pure water: state of knowledge

Nature of the incidental radiation



- The very pure water irradiated by highly penetrating radiation (γ, X) seems inert to radiation ⇨ Recombination in a closed environment

- For penetrating particles (α), the production of free radicals is too low compared to the production of molecular products and their recombination is incomplete: there is still a decomposition of water.



Physico-chemical conditions

$H + H \rightarrow H_2$
$OH + OH \rightarrow H_2O_2$

- **Closed system with H_2**

Results : $H_2 + H_2O_2 \rightarrow 2\ H_2O$

Effective chain reaction ⇨ Stabilization due to the effective recombination

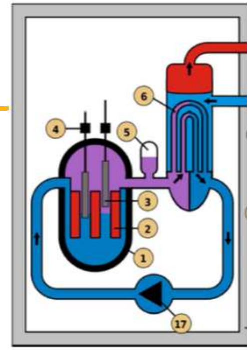
$V_{formation}$ (H2) ⇔ $V_{decomposition}$(H2)

⇨ All the species reacting with H and OH radicals make the process less efficient.

- **Open system :** $[O_2]$ sufficient

⇨ O_2 compete with H_2 to react on OH ⇨ H_2 production

Water radiolysis in the PWR

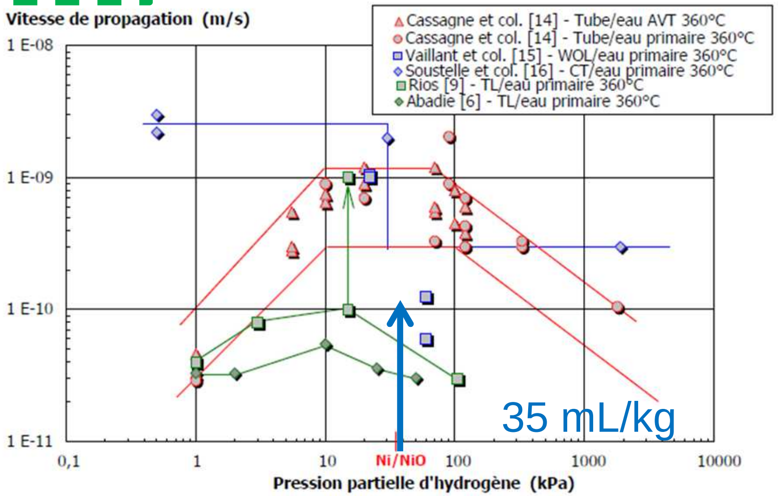


Water radiolysis produce corrosive species such as H_2O_2 responsible for localized corrosion

1- To maintain reductive conditions
2- To avoid the decomposition of water by promoting chemical recombination with H_2O_2 hydrogen is added. (20-50 mL/kg water)
Global results $H_2 + H_2O_2 \rightarrow 2\ H_2O$

[H2] Optimization

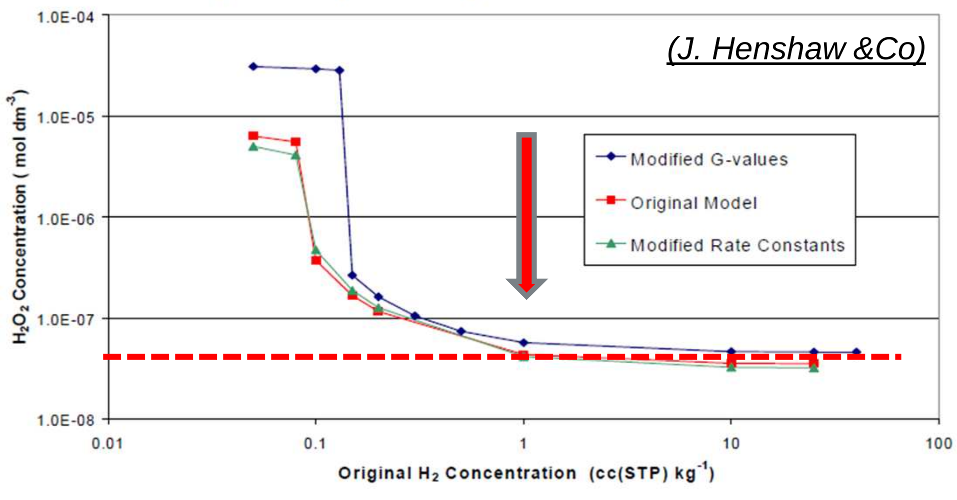
But H_2 is also responsible for stress corrosion phenomena.
Maintenance shutdown : H_2 elimination by O_2 introduction (time is money !)



- **Key point : [H2] optimization**
  - > Increasing and reducing have both advantages and drawbacks

Optimizing the management of radiolysis in the PWR

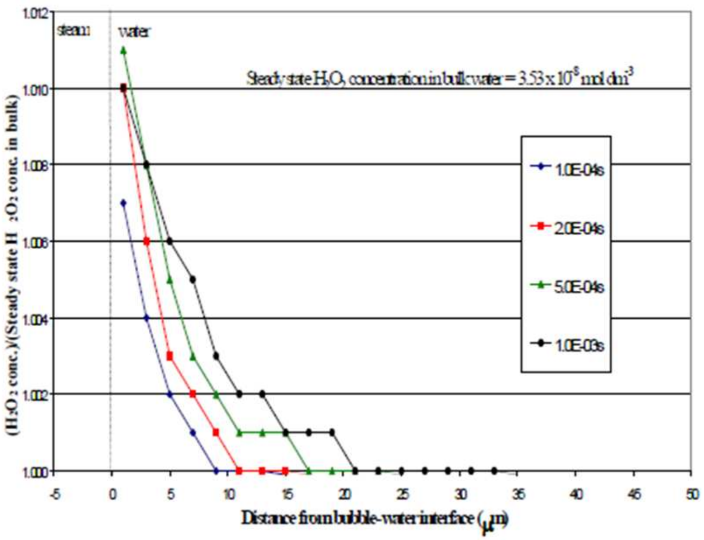
- **1 cm³/kg is more than enough to reduce hydrogen peroxide generated by radiolysis…**



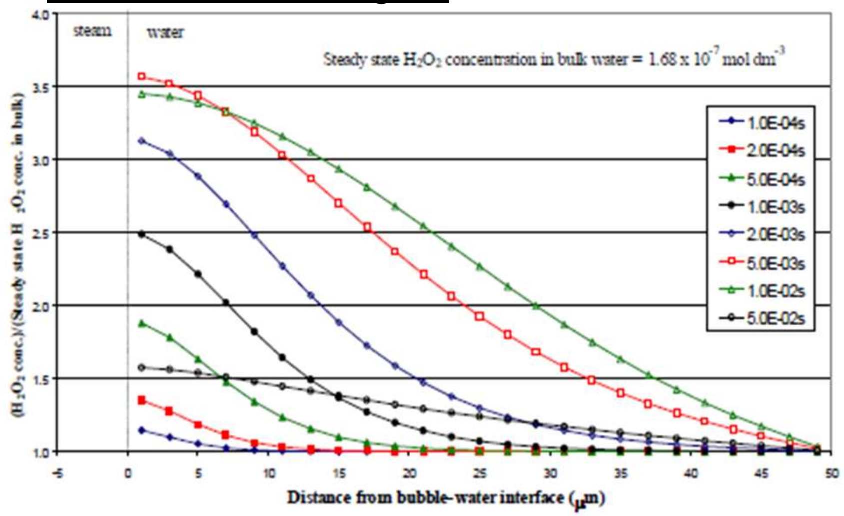
T = 344 °C, typical PWR dose rate, 1200ppm B

- **except for boiling. Possible cause of abnormal flow**

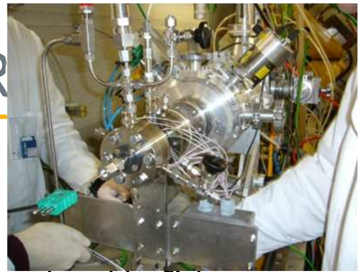
<u>Bulk water 40cc/kg H2</u>



<u>Bulk water 0.15cc/kg H2</u>

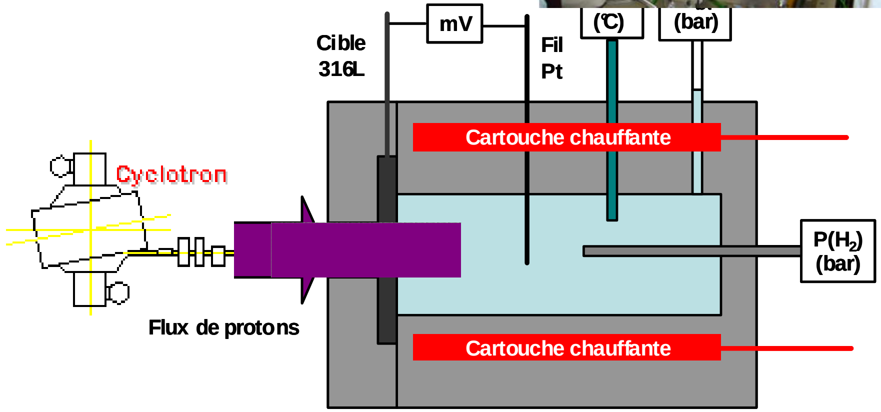


Optimizing the management of radiolysis in the PWR



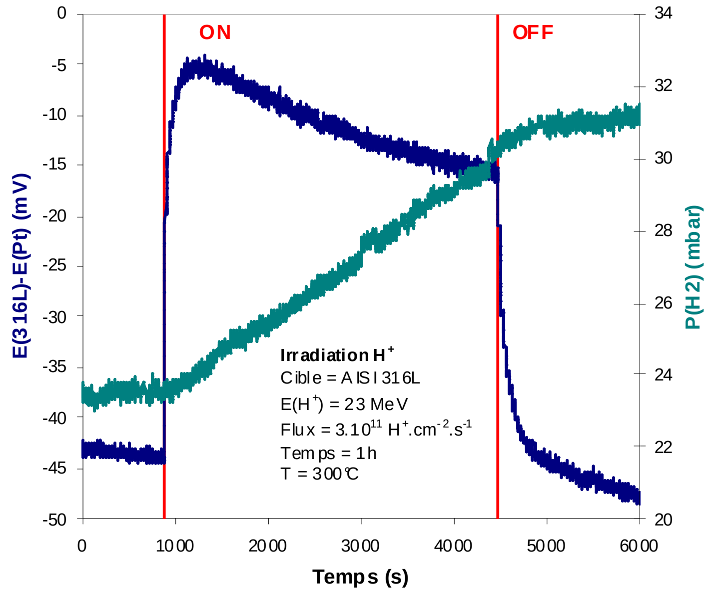
- **Scientific issues concerning the water radiolysis in PWR**
  - > **[H_2] optimum**
  - > **less corrosion**
  - > **with a wide operating range**

  ⇨ Acquiring data in a large range of P and T (300℃, 15 Bar)



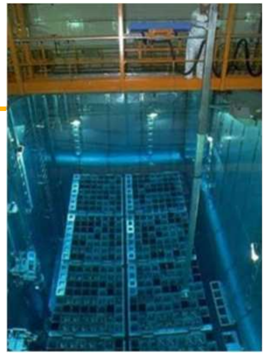
Proton irradiation (CEMTHI Orléans) 34 MeV (patented

- **Development of an innovative experiment**
  - > with proton irradiation
  - > operating conditions (up to 330℃ and 16 bar)
  - > monitoring of the redox potential of the aqueous solution
  - > on line [H_2] measurement
  - > post-mortem characterization of surface sample (MEB, DRX,….)



DEN-DPC / CEMTHI

Water radiolysis in spent fuel pool



- **[31/03/2011] IRSN website** "*The release of hydrogen in Fukushima is not only due to the oxidation of zirconium cladding but also due to water radiolysis?"*
- **For safety demonstration : H_2 production by radiolysis**

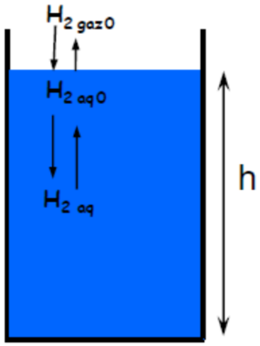
⇨ *RISK : calculation in first approach is too conservative*

- > pure water
- > open system (aerated)
- > no recombination
- > all the energy released in water

$V(H_2)$ calculation : $V(H_2) = *G(H_2) \times a\ P$

*G(H2)=0,45 mol/100ev

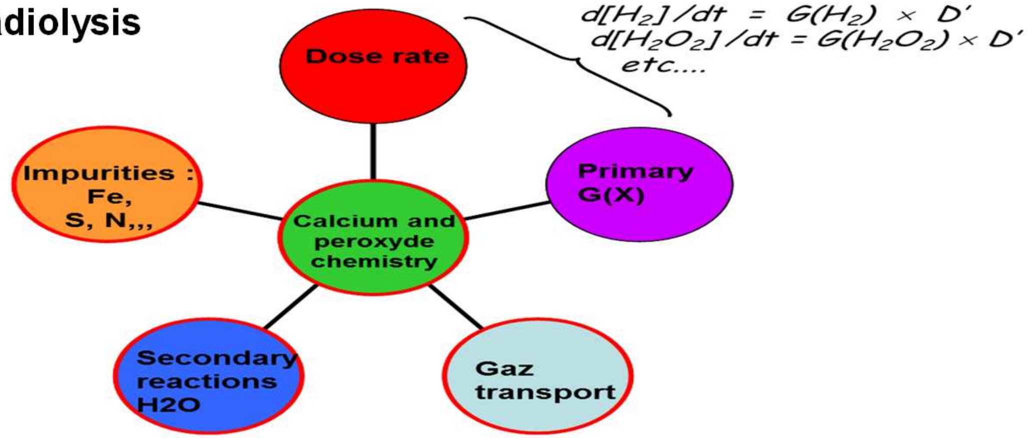
- **Scientific issues :**
  - > determination of dose rate and the energy deposition by taking into account the geometry of the assemblies (TRIPOLI)
  - > open or partially closed system : difference between the top, in contact with the air and the bottom of the pool
  - > In case of incident or accident : evolution of $G(H_2)$ with impurities (salt, dissolved metal or organic species, gazeous atmosphere)?

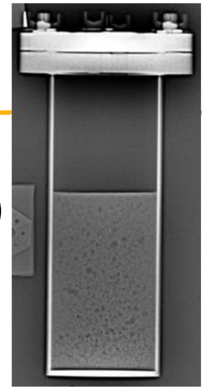


DEN-DPC

Impurities : case of cement radiolysis

- **Radiolysis of water cementitious materials :**
  - **DOREMI (Operational Description of water radiolysis in Irradiated Materials)**
  - **Water radiolysis**





DEN-DPC

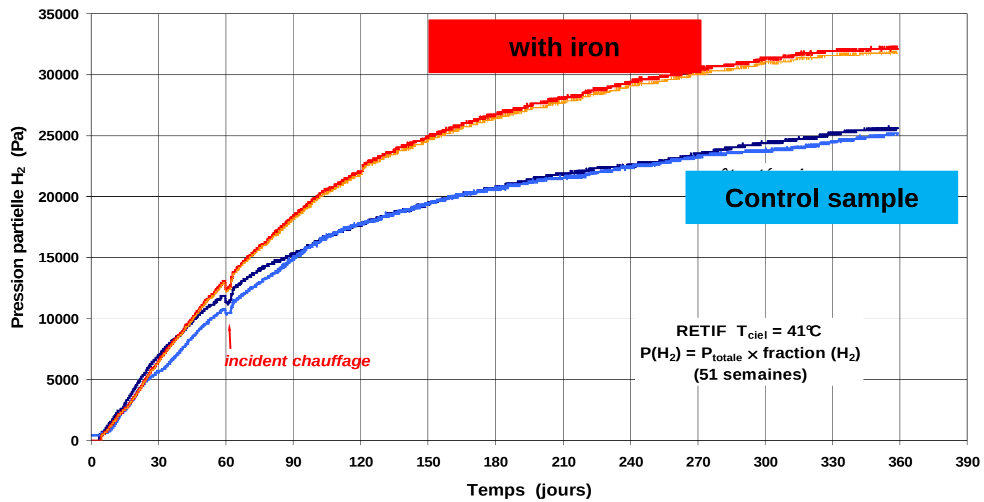
Reactions in alkaline medium (pH > 13) :

$$O^- + H_2 \rightarrow e^-_{aq}$$
$$e^-_{aq} + HO_2^- \rightarrow O^- + OH^- + H_2O$$
$$\Rightarrow \quad H_2 + HO_2^- \rightarrow OH^- + H_2O$$

Iron effect *:

$$O^- + Fe(II) \rightarrow O^{2-} + Fe(III)$$
$$e^-_{aq} + Fe(III) \rightarrow H_2O + Fe(II)$$
$$\Rightarrow \quad O^- + e^-_{aq} \rightarrow O^{2-} + H_2O \rightarrow 2\ OH^-$$

Experimental data



* Bouniol 2011

⇨ Iron tend to increase indirectly H_2 production.

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- **Exemple of an operationnal approach : case of the radiolysis of waste packages.**

Gaz radiolysis

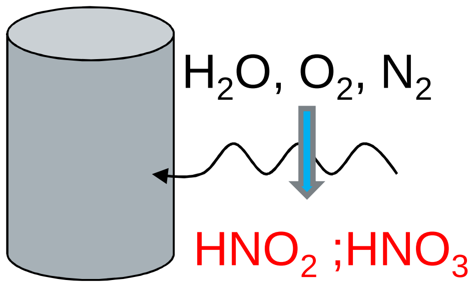
- **Air radiolysis**
  - > leads to an oxidizing environment ⇨ O_3, NO_2
  - > dry air ⇨ N_2O_5
  - > moist air ⇨ HNO_2 ; HNO_3

Andra website

- **Impact**
  - > damage - corrosion ⇨ (CSDC)
    - ZYR-4 tube
    - alloy 718 (grid)
  - > impact on container corrosion ⇨ stainless steel
  - ⇨ Evaluation of the consequences on the long life storage

Species	Dry air		Moist air	
	Production rate		Production rate	
O_3	$7,9x10^{-2}$	1	$7,6x10^{-2}$	1
NO_2	$7,7x10^{-3}$	0,10	$5,6x10^{-3}$	0,07
N_2O_5	$1,2x10^{-2}$	0,15		
HNO_3			$1,4x10^{-2}$	0,19
HNO_2			$7,1x10^{-4}$	0,009

[KANDA-1], [ARMSTRONG].

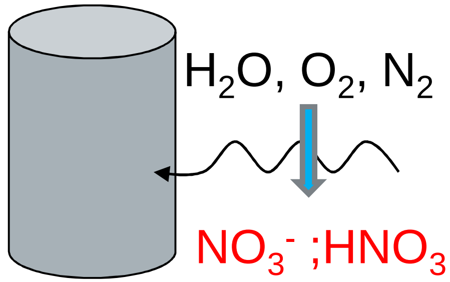


Gaz radiolysis

- **Integrated irradiation experiment CASIMIR (Corrosion AtmoSphérIque des Matériaux sous Irradiation)**
  > **Irradiation of mini-container**

  > **Conditions**

  - Température : 80°C
  - Different dose rate [300-10 Gy/h]
  - Different duration : from 6 to 12 months
  - Different relative humidity HR [70%-100%]
  - Different steels composition



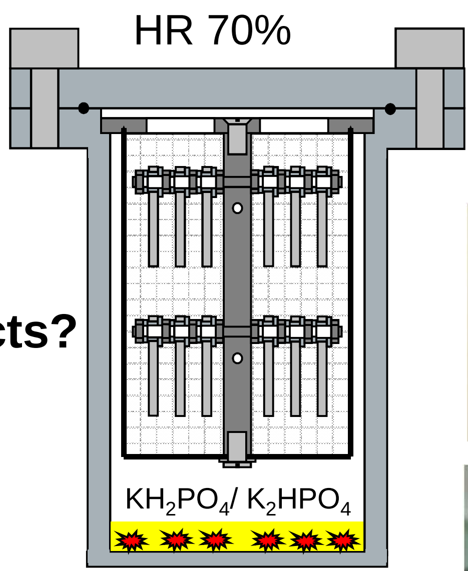
- **Output**
  > **Production of HNO_3 or not ?**

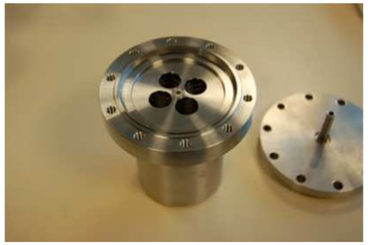
  > **Determination [HNO_3]**

  > **Observation of corrosion products?**

  > **Identification**

  > **And kinetic**





DEN-DPC / DRSN-LABRA

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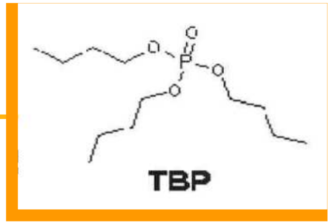
Organic molecules radiolysis



R A D I O L Y S I S

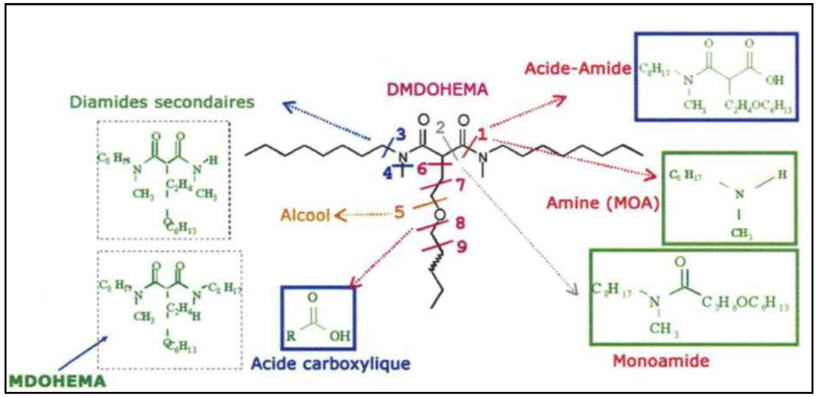
- **Radiolysis on extractants used in liquid liquid extraction for spent fuel reprocessing**
  - > TBP (Tributyl Phosphate) Solvant used in the french reprocesing process (PUREX process): allowed the extraction of U(VI) and Pu(IV)
  - > Partitioning concept : New solvents based on diamides,…

⇨ Consequences on Process reliability and robustness

- **Decrease in the extractant concentration**
  - > Control of the process : follow up and adjustment of the concentration
- **Formation of degradation products derivatives (ex for TBP : MBP,HDBP) :**
  - > Impact on performance extraction
  - > Risk of Pu retention and accumulation
  - > Risk of precipitation with the new species formed,
- **Need to developp effective treatment for solvent recycling**

⇨Typical studies :

- > Identification and quantification of species
- > Degradation mechanisms

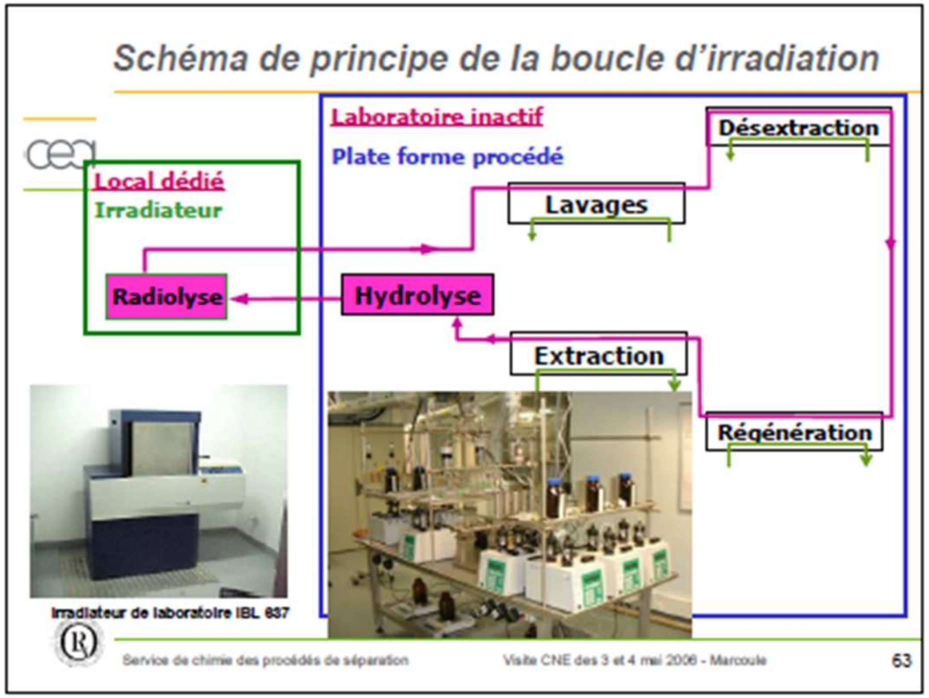


** Diamide degradation Berthon 2009*

Organic molecules based compounds : solvent

- **Scientific issues concerning the radiolysis of extractants**
  - > Increase the understanding of degradation mechanisms of extracting molecules and complexes in order to:
    - define appropriate treatment
    - propose new more stable molecules
  - > Study of the behavior of redox systems in radiolysis: the radiolysis of nitric solutions significantly affect the oxidation of actinides in the dissolving solution and the extraction cycles
  - > Radiolysis of water dissolved in organic phase

- **Thanks to Marcel facilities in CEA Marcoule :**
  - > Liquid-liquid extraction system
  - > Coupled with an irradiator ^{137}Cs



DEN-DRCP

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Operationnal approach : radiolysis of organic wastes packages

INPUT DATA

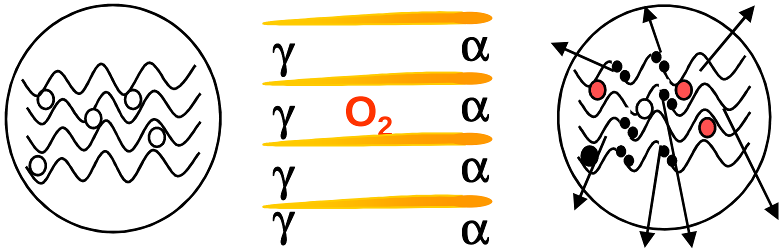
Irradiated Technological wastes with organic materials

OUTPUT DATA

Gaz production ⇨ **H2**

- Small complexant formation

- elimination
- reticulation
- chain ruptures



- transport considerations
- gas emission for a safe and optimal dimensioning of storage cells
- production of water soluble chemical complexing agents which could enhance radionuclide migration.

Predictive Model development

DEN-DPC / DEN-DSN / DEN/DTCD / DEN-DRCP / IRAMIS-LRAD

Operating model : Inventory

$$V^j(gaz) = \lambda_j \left(1-\bar{a}^j\right) P^j_{em} \sum_k f^j_k G^j_k \; V_m(T)$$

$V_{gaz}(X) = a \, E_{émise} \times G(X)$

Need	Operating data
Emission source : Activity of the different emitters (α, β, γ)	Typical radiological spectrum from PWR, BWR, UNGG reactor
Nature of the target: thickness, weight, density, volume.	Nature of waste: paper, bottle, pipes,… Crushed,,,,
Chemical nature and gaz emission: **G(H2)**	Nature of polymers. PE, PP, PUR,,,,
Energy deposition: **a** α ; β ; γ	Chemical and physical forms (particle size) Contact : on, inside,…

❶ Knowledge of the waste packages

❷ Development of a data base

❸ Energy deposition and dose effect

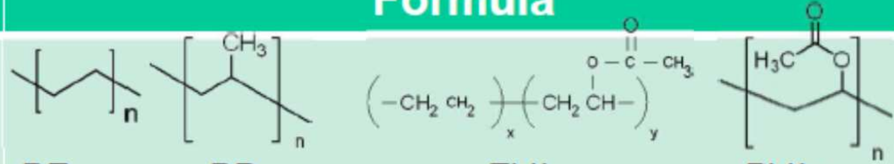
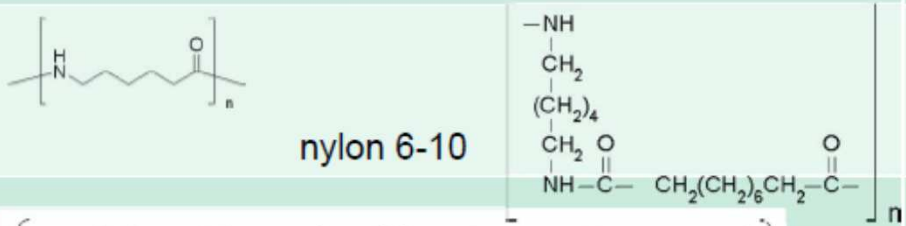
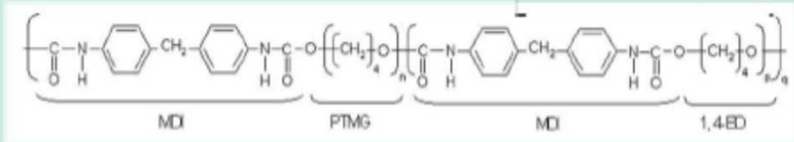
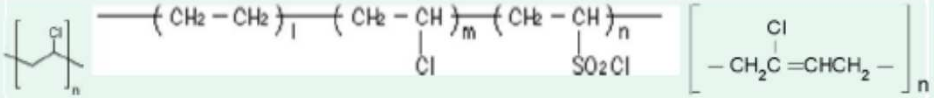
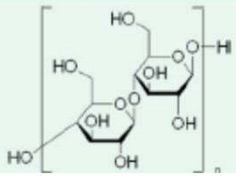
❹ Validation : measurements

1- Knowledge of the waste packages







Polymer	Formula	Use
Polyethylene and derivatives	 PE PP EVA PVAc	Bottles Cables Pipes
Polyamide	 nylon 6-10	Clothes
Polyurethan		Gloves Cable sheath Insulation material
Chlorinated Polymer	 PVC Polyéthylène chlorosulfon (CSPE) Neoprene®	Hot cell sleeves Sheet protection
Fluoropolymer	 PTFE PVDF	Seal (Teflon®, Fluon®, Viton-A®...)
Cellulose		Tissue Absobent paper

PRELOG : Polymère sous Radiolyse pour l'Etude des Lixiviats Organiques et des Gaz

- **Goals**
  - Have a common database used by the partners involved in the management and transport of nuclear waste containing organic compounds.
  - Prediction tool (time evolution, oxydation)
- **Part I : Bibliography (more than 300 publications)**
- **Part II : Completed by experimental work**
  - Gaz production G(X)
  - Small organic compound determination
- **Part III : Prediction tool**
  - Evolution of G(X) with accumulated doses.

2- Experimental data

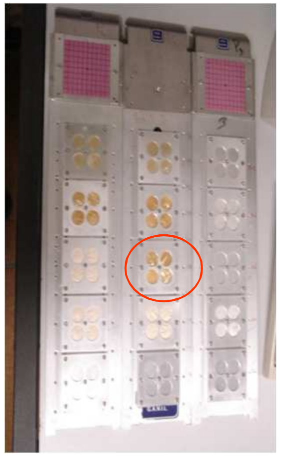
❑ Irradiation experiments

- $G_0(X)$: new material

✓ Gamma radiolysis

source ^{60}Co ou ^{137}Cs DD 1-2 kGy/h, Dose 150-300 kGy.

✓ alpha radiolysis: simulation with heavy ions in Ganil facilities



G_0 insufficient to model the long-term behavior

Evolution G = f(agig)

- Pre-aging material

✓Dose 6-8 MGy

✓Environnement : inert or aerated

✓Formulation : charge effect,

- Temperature

PUR Mapa

PVC Plastunion

❑ caractérisations

- evolution of materials : IRTF,
- gaz quantification : HRMS
- small organic compounds identifications IC, HPLC-MS,,,

2- PRELOG

- **More than 2000 data**
  - **Industrial polymer**
  - **Pure polymer**
  - **Temperature effect**
  - **Dose effect**
  - **Atmosphere (inert ; air)**
  - **…**

- **Output data base**
  - **formulation**
  - **$G(H_2)$ and other gases (CH_4, CO_2,…)**
  - **references**

Step 1: choice of a reference material in the database

46% NORDEL 2722
2% carbon blacks
37% kaolin
5% vulcanizing agents
5% oils implementation
3% stabilizers

Step 2: calculation of G_{max} and G_{min}

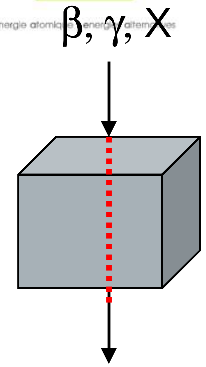
$$G_{max}(H_2) \approx 1{,}2\,10^{-7}\ mol/J$$

$$G_{min}(H_2) \approx 0{,}6\,10^{-7}\ mol/J$$

Cable insulation

PIRELLI
(EVA)

3- Energy deposition



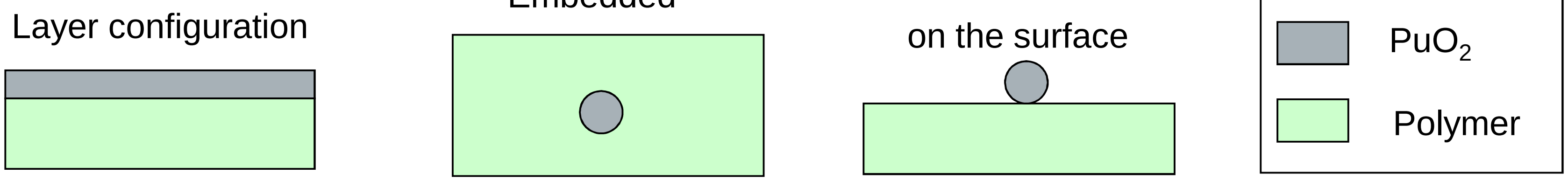
- Energy deposition a
  - type of emitters
  - contact mode

$$V_{gaz}(X) = a\, E_{émise} \times G(X)$$

- gamma , X et (β)
  - ✓ no auto-absorption penetrant radiation a = 1
  - ✓ energy deposition : from 0 to 100%
  - ✓ consideration of the volume of the target

- α
  - ✓Auto-absorption ⇨ code 3DIP
  - ✓Dependant on contact mode
  - ✓Complete energy deposition
  - ✓Consider the surface of the target

Contact mode

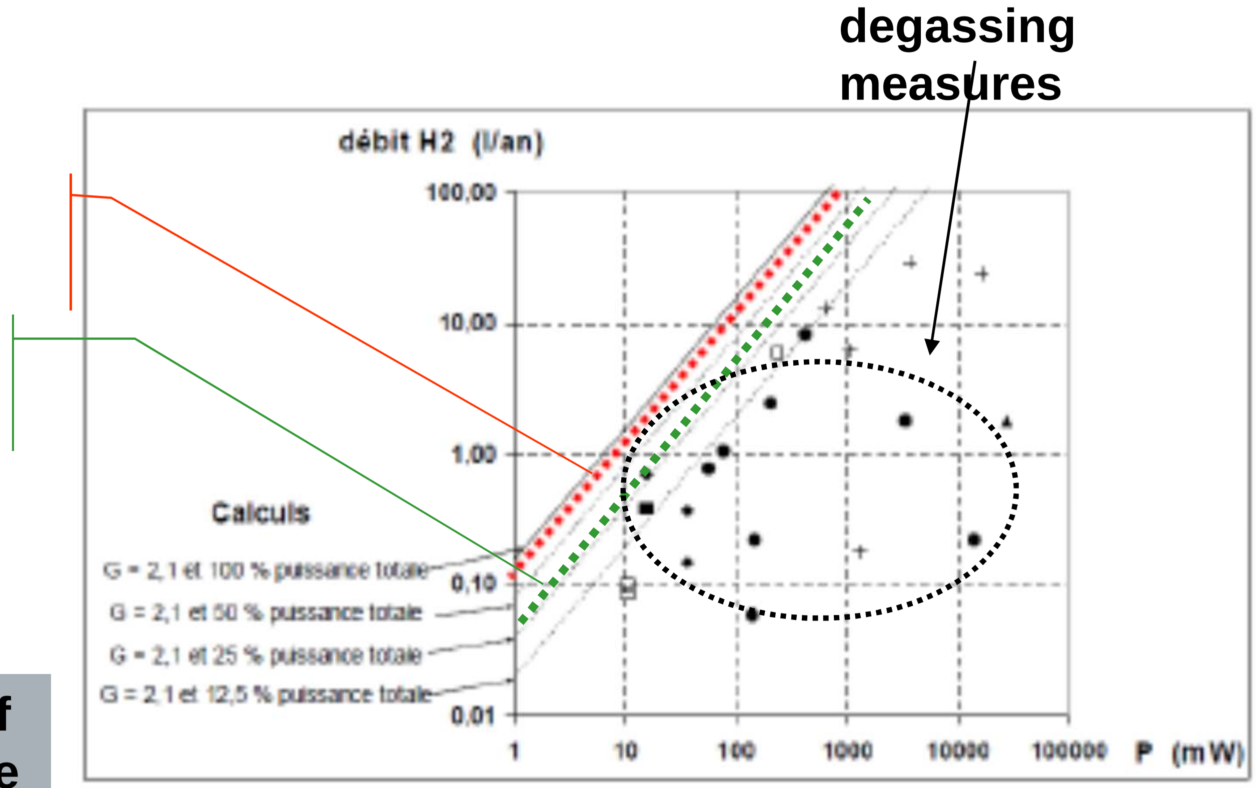


4- Validation

Weight weighting

Surface weighting

Importance of the knowledge of the composition



⇨The model is still conservative but takes into account realistic assumptions.

CONCLUSION

- **Wide range of relevant field**
  - > **Water radiolysis**
  - > **Polymer radiolysis**
  - > **Materials and corrosion**
  - > **Dosimetry**
  - > **…**
- **But also**
  - > **confined spacies**
  - > **hydrated species**
  - > **porous materials**
  - > **…**
- **Need a strong link between basic and applied research**
- **Requires heavy and expensive installations**

Thanks

- **DEN/DISN**
  - Program Reactor Gen II-III
  - Program current back end fuel cycle (ACA)
  - Program future back end fuel cycle (ACF)
  - Basic research (RSTB)
- **DEN-DADN**
  - R&D waste package radiolysis
- **DEN-Department involves in radiolysis topics**
  - DPC basic research and development of operational model (reactor, corrosion, long term behaviour of cement and polymer materials in waste packages, spent fuel pool)
  - DRCP (back end fuel cycle : solvent, nitric acid solution, PuO_2)
  - DTCD (Long term behaviour of bitumen, Ion Exchange Resins, nuclear glasses) with future gammatech facilities
  - DSN (measure on waste packages, instrumented waste packages, integrated experiments) and chicade facilities
  - DTCD (DRSN Labra facilities)
- **IRAMIS - LRAD**
- **The radiolysis network**
- **Our industrial partners**