Approche « durée de vie » d’équipements polymères soumis à la thermo radio oxydation dans les installés dans le bâtiment réacteur des REP du parc français

7 December 2023

Dr. Marc Kuntz, EDF R&D

Content

1. Role and place of the nonmetallic materials in the nuclear industry
2. Specificities of the nuclear sector for SLP of polymers
3. Development of gamma-stabilized polymers
4. Low-aging philosophy
5. Service life prediction for Epoxy Coating
6. International research program

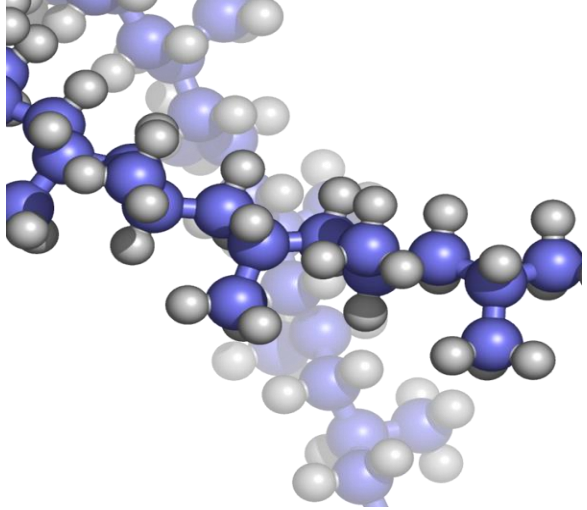
Content

1. Role and place of the nonmetallic materials in the nuclear industry
2. Specificities of the nuclear sector in the SLP
3. Development of gamma-stabilized polymers
4. Low-aging philosophy
5. Service life prediction for Epoxy Coating
6. International research program

Nonmetallic materials in the energy sectors, a game changer!

Has allowed development of new technologies like Wind turbine or hydro turbine

Optimization of business model (solar farm distribution poles)



Yes nonmetallic materials can protect !!

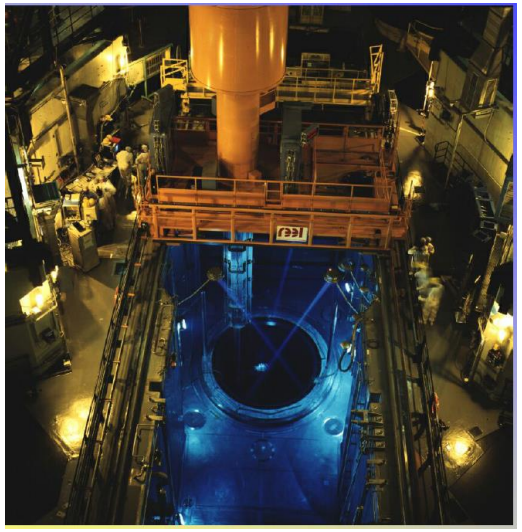
Safety-related !!!

Major functionalities of nuclear polymers

- Corrosion protection
- Fire protection
- Decontamination
- Repair concrete and metal
- Seismic protection
- Water tightness
- Airtightness
- Thermal insulation
- Electrical insulation

Nonmetallic materials and nuclear sector

Composite Floors (Polyepoxy)



Jacket and Insulated Layer for cable (PE, PI, PEEK, PSU)

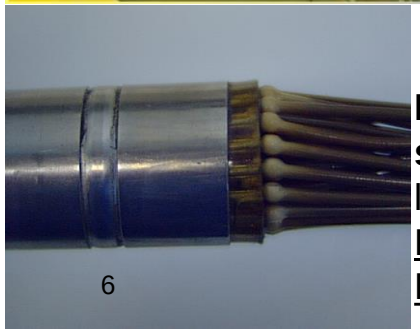
Membranes of pneumatic actuator/ effector Rubber- Polyisoprene, EPDM)

Roof & structure's Coating

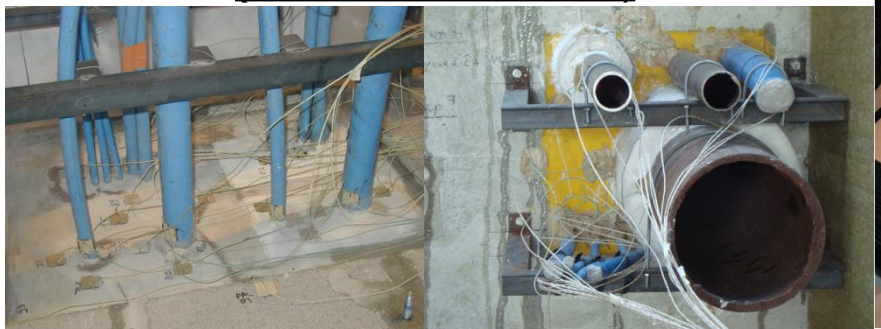
Valves with EPDM seals

Tap washer / gasket (EPDM)

Draught proofing polymer material for fireguard penetration seals (Elastomer and silicone)



Penetration seal Isolated layer, PEEK, PI, Polysulfone



Nonmetallic materials and nuclear sector

HDPE

Pipe's coating, inside and outside (Polyepoxy, PolyUrethane, Polyacrylique)

Cooling tower, condensation system (Polyester-glassfiber)

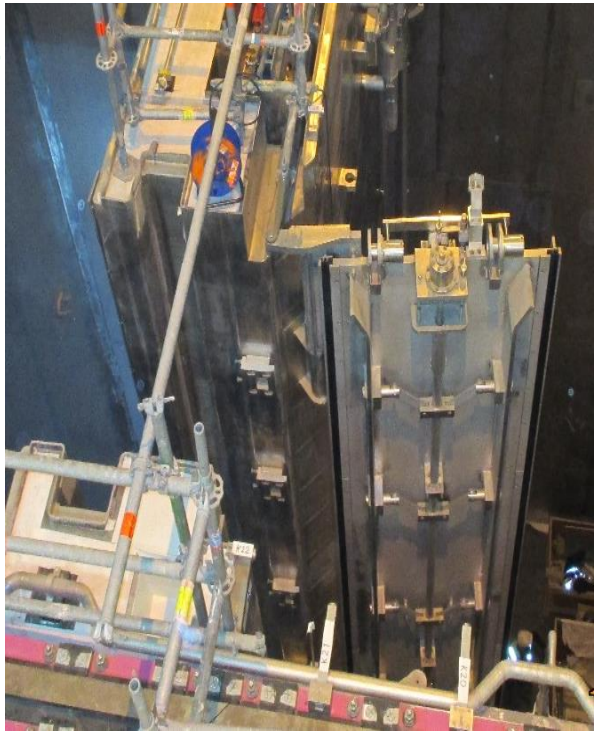
Neoprene, protection liner for pipe

Jacket and Insulated Layer for cable (PE, PVC)

Rubber Expansion joint diaphragm (Polyisoprene)

Rubber dog bone (Polyisoprene)

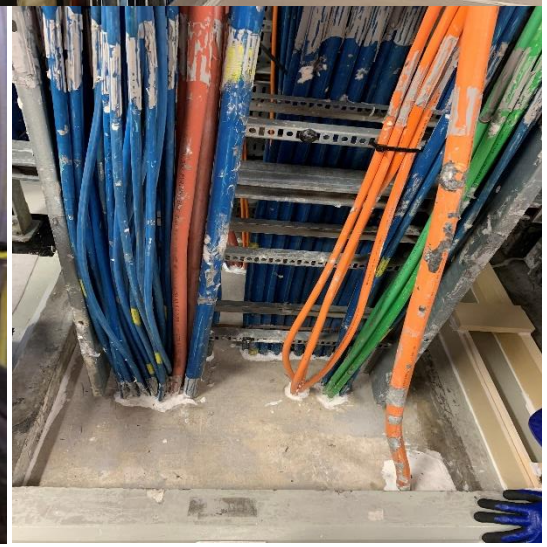
Few ex. of current polymeric projects for new buildings [EDF]



Qualification of the seal of Fla3 cofferdam

UK NPP Evaluation of the compressibility limit of a polymeric backfill (PSE)

Development, qualification and installation of new fireproofing materials (penetration seals and cable ways)



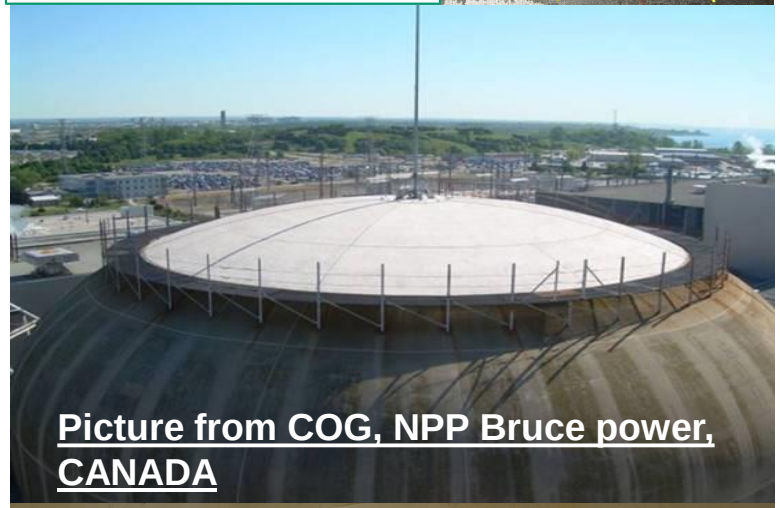
Nonmetallic materials and nuclear sector

- A class of material that is developing in nuclear power, margin for progress
- 5 tones today
- The French nuclear sector gives a good indicator, part has doubled in 25 Years
- Some repairs are only possible with polymers
- **A connection between use of polymers and cost of production for nuclear power**

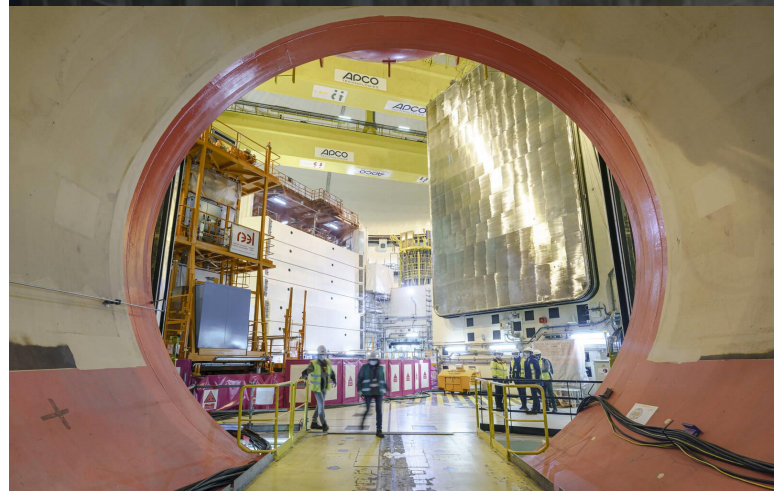
- **On utility' side, polymers needs are real**
  - **New and "Specific" polymers : much more than ever**
    Due to reinforcement of accidental scenario and qualification procedure + polymer-based material have not changed: reduction of operational margin
  - **Key solutions for safe and affordable maintenance**: some maintenance operations are impossible without polymers

STELLANTIS

EDF power plant, DAMPIERRE 2, Cooling tower, damaged area observed – halfway up - Circular composite – carbon epoxy plates -



Picture from COG, NPP Bruce power, CANADA



Content

1. Role and place of the nonmetallic materials in the nuclear industry
2. Specificities of the nuclear sector for SLP of polymers
3. Development of gamma-stabilized polymers
4. Low-aging philosophy
5. Service life prediction for Epoxy Coating
6. International research program

Service life prediction : why do we care about it?

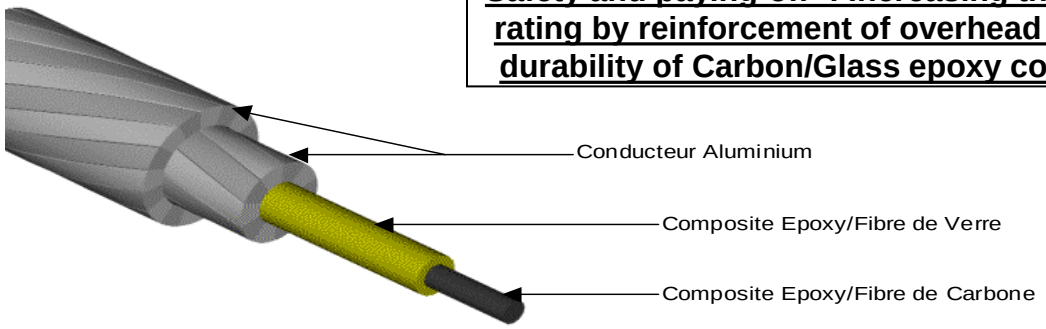
Security of the supply ➔ Capability of water transport in PE Sheath vs thermal ageing

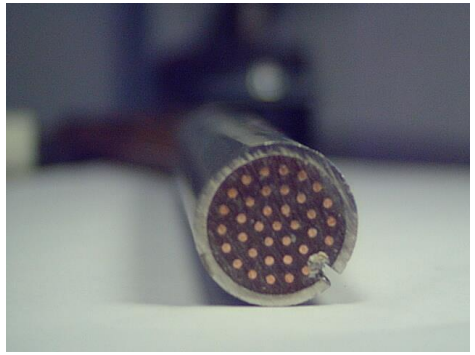
Examples of service life prediction studies dealing with polymer
- **various**
- **input for EDF**

Safety of the reactor and durability of nuclear components ➔ RO

1000 V copper conductor

Safety and paying-off : Increasing the current rating by reinforcement of overhead lines ➔ durability of Carbon/Glass epoxy composite

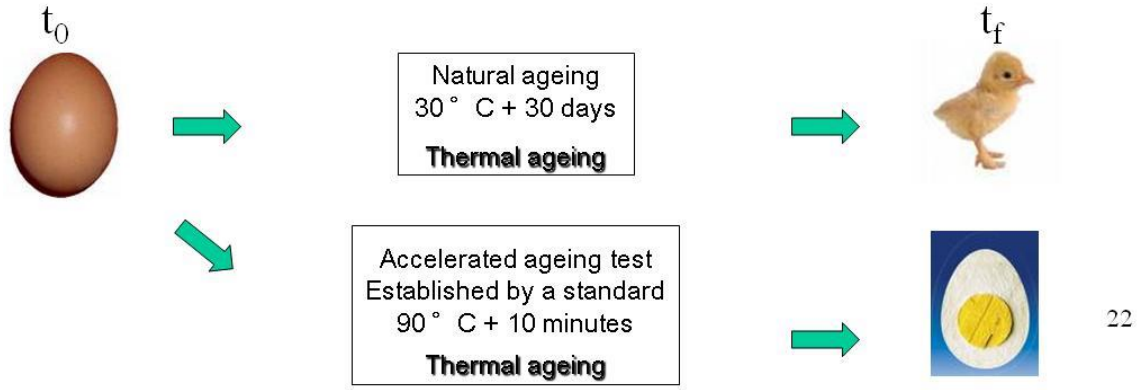


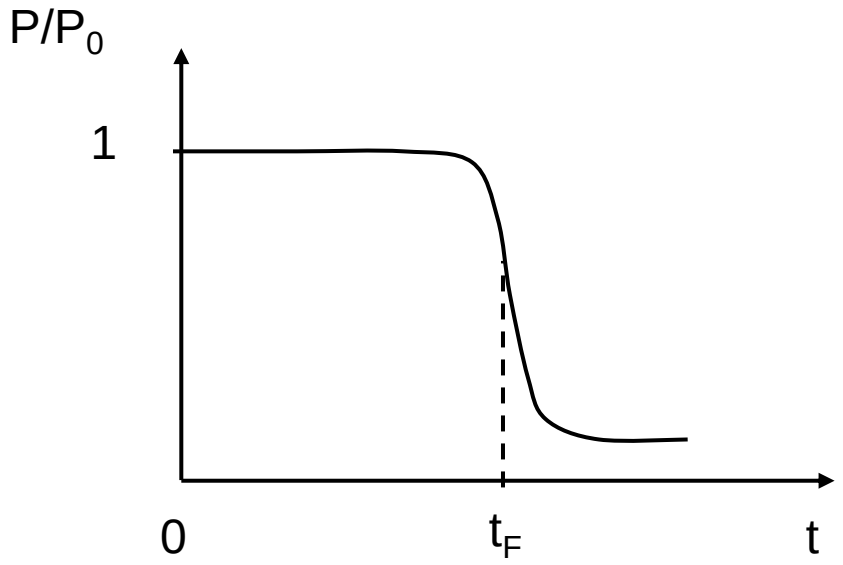


Building penetration

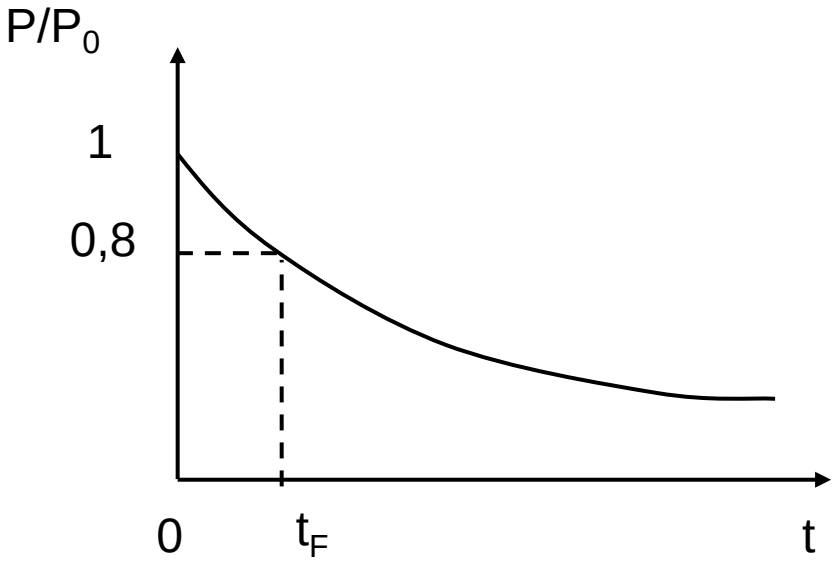
Specificities of the nuclear sector for SLP of polymers

- **Nuclear usage are based on Standards and accelerated testing protocols**





- **Particularly for the nuclear field** :
  - Polymers are the most sensitive to environment
  - Predicting not only the in-service durability but also the behavior during an accident + taking into consideration the cumulative effect of the service degradation and its possible contribution to decrease properties and functionalities
  - No code, no standard, no method available for determining such a duration
  - Definition of the threshold value
  - Industrial feedback provides input for SLP



Specificities of the nuclear sector for SLP of polymers

- Ageing ? Slow and irreversible change due to in-service conditions of the chemical structure, the morphology or the formulation because of its own instability or environmental effects.
- Physical ageing, when the environment changes the formulation of the polymer and so M = constant.
  - Formulation change (Loss of adjuvant, solvent)
  - Percolation and migration of fillers
  - Structural relaxation
  - Absorption of solvent (organic and inorganic)
  - Fatigue
- Chemical ageing when the environment reacts with the polymer and so modifies its M
  - Thermal degradation (thermo oxidation, thermolyse)
  - Radiative degradation (radio oxidation, radiolyse, photo oxidation)
  - Electrical
  - Interaction with chemistry of the medium (pH, Cl-, Cu+, Cu++, …..)
  - Bio degradation
- Combined ageing
  - Thermo and radio [inside the containment]
  - Thermo, hydro and electrical leading to water trees development ? [isolated layer of underground cable]
  - Fatigue et thermal degradation [valve gasket, ….]
  - ……

Specificities of the nuclear sector for SLP of polymers

« Nuclear » polymers are submitted to radio and thermo oxidation inside the containment

Radio oxidation

Radiative exposure is a high energy process, the conferred energy is 10 times higher than covalent bond energy

Depositing is randomly. Scission and radicalar process

Degradation is limited by the oxygen diffusion into the material otherwise radiolyse

Thermo oxidation

Thermal degradation of polymers is molecular deterioration as a result of heating. It can occur at room temperature but slowly.

Scission and radicalar process

Basic Scheme of oxidation for Polyolefine (PE, PP, PS)

Initiation	Polymer	→	$R^{\cdot}$
Propagation	$R^{\cdot} + O_2$	→	$RO_2^{\cdot}$
	$RO^{\cdot} + RH$	→	$ROOH + R^{\cdot}$
Bimolecular termination	$R^{\cdot} + R$	→	Products
	$RO_2^{\cdot} + R$	→	Products
	$RO_2^{\cdot} + RO_2$	→	Products
Unimolecular termination	$RO_2^{\cdot}$	→	Products
	$R^{\cdot}$	→	Products

Chain Branching Reactions from Hydroperoxides - ROOH			
	ROOH	→	$RO^{\cdot} + OH^{\cdot}$
	$OH^{\cdot} + RH$	→	H2O + $R^{\cdot}$
	$RO^{\cdot} + RH$	→	ROH + $R^{\cdot}$

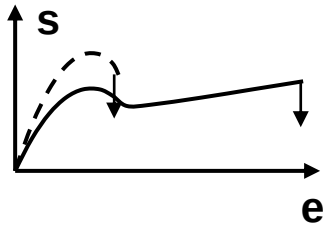
Czechoslovak Journal of Physics, Vol. 49(1999), Suppl. S1

Specificities of the nuclear sector for SLP of polymers

Effect of the ageing type on mechanical properties
Examples : stress- strain curves

Physical Ageing (amorphous thermoplastic)

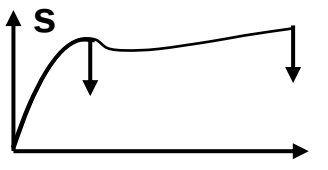
(structural relaxation) $T < T_g$



M = cte

Chemical ageing by chain scissions

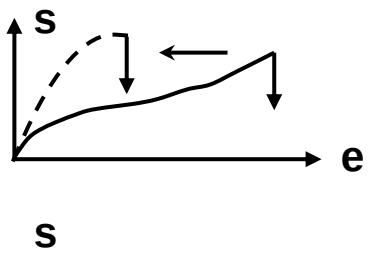
(semi-crystalline)



M ↘

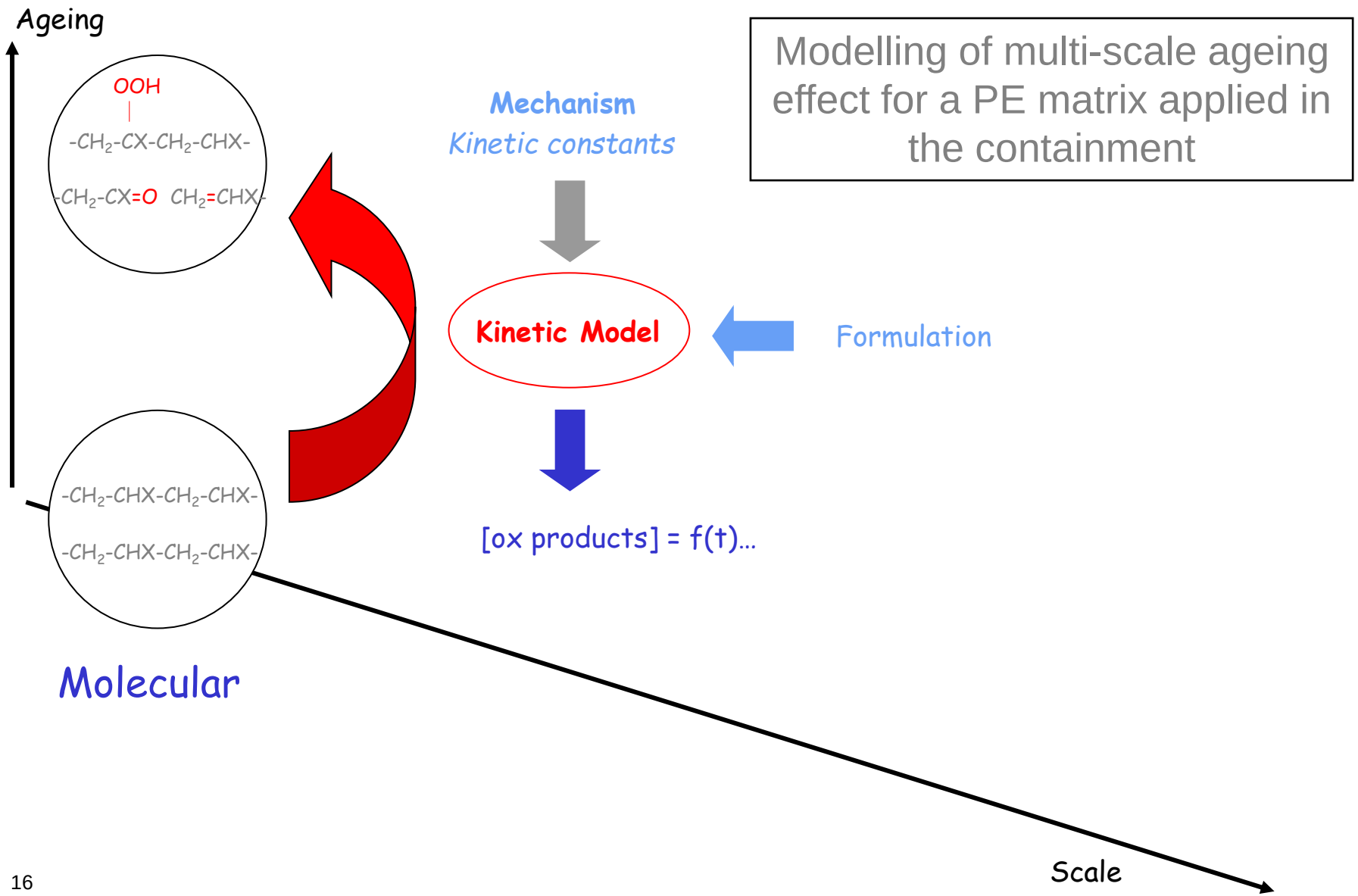
Chemical ageing by crosslinking

(elastomer)



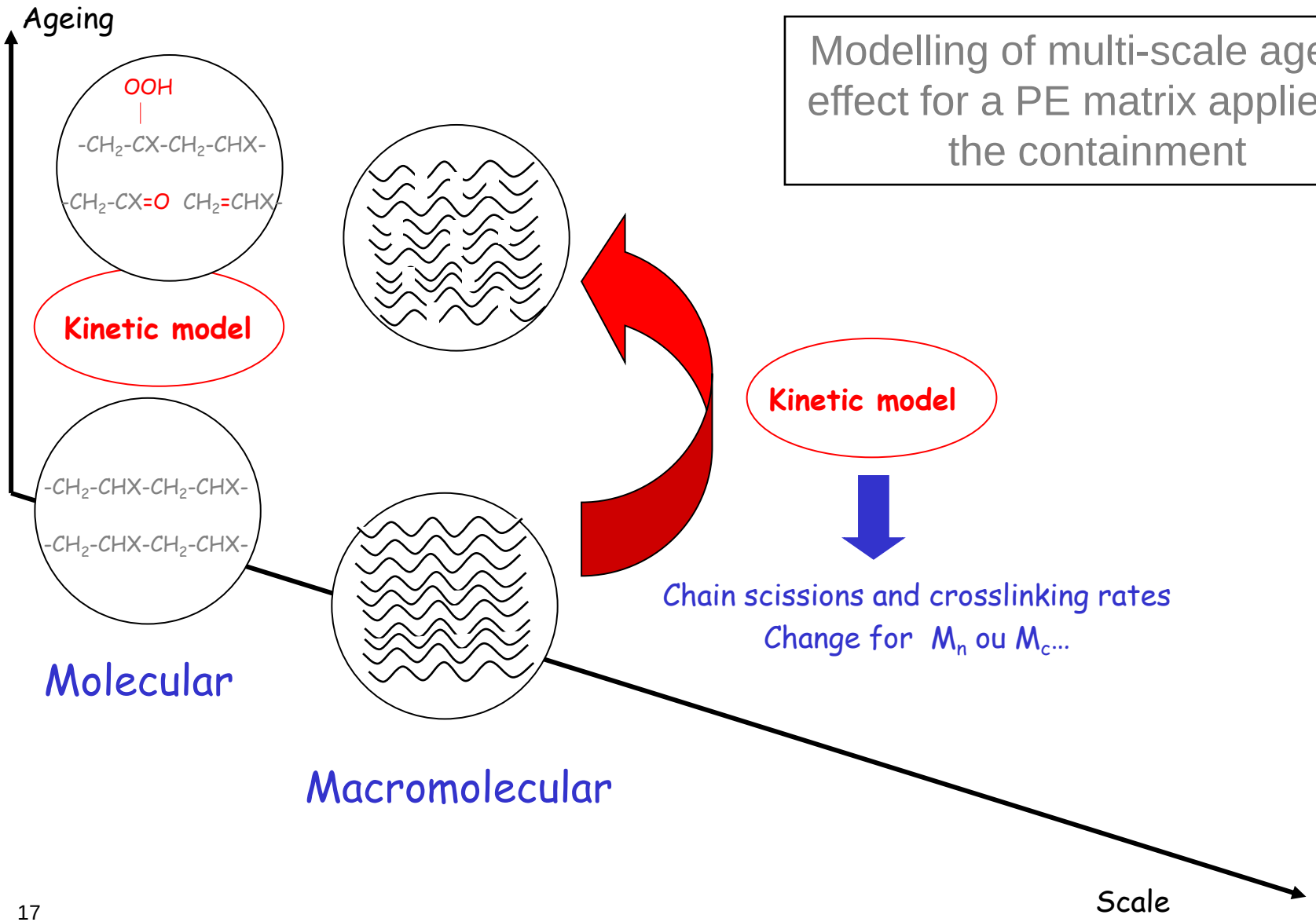
M ↗

Specificities of the nuclear sector for SLP of polymers

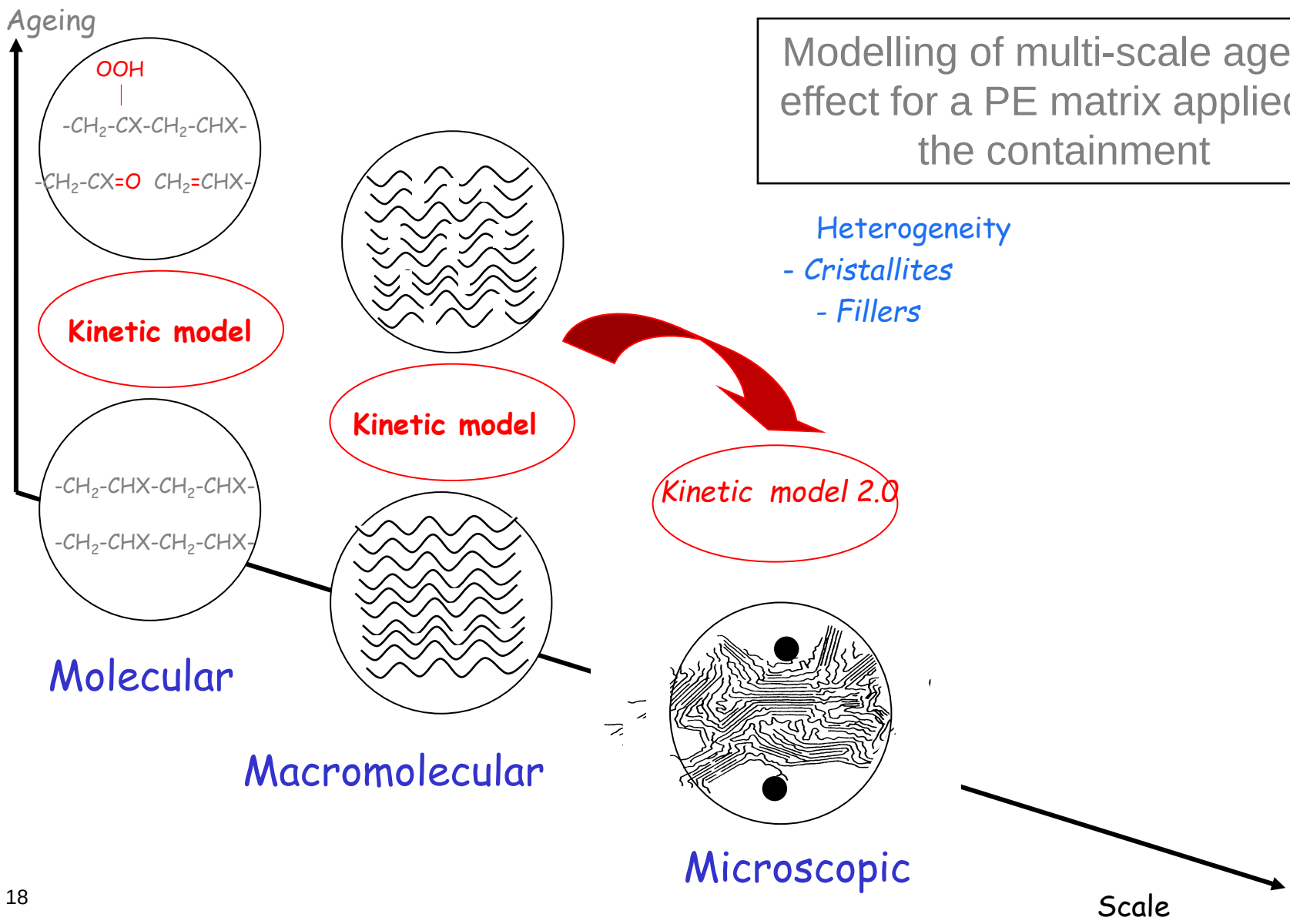


Modelling of multi-scale ageing effect for a PE matrix applied in the containment

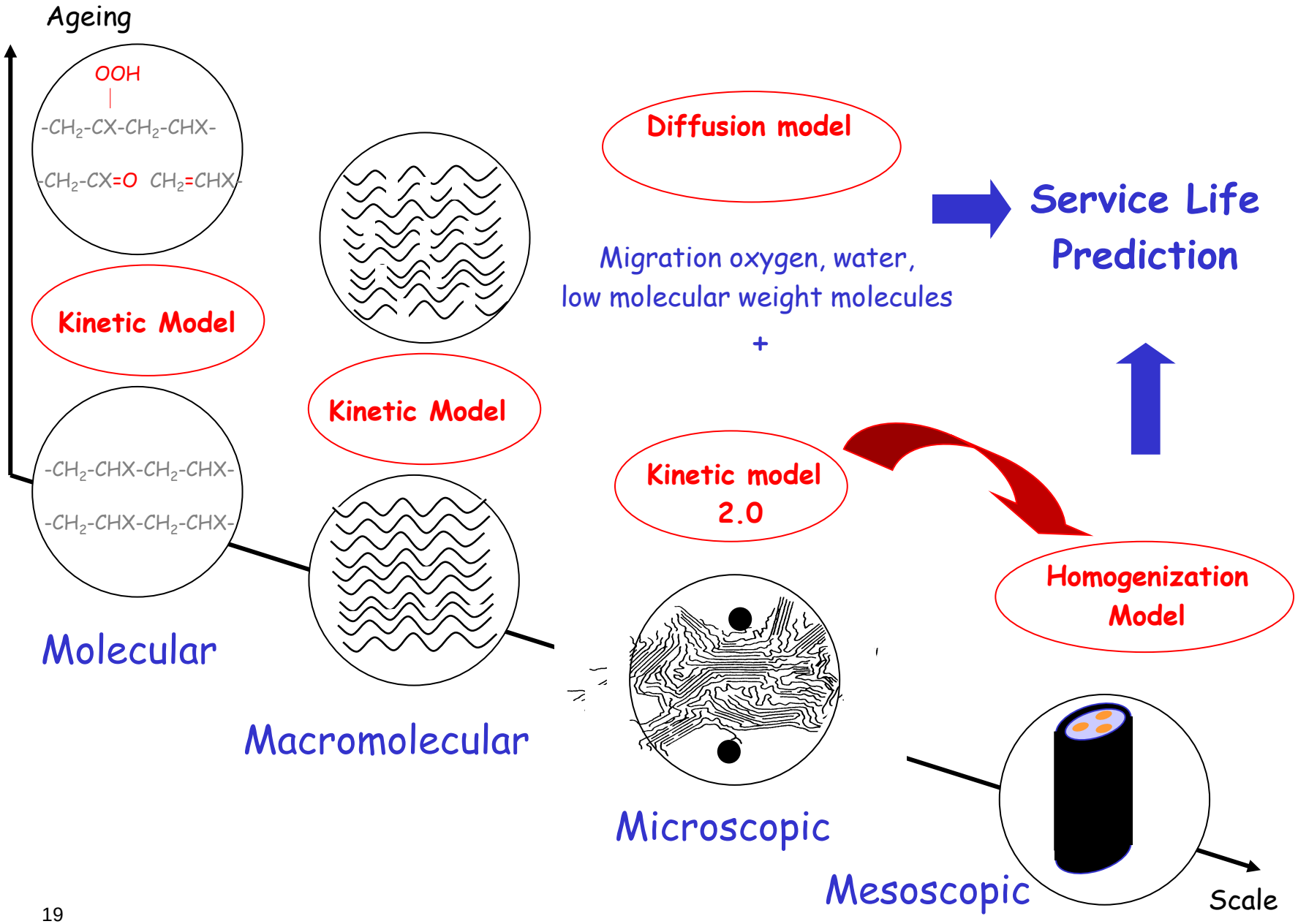
Specificities of the nuclear sector for SLP of polymers



Specificities of the nuclear sector for SLP of polymers



Specificities of the nuclear sector for SLP of polymers



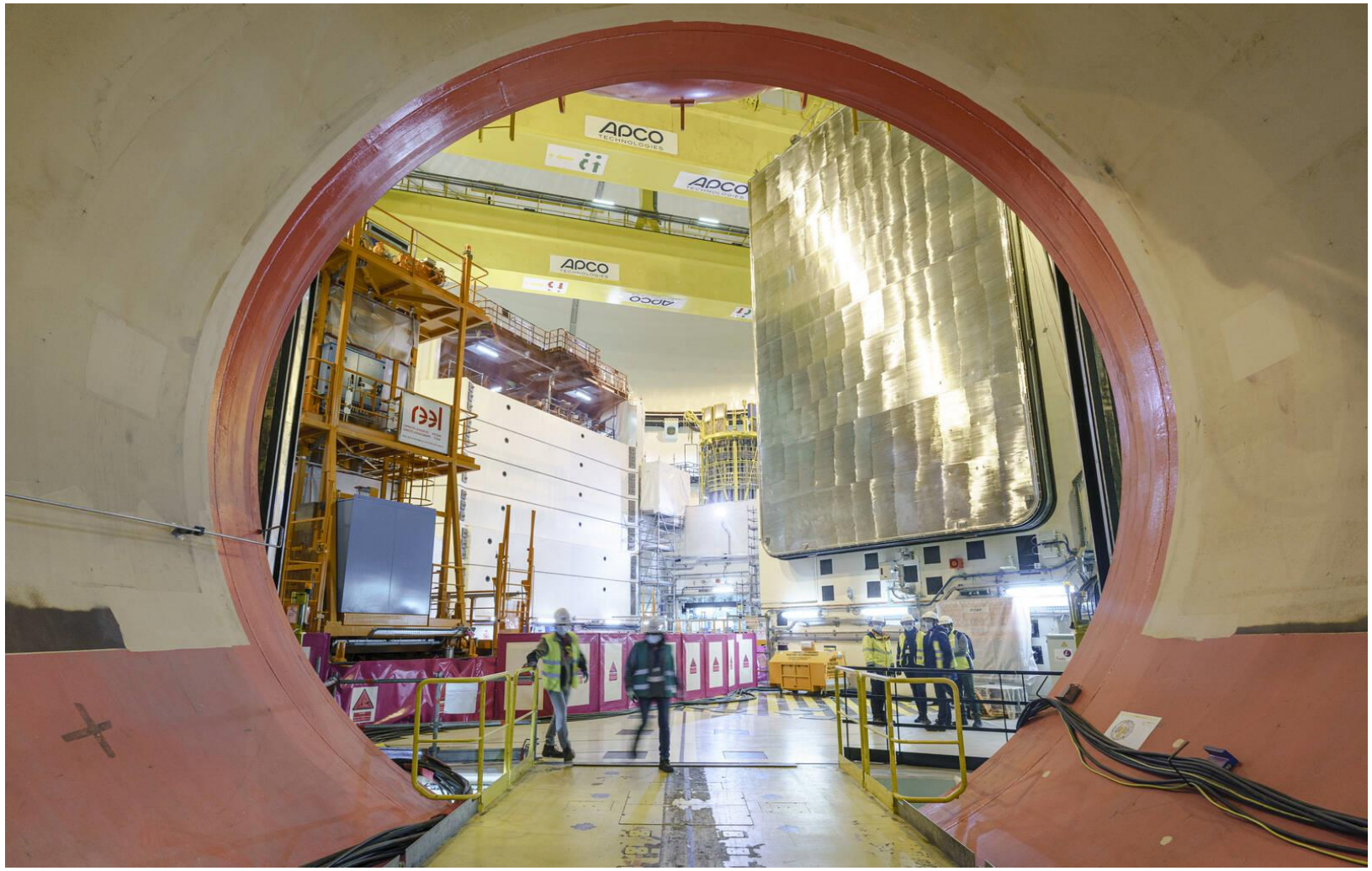
Assessment of EDF knowledge

Polymer	Component / installation	Mechanism under radiation oxidation	Mechanism under thermo hydro (chlorinated water)	Identification of ageing tracers	Threshold value for modeling SLP
Epoxy	Coating, floor, concrete repair	x		x	Chemical
PE/EPDM	Cable	x		x	Physico-chemical (Molecular weight)
Neoprene	Shock absorber, diaphragm	x		x	
Silicone	Shock absorber, diaphragm	x		x	Chemical
HDPE	Piping		x	x	Oxidized layer

Content

1. Role and place of the nonmetallic materials in the nuclear industry
2. Specificities of the nuclear sector for SLP of polymers
3. Development of gamma-stabilized polymers
4. Low-aging philosophy
5. Service life prediction for Epoxy Coating
6. Service life prediction for Nuclear cables
7. International research program

Development of a gamma-stabilized Silicone (PDMS)



Context

- Gasket of the hatch
- PDMS
- Qualified NFT30-900
- 20-30 years of longevity

Means

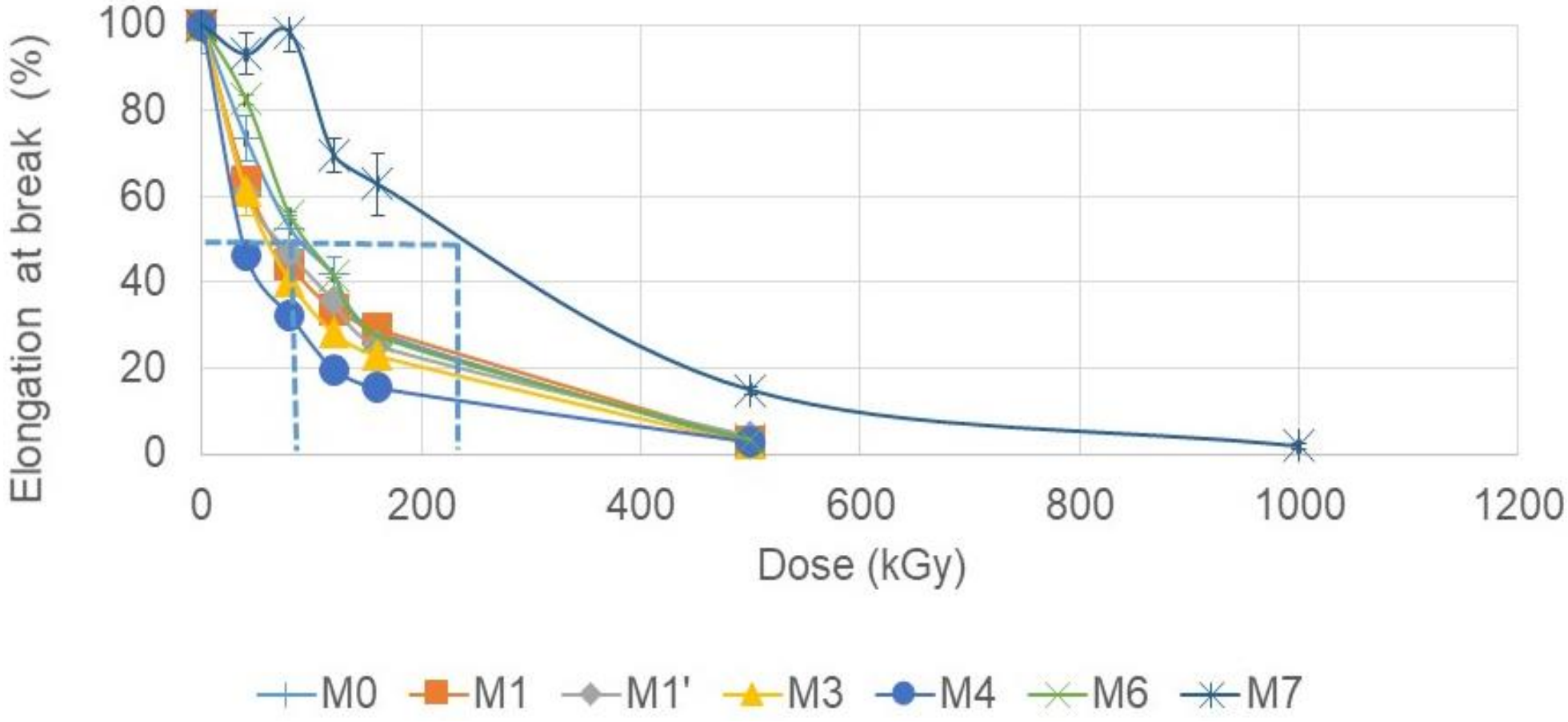
- Shielding
- Radicals trapping
- Other [formation of a copolymer whose chain cutting acts and crosslinking acts would be balanced within the irradiated material]

Requisite

- Strategie: slight change of the formulation in avoiding requalification
- Done with suppliers

Development of a gamma-stabilized Silicone (PDMS)

Traction uniaxiale (valeurs normalisées)



Content

1. Role and place of the nonmetallic materials in the nuclear industry
2. Specificities of the nuclear sector for SLP of polymers
3. Development of gamma-stabilized polymers
4. Low-aging philosophy
5. Service life prediction for Epoxy Coating
6. Service life prediction for Nuclear cables
7. International research program

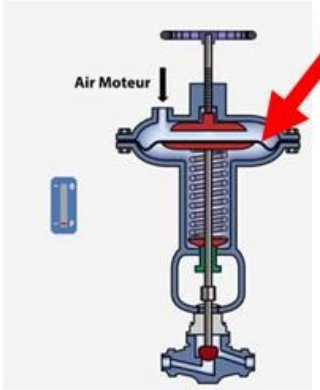
Low ageing approach for the extension of the service life of nuclear elastomers

- Elastomers are widely involved in nuclear installations
- Service conditions produce ageing effects and reduce longevity however additional margin exists. In this sense, this deliverable has been proposed.
- Contributors: COG, EPRI, FRAMATOME, CNNC/CNPO, EDF,

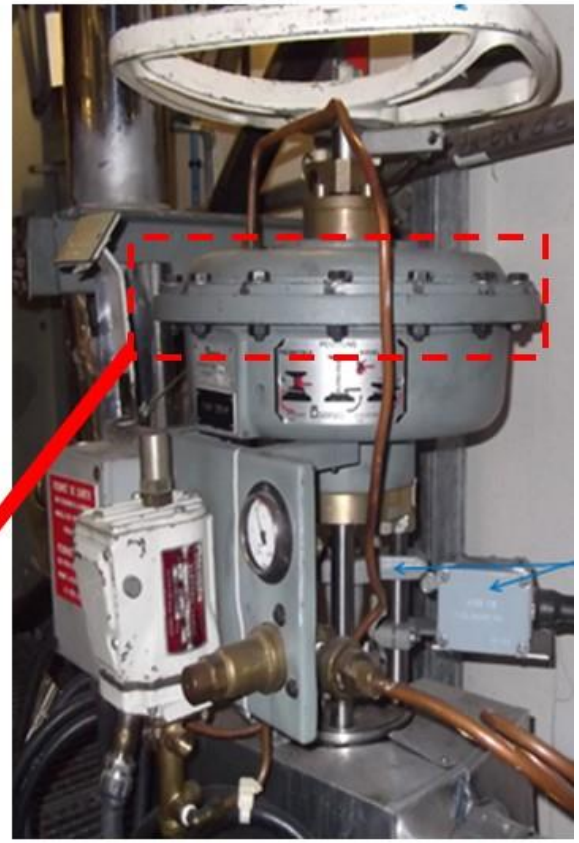
Application

Industrial case	Pneumatic valve actuator diaphragm (SEREG)
Operating mode	Use of air pressure to operate the valve
Qualification procedure	K3AD (EDF procedure) ASTM C1068 - 15

Main operating air leaks identified

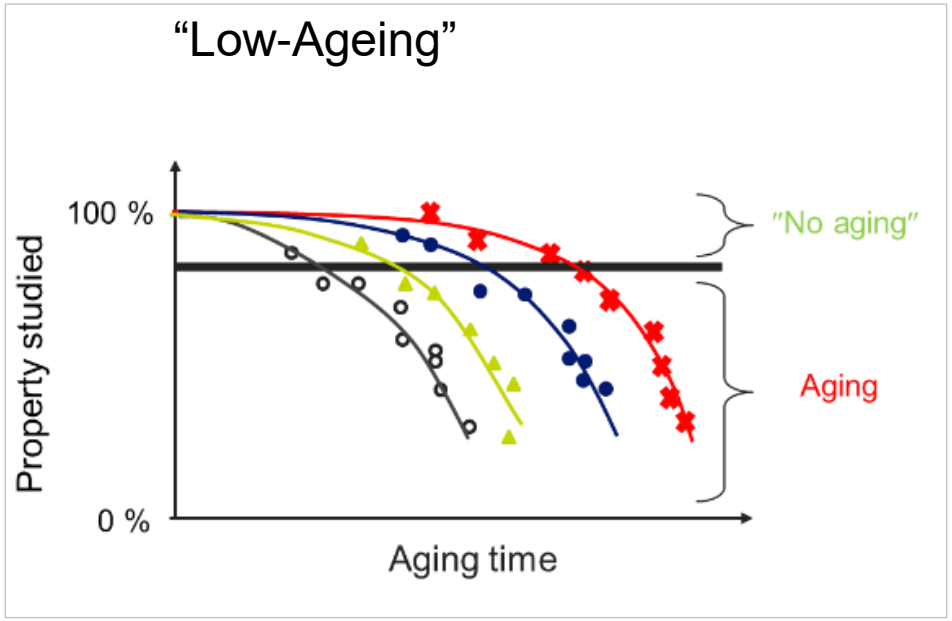


Operating mode



Low ageing approach for the extension of the service life of nuclear elastomers

How to justify service time increase?



Do Lab tests to chase no ageing indicator

Scale	Property / feature	Method	Criteria		Extra Time if all criteria are fulfilled
Molecular scale	Oxydation products C=O	IRTF	C1	$[CO]_t = 0$ or $[CO]_i$	**Extension →**
	Oxidative induction time (OIT)	DSC	C2	OIT ≥ 5 minutes	**½ time already spent in service**
Macromolecular scale	Crosslinking rate (X) Scission rate (S)	Swelling	C3	X = ± 10 % of initial value	**Max 6 years**
			C4	S = ± 10 % of initial value	**Then set up**
Macroscopic scale	Elongation at break	Tensile test	C5	$e_{R\,nom}$ ± 25 % of initial value	**Case 1 for 3 years**
	E-Modulus		C6	E = ± 25 % of initial value	**Or**
	Shore hardness	Indenter	C7	Value = ± 10% of initial value	**Case 2 For ½ time or 6 years**

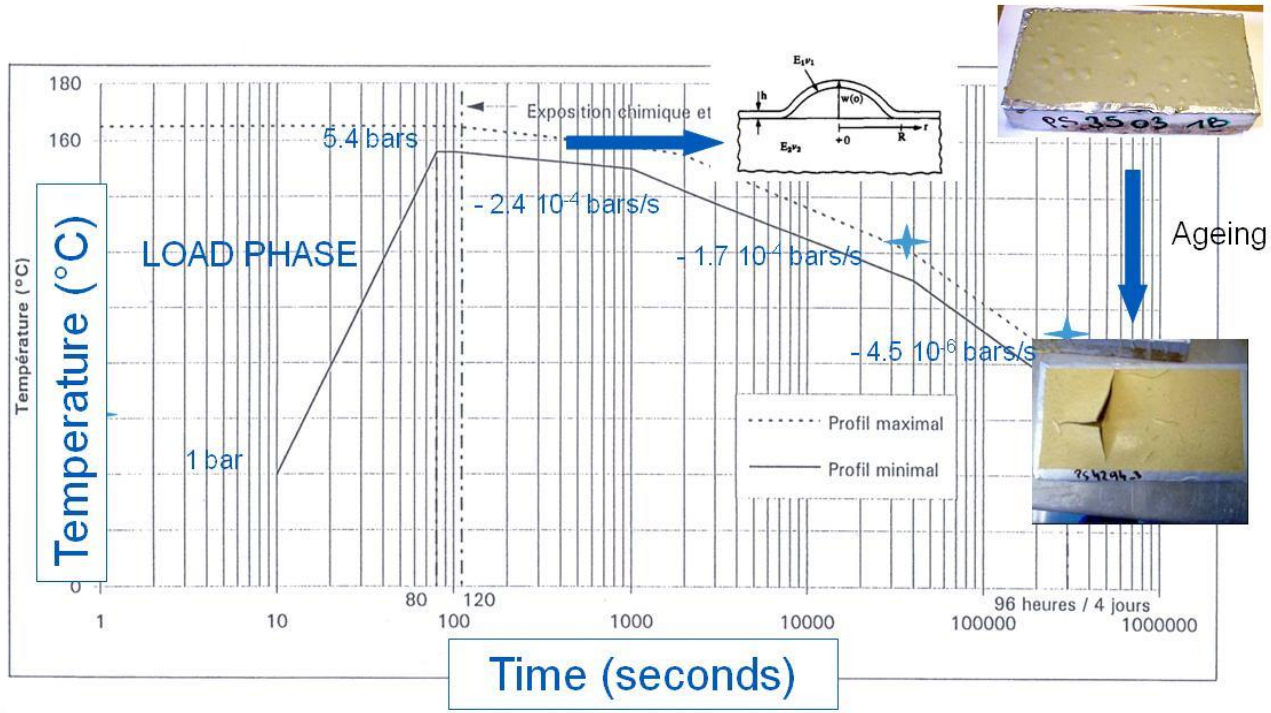
Content

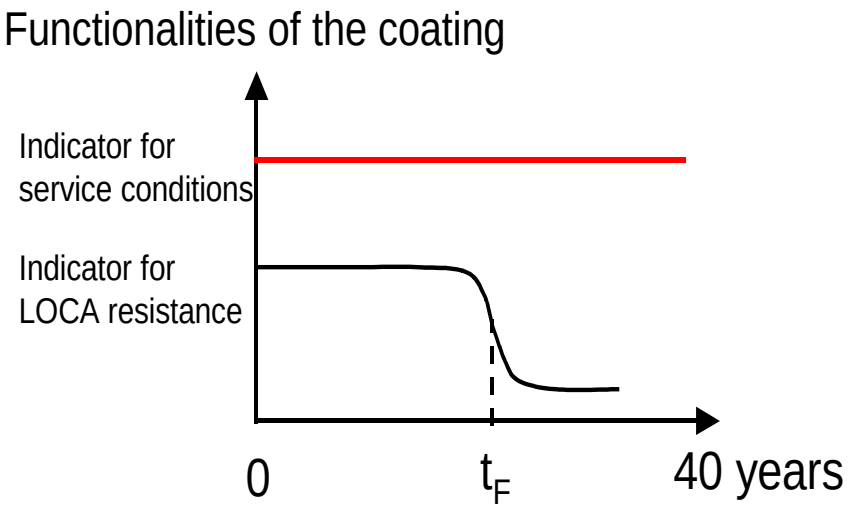
1. Role and place of the nonmetallic materials in the nuclear industry
2. Specificities of the nuclear sector for SLP of polymers
3. Development of gamma-stabilized polymers
4. Low-aging philosophy
5. Service life prediction for Epoxy Coating
6. International research program

SL1 Nuclear Coatings

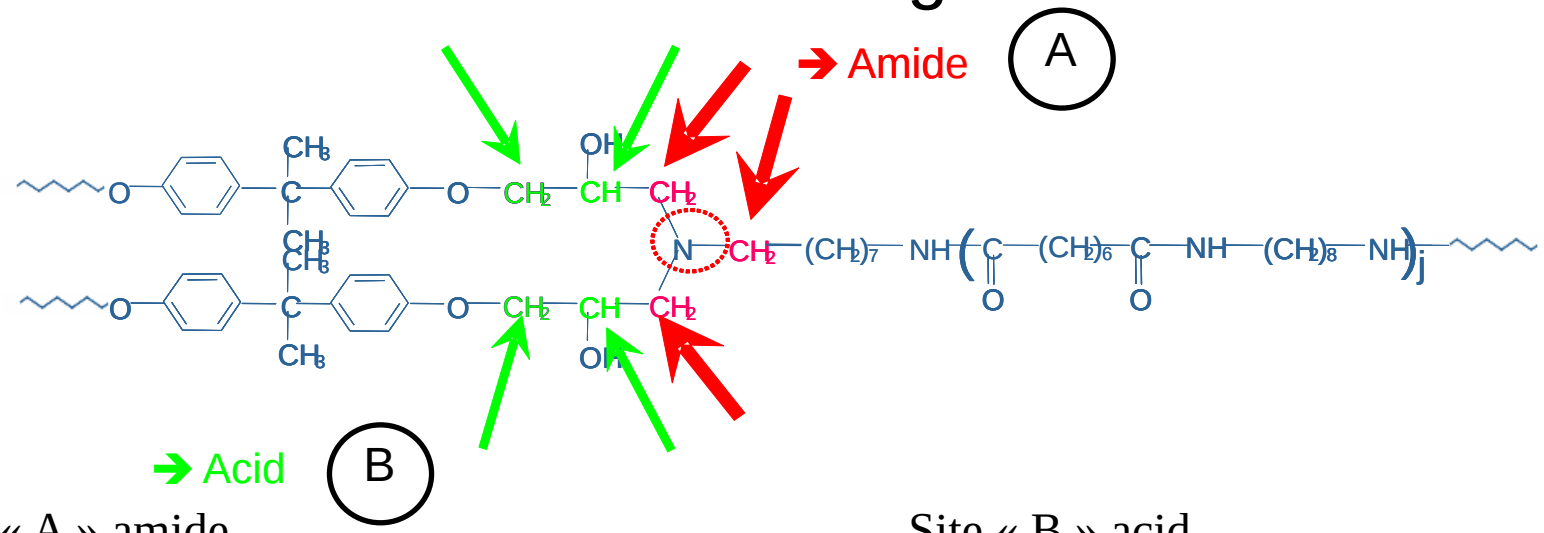
- **EDF has SL1 qualified coatings for steel and concrete applications**
- **Follow-up procedure performed on coupons**
- **Some coatings have shown a LOCA resistance change during follow-up : service conditions considered as non degrading conditions but some coatings exceed end-of-life criterion during follow-up procedure by LOCA performed on coupon (20-25 years).**
- **Effect of service aging or bad preparation of the coupons?**

What happens to the coating to explain this behaviour change during LOCA?





SL1 Nuclear Coatings



Site « A » amide

$P_aOOH \rightarrow 2P_a^\circ + P{=}O + s$ k_{ua}

$P_a^\circ + O_2 \rightarrow P_aOO^\circ$ k_{2a}

$P_aOO^\circ + P_aH \rightarrow P_aOOH + P_a^\circ$ k_{3a}

$P_a^\circ + P_a^\circ \rightarrow$ produits inactifs k_{4a}

$P_a^\circ + P_aOO^\circ \rightarrow$ produits inactifs k_{5a}

$P_aOO^\circ + P_aOO^\circ \rightarrow$ amides k_{6a}

Site « B » acid

$P_bOOH \rightarrow 2P_b^\circ + P{=}O + s$ k_{ub}

$P_b^\circ + O_2 \rightarrow P_bOO^\circ$ k_{2b}

$P_bOO^\circ + P_bH \rightarrow P_bOOH + P_b^\circ$ k_{3b}

$P_b^\circ + P_b^\circ \rightarrow$ produits inactifs k_{4b}

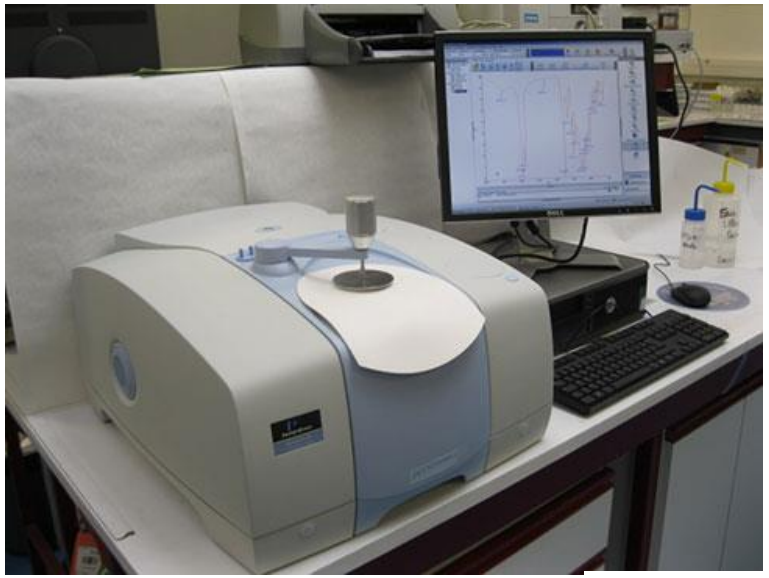
$P_b^\circ + P_bOO^\circ \rightarrow$ produits inactifs k_{5b}

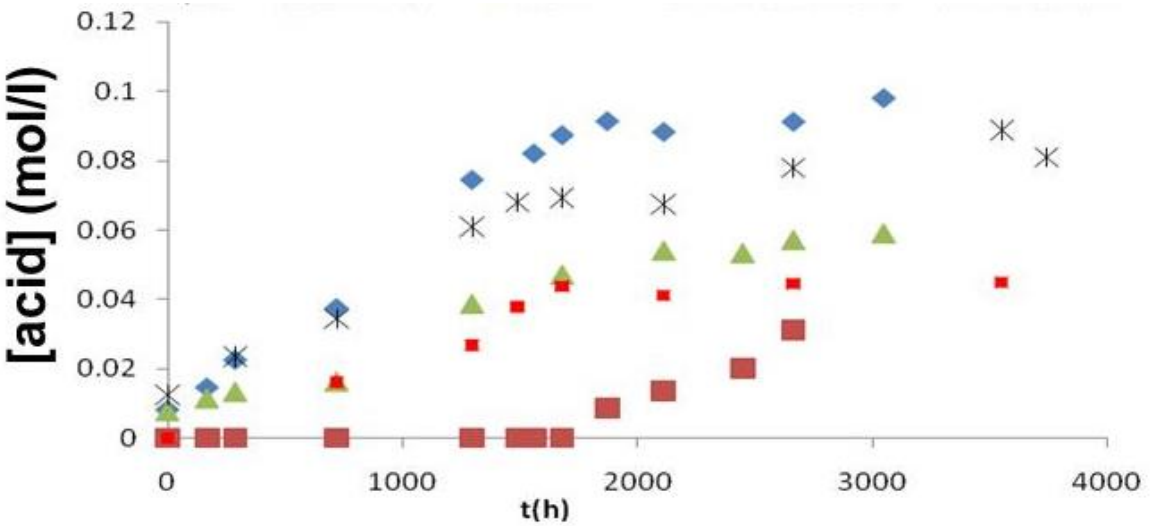
$P_bOO^\circ + P_bOO^\circ \rightarrow$ acides k_{6b}

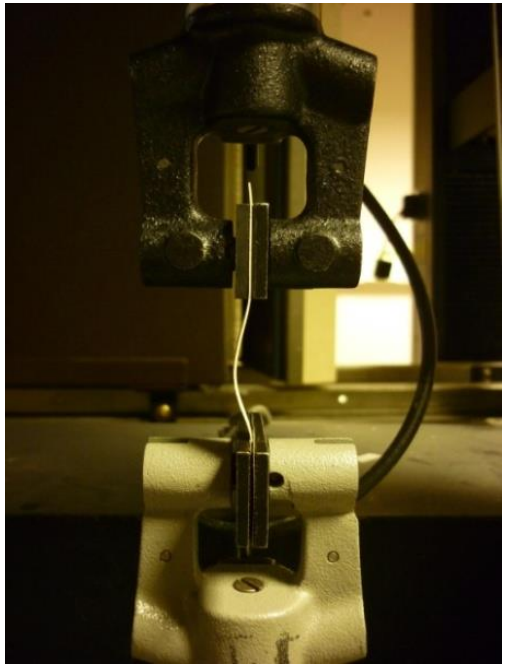
Assessment of each kinetic rates from experimental data

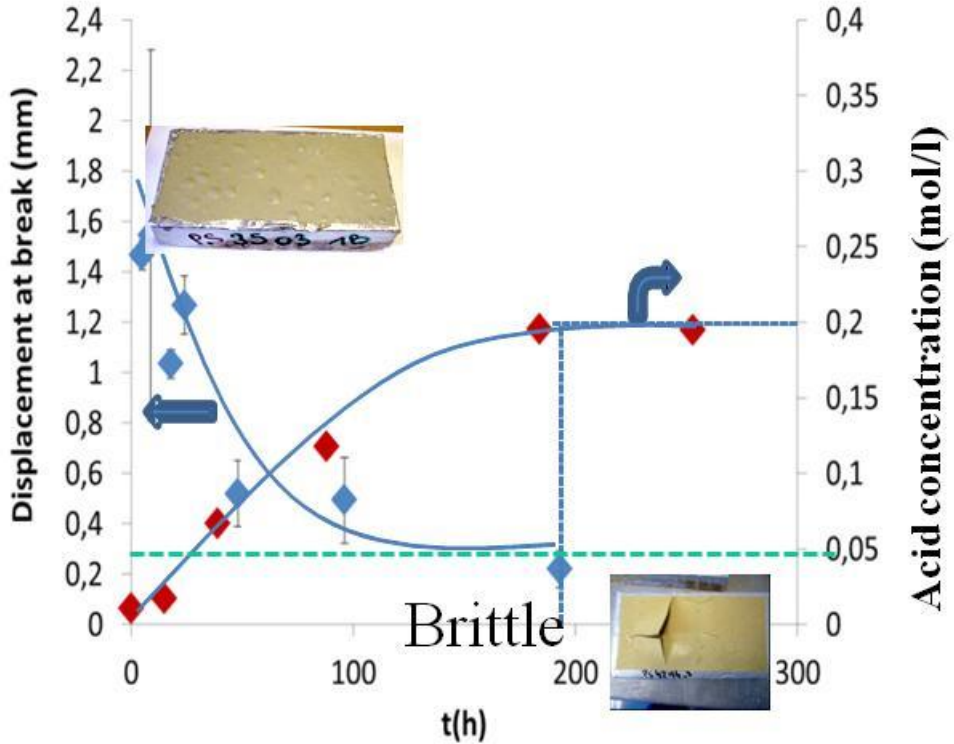
EPOXY COATING	k1	k3	k6
E (kJ)	150	61,3	40
70 ° C	2.06*10^(-6)	0.01	388
110° C	10^(-5)	0.16	0.4*10^4
150° C	0.0042	0.72	10^5

SL1 Nuclear Coatings









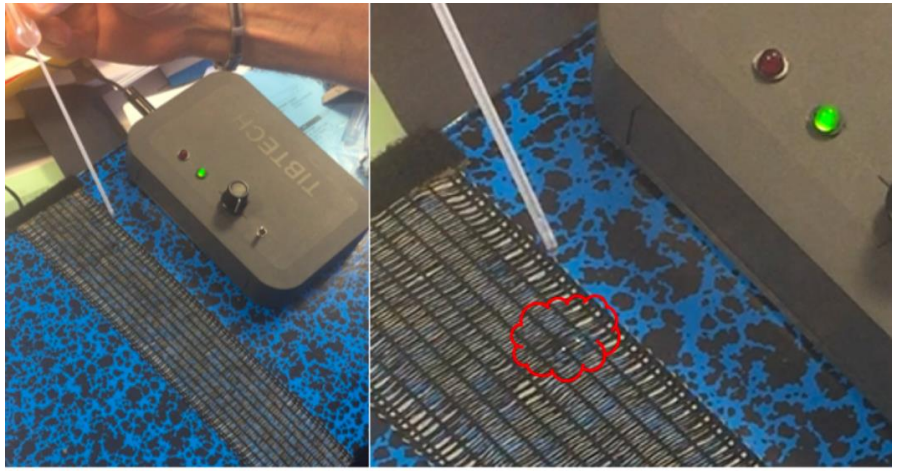
Nuclear coating systems	1	2	3	
Nuclear coatings	2-coat	2-coat	Coat 1	Coat 2
Exposure conditions	In-service life (years)			
25 °C & 0.1 Gy/h (in-service at the floor)	48	58	48	66

Content

1. Role and place of the nonmetallic materials in the nuclear industry
2. Specificities of the nuclear sector for SLP of polymers
3. Development of gamma-stabilized polymers
4. Low-aging philosophy
5. Service life prediction for Epoxy Coating
6. International research program

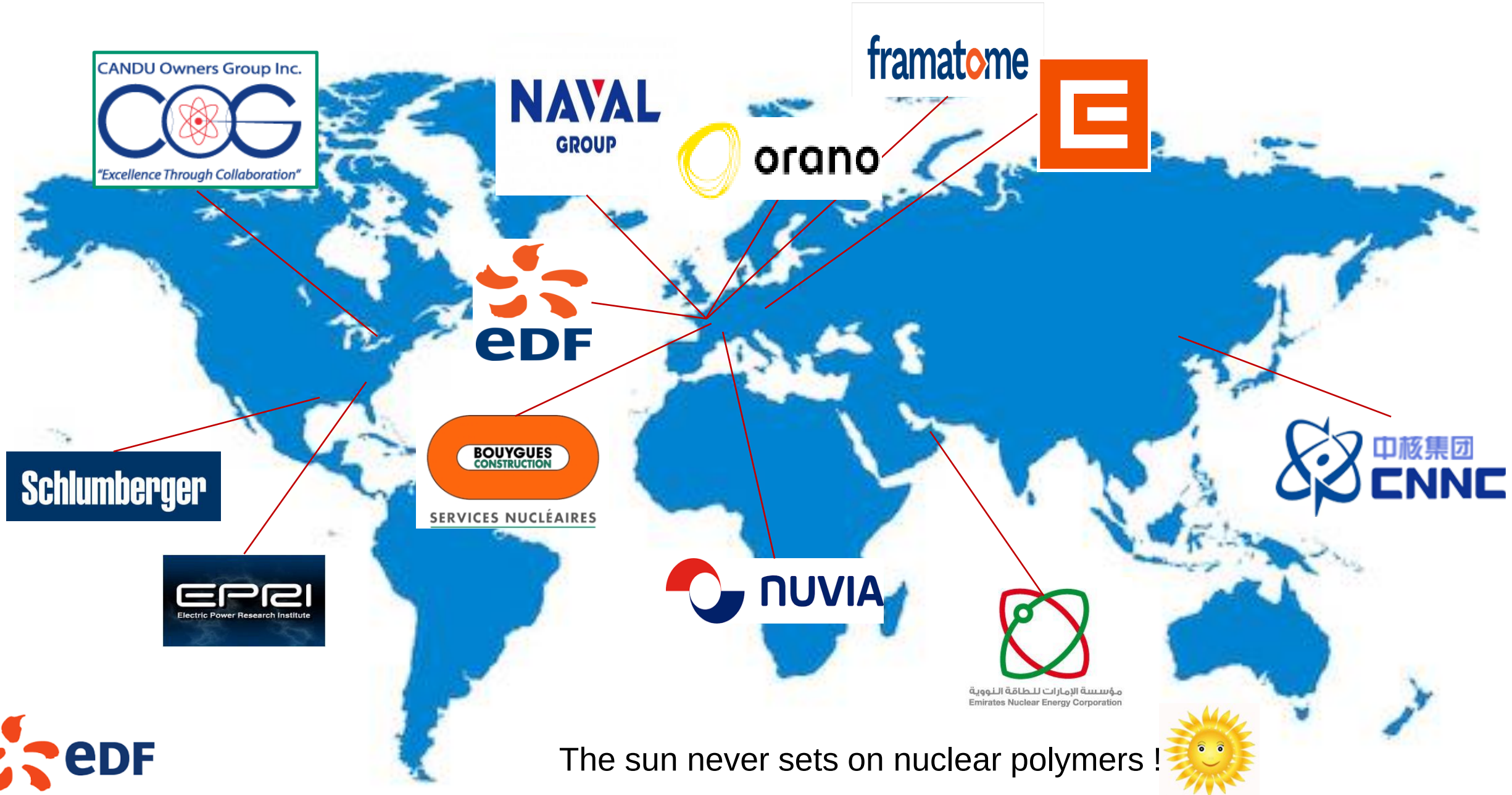
MEGAPOOL

Formalism and Outcomes for members, 4 ways to generate value



- **Capitalization of know-how: extension of use**
- **Innovation: emergency repair, leak detection with tape:**
- **Benchmark: test of several decon solution, test of fireproofing materials**
- **Bibliographic research: composite in the nuclear sector, geopolymer applications**

Members & Partners



EDF

The sun never sets on nuclear polymers !

Membres & Partners

MEGAPOOL

orano

[2022-2025] Research Program

Topics	Section	Scope / target	Type of study	Expected outcomes
D1+. Aging of nuclear elastomers	LTO	Justification of service life extension of nuclear elastomers	Experimental work based on component testing “in-service requalification”	Guideline to get more than 10 years of extra time in service
D2+. Underwater emergency repair	SAFETY	Repairing from the surface a leak of the floor that overpasses the drainage system, fast and efficiency Seismic or fallen objects (used fuel containers)	Experimental development in full scale pool	Having a proven solution at disposal, knowing limitations, knowing how to industrialize
D3+. Superhydrophobic surface engineering	LTO (Performance of the plant)	Improving functioning Durability of solution	Survey, tests of solution	Benchmark of solutions
WP2. NDE	LTO	Evaluation of applicability of several technics for follow-up ageing polymers (55 aged materials) Thz, indenter, light emitting, hyperspectral imaging	Experimental work	Round robin; knowledge
WP3. Fire	SAFETY	Inventory of fireproofing material applications and expected level of performance. Comparative fire testing Development of new applications, possibly fire upgrade of existing polymers and composites	Survey, comparative tests, prospective new applications	Round robin; knowledge

[2022-2025] Research program

Topics	Section	Scope	Type of study	Expected results
WP4. Composite applications	LTO	Compilation of composite repairs realized and existing composite applications for all nuclear power plant designs New applications investigations	Survey and bibliographic study	Knowledge, Feedback of the nuclear sector, prospective new applications
WP5. Gamma stabilized polymers	LTO	Formulation of a gamma-stabilized elastomeric grade for nuclear application Test of the gamma-stabilized elastomeric grade to evaluate gain	Survey, bibliographic study, test	One grade of elastomer gamma stabilized in accordance with existing application- proven gain
WP6. Beta stabilized polymers	LTO	Formulation of beta-stabilized polymers for nuclear applications Test of the beta stabilized polymer grade defined in task 1	Survey, bibliographic study, test	One grade of elastomer beta stabilized in accordance with existing application-proven gain
WP8. Decon polymeric process	LTO	Test of commercial solutions for 3 applications Development of new applications of strippable coating for Megapol2 members	Survey, test and prospective new applications	Benchmark of solutions, prospective new applications
WP9. 3D printing	LTO	Inventory of 3D printable components for the nuclear sector that constitutes value for maintenance program. Manufacturing and test of 3 applications	Survey, state-of-the-art, manufacturing and test	Knowledge about new technologies, Prospective new applications
WP11. Geopolymers	LTO, SAFETY	State-of-the art for geopolymer applications for nuclear sector.	Survey, bibliographic study	Knowledge about new technologies, Prospective new applications