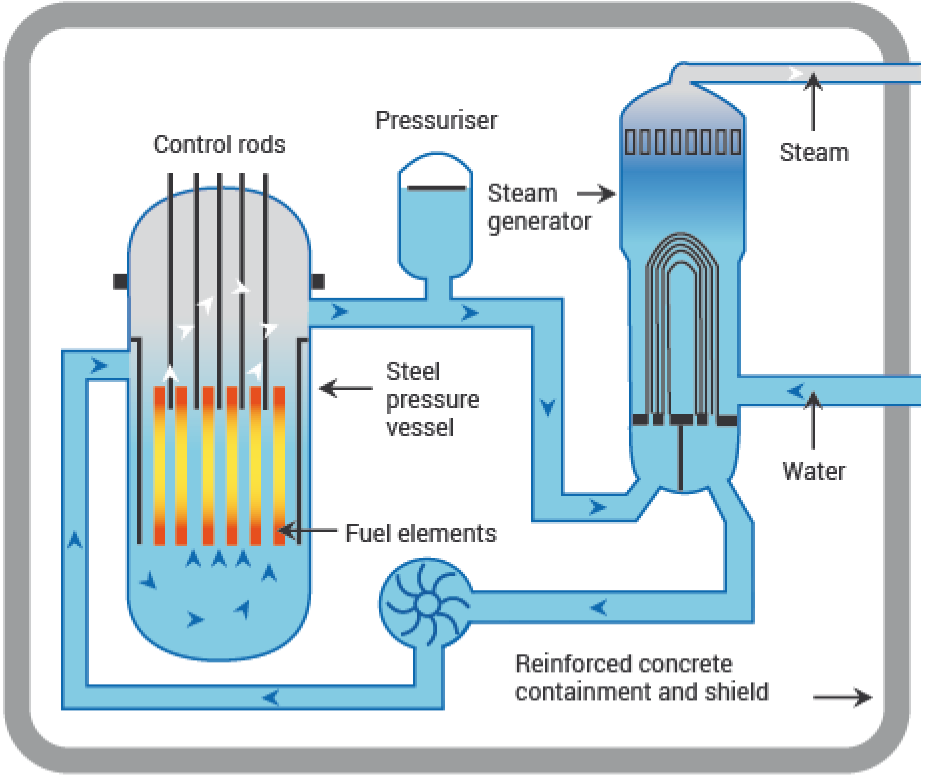
# Zirconium alloys high temperature oxidation laws determination and MFront implementation

Ali Charbal, Thomas Guilbert, Maxence Wangermez, Jean-Christophe Brachet and Thomas Helfer

# Loss Of Coolant Accident conditions (postulated scenario)

Pressurized Water Reactor




- Nuclear core generates heating
- Heat is extracted by the water coolant
- Water is pressurized to maintain its liquid state at temperatures ~300°C

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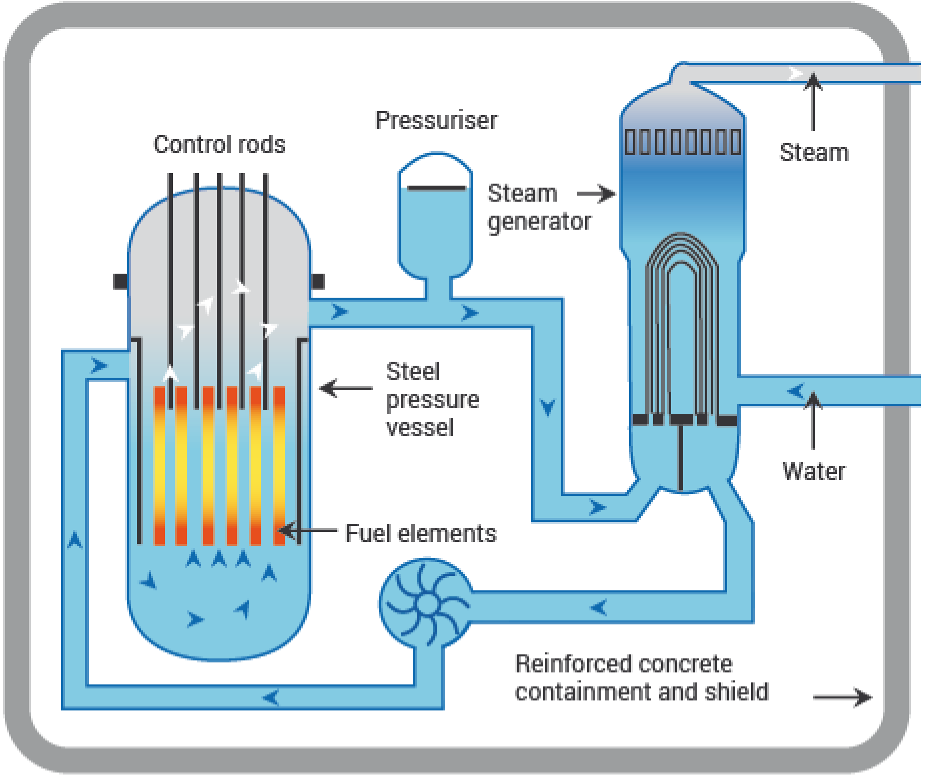
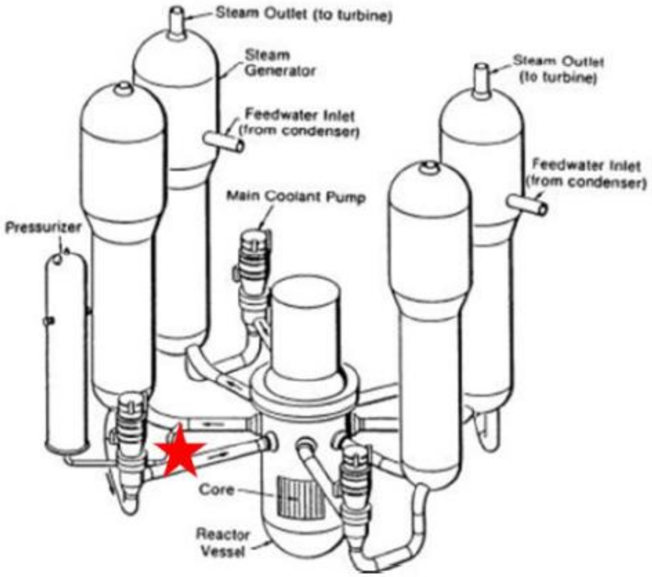
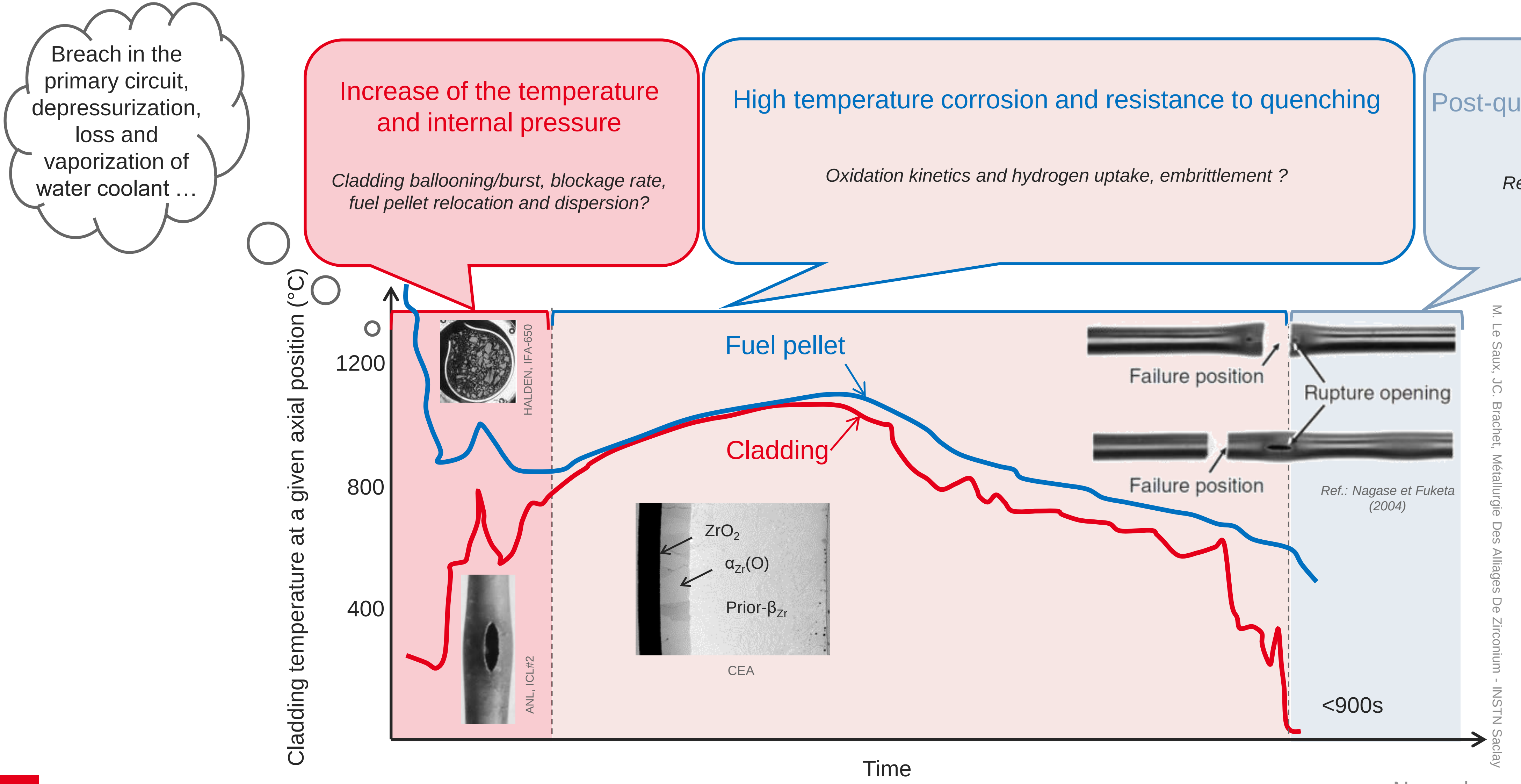


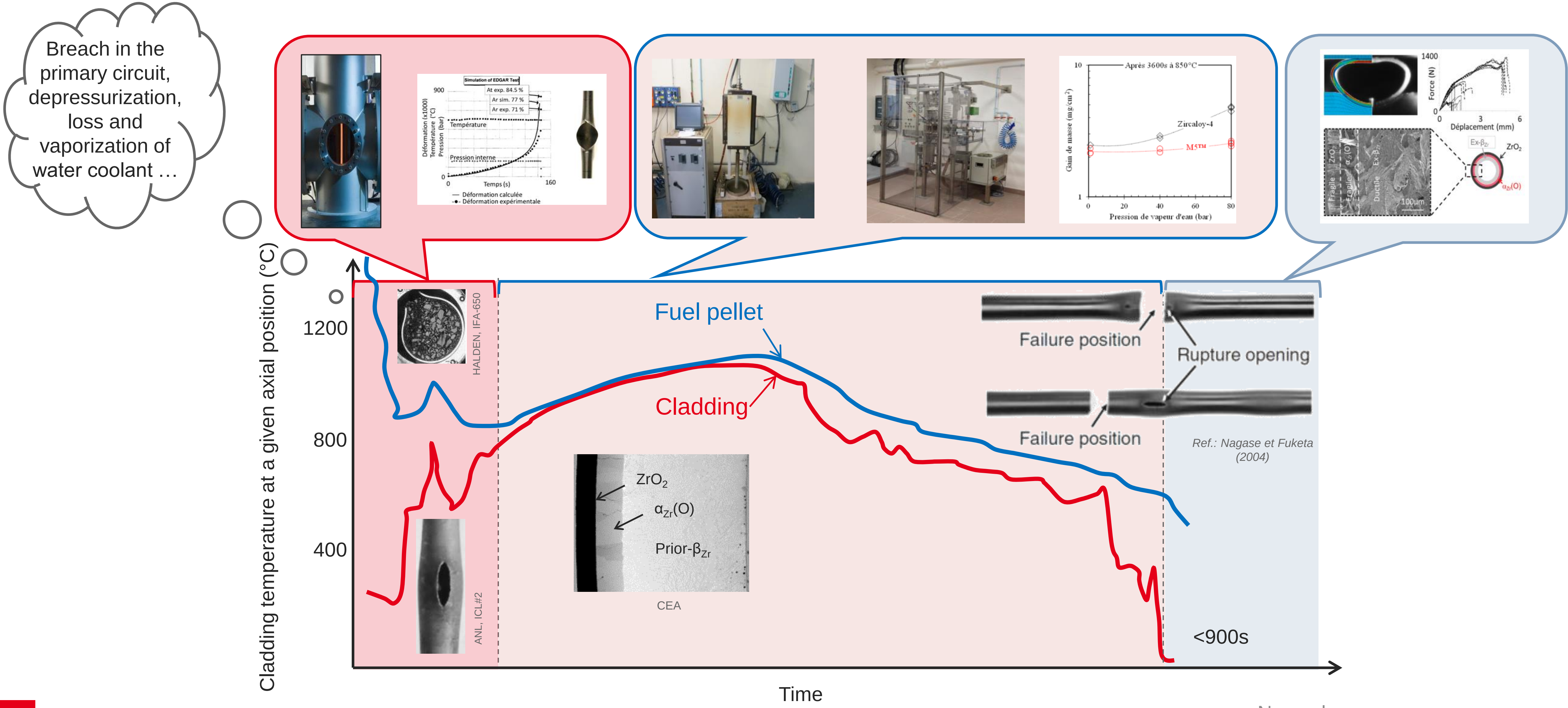



# LOCA and consequences on the fuel rods :
## *Example of a « large break » LOCA scenario.*



# LOCA and consequences on the fuel rods cladding:

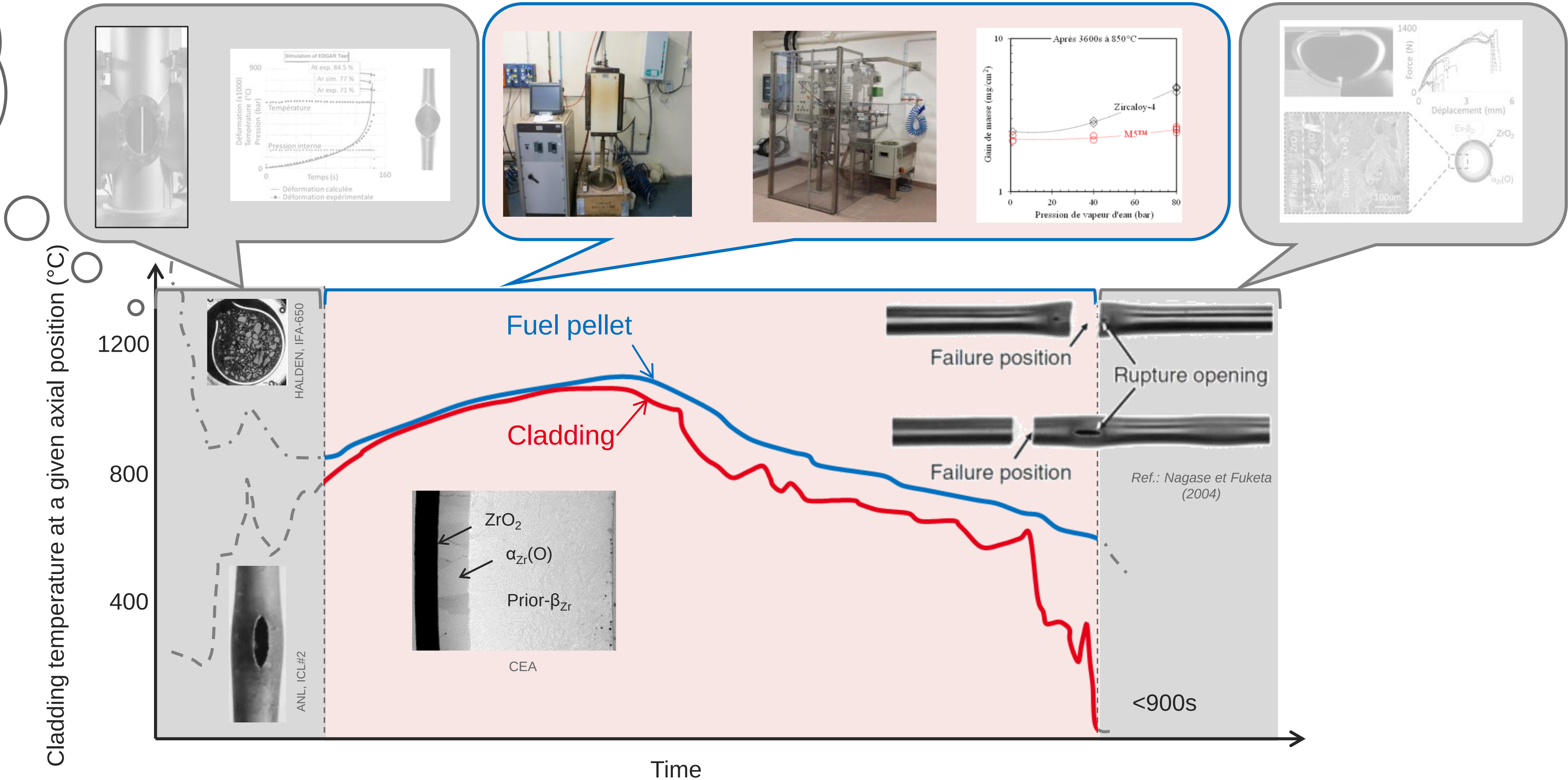
## *Experimental facilities for separate-effects studies*



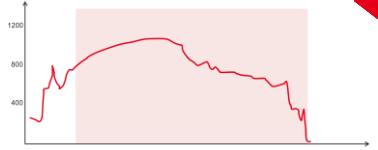
# LOCA and consequences on the fuel rods cladding:

## *Experimental facilities high temperature oxidation studies*

Breach in the primary circuit, depressurization, loss and vaporization of water coolant …

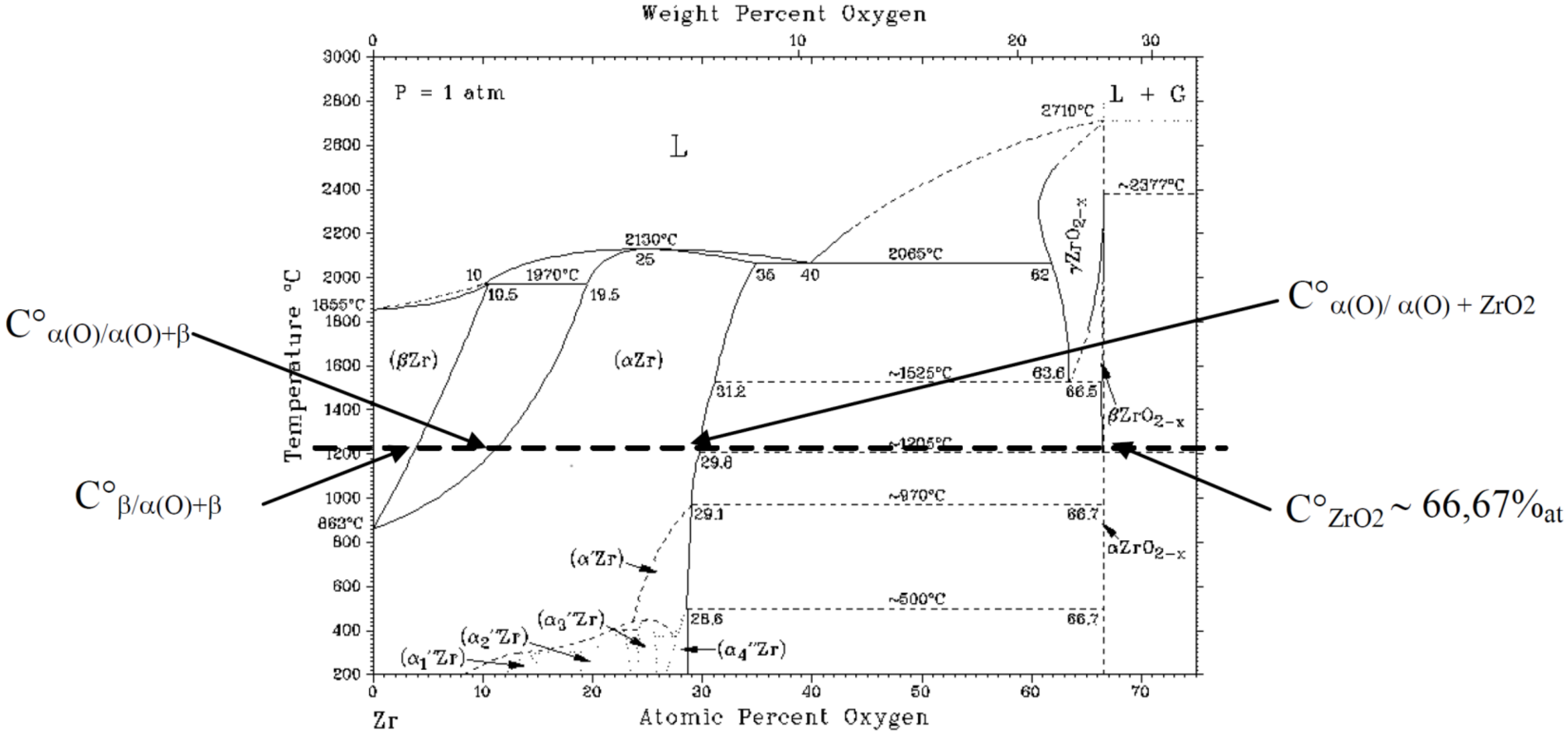


# HT Oxidation, effect of Oxygen on Zr phase formation



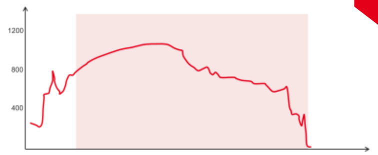
## Zr phases diagram vs. O at atmospheric pressure

Abriata et al. , 1986



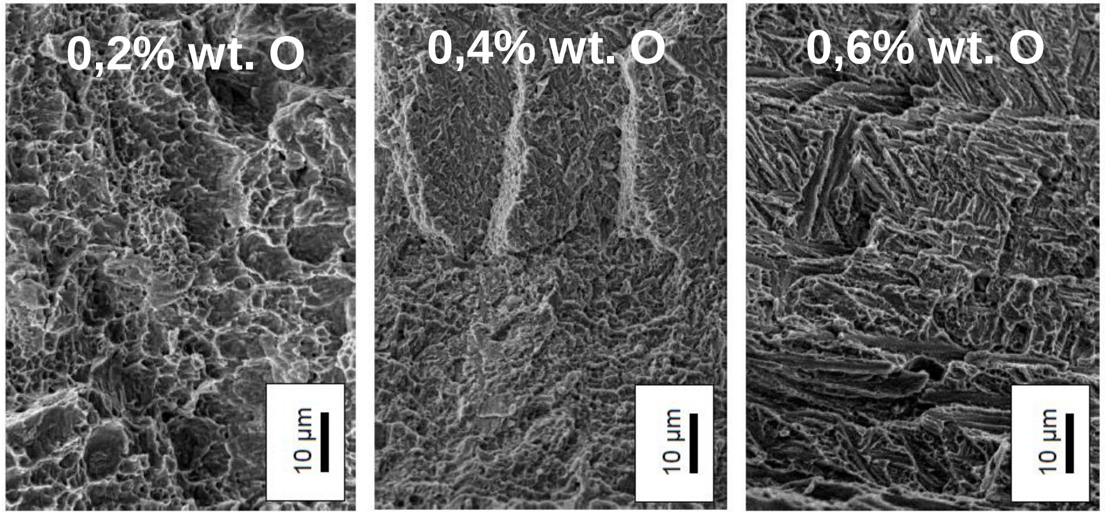

- Oxidation temperature will affect the phases formation
- The oxygen concentration will affect the mechanical response of the cladding : ZrO2 et Alpha(O) are brittle

# HT Oxidation, effect of Oxygen on Zr cladding




## Mechanical response affected by oxygen concentration

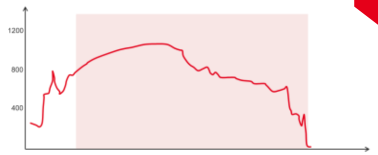
Cabrera. PhD Thesis, 2012




Ductile → Brittle

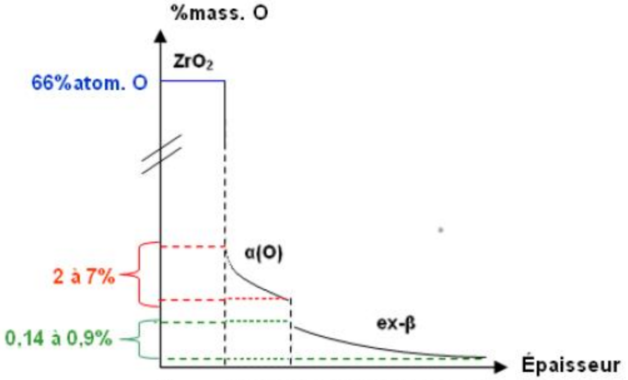
- The phases formation need to be quantified → use of metallographic observations and weight gain measurements
- They are correlated to the (post-quench) mechanical testing response to determine the remaining cladding ductility

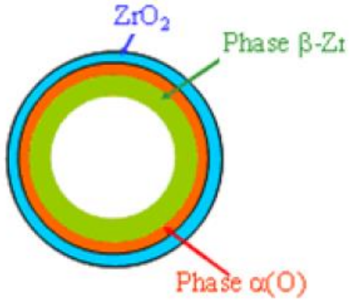
# HT Oxidation, effect of Oxygen on Zr cladding

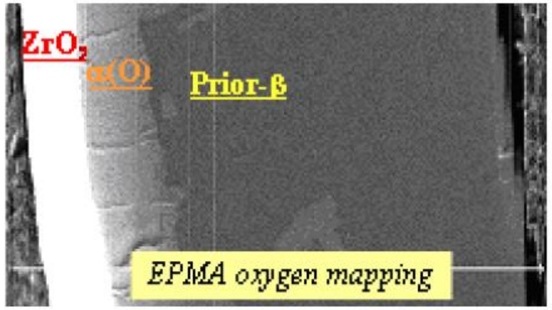


## Representation and observations of the generated phases (post-quenching)

Brachet et al. , 2001



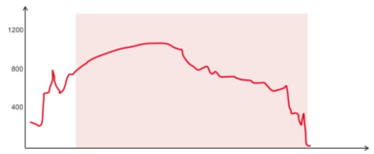



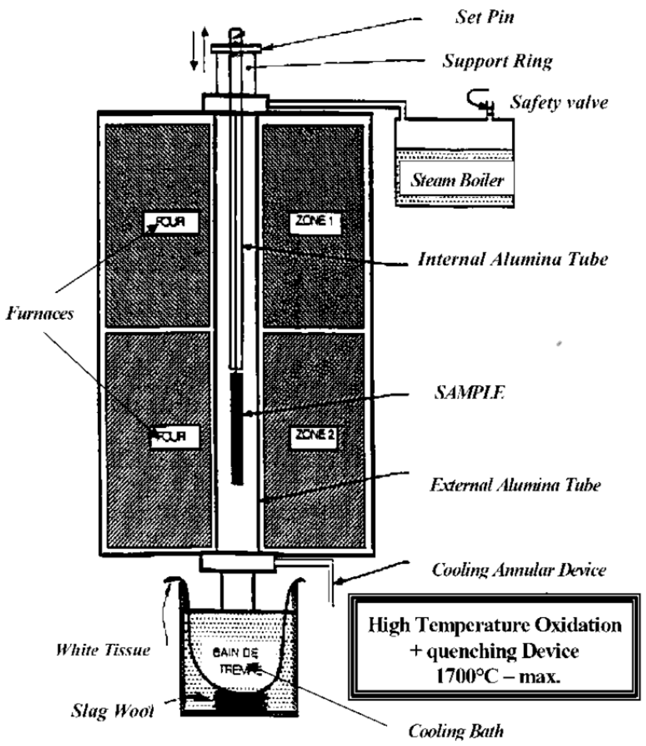

- The cladding tube will have a multi-layered structure with Alpha (O), ex-Beta and zircone
- The formed phases  post-oxidation are correlated to the oxygen local concentration

# DEZIROX, high temperature oxidation kinetics

## *Reference HT oxidation device with more than 2000 realized tests*




Brachet et al. ,2001, AIEA Halden




## DEZIROX : HT oxidation

- Heat generated by two ovens : from **700°C to 1250 °C**
- Experiments are carried **at constant temperature**
- Sample suspended **in steam environment** :
  - Plates
  - **One** (mostly) or two **sided HT oxidation test on cladding**
  - **Cladding after burst testing** on EDGAR
    - → sequenced semi-integral testing
    - → investigation of secondary hydriding mechanism and effects
- Samples are water-quenched or step-cooled

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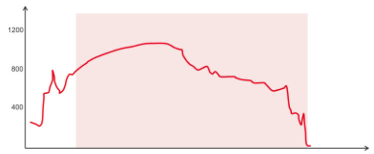


Brachet et al. ,2001, AIEA Halden

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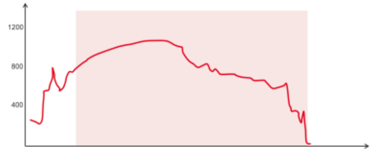
# I2TOX, high temperature oxidation kinetics

## Controlled environment

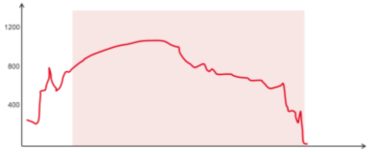



Brachet et al., 2020, Corr. Sc.

### I2TOX : Oxydation HT

- Heat generated by two ovens : from **400°C to 1600 °C**
- Experiments can be carried **at constant temperature or thermal ramps in dynamic conditions (>1°C/s, up to 50°C/s)**
- Samples can be suspended to **neutral or steam** environment:
  - Plate
  - One or two sided HT oxidation on cladding tubes
  - **Cladding after burst testing** on EDGAR
- **Controlled** steam flow rate
- Samples can be quenched by air or water

# I2TOX, high temperature oxidation kinetics
## Controlled environment

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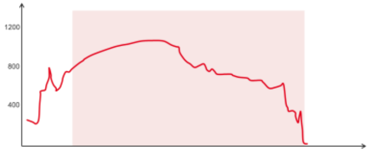
# CINOG-HP, high temperature oxidation kinetics

## Effect of external pressure

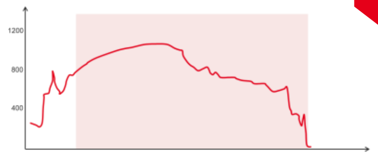
Le Saux et al. , 2014, ASTM




### CINOG : Oxydation HT

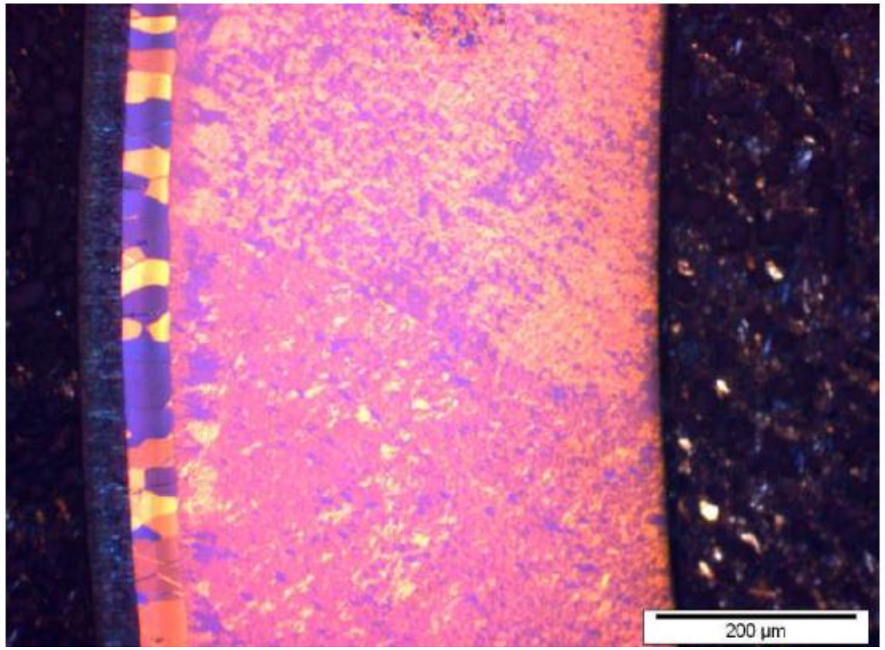
- Heat generated by induction : from **400°C to 1550 °C**
- **Steam (external) pressure** can be raised **up to 80 bars**
- Experiments are usually carried **at constant temperature**
- Sample suspended **in steam environment**:
    - Plates
    - **Two sided cladding HT** oxidation testing
- **Monitored and controlled** temperature by IR pyrometers
- Samples can be water-quenched

# HT Oxidation, phases distribution quantification

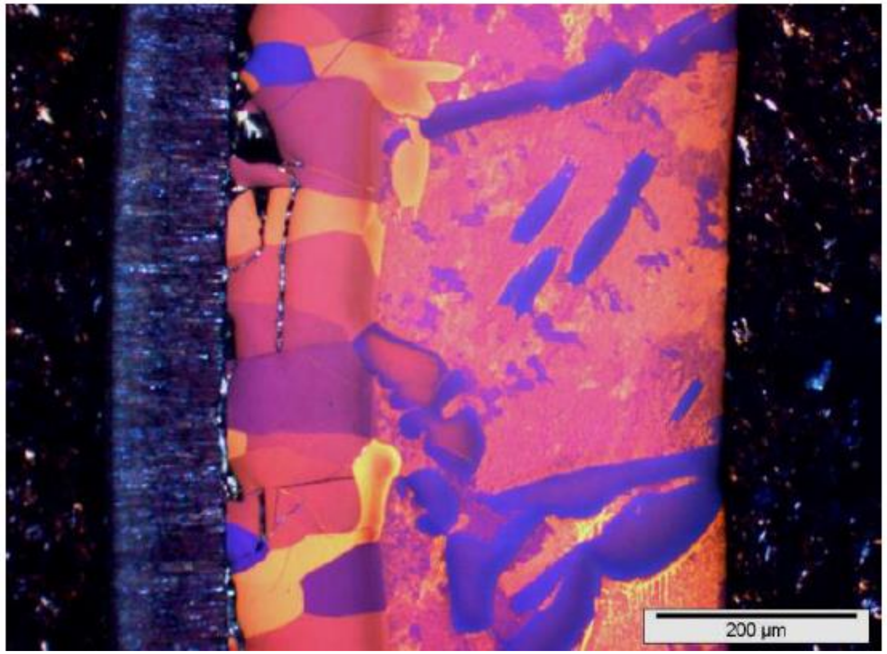



## Observations of the generated phases (post-quenching)

Cabrera. PhD Thesis, 2012



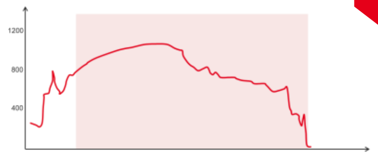

470 s 1100°C




1500s 1200°C

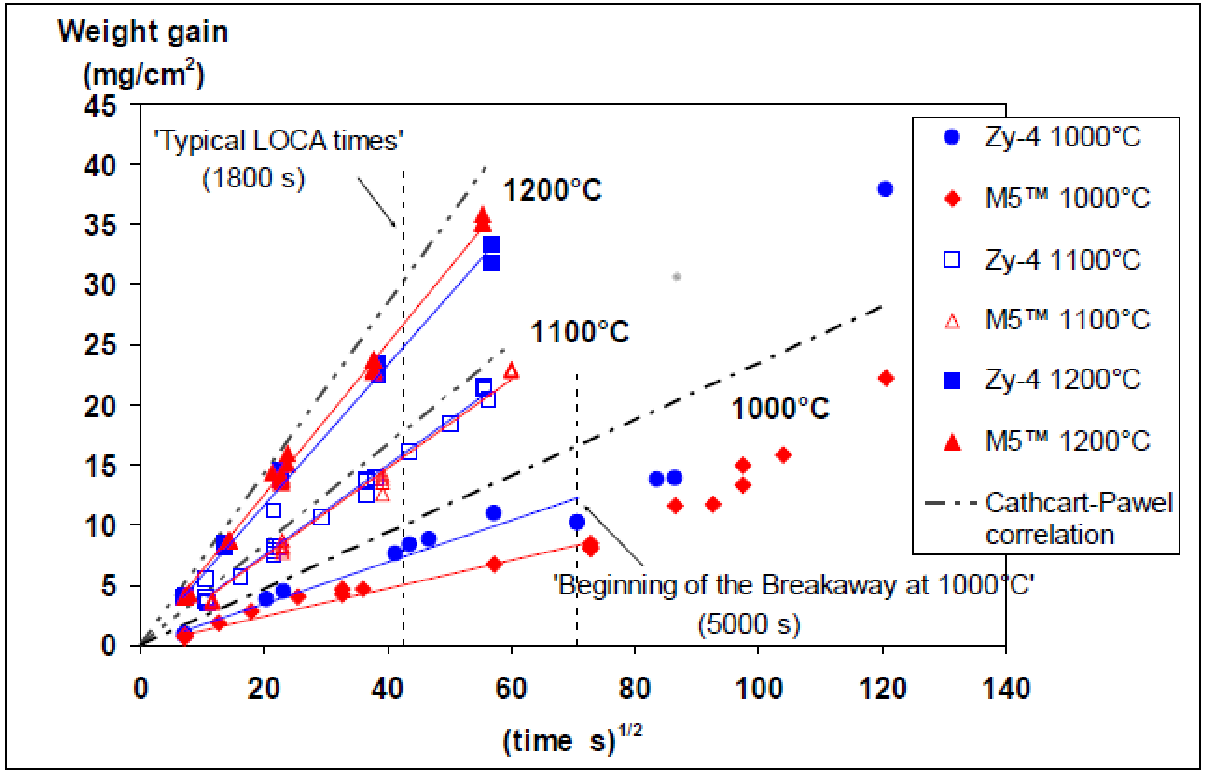
- The mass gain (g/cm2) , ZrO2 and Alpha(O) thicknesses (µm) can be measured after each oxidation tests
- Parabolic correlations can be determined as a function of the oxidation temperature (T) and duration (t)

# HT Oxidation, parabolic time dependences




## Weight gain

Portier et al. 2005, ASTM




## Example of the mass gain

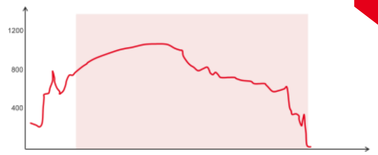
$$(gdm)^n = \left(\frac{m}{S}\right)^n = K^{gdm}.t$$

gdm : mass gain expressed in $(kg/m^2)^n$
m : mass (kg)
S : exposed surface ($m^2$)
t : time (s)
n : 2 (depends on the oxidation regim)

$$K^{gdm} = K_p^{gdm\_o}.\exp\left(-\frac{E_a}{RT}\right)$$

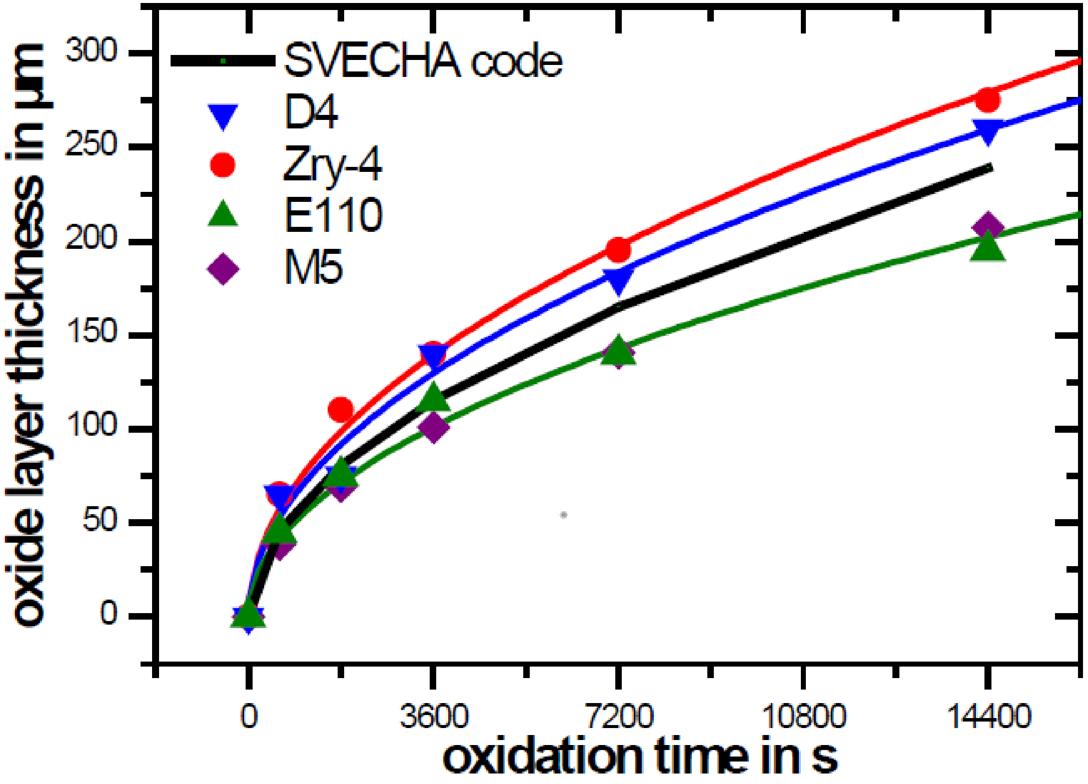
$K_p^{gdm\_o}$ : constant parameter $(kg^n.m^{-2n}.s^{-\frac{1}{n}})$
$E_a$ : activation energy $(J\ mol^{-1})$
T : Temperature (K)
R : 8,314 $(J\ K^{-1}mol^{-1})$

# HT Oxidation, parabolic time dependences




## Oxide layer thickness

Grosse et al. 2010




## Example of the ZrO2

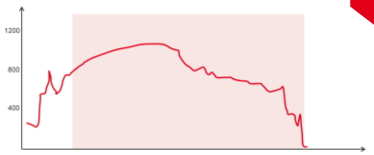
$$(e\_ZrO2)^n = K^{ZrO2}.t$$

ZrO2 : Thickness (m *or µm*)
t : Time (s)
n : 2 (depends on the oxidation regim)

$$K^{ZrO2} = K_p^{ZrO2\_o}.\exp\left(-\frac{E_{a-ZrO2}}{RT}\right)$$

$K_p^{ZrO2\_o}$ : Constant parameter ($m^n.s^{-\frac{1}{n}}$)
$E_{a-ZrO2}$ : Activation energy ($J\ mol^{-1}$)
T : Temperature (K)
R : 8,314 ($J\ K^{-1}mol^{-1}$)

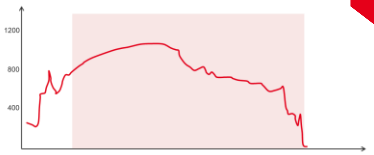
# HT Oxidation, Mfront Implementation - description




```
@DSL Model;
@Model CP1977_HighTemperatureOxidationModel;
@Material Zy4;
@Author   Thomas Guilbert / Maxence Wangermez / Thomas Helfer / Ali Charbal;

@Description{Oxidation laws describing the Zy4 cladding alloy : mass gain, Alpha(O) and ZrO2 thicknesses
evolution identified by CATHCART-PAWEL
Remark               : parameters were adapted in order to use the physical constant R = 8.314 J K-1 mol-1
                             Mass gain unit     : kg / m2  - SI unit
                             Thickness unit     : m        - SI unit
                             Thickness unit     : m        - SI unit
                             Alloy              : Zy4
                             Temperature range  : 1000 - 1500
Reference            : Cathcart, J.V., Pawel, R.E., McKee, R.A., Druschel, R.E., Yurek, G.J., Campbell, J.J., &
Jury, S.H. (Jul 1977). Zirconium metal-water oxidation kinetics IV Reaction rate studies (ORNL/NUREG--17).
United States "https://www.nrc.gov/docs/ML0522/ML052230079.pdf"};
```

# HT Oxidation, Mfront Implementation – Output/Input




```
@Output real gdm;
gdm.setEntryName("MassGain");
gdm.setDepth(1);

@Output length eAlphaO;
eAlphaO.setEntryName("AlphaOLength");
eAlphaO.setDepth(1);

@Output length eZrO2;
eZrO2.setEntryName("ZrO2Length");
eZrO2.setDepth(1);

@Input temperature T;
T.setGlossaryName("Temperature");
T.setDepth(1);

@PhysicalBounds T in [0 : *[;
@Bounds T in [1273.15 : 1773.15];
```

# HT Oxidation, Mfront Implementation - Models

```
// *********************************************************************
// Mass gain parameters - T 1000 - 1500 °C
@Parameter quantity<real, 2, -4, -1>              K0_gdm     = 3.62e+1;
@Parameter quantity<real, 1, 2, -2, 0, 0, 0, -1> Ea_gdm     = 167116.0;
// *********************************************************************
// Parameters for the Alpha(O) thickness  - T 1000-1500 °C
@Parameter quantity<real, 0, 2, -1>              K0_AlphaO  = 1.53e-4;
@Parameter quantity<real, 1, 2, -2, 0, 0, 0, -1> Ea_AlphaO  = 201428.0;
// *********************************************************************
// Parameters for the the ZrO2 thickness  - T 1000-1500 °C
@Parameter quantity<real, 0, 2, -1>              K0_ZrO2    = 2.25e-6;
@Parameter quantity<real, 1, 2, -2, 0, 0, 0, -1> Ea_ZrO2    = 150170.0;
// *********************************************************************

@Function CP1977_HighTemperatureOxidationModel{
  constexpr auto R          = PhysicalConstants::R;
  const auto     T_mts      = (T + T_1) / 2;

  const auto     K1         = K0_gdm * exp(-Ea_gdm / (R * T_mts));
                 gdm        = power<1,2>(gdm_1 * gdm_1 + K1 * dt);

  const auto     K2         = K0_AlphaO * exp(-Ea_AlphaO/ (R * T_mts));
                 eAlphaO    = power<1,2>(eAlphaO_1 * eAlphaO_1 + K2 * dt);

  const auto     K3         = K0_ZrO2 * exp(-Ea_ZrO2 / (R * T_mts));
                 eZrO2      = power<1,2>(eZrO2_1 * eZrO2_1 + K3 * dt);}
```

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```
 @DSL Model;
@Model CP1977_HighTemperatureOxidationModel;
@Material Zy4;
@Author   Thomas Guilbert / Maxence Wangermez / Thomas Helfer / Ali Charbal;

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                                                                     Thickness unit     : m                         - SI unit
                                                                     Thickness unit     : m         - SI unit
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States "https://www.nrc.gov/docs/ML0522/ML052230079.pdf"};

//@UseQt true;

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// ************************************************************************

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  const auto     T_mts      = (T + T_1) / 2;

  const auto     K1         = K0_gdm * exp(-Ea_gdm / (R * T_mts));
                 gdm        = power<1,2>(gdm_1 * gdm_1 + K1 * dt);

  const auto     K2         = K0_AlphaO * exp(-Ea_AlphaO/ (R * T_mts));
                 eAlphaO    = power<1,2>(eAlphaO_1 * eAlphaO_1 + K2 * dt);

  const auto     K3         = K0_ZrO2 * exp(-Ea_ZrO2 / (R * T_mts));
                 eZrO2      = power<1,2>(eZrO2_1 * eZrO2_1 + K3 * dt);
                                                                                         }
```
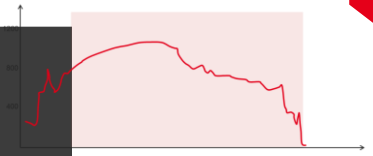
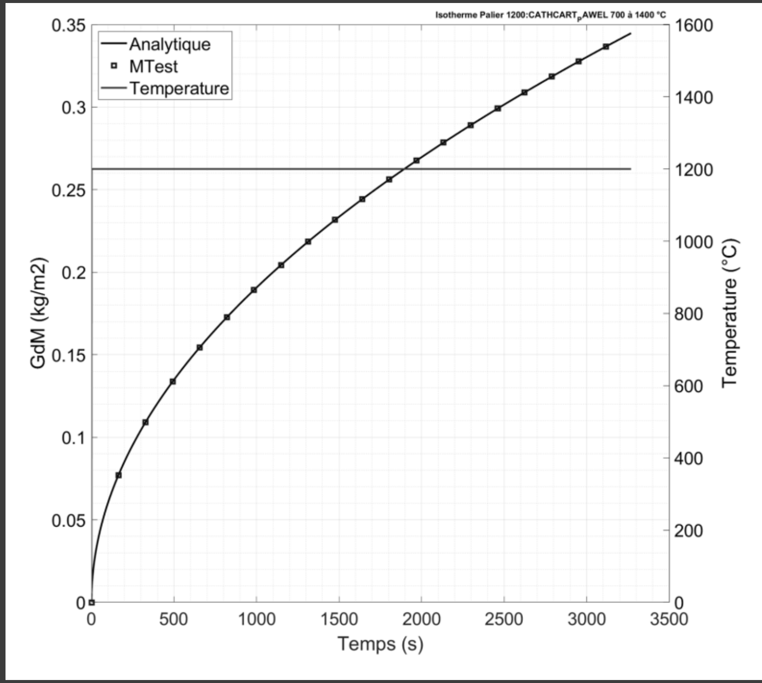
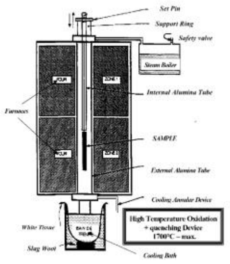



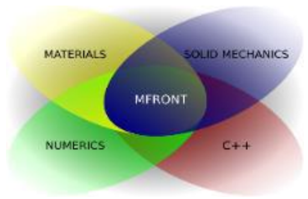


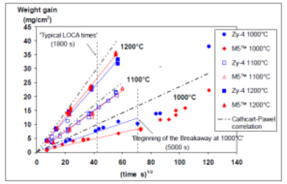
# Integrating “LOCA material laws” into ALCYONE

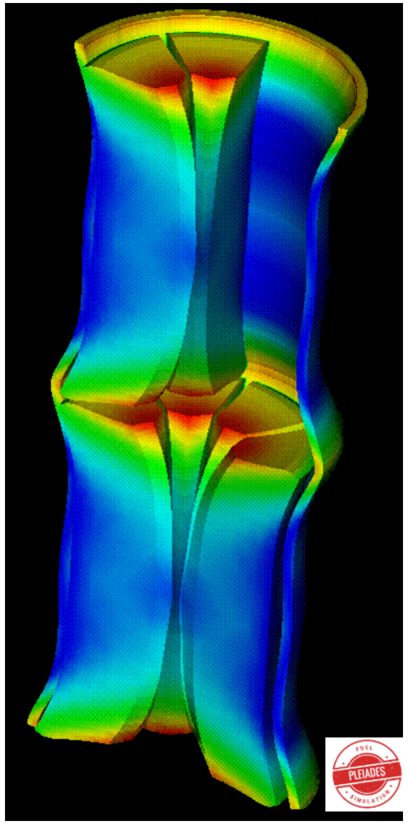
## MFront bridges the “gap” between various experts

### ALCYONE : fuel performance code








https://doi.org/10.1016/j.anucene.2024.110711

### Few ALCYONE features

- Multiphysics partitioned scheme
- Multiscale modelling
- From 1D to 3D modelling
- From nominal to postulated accidental scenario
- Integrates a large number materials behaviour

# Thank you for your attention