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The OXNIT density law in CRISTAL package

An easy way to predict the composition of dissolved oxide in
nitrate solutions

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Context

➤ Reprocessing of fuel

- UO_2 and $\text{UO}_2\text{-PuO}_2$ fuel rods sheared in small 5-cm pieces
 - Sent into nitric acid in the rotary dissolver
 - Separation of oxide pellets, Zircaloy claddings and non fissile elements
 - Uranium and plutonium move to uranyl and plutonium nitrate
 - Coexistence of nitrate and oxide

- Criticality calculations performed with both chemical forms
 - Assess criticality safety margins w.r.t dissolution kinetics
 - Optimization of dissolution process for high plutonium content

- Need for specific density laws called “OXNIT”



Users' needs

➤ Established in collaboration with ORANO Projects

- Dissolution of pellets or fragments of pellets in continuous process (with a continuous addition of acid)
- Dissolution of pellets or fragments of pellets in discontinuous process (addition of acid per batch)
- Dissolution of oxide powder
- Presence of residues (low solubility) in the dissolution solution



Modelled as a regular array of oxide pellets in dissolution solution

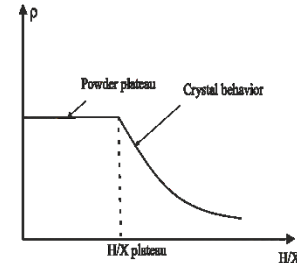
Users' needs (2)

➤ Established in collaboration with ORANO Projects

■ $UPuO_2$ modeled as a powder or a crystal

■ Various Pu/UPu ratios

- Kinetics of dissolution of uranium and plutonium may be different
- Consider separate Pu/UPu ratio in oxide and nitrate



■ Different isotopic vectors

- In continuous loading process of the oxide (no renewal of acid), fragment of oxide arriving in the dissolver have not the same isotopic vector as the uranyl/plutonium nitrate solution (BWR with axial enrichment heterogeneities)
- Calculations with bounding isotopic vector

■ Poison

- Necessary to keep a constant dissolution rhythm in sub-critical conditions (e.g. dissolution residues with a high content in Pu)
 - Small quantities defined in the density law

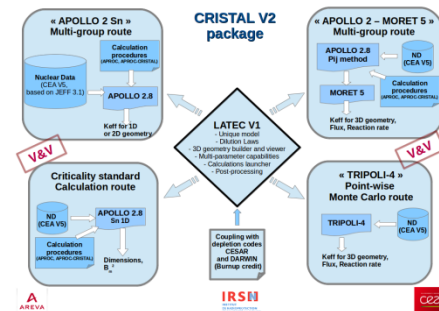
Density laws in the LATEC workbench

Density laws, why?

- Knowledge of fissile and moderator concentrations is required to assess NCS
 - The density of a solution generally not known
 - Need to study the behavior (k_{eff} vs H/X) in terms of criticality on the whole moderation range
 - Associated with a bounding fissile medium: **conservatism**
- Mathematical relationship: $\rho=f(C(X), H^+, C(\text{poison}), T\dots)$

LATEC workbench

- Interface that drives criticality calculations
- Generates input deck for CRISTAL package codes
 - Determination of composition of fissile mixtures using density laws
- Geometry of modeling (1D, 2D and 3D)
- Variables for parametric study
- Launches calculations and manages results
- Verification mode



Use of the OXNIT density law

➤ Definition of the oxide

Density of crystal calculation

The screenshot displays the CRISTAL software interface for material UO2. Key sections include:

- Chemical elements:** Shows ^{92}U and O_2 [massic] tot:100 %.
- Density:** Includes a checked box for "calc. Theoric density". Fields for "Powder (g/cm3)" (0) and "Cristal (g/cm3)" (10.8487053) are visible.
- Temperature:** A field for "°C" is set to 21. A red note states: "Update of cross sections and water density (density calculation is valid only for temperatures between 1 and 59°C).".
- Moderation:**
 - Variable (Ctrl + click): moderation
 - Definition of moderation: Density (g/cm3) 0.99799
 - Composition: H_2O H2O 100.0
 - Moderation expressed in: Type: Mod/X, Moderator element: ^1H , Value = 0
- Element links:** Expressed as: massic

Isotopic vector

Nature of moderator

Not taken into account

Use of the OXNIT density law

The screenshot shows the 'Nitrate' software interface. The 'Chemical elements' panel on the left lists ^{92}U O₂(NO₃)₂ [massic] tot:100 % with an arrow pointing to it labeled 'Isotopic vector'. The 'Moderation' panel on the right shows 'Variable (Ctrl + click) : H₂O', 'Definition of moderation : Density (g/cm3) 0.99799', and 'Moderation expressed in : Type : C(X) g/l' with a 'Value = 500.0' field. An arrow points to this field labeled 'Moderation'. At the bottom, the 'Element links' panel has 'Acidity' and 'Mixture' tabs, with arrows pointing to them labeled 'Acidity' and 'Mixture' respectively. A red warning message is visible: 'Update of cross sections and water density (density calculation is valid only for temperatures between 1 and 59°C)'.

Use of the OXNIT density law

The screenshot shows the OxNit software interface with the following fields and annotations:

- Temperature:** °C: 21
- Powder density:** g/cm3 5.5 (An arrow labeled "Powder density" points to this field.)
- Oxide medium:** Moderation expressed in C(X) g/l Value = 50. The dropdown menu is set to UO2 (An arrow labeled "Drag & drop oxide" points to this dropdown.)
- Nitrate medium:** Nitrate (An arrow labeled "Drag & drop nitrate" points to this dropdown.)
- Radio buttons:** Solution (selected) and Mixture.
- Warning:** Warning: only acidity in nitrate is taken into account here.

Powder density

Drag & drop oxide

Drag & drop nitrate

Concentration expressed before mixing with the oxide

Programming of the OXNIT density law

Volume addition principle

- Addition of the volume of the oxide (crystal/powder) and the nitrate solution
 - Two phases: oxide and nitrate solution

Density of the nitrate solution determined using the “isopiestic” density law (see Leclaire & al ICNC2015, Charlotte)

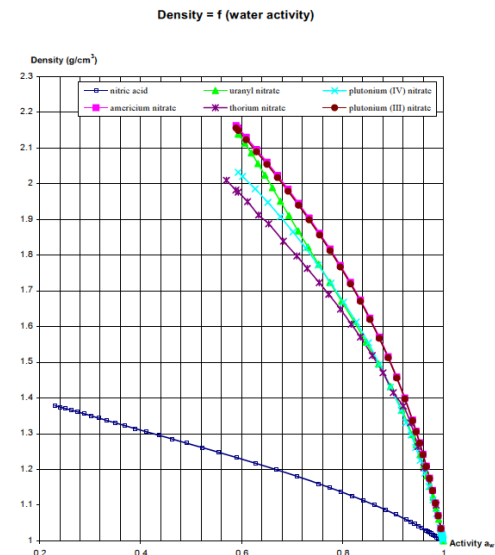
- Need to split a mixture of several nitrate compound in “binary” solutions (1 nitrate + water) having the same water activity a_w

$$a_w = \frac{p_{H_2O}}{p_{H_2O}^{St}}, \text{ standard: pure, 1atm, } 25^\circ C \quad (1)$$

$$\rho = \sum \frac{C_i}{C_i^{bi}} \times \rho_i^{bi} \quad (2)$$

- Knowledge of the “binary” solutions characteristics having same water activity looping on equation

$$\sum \frac{C_i}{C_i^{bi}} = 1 \quad (3)$$



Programming of the OXNIT density law

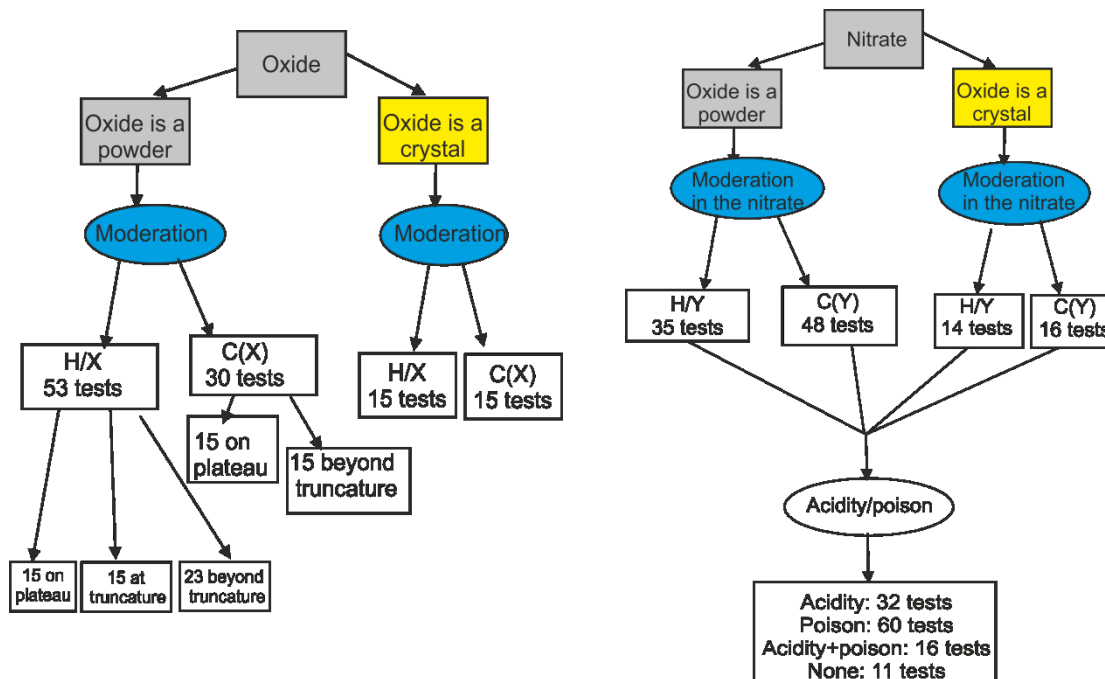
Type	CRYSTAL			
Moderation of oxide in the mixture	C(X) in g/cm ³		H/X	
Moderation of nitrate solution	C(Y) in g/cm ³	H/Y	C(Y) in g/cm ³	H/Y
Type	POWDER			
Moderation of oxide in the mixture	C(X)		$\left(\frac{H}{X} < \left(\frac{H}{X} \right)_{\text{plateau}} \right)$ H/X else crystal resolution	
Moderation of nitrate solution	C(Y)	H/Y	C(Y)	H/Y

Use and validation of the law

➤ Automated validation tool

Creation of tests

- Cover all options (crystal/powder, moderation of the oxide expressed in moderation ratio H/X, moderation in the nitrate solution expressed in H/Y...)
- Easy addition and checking of consistency with reference compositions (EXCEL sheets)



Isotopes	Concentrations LATEC (at./barn.cm)	Ecart relatif %	
		Vérification expert	code CIGALES
H1_H2O	1.03522E-02	-1.49E-04	-
H1_ZRH	6.06320E-02	-4.13E-03	-
H2_H2O	1.19064E-06	-1.49E-04	-
H2_ZRH	6.97348E-06	-4.13E-03	-
O16	5.16411E-03	-1.49E-04	-
O17	1.96714E-06	-1.49E-04	-
O18	1.06122E-05	-1.49E-04	-
U235	2.09181E-04	-2.63E-04	-
U238	8.26157E-04	-1.20E-04	-
Zr90	1.56000E-02	2.68E-04	-
Zr91	3.40199E-03	2.68E-04	-
Zr92	5.20001E-03	2.68E-04	-
Zr94	5.26975E-03	2.68E-04	-
Zr96	8.48982E-04	2.68E-04	-

➤ More than 100 tests

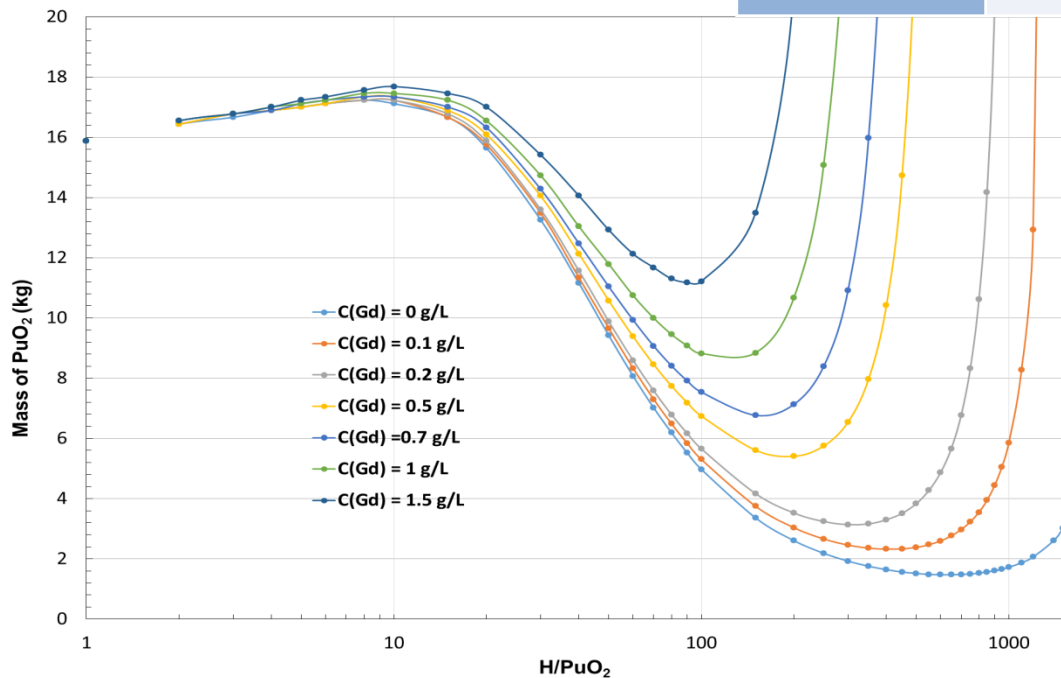
Use and validation of the law

➤ Criticality standards with CRISTAL V2.0.3 package

■ APOLLO2-S_n 20 groups, calculation

- Target $k_{\text{eff}} = 0.95$

	Oxide	Nitrate
	PuO ₂ crystal	Uranyl/Plutonium nitrate
Isotopics	71/17/11/1 (%)	Pu (71/17/11/1), U _{natural} , Pu/UPu = 12.5 %
Concentration	Variable (H/Pu)	400 g/L in the solution
C(Gd)		Variable, in the solution



[Video](#)

Conclusion

- The OXNIT density law was developed to cover maximal application domains and meet CRISTAL V2 user requests
- Possible to differentiate isotopic vectors for the oxide and the nitrate
- Uranium/plutonium ratios can differ between the oxide and the nitrate
- The oxide can be defined as a powder or a crystal
- Extensive validation with automated tool has been performed
- Further release
 - Definition of the nitrate concentration after dissolution of the oxide in the mixture

Thanks for your attention!

