



International Workshop on Developments in Safety Assessment Approaches and Safety Management Practices of Fuel Cycle Facilities

Chemical hazards in nuclear fuel cycle facilities

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Youcef HEMIMOU

ASN/DRC/FUEL CYCLE FACILITIES UNIT

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- 1. ASN in a glance**
- 2. The dangerous substances in nuclear fuel cycle facilities**





ASN in a glance

- The French Nuclear Safety Authority is tasked, on behalf of the State, with regulating **nuclear safety** and **radiation protection** in order to protect **workers**, **patients**, the **public** and the **environment** against the risks related to nuclear activities in France. It also contributes to **informing the citizens**.

- ASN Missions : **Regulate, Control, Inform**

- A State Authority (does not belong to a Ministry)
 - Reports to the Parliament

- ASN Scope
 - 150 civilian nuclear installations in France (58 NPPs, Fuel Cycle Facilities, Research Reactors, construction, decommissioning, waste/decommissioned facilities, etc)
 - Transport of radioactive materials
 - Proximity nuclear (medical uses, construction)





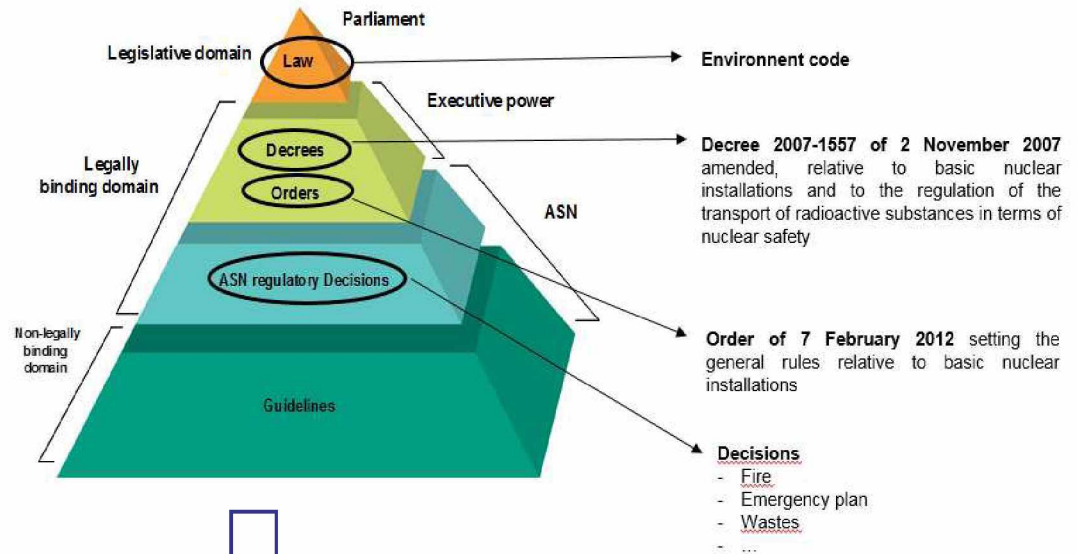
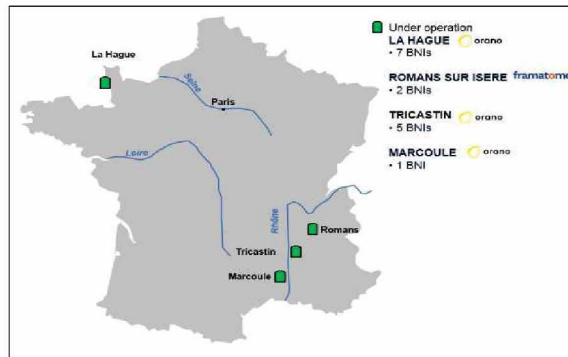
1. ASN in a glance

2. **The dangerous substances in nuclear fuel cycle facilities**





The general french regulatory framework

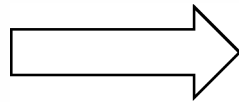


What is the regulatory framework for dangerous substances in the nuclear facilities ?

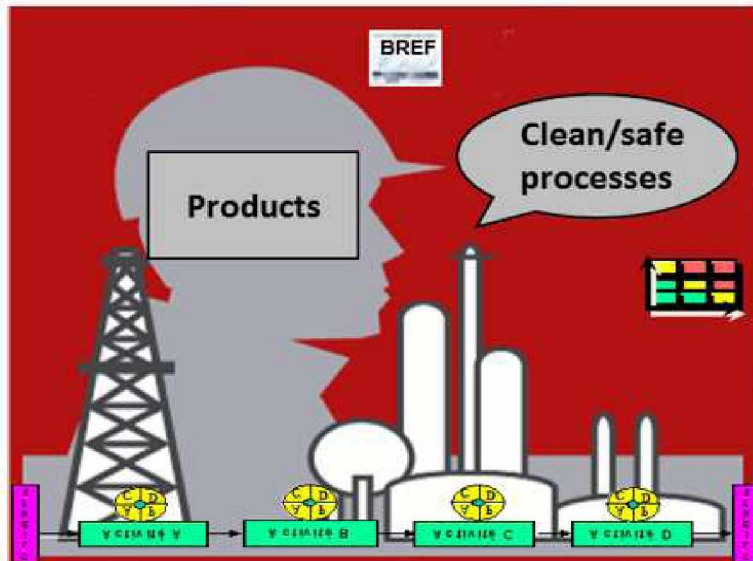


asn Overview of main regulations involving chemicals

CLP
REGULATION



To take inventory of the categories of dangerous substances present in the BNI with the respective amounts



The European regulation EC n° 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures

Hazard statement

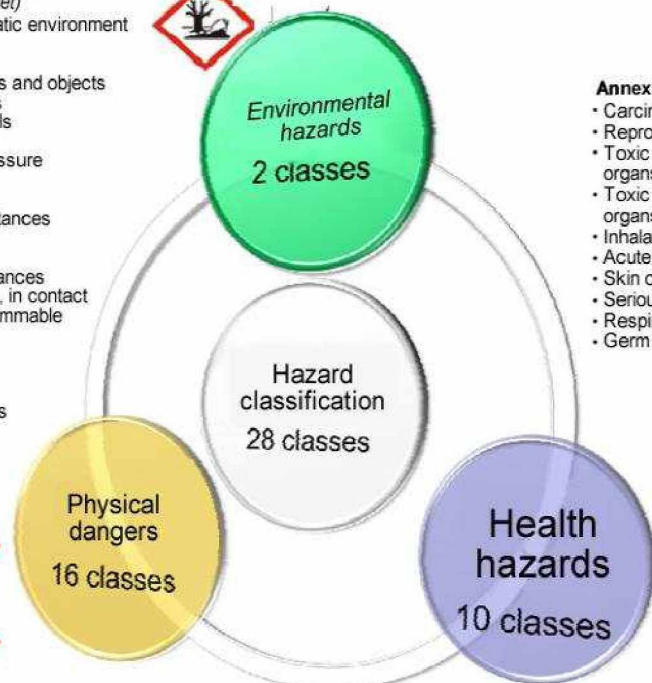
- H2xx : physical hazards
- H3xx : health hazards
- H4xx : environmental hazards

Hazard pictogram

- Danger to the ozone layer
(no pictogram as yet)
- Danger to the aquatic environment

Annex 1 Chap 2

- Explosive materials and objects
- Flammable gasses
- Flammable aerosols
- Oxidizing gasses
- Gasses under pressure
- Flammable liquids
- Flammable solids
- Self-reactive substances
- Pyrophoric liquids
- Pyrophoric solids
- Self-heating substances
- Substances which, in contact with water, emit flammable gasses
- Oxidizing liquids
- Oxidizing solids
- Organic peroxides
- Corrosive to metals



Annex 1 Chap 3

- Carcinogenic
- Reproductive toxicity
- Toxic to certain target organs - one off-exposure
- Toxic to certain target organs - repeated exposure
- Inhalation hazard
- Acute toxicity
- Skin corrosion/skin irritation
- Serious eye injury/irritation
- Respiratory or skin sensitivity
- Germ cell mutagenity



Inventory of the categories of dangerous substances present in the BNI with the respective amounts



Echa.europa.eu

Website from European union



CLP regulation

The European regulation EC n° 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures

Hazard statement
H2xx : physical hazards

Hazard Class
Explosives
Flammable gases
Flammable aerosols and aerosols
Oxidising gases
Gases under pressure
Flammable liquids
Flammable solids
Self-reactive substance/mixture
Pyrophoric liquids
Pyrophoric solids
Self-heating substance/mixture
Water-reactive - emits flammable gases
Oxidising liquids
Oxidising solids
Organic peroxides
Corrosive to metals

Hazard statement
H3xx : health hazards

Hazard Class
Acute toxicity
Skin corrosion / irritation
Eye damage / irritation
Respiratory / skin sensitisation
Mutagenicity
Carcinogenicity
Toxic for reproduction
Specific target organ toxicity (single exposure)
Specific target organ toxicity (repeated exposure)
Aspiration hazard

Hazard statement
H4xx : environment hazards

Hazard Class
Hazardous to the aquatic environment



asn Example : HF (Hydrogen fluoride)

Hazard classification & labelling



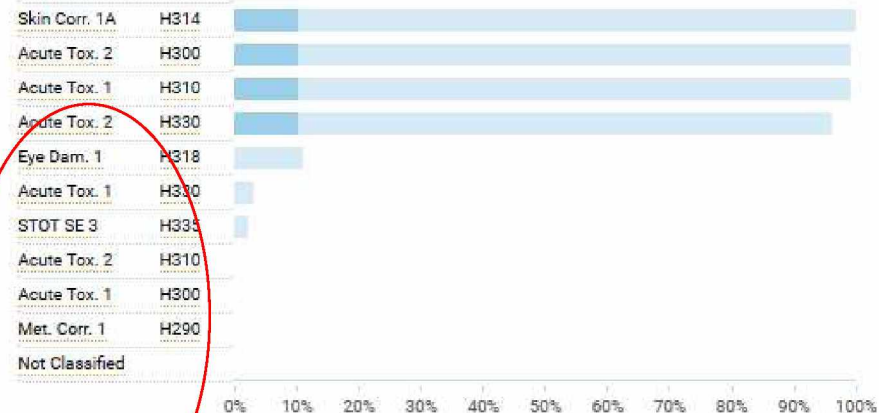
Danger! According to the classification provided by companies to ECHA in **REACH registrations** this substance is fatal if swallowed, is fatal in contact with skin, is fatal if inhaled and causes severe skin burns and eye damage.

Additionally, the classification provided by companies to ECHA in **CLP notifications** identifies that this substance causes serious eye damage.

This substance is covered by several Harmonised Classifications and Labelling's (CLH) entries approved by the European Union. Differentiating between the different CLH's entries requires manual verification. To know more about the CLH please visit the [C&L inventory](#).

Classification	
Hazard Class and Category Code(s)	Hazard Statement Code(s)
Acute Tox. 2 *	H300
Acute Tox. 1	H310
Skin Corr. 1A	H314
Acute Tox. 2 *	H330

Breakdown of all 625 C&L notifications submitted to ECHA



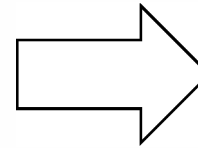
- Harmonised Classification
- REACH registration dossiers notifications
- CLP notifications

ⓘ At least one notifier has indicated that an impurity or an additive present in the substance impacts the notified classification.

asn Example : heavy fuel oils

34. Petroleum products and alternative fuels

- (a) gasolines and naphthas,
- (b) kerosenes (including jet fuels),
- (c) gas oils (including diesel fuels, home heating oils and gas oil blending streams)
- (d) heavy fuel oils
- (e) alternative fuels serving the same purposes and with similar properties as regards flammability and environmental hazards as the products referred to in points (a) to (d)



asn Example : Nitric acid

Hazard classification & labelling



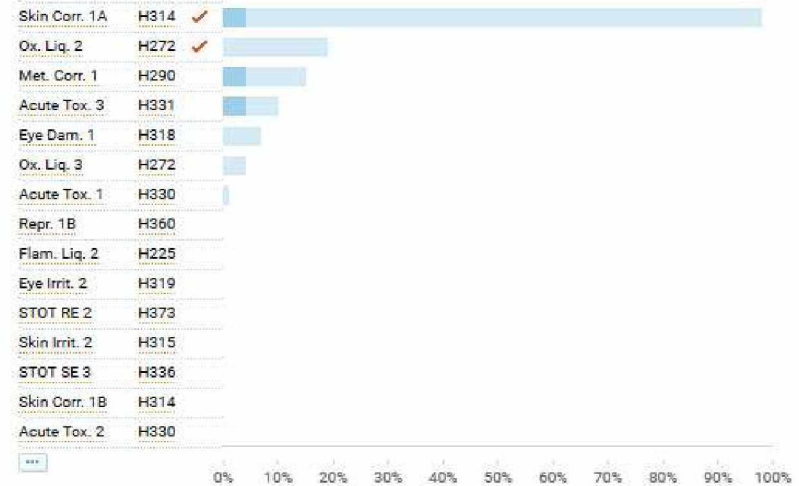
Danger! According to the **harmonised classification and labelling** (ATP07) approved by the European Union, this substance causes severe skin burns and eye damage and may intensify fire (oxidiser).

Additionally, the classification provided by companies to ECHA in **REACH registrations** identifies that this substance is toxic if inhaled and may be corrosive to metals.



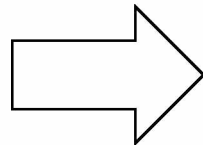
Additionally, the classification provided by companies to ECHA in **CLP notifications** identifies that this substance causes serious eye damage.

Breakdown of all 2455 C&L notifications submitted to ECHA



- ✓ Harmonised Classification
- REACH registration dossiers notifications
- CLP notifications

ⓘ At least one notifier has indicated that an impurity or an additive present in the substance impacts the notified classification.



asn Example : Hydrogen fluoride

Hazard classification & labelling

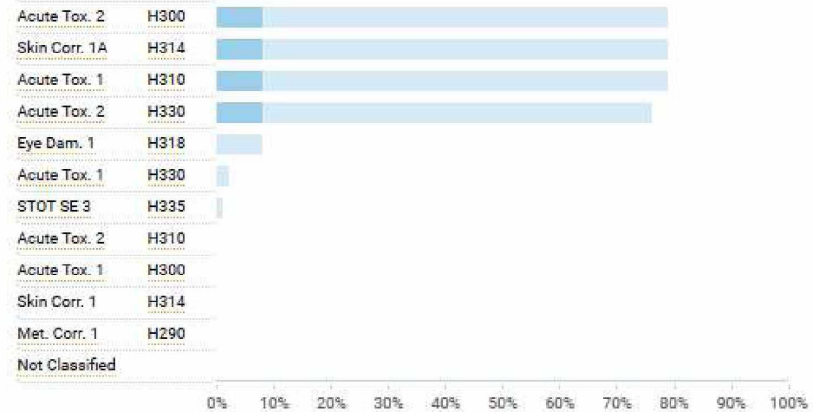


Danger! According to the classification provided by companies to ECHA in **REACH registrations** this substance is fatal if swallowed, is fatal in contact with skin, is fatal if inhaled and causes severe skin burns and eye damage.

Additionally, the classification provided by companies to ECHA in **CLP notifications** identifies that this substance causes serious eye damage.

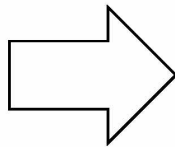
This substance is covered by several Harmonised Classifications and Labelling's (CLH) entries approved by the European Union. Differentiating between the different CLH's entries requires manual verification. To know more about the CLH please visit the [C&L Inventory](#).

Breakdown of all 833 C&L notifications submitted to ECHA



- ✓ Harmonised Classification
- REACH registration dossiers notifications
- CLP notifications

i At least one notifier has indicated that an impurity or an additive present in the substance impacts the notified classification.





Minimum data and information to be considered in the safety demonstration

For each scenario, this assessment includes :

- ❑ A presentation of the assumptions used in the release calculations and exposure scenarios :
 - the release calculation assumptions must be **reasonably pessimistic and the exposure scenarios must be based on realistic parameters**, but without considering any population protection actions that could be implemented by the public authorities

- ❑ An estimation of the intensity of the non-radiological phenomena to which persons and the environment could be exposed in the short, medium and long term, distinguishing the different age classes where necessary, and considering the different hazardous substance transfer pathways

- ❑ An estimation of the extent of the areas likely to be affected ;

- ❑ For incidents or accidents having consequences outside the site, **the kinetics of the development of the hazardous phenomena and the propagation of their effects.**

- ❑ The demonstration must prove **that accidents** that could lead to hazardous effects off the site that develop **too rapidly to allow timely deployment of the necessary population protection measures** :
 - are physically impossible,
 - if physical impossibility cannot be demonstrated, **that the measures taken on or for the installation render such accidents extremely improbable with a high level of confidence.**



Minimum data and information to be considered in the safety demonstration

Deterministic approach :

- ❑ This procedure integrates the **technical, organisational and human dimensions**,
- ❑ Takes into account **all the possible statuses of the installation**, whether permanent or transient.
- ❑ In addition to the postulated single initiating events, the demonstration of safety addresses plausible situations of **combined initiating events**.

Probabilistic approach :

- ❑ The safety demonstration shall also include **probabilistic analyses** of accidents and their consequences.





General principle of the safety demonstration involving dangerous chemicals

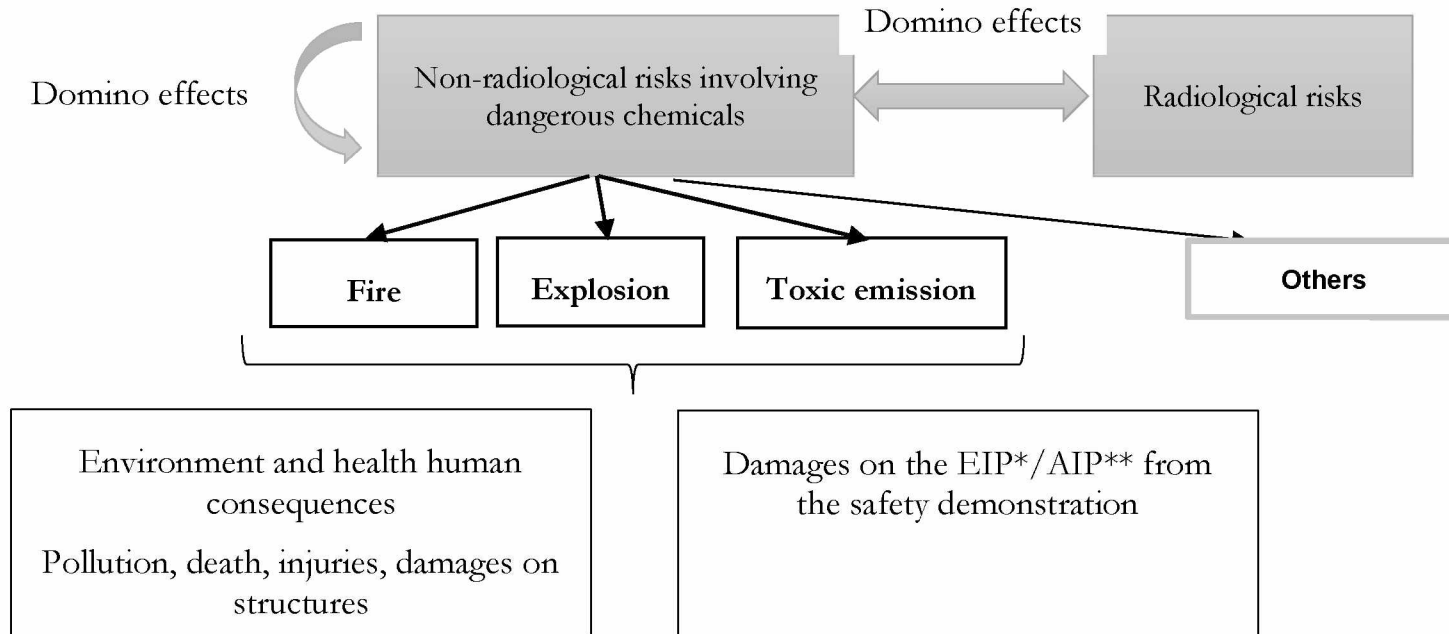


Figure 7 : consequences linked to non-radiological risks involving dangerous chemicals

EIP* : Important Element for the Protection of public security, health and safety, nature and environment. That is to say a structure, an equipment, a system (programmed or not), hardware, a component or software present in a basic nuclear installation or placed under the responsibility of the licensee, fulfilling a function necessary for the demonstration mentioned.

AIP**: Important Activity for the Protection of public security, health and safety, nature and environment. That is to say activities participating in the technical or organizational provisions.





3 EXAMPLES



Sintering process and explosion hazard

- Function : sintering of UO_2 and $(\text{U-Pu})\text{O}_2$ green pellets for fuel assembly manufacturing



Sintering process and explosion hazard

- Function : sintering of UO_2 and $(\text{U-Pu})\text{O}_2$ green pellets for fuel assembly manufacturing
 - ✓ Furnaces are operated under a light overpressure compared to the room.
 - ✓ Pressure and oxygen content measurements are performed inside equipment and they are associated to automatic actions.
 - ✓ Furnace design takes into account the overpressure that could be generated by an explosion defined by deterministic methods.
 - ✓ In case of an earthquake, specific systems that detect earthquake movements close process gas supply, outside the buildings.

Sintering process and explosion hazard

- Function : sintering of UO_2 and $(\text{U-Pu})\text{O}_2$ green pellets for fuel assembly manufacturing

	UO_2 process	Mox process
Sintering gas	75% H_2 + N_2	9% H_2 + Ar
Inerting gas	3,75% H_2 + N_2	Ar

Sintering process and explosion hazard

- Function : sintering of UO_2 and $(\text{U-Pu})\text{O}_2$ green pellets for fuel assembly manufacturing

UO_2 process	Mox process
Two static containment barriers	Three static containment barriers
Furnace under pressure when doors are closed	Airtight furnace
Automatic control of the entrance and exit gates Flame curtain at opening entrance or exit gate	Entrance and exit equipped with airlocks allowing atmosphere change (process gas to nitrogen)
Process gas released by two stacks	Process gas extracted directly by process ventilation

Sintering process and explosion hazard

- Function : sintering of UO_2 and $(\text{U-Pu})\text{O}_2$ green pellets for fuel assembly manufacturing

UO_2 process	Mox process
<p>A flare (<i>torchère</i>) burns process gas in each stack, using:</p> <ul style="list-style-type: none">- methane gas and- hot wire (also after an earthquake)	<p>Four steps:</p> <ul style="list-style-type: none">DecantationFiltration (metallic filter)CoolingVery high efficiency (VHE) filtration (2 filters in a row)
<p>Extraction hood above the two stacks and the doors: collection of combustion gas, dilution with the room air, VHE filtration and release in the building ventilation network.</p>	<p>Release in the glove boxes ventilation network.</p>

Sintering process and explosion hazard

- Function : sintering of UO_2 and $(\text{U-Pu})\text{O}_2$ green pellets for fuel assembly manufacturing



©FBFC

Sintering process and explosion hazard

- Function : sintering of UO_2 and $(\text{U-Pu})\text{O}_2$ green pellets for fuel assembly manufacturing
- In case of an earthquake:

UO_2 process	Mox process
Keeping location of the fissile material in order to avoid any criticality accident	Leak tightness of furnaces including gas and ventilation pipes

On-site transportation of uranium hexafluoride

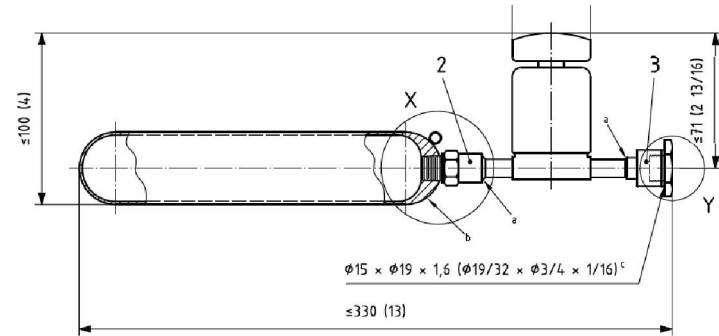
- Uranium hexafluoride (UF_6) is a radioactive material that has significant non-radiological hazardous properties.
- Talking about UF_6 on-site transportation, two specific cases are interesting:
 - the transport of UF_6 samples and
 - the transport of cylinders partially filled.



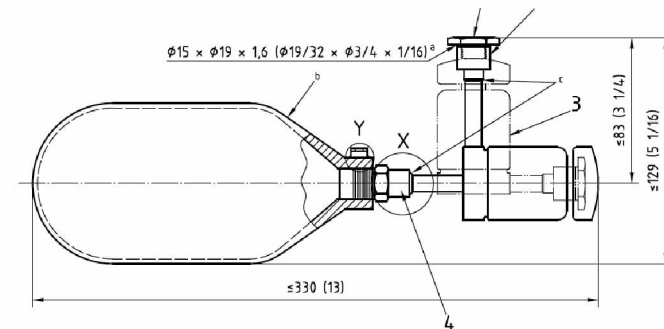
On-site transportation of uranium hexafluoride

transport of UF₆ samples:

- Even if the mass of UF₆ is low, samples are conditioned in specific cylinders for their transportation between industrial facilities and laboratories: mainly in metallic bottles type 1S or 2S containing between 100 and 2,200 grams of UF₆, loaded in a packaging agreed for transportation (container, drum...).
- The vehicle used is a common car, equipped with stowage tools and adequate signaling; the car speed is limited to 30 km/h.



1S cylinder



2S cylinder

©Norme ISO 7195

On-site transportation of uranium hexafluoride

transport of cylinders partially filled :

- Cylinders used for UF₆ transportation are 30B and 48Y cylinders,
- These cylinders can be transported full (2,277 kg of UF₆ for 30B cylinder and 12,501 kg for 48Y cylinders), partially full, or empty (containing only heels).
- A specific fire test (800 °C during 15 minutes) has been defined by the licensee for on-site transportation.
- Criteria associated to this test applicable to all cylinders are:
 - mechanical stresses on the cylinder wall must be lower than the ultimate strength of the steel used,
 - pressure in the cylinder must not overcome pressure of the critical point of UF₆ (233 °C and 46,6 bars) in order to avoid reaching a super-critical phase of UF₆ which properties are difficult to be modeled.

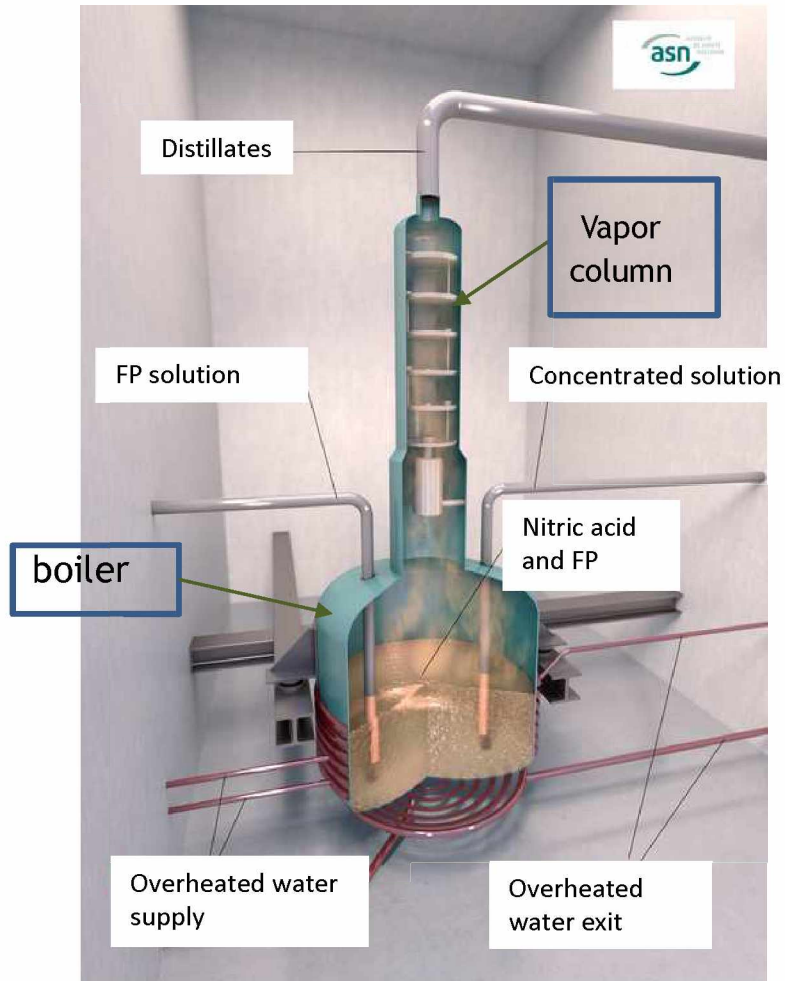
On-site transportation of uranium hexafluoride

transport of cylinders partially filled:

- Partially filled cylinders are sometimes transported on-site, between enrichment plants and storage pads. They could contain from 150 to 6,250 kg of UF₆ (48”) or from some kg to 450 kg (30B).
- Due to this limited mass of material, the thermal inertia is low and the pressure increase during a fire is greater than in a full cylinder. As a consequence, the criteria could be not always respected.
- Licensees have defined specific dispositions to compensate this issue: a vehicle with fire extinguishing means escorts the transport on a predetermined itinerary on which no other circulation is permitted.

Fission product concentrators

- Function : concentration of PF solutions, after U+Pu partitioning and before vitrification



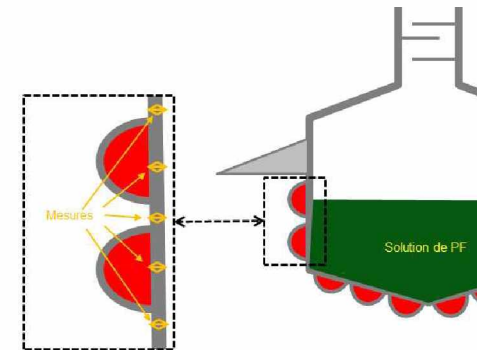
	UP2 facility	UP3 facility
Number of concentrators	3	3
Commissioning date	1994	1989
Usefull Volume	10 m ³	10 m ³

- ✓ Material: stainless steel resistant to corrosion (URANUS S1N)
- ✓ Designed in 80s with an over-thickness of the shell
- ✓ Sited in individual concrete cells, not accessible (high dose rate zone)

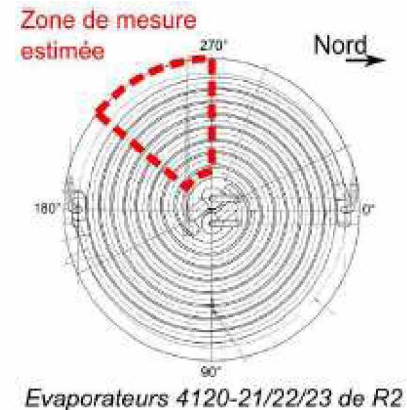
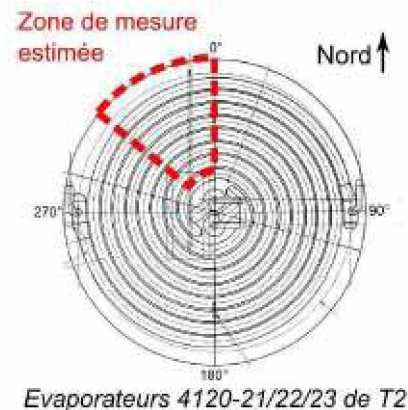
FP evaporator corrosion

Thickness measurements of evaporator shell (2012 - 2015):

- Thickness measurement by ultra-sound:
 - ✓ External measures, between turns of heating circuit;
 - ✓ Measures inside the heating circuit.



- Zones accessible to ultra-sound measurement: 1/8 of boiler surface
⇒ Recommendation to increase measurement area.



FP evaporator corrosion

- Measured thickness lower than expected = corrosion rates higher than expected at the design

Part of the evaporator	Decrease of the corrosion over-thickness (end of 2016)	
	R2	T2
Boiler	76 %	74 %

- Evaporator of both plants will reach minimal thickness to guaranteeing mechanical integrity in between 2 and 10 years

FP evaporator corrosion

- Origin of increased corrosion rate: 2 hypotheses from Orano
 - presence of more important than expected fluoride anions;
 - presence of deposit on the boiler walls leading to the creation of hot spots.
- Deterministic accidental scenario:
 - Simultaneous breaches of the overheated water circuit and of the boiler and leaks in the cell.
 - Steam and radioactive solution extracted by the ventilation system
 - Contamination and irradiation in the building
 - Last VHE filter degradation and potential release in the environment.

FP evaporator corrosion

Orano proposals:

- Chemistry evolution: injection of fluorine complexant
- Decrease of operating temperature and pressure
- Increase of the rinsing frequency

IRSN recommendations:

- an annual surveillance program should be implemented,
- containment of FP solutions in case of accidental situations (worst case: leak of FP solution and of overheated water in the cell) should be improved.

Nuclear safety authority decision (Decision n° 2016-DC-0559) with requirements related to:

- the monitoring of the corrosion phenomena;
- the reduction of the phenomena by limiting the operating pressure, temperature and fluorine content, and by periodic rinsing;
- the detection and mitigation of accidental situations.

FP evaporator corrosion

- | In parallel to the implementation of these improvements, Orano decided to replace the evaporators and started the construction of two new concentration workshops, one for each plant.
- | Assessing the design options of these new workshops, IRSN considered that:
 - in order to perform US measurements and visual controls, the whole external surface of the evaporators shall be accessible, especially the surface located under the liquid level;
 - the inspection of the internal surface of the boilers shall be possible in order to monitor the deposit formation;
 - the volume of overheated water, and the consecutive overpressure, that could leak in the evaporator cell shall be reduced in order to minimize the consequences on the ventilation filters of the second static containment barrier.
- | This corrosion issue is an example of the ageing effect related to chemical action in a fuel cycle facility and it underlines the importance of a surveillance programme implemented from the beginning of the operation.

Thank you for your attention