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## Determination of Cl-36 in various radioactive waste

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# DEM 2021

International Conference on Decommissioning Challenges: Industrial Reality, Lessons Learned and Prospects



DE LA RECHERCHE À L'INDUSTRIE

## Determination of $^{36}\text{Cl}$ in radioactive waste

15<sup>th</sup> September 2021

Céline GAUTIER - DES/ISAS/DPC/SEARS/LASE



## Context of the study

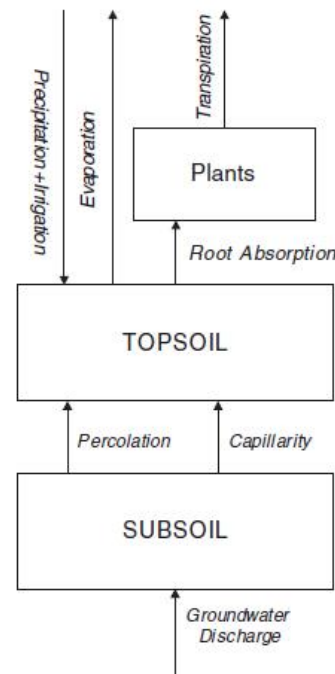
## Management of low and intermediate level nuclear waste in France

In France, the National Radioactive Waste Management Agency **ANDRA** requests a radiological characterization of nuclear waste and specifies acceptance criteria for packages that waste producers have to respect.

**$^{36}\text{Cl}$  is one radionuclide of interest for decommissioning and disposal of nuclear waste**

$^{36}\text{Cl}$  exists as chloride anion in the environment and can be very soluble and mobile  $\Rightarrow$  risk for the safety of waste disposal  $\Rightarrow$  **its acceptance limit is only 5 Bq/g**

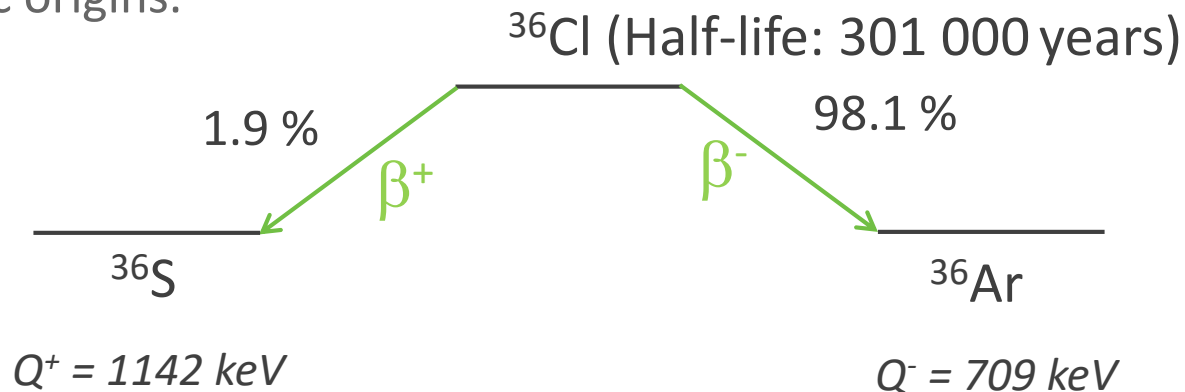
Radionuclide	Declaration threshold (Bq/g) - Acceptance limit (Bq/g) for ANDRA surface disposal
$^3\text{H}$	$10 \rightarrow 2 \times 10^5$
$^{60}\text{Co}$	$10 \rightarrow 1 \times 10^8$
$^{14}\text{C}$	$10 \rightarrow 9 \times 10^4$
<b><math>^{36}\text{Cl}</math></b>	<b><math>0.01 \rightarrow 5</math></b>



*Model for the transport of  $^{36}\text{Cl}$  in soils and its uptake by plants (Pérez-Sánchez et al. (2009))*

## Determination of $^{36}\text{Cl}$ in low and intermediate level nuclear waste

- $^{36}\text{Cl}$  is a long-lived beta-emitting radionuclide with both natural and anthropogenic origins.



- $^{36}\text{Cl}$  is produced from **neutron activation of stable  $^{35}\text{Cl}$**  present as an impurity in materials.
- $^{36}\text{Cl}$  can be present in nuclear graphites but also in steels, ion exchange resins, effluents and sludges.
- As a pure beta-emitter,  $^{36}\text{Cl}$  needs to be isolated from the matrix elements and the interfering radionuclides ( $^{60}\text{Co}$ ) through chemical purification prior to nuclear measurement, mainly liquid scintillation counting (LSC).



## Bibliography

## Determination of $^{36}\text{Cl}$ in nuclear waste

- Literature review: for  $^{36}\text{Cl}$  extraction step, all the published radiochemical methods use the **volatile nature of chlorine** at high temperatures

1

- Chlorine extraction: oxidative acid digestion and thermal decomposition after addition of Cl carrier

2

- Trapping in bubbler: mainly alkaline solutions of NaOH or  $\text{Na}_2\text{CO}_3$

3

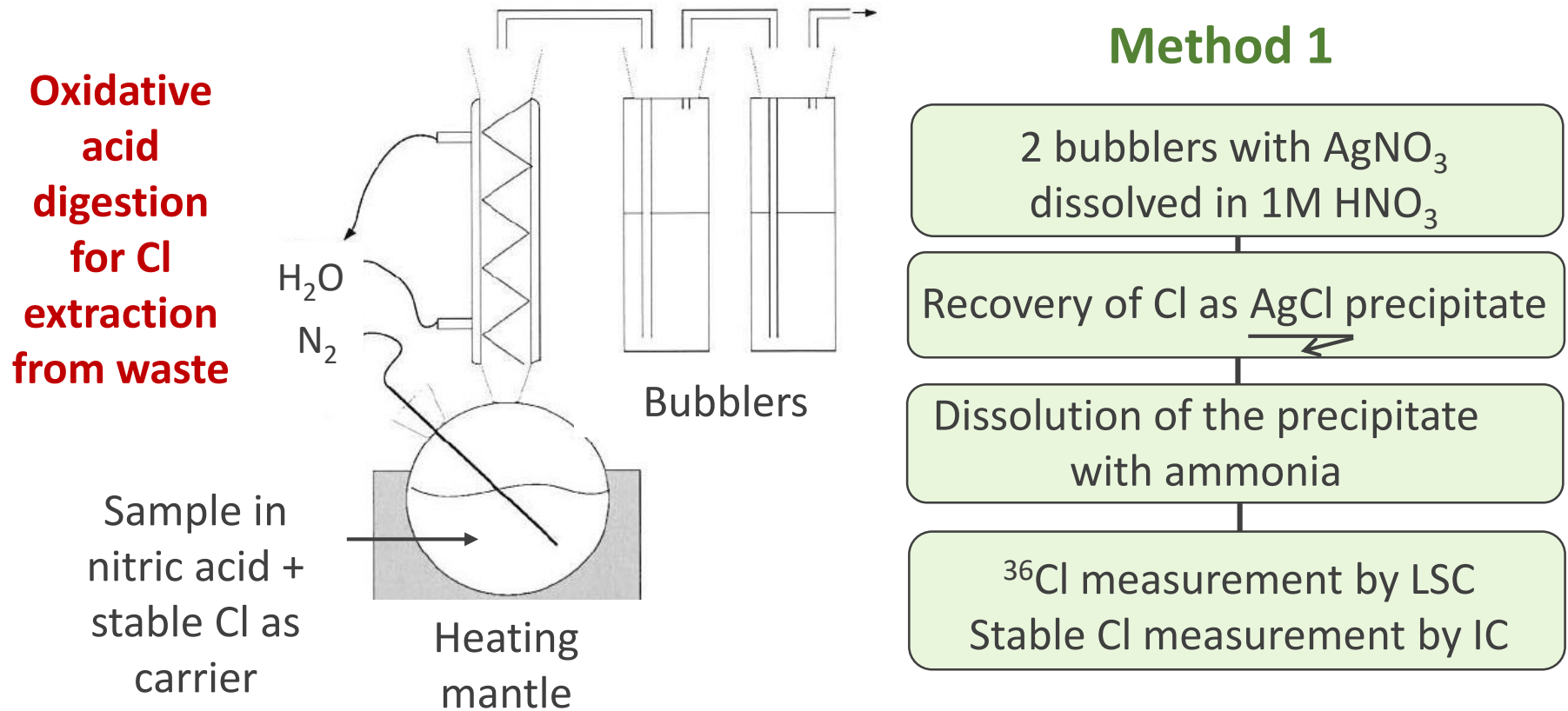
- Purification: mainly AgCl precipitation but also anion exchange chromatography or extraction chromatography ( $\text{Cl}^\text{®}$  resin)

4

- Measurements
  - Stable chlorine: ion chromatography, ICP
  - $^{36}\text{Cl}$ : mainly LSC for routine analysis

## Determination of $^{36}\text{Cl}$ in low and intermediate level nuclear waste

- French M60-332 standard  $\Rightarrow$  two radiochemical methods to characterize  $^{36}\text{Cl}$  in radioactive waste after radiochemical separation



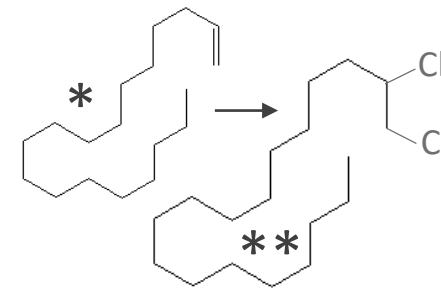
**Radiochemical method only relevant for samples with few  $\beta$  and  $\gamma$  emitters and with no other halogens or volatile RNs (ex:  $^{129}\text{I}$ )**



Method 2 of the French M60-332 standard = CEA method = advanced purification

- Extraction after Cl and Ag addition: oxidative acid digestion in micro-wave oven or thermal decomposition
- AgCl precipitation
- Dissolution of AgCl precipitate using ammonia
- Elimination of Ag by reduction using hydrazine sulfate
- Octadecene\* spiking by chlorine using an oxidant mixture (sulphuric acid + potassium iodate) and dichloromethane
- Recovery of the organic phase containing dichloro-octadecane\*\* and purification on silica gel column using hexane
- Liquid-liquid extraction using diethyl ether and sodium biphenyl
- Back extraction using nitric acid, heating and dilution in water
- Ion chromatography for Cl determination and LSC for  $^{36}\text{Cl}$  determination (LOD ~ a few Bq/g)

**Method 2:**  
method based on  
the chlorination  
of an alkene



**Radiochemical  
method  
relevant for  
all types of  
radwaste: high  
selectivity**

# Strategies developed to extract $^{36}\text{Cl}$ in radioactive waste

► Demands to characterize  $^{36}\text{Cl}$  in various types of nuclear waste

- Various amounts to characterize: <1 g up to 10-20 g
- Two types of contamination: in-depth or surface contamination

Small amounts to  
characterize (< 1 g)

Steel chips



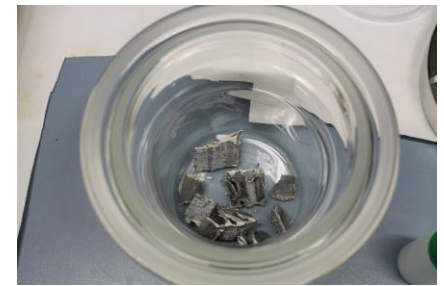
Concrete



Resin

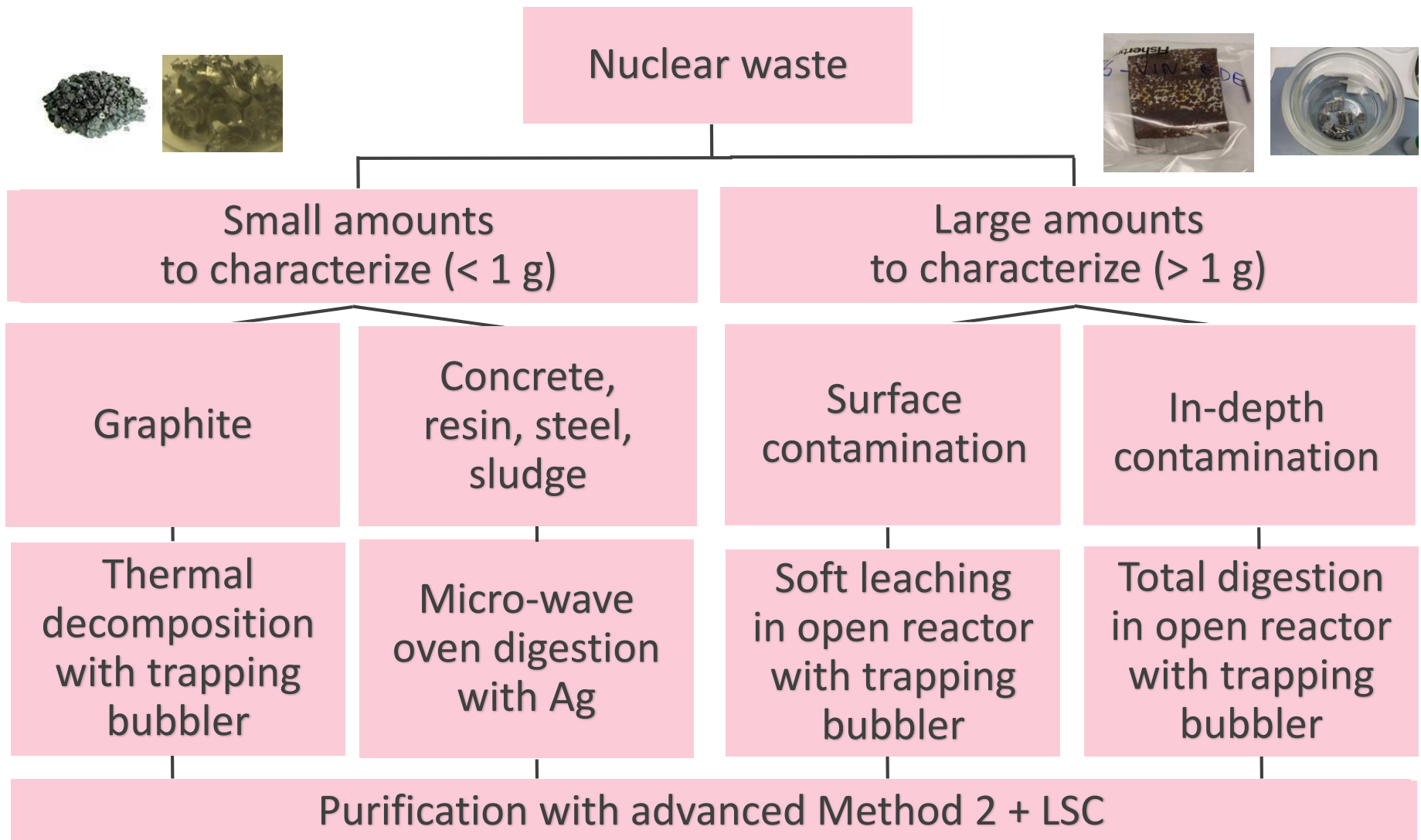
Large amounts to  
characterize (> 1 g)

Steel block



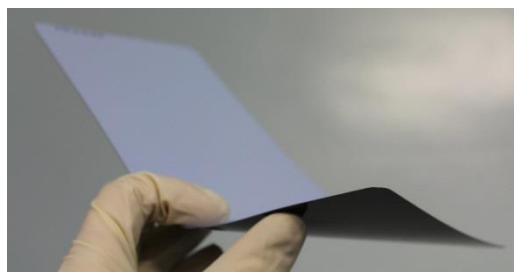
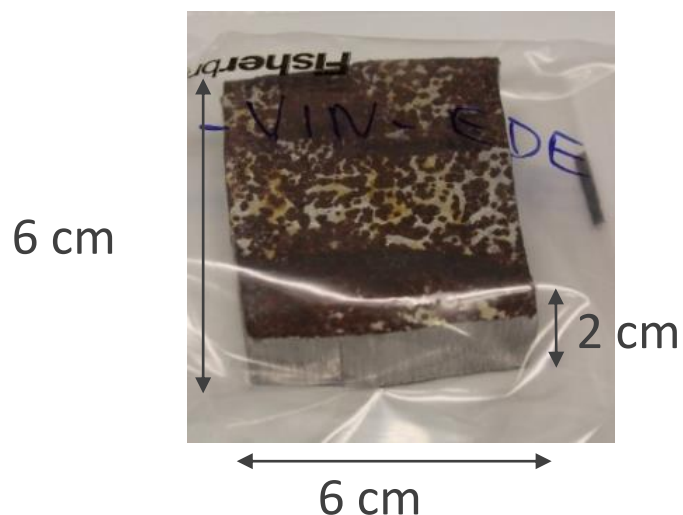
Magnesium cladding

**Development of different strategies  
to extract  $^{36}\text{Cl}$  in nuclear waste**



## ► Example 1: steel blocks with surface contamination

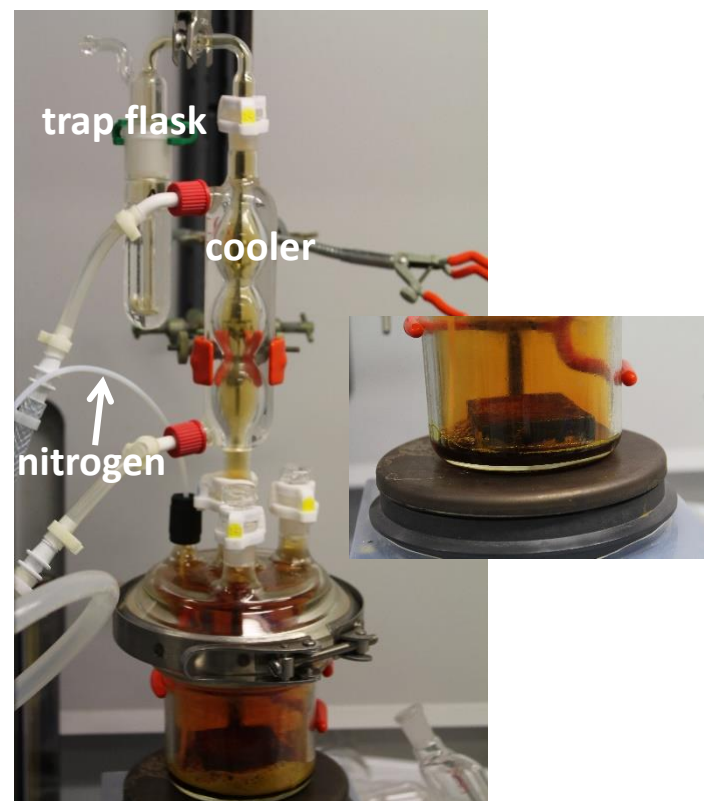
- Soft leaching in open reactor to remove only the contamination layers: adaptation of the reactor (flat bottom) to treat large blocks
- Application of digital autoradiography technique to monitor the decontamination steps



Radiosensitive phosphor screen

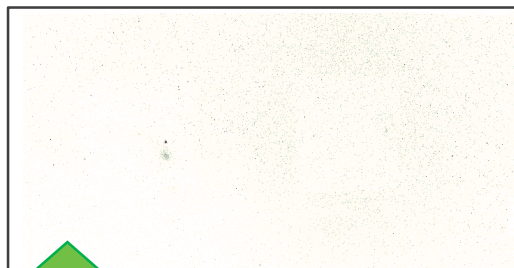


Scanner

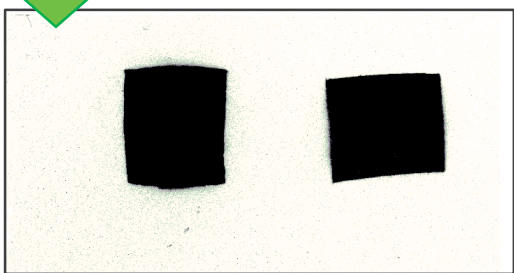
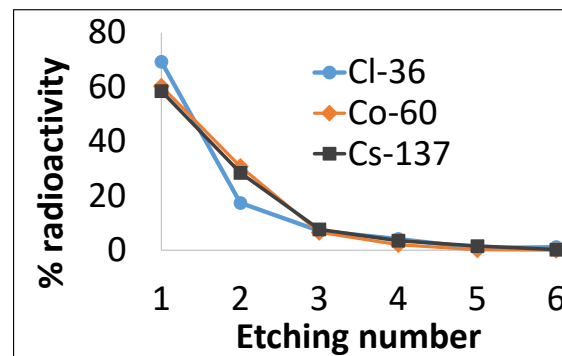


### ► Example 1: steel blocks with surface contamination

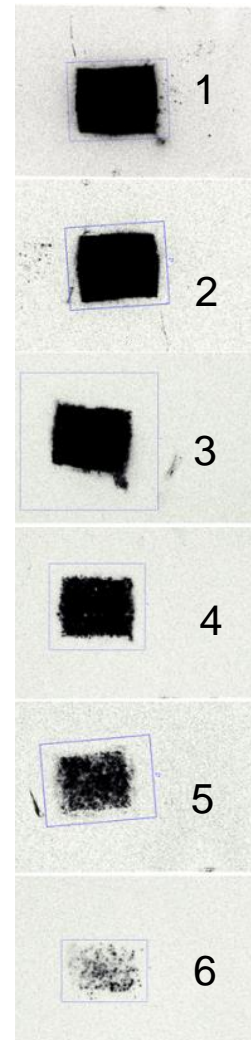
- Application of digital autoradiography technique to monitor the decontamination steps



Top screen

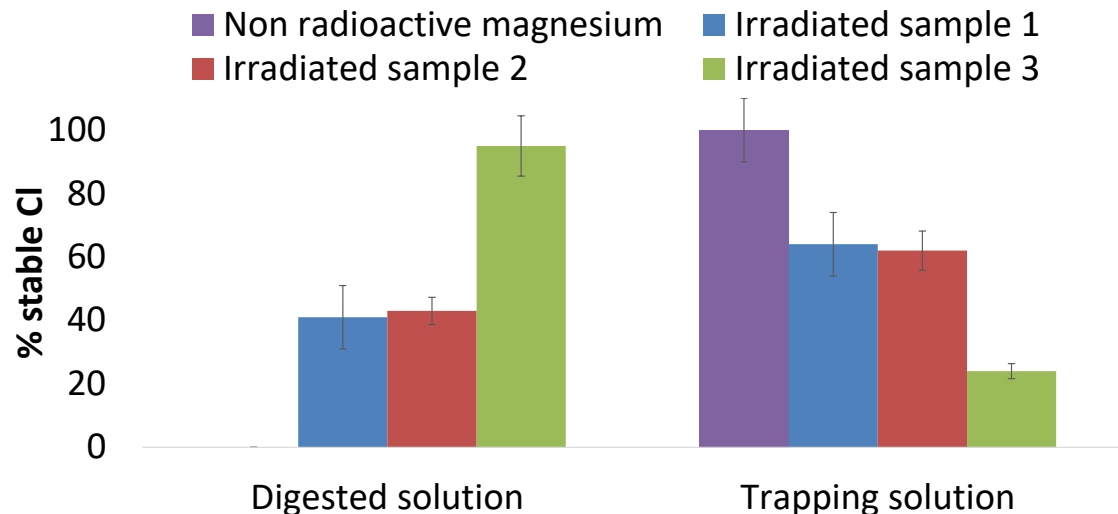
Only one side  
contaminated to treatBottom  
screenSample after several etchings  
( $\approx 100\ \mu\text{m}$  thickness removed  
at each etching)

**Same  
decontamination  
profile for all RNs**



## ► Example 2: magnesium claddings with in-depth contamination

- Total digestion to decompose the entire samples of  $\sim 10\text{-}15\text{ g}$ 
  - Magnesium digested easily in nitric acid but solubility of  $\text{Mg}(\text{NO}_3)_2$  limited at room temperature ( $\sim 70\text{-}420\text{ g/L}$  at  $20\text{ }^\circ\text{C}$ ) :  $\sim 100\text{ ml}$  of  $\text{HNO}_3$  needed  $\Rightarrow$  not compatible with our micro-wave oven
- Total digestion in open reactor with nitric acid



**Different behaviors of irradiated samples: purification procedures applied to digested or trapping solutions**

**$^{36}\text{Cl}$  measurement at low level**



- Maximum activity limit in low and intermediate level nuclear waste in France=5 Bq/g and clearance limit in 2013/59 Euratom directive=1 Bq/g

⇒ **Application of accelerator mass spectrometry (AMS) to measure  $^{36}\text{Cl}$  at low level**

1

- Sample purified with our in-house radiochemical procedure

2

- AgCl precipitate and dissolution in ammonia

3

- Elimination of sulfur by precipitation using baryum nitrate

4

- AgCl precipitate

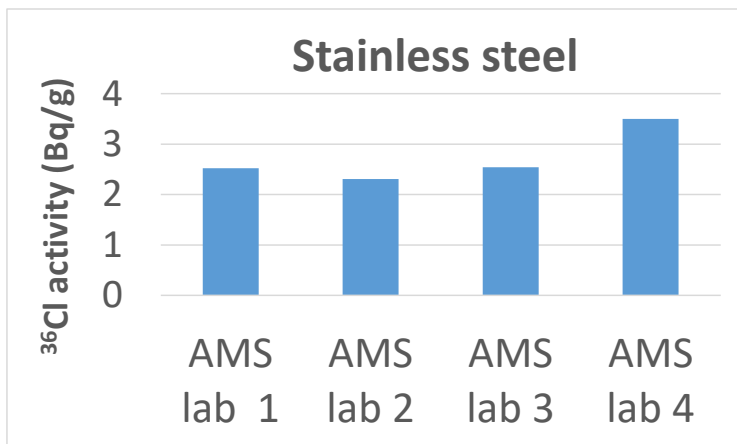
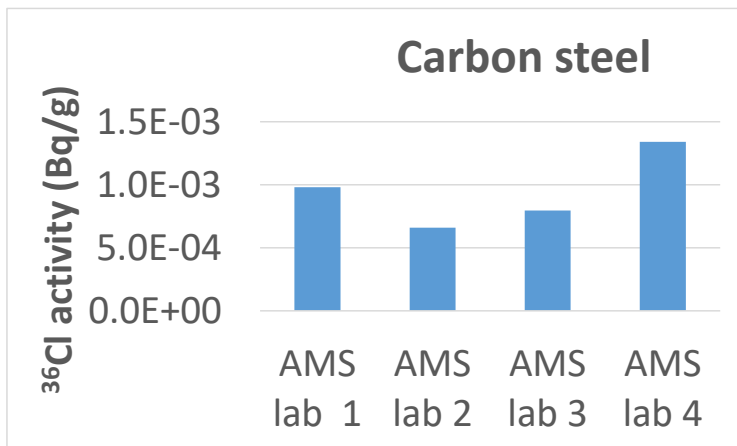
5

- Sample sending to AMS facility to measure  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio

**Necessity to adapt our purification procedure for AMS detection:  $^{36}\text{S}$  elimination (to avoid interferences at m/z 36) and special care to the laboratory environment and materials (to avoid sample contamination)**



- ▶ Application of AMS to measure  $^{36}\text{Cl}$  at low level in irradiated steels
  - Comparison with LSC measurements



$^{36}\text{Cl}$ (Bq/g)	LSC	AMS mean
<b>Carbon steel</b>	< 0.5	9.44E-04 (30 %)
<b>Stainless steel</b>	6 (50 %)	2.72 (20 %)

**Consistency of the results obtained with the different AMS laboratories and with LSC measurements at CEA**

**Improvement of  $^{36}\text{Cl}$  detection limit by at least a factor of 500**

## Conclusions and prospects

## Determination of $^{36}\text{Cl}$ in low and intermediate level nuclear waste

- ▶ Development of a highly selective radiochemical procedure based on the chlorination of an alkene molecule
  - Initial validation by preparing in-house spiked resins
  - Check of its validity over time by participating to proficiency tests
- ▶ Development of different extraction methods to treat all natures of nuclear waste (graphite, concrete, resin, steel, sludge, magnesium cladding...) and all types of contamination (in depth or surface contamination)
  - Potentialities of digital autoradiography to monitor the decontamination steps in case of surface contamination
  - Successful application of AMS to measure  $^{36}\text{Cl}$  at low level

**Each sample is almost unique: we have to adapt each time !**



**Thank you for your attention**

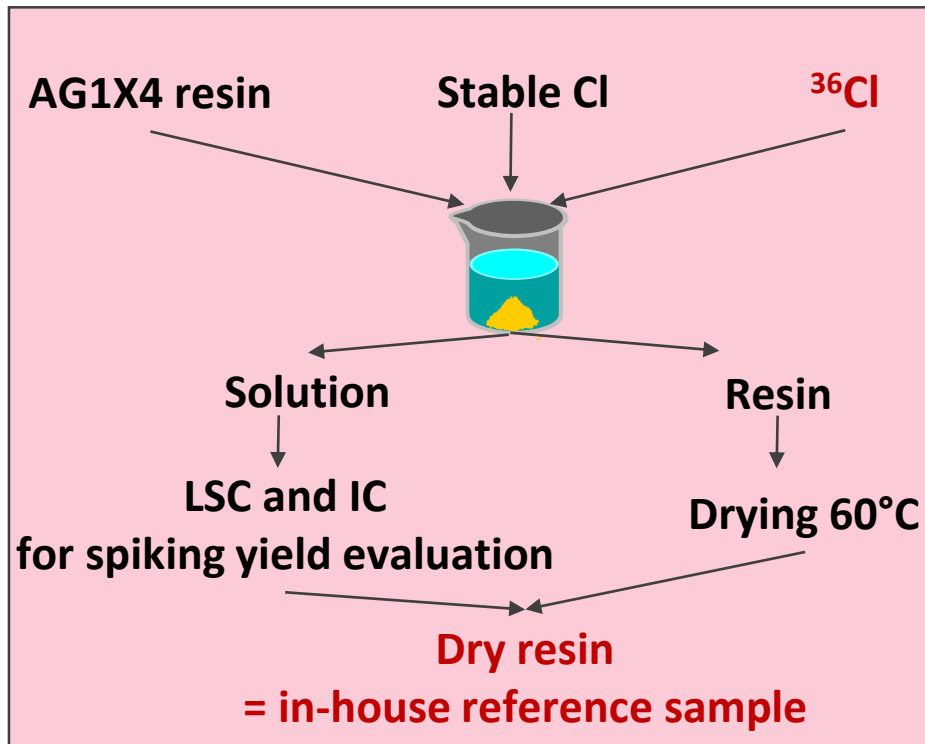
Christèle Colin, Margaux Giuliani, Elodie Laporte,  
René Brennetot, Pascal Fichet

# Validation of the developed radiochemical method

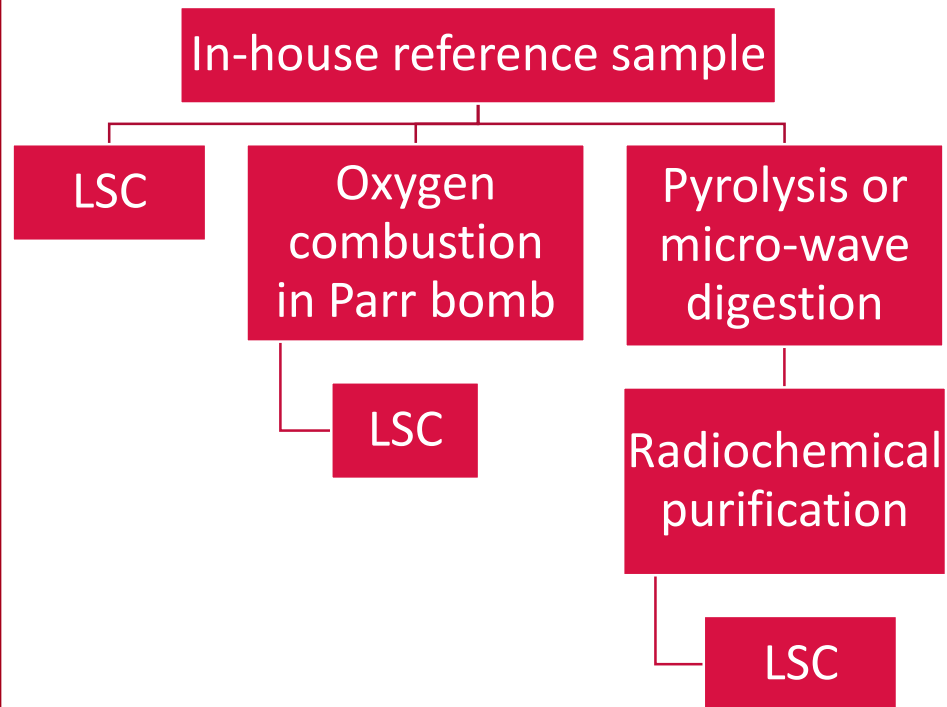
## ► Initial validation

- Lack of certified solid standards for  $^{36}\text{Cl}$  measurement in nuclear waste
- Preparation of in-house solid reference samples in 2 steps

### 1. Spiking of ion exchange resins with $^{36}\text{Cl}$

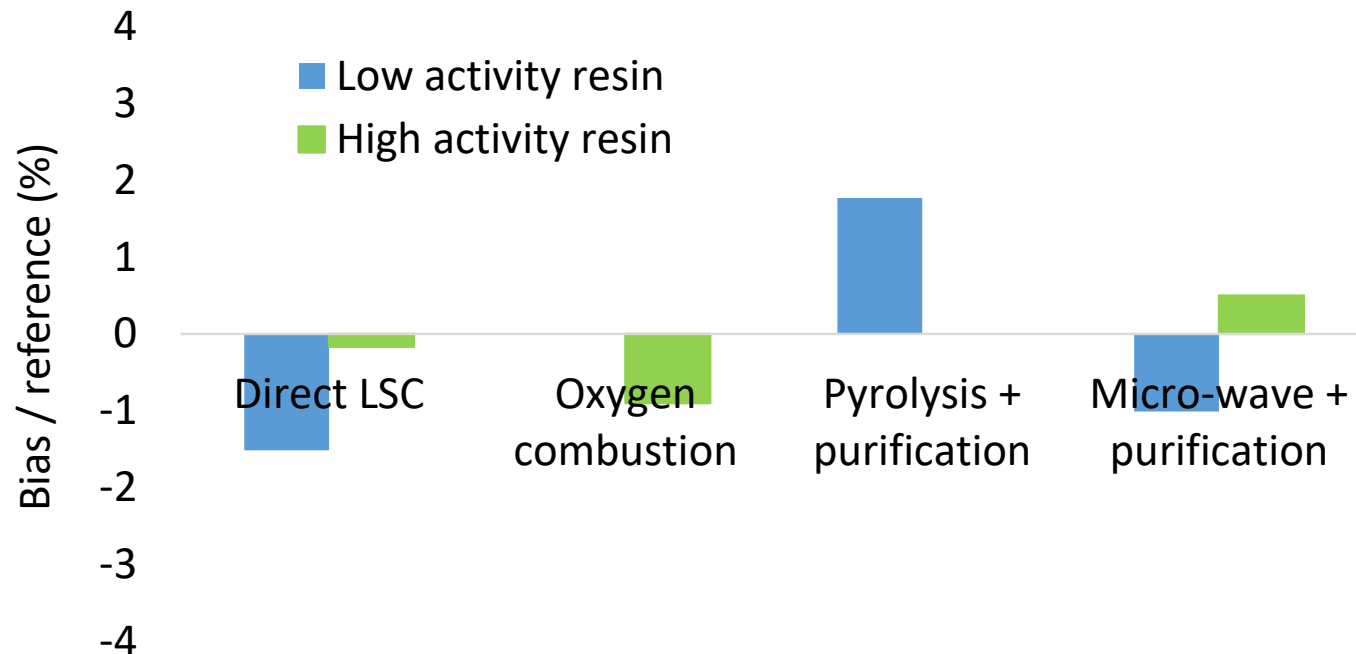


### 2. Comparisons of different methods



## ► Initial validation

- Preparation of **two spiked resins** with low and high activities (40 and 3000 Bq/g)

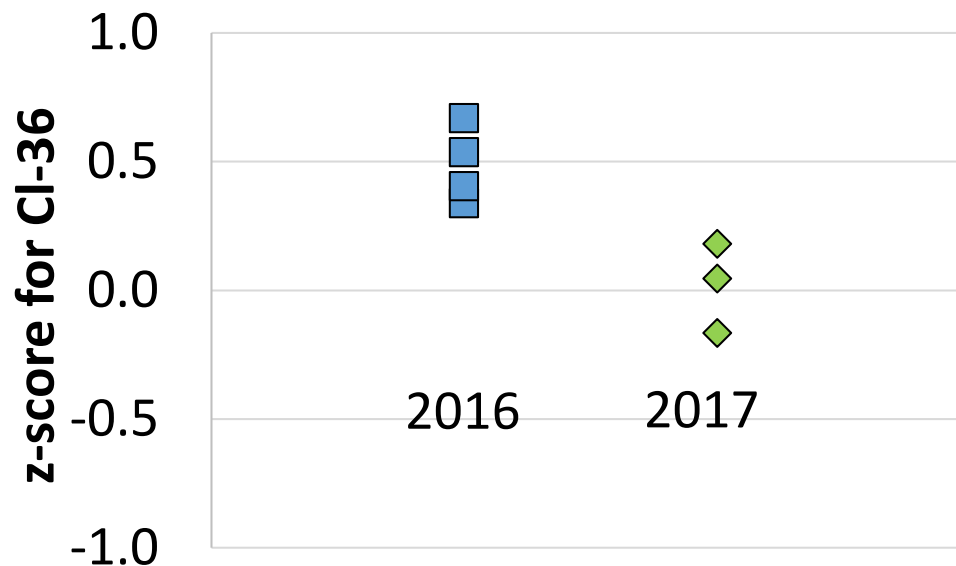


**No bias for  $^{36}\text{Cl}$  analysis in comparison to direct LSC (= reference) whatever the applied procedure including our developed radiochemical purification  $\Rightarrow$  validation**



► **Quality assurance: validity of the results over time**

- Participation in interlaboratory comparisons and proficiency tests: Environmental Radioactivity Proficiency Test Exercises organized by NPL (UK)



**z-score < 2 ⇨ trueness of our developed method over time**

# Strategies developed to extract $^{36}\text{Cl}$ in radioactive waste

**► Example: irradiated graphites with in-depth contamination**

- Extraction step performed with a thermal decomposition by combustion so as to eliminate  $^{14}\text{C}$  more easily



- 1 Preparation of the graphite sample in a boat
- 2 Introduction in the pyrolysis oven ( $950^\circ\text{C}$ ) and addition of oxygen circulation
- 3 Trapping of  $^{36}\text{Cl}$  in bubblers containing sodium carbonate, hydrogen peroxide and water
- 4 Recovery of the trapping solution and application of our purification procedure
- 5 LSC and ion chromatography measurements