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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}Cl in radioactive waste

15th September 2021

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



Context of the study

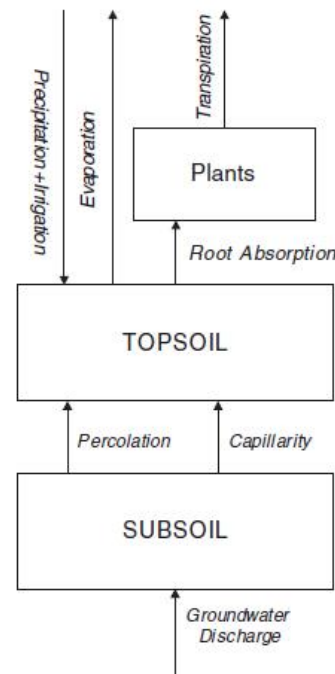
Management of low and intermediate level nuclear waste in France

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}Cl is one radionuclide of interest for decommissioning and disposal of nuclear waste

^{36}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**

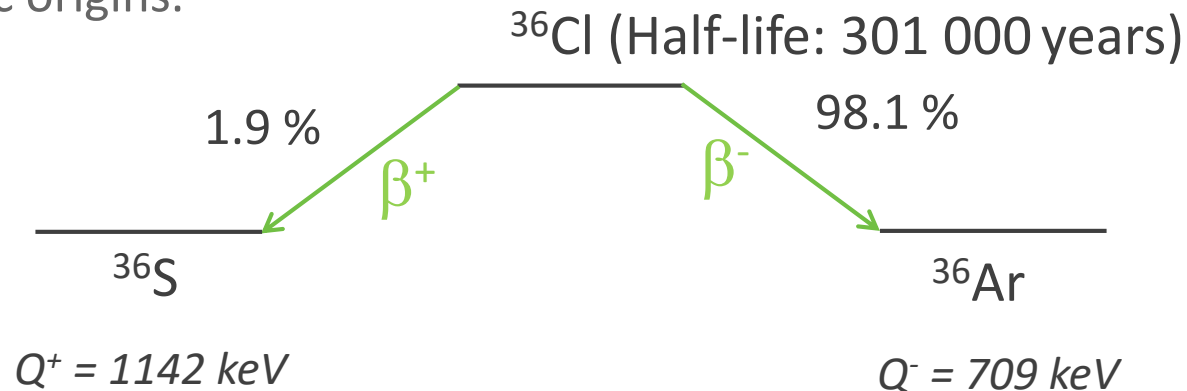
| Radionuclide | Declaration threshold (Bq/g) - Acceptance limit (Bq/g) for ANDRA surface disposal |
|------------------------------------|---|
| ^3H | $10 \rightarrow 2 \times 10^5$ |
| ^{60}Co | $10 \rightarrow 1 \times 10^8$ |
| ^{14}C | $10 \rightarrow 9 \times 10^4$ |
| ^{36}Cl | $0.01 \rightarrow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



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

Determination of ^{36}Cl in low and intermediate level nuclear waste

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



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



Bibliography

Determination of ^{36}Cl in nuclear waste

- Literature review: for ^{36}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 Na_2CO_3

3

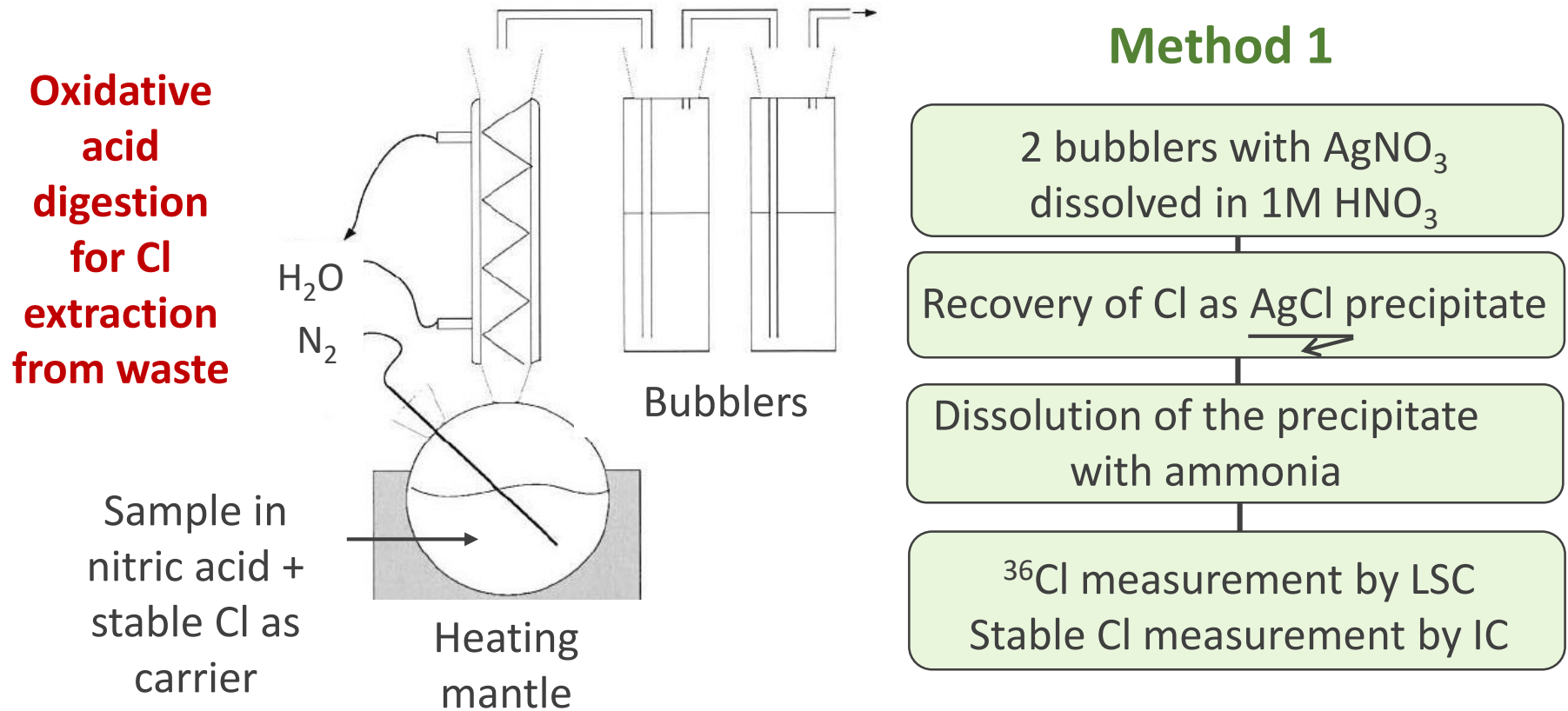
- Purification: mainly AgCl precipitation but also anion exchange chromatography or extraction chromatography (Cl^\circledast resin)

4

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

Determination of ^{36}Cl in low and intermediate level nuclear waste

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

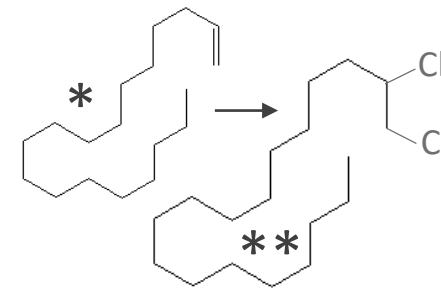


Radiochemical method only relevant for samples with few β and γ emitters and with no other halogens or volatile RNs (ex: ^{129}I)

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}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}Cl in radioactive waste

► Demands to characterize ^{36}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)

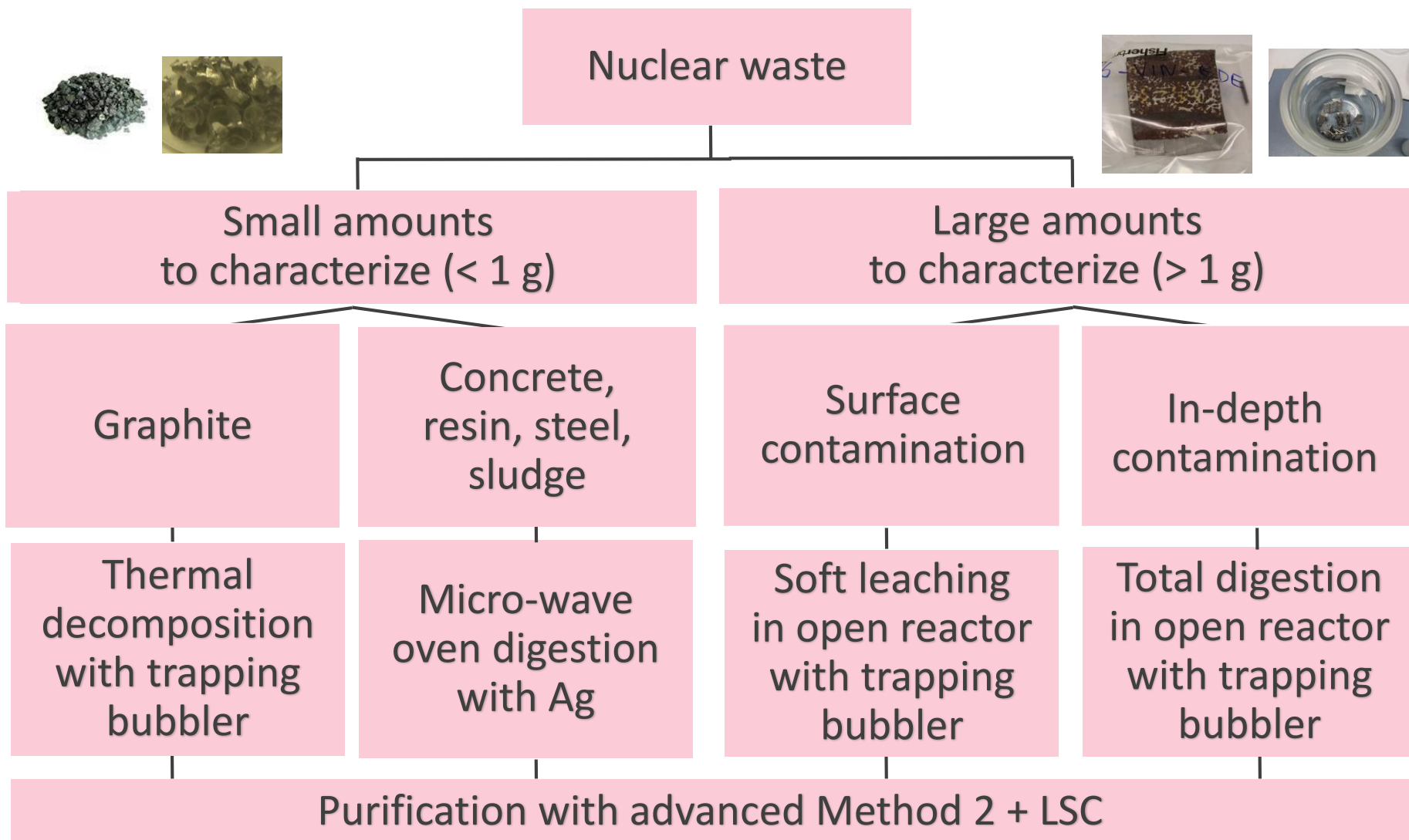


Steel block



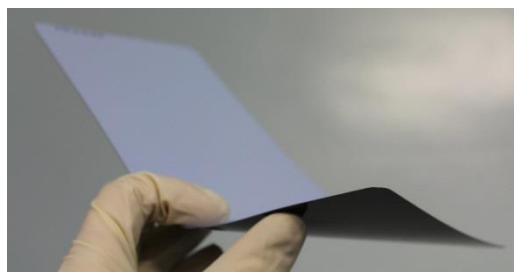
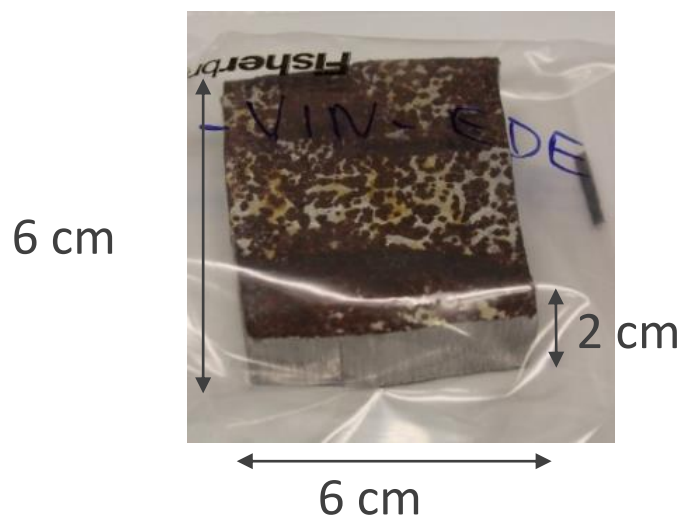
Magnesium cladding

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



► Example 1: steel blocks with surface contamination

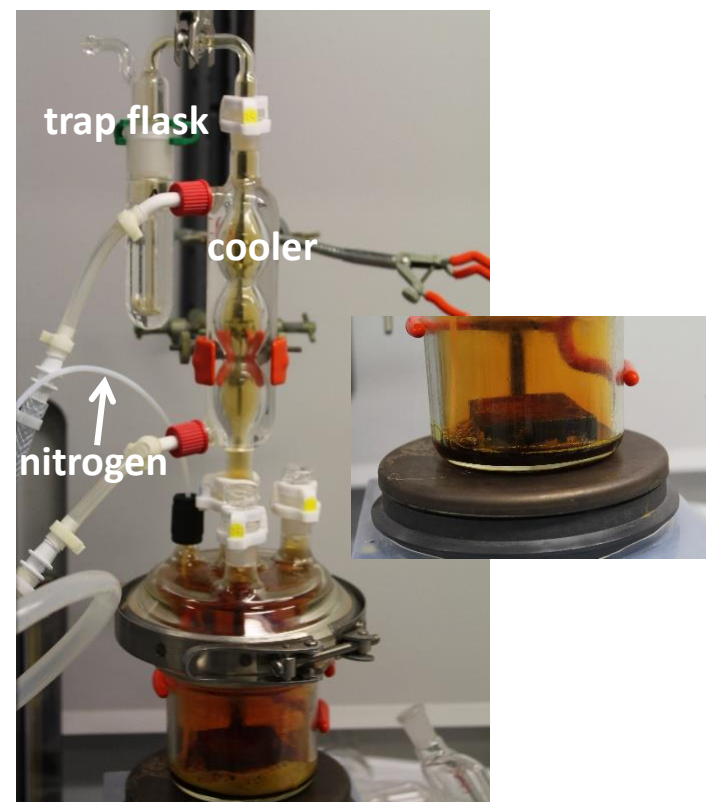
- Soft leaching in open reactor to remove only the contamination layers: adaptation of the reactor (flat bottom) to treat large blocks
- Application of digital autoradiography technique to monitor the decontamination steps



Radiosensitive phosphor screen

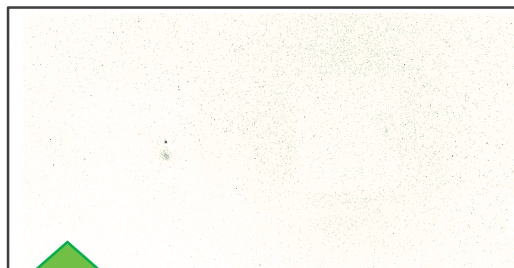


Scanner

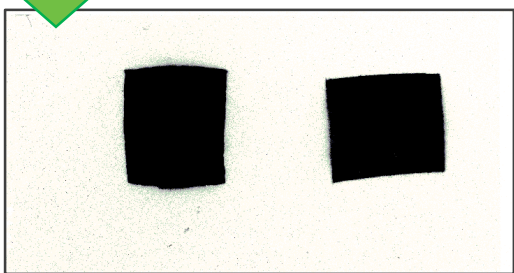
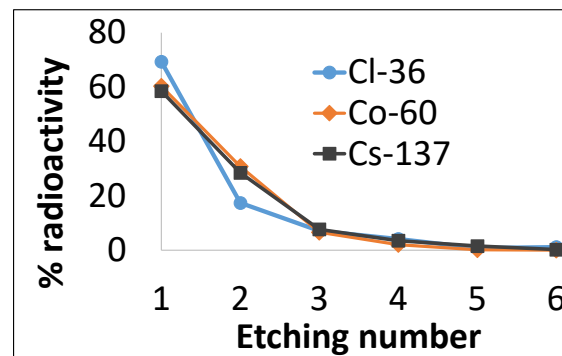


► Example 1: steel blocks with surface contamination

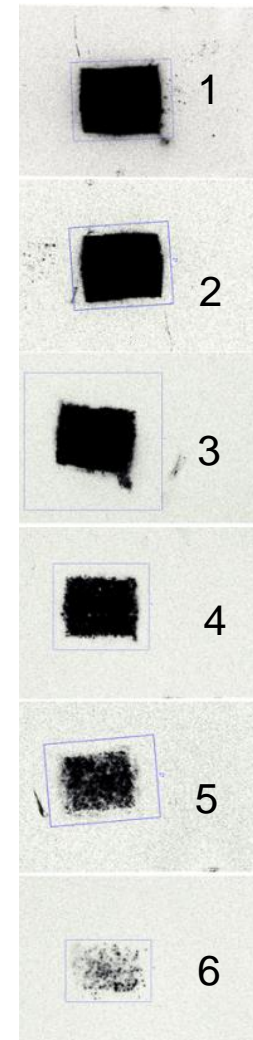
- Application of digital autoradiography technique to monitor the decontamination steps



Top screen

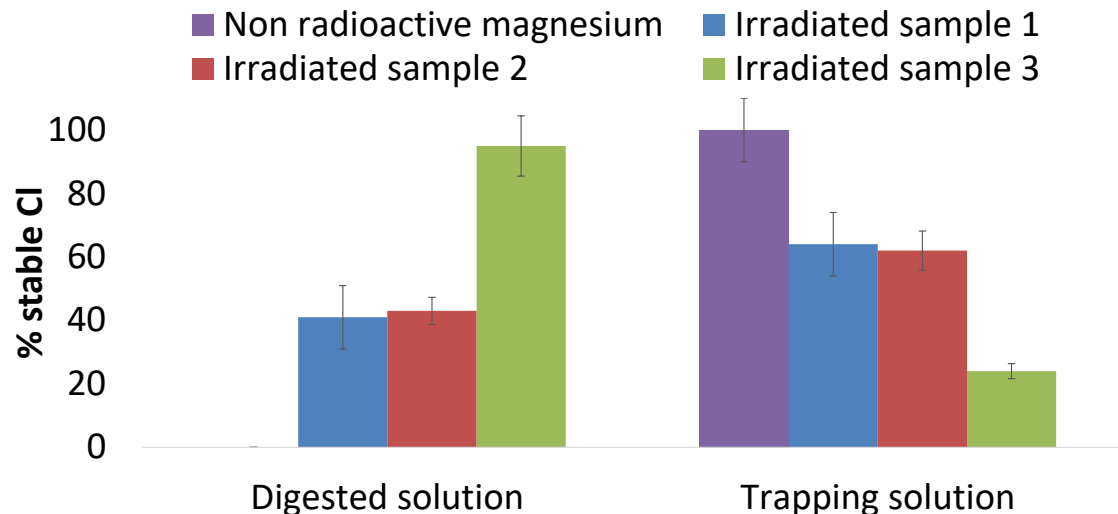
Only one side
contaminated to treatBottom
screenSample after several etchings
($\approx 100\ \mu\text{m}$ thickness removed
at each etching)

**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 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}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}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

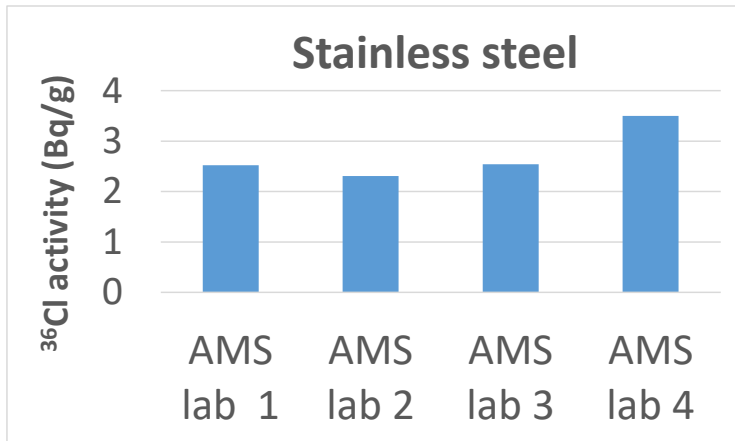
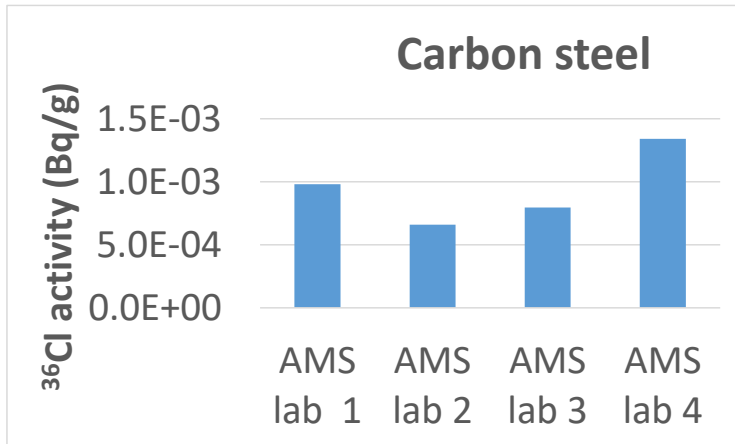
5

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

Necessity to adapt our purification procedure for AMS detection: ^{36}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}Cl at low level in irradiated steels
 - Comparison with LSC measurements



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

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

Improvement of ^{36}Cl detection limit by at least a factor of 500

Conclusions and prospects

Determination of ^{36}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}Cl at low level

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



Thank you for your attention

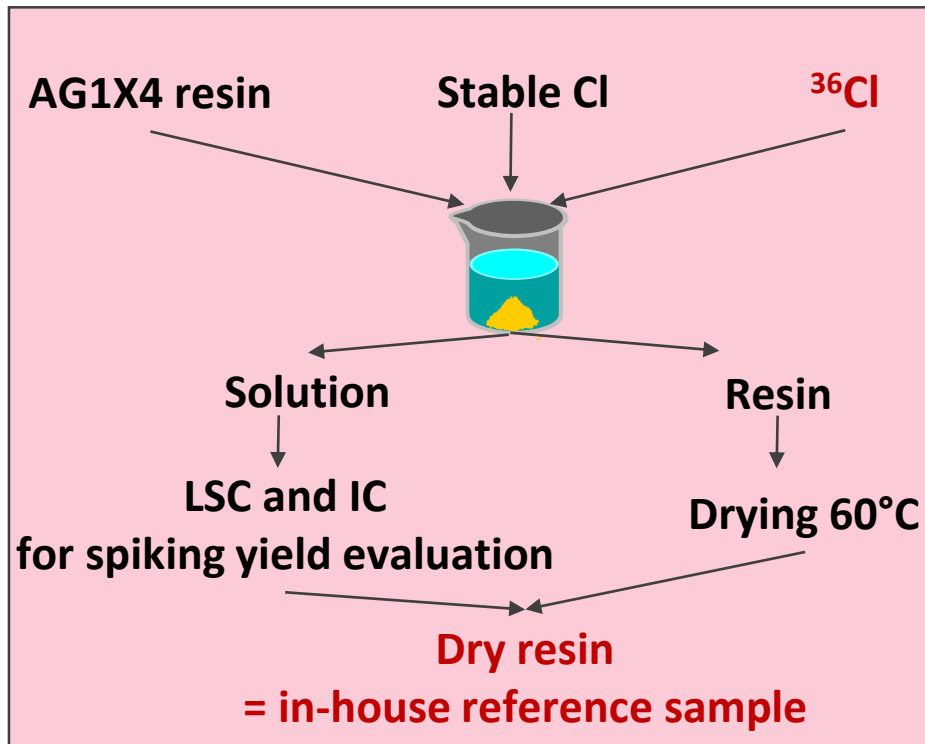
Christèle Colin, Margaux Giuliani, Elodie Laporte,
René Brennetot, Pascal Fichet

Validation of the developed radiochemical method

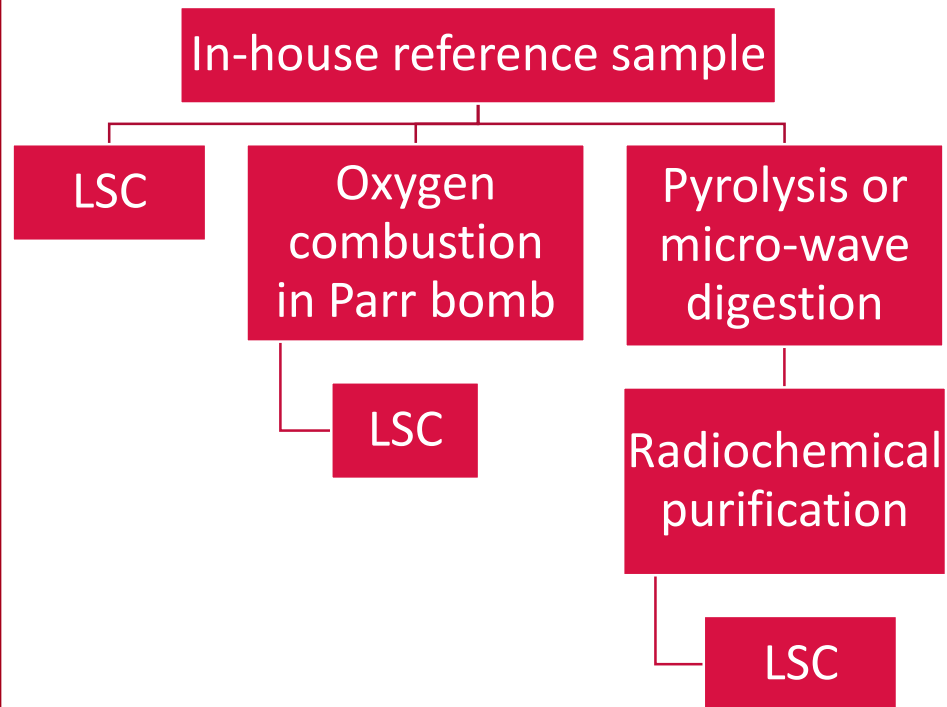
► Initial validation

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

1. Spiking of ion exchange resins with ^{36}Cl

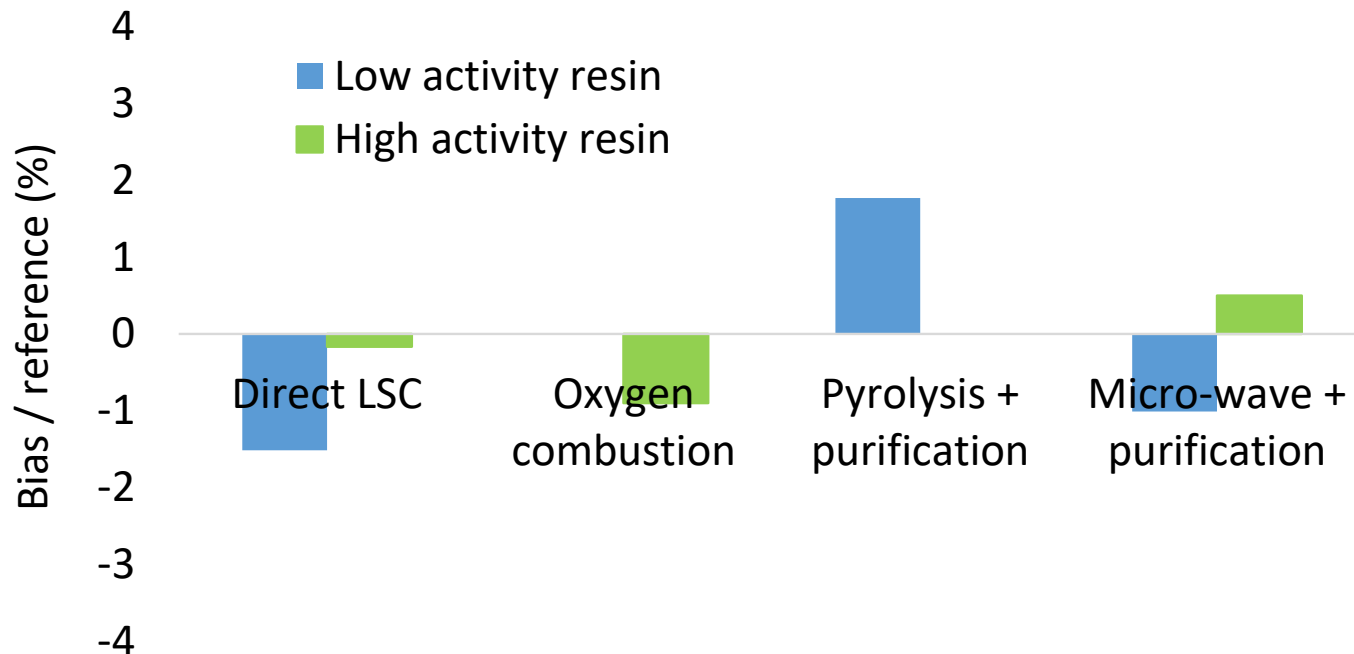


2. Comparisons of different methods



► Initial validation

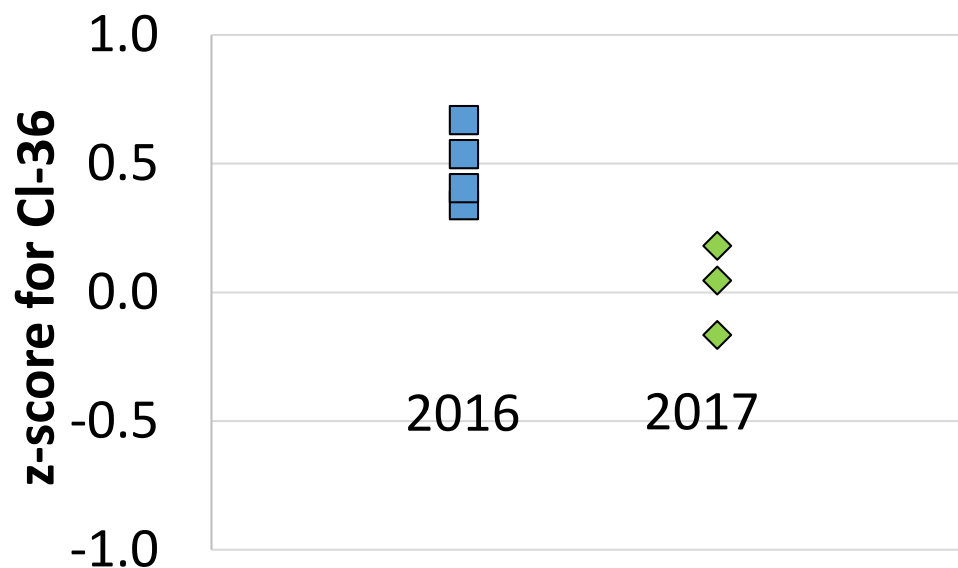
- Preparation of **two spiked resins** with low and high activities (40 and 3000 Bq/g)



No bias for ^{36}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}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}C more easily



- 1** Preparation of the graphite sample in a boat
- 2** Introduction in the pyrolysis oven (950°C) and addition of oxygen circulation
- 3** Trapping of ^{36}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