



Determination of Cl-36 in various radioactive waste

Celine Gautier, Christèle Colin, Margaux Giuliani, Elodie Laporte, René Brennetot, Laëtitia Kasprzak, Pascal Fichet

► To cite this version:

Celine Gautier, Christèle Colin, Margaux Giuliani, Elodie Laporte, René Brennetot, et al.. Determination of Cl-36 in various radioactive waste. International Conference on Decommissioning Challenges: Industrial Reality, Lessons Learned and Prospects (DEM 2021), SFEN, Sep 2021, Avignon, France. cea-03784779

HAL Id: cea-03784779

<https://cea.hal.science/cea-03784779>

Submitted on 23 Sep 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



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

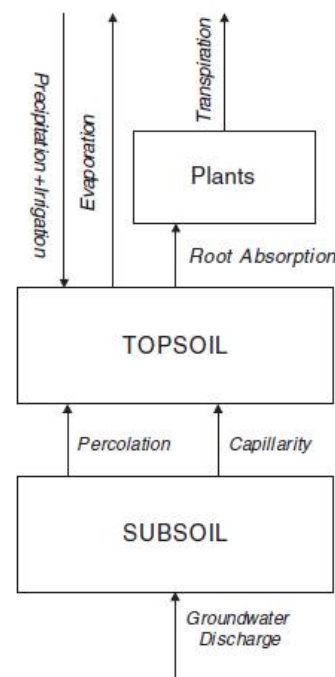
Management of low and intermediate level nuclear waste in France

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

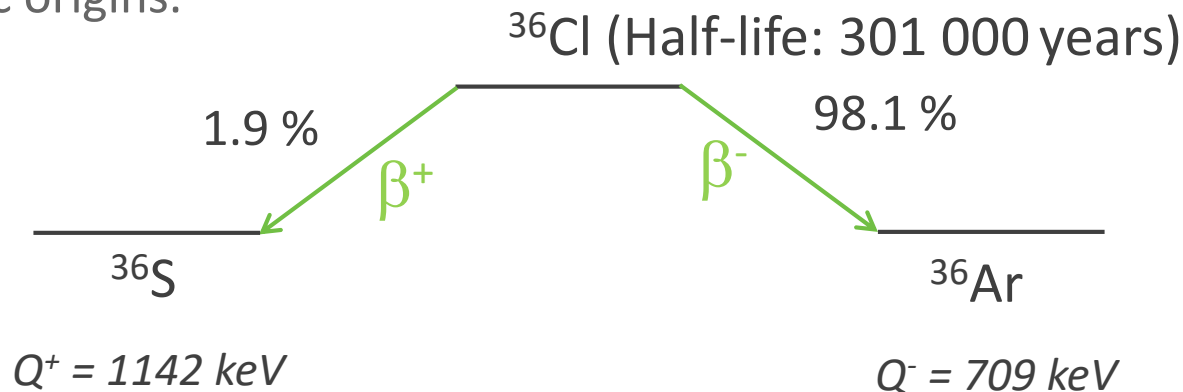
Radionuclide	Declaration threshold (Bq/g) - Acceptance limit (Bq/g) for ANDRA surface disposal
^3H	$10 \rightarrow 2 \times 10^5$
^{60}Co	$10 \rightarrow 1 \times 10^8$
^{14}C	$10 \rightarrow 9 \times 10^4$
^{36}Cl	$0.01 \rightarrow 5$



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

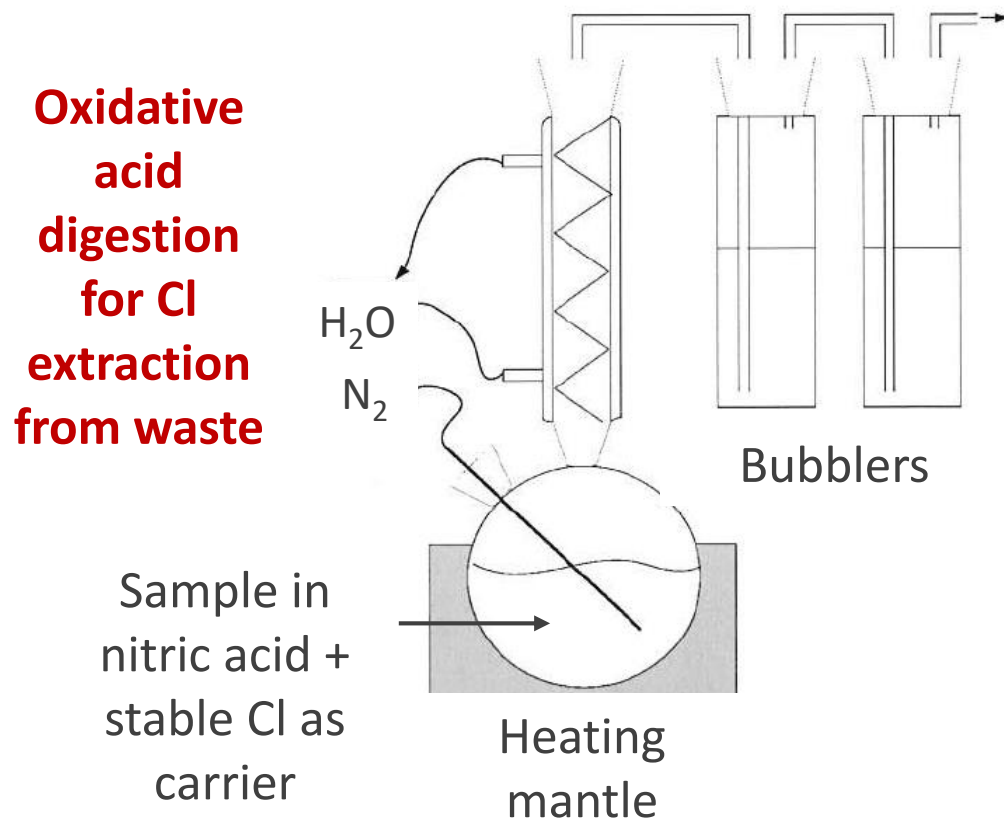
- Purification: mainly AgCl precipitation but also anion exchange chromatography or extraction chromatography (Cl^\circledast resin)

4

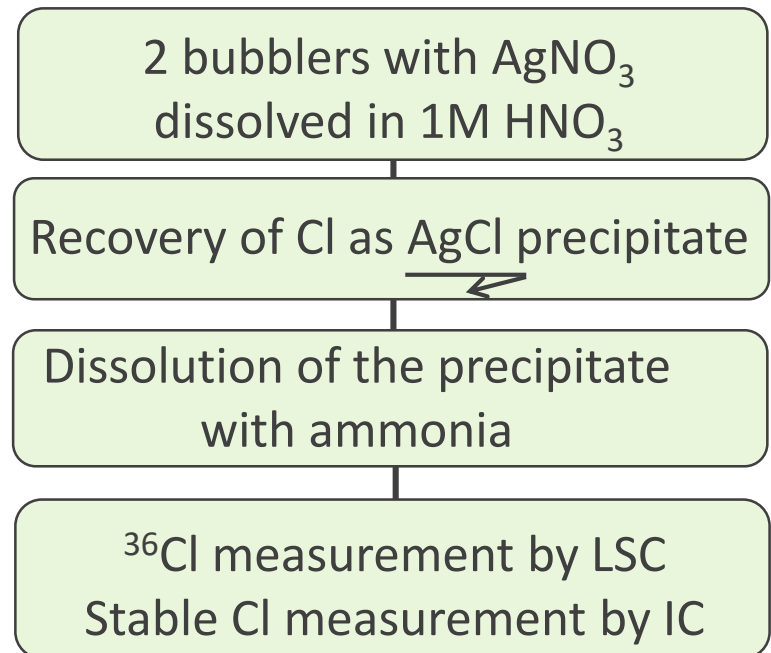
- Measurements
 - Stable chlorine: ion chromatography, ICP
 - ^{36}Cl : mainly LSC for routine analysis

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



Method 1

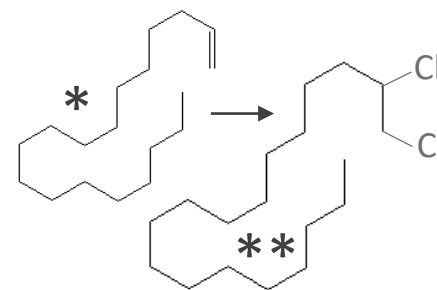


Radiochemical method only relevant for samples with few β and γ emitters and with no other halogens or volatile RNs (ex: ^{129}I)

■ 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)

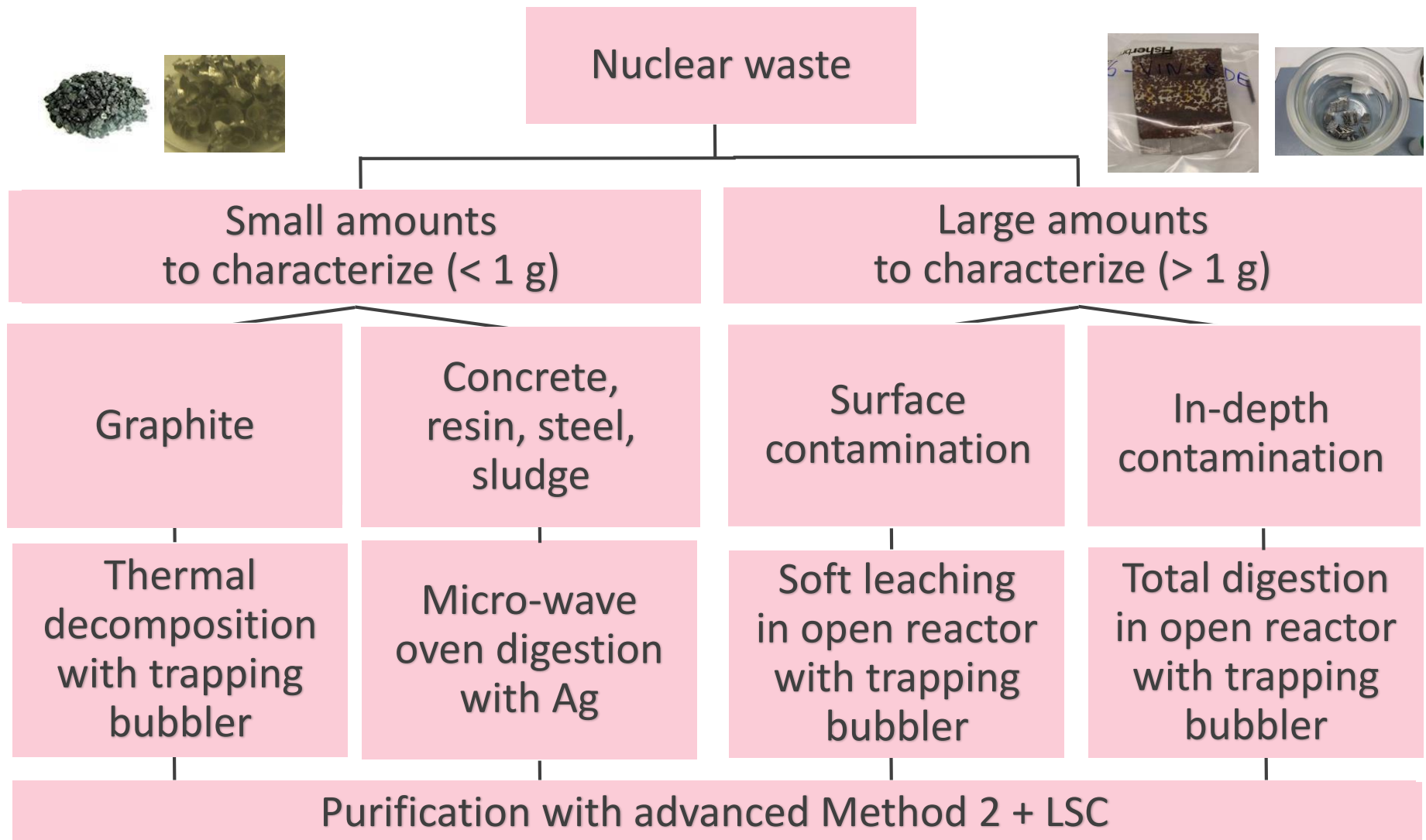


Steel block



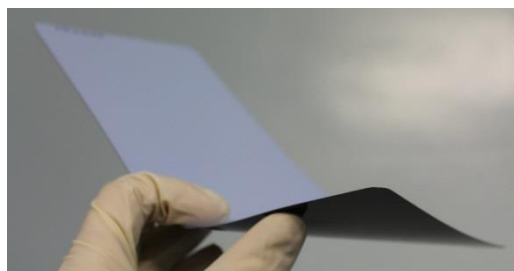
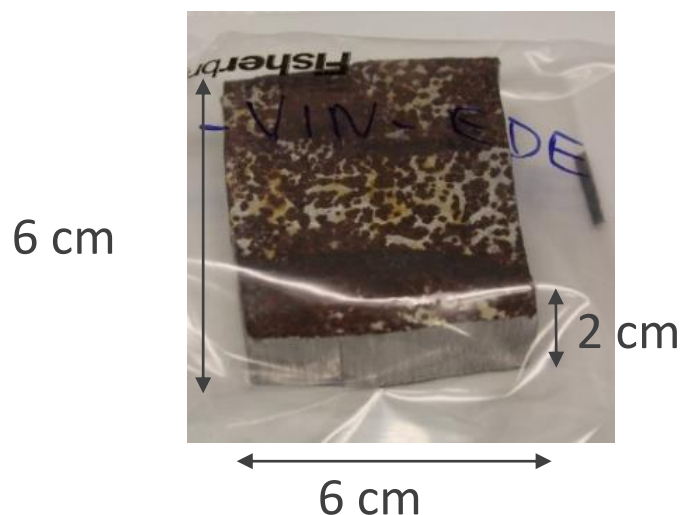
Magnesium cladding

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



► Example 1: steel blocks with surface contamination

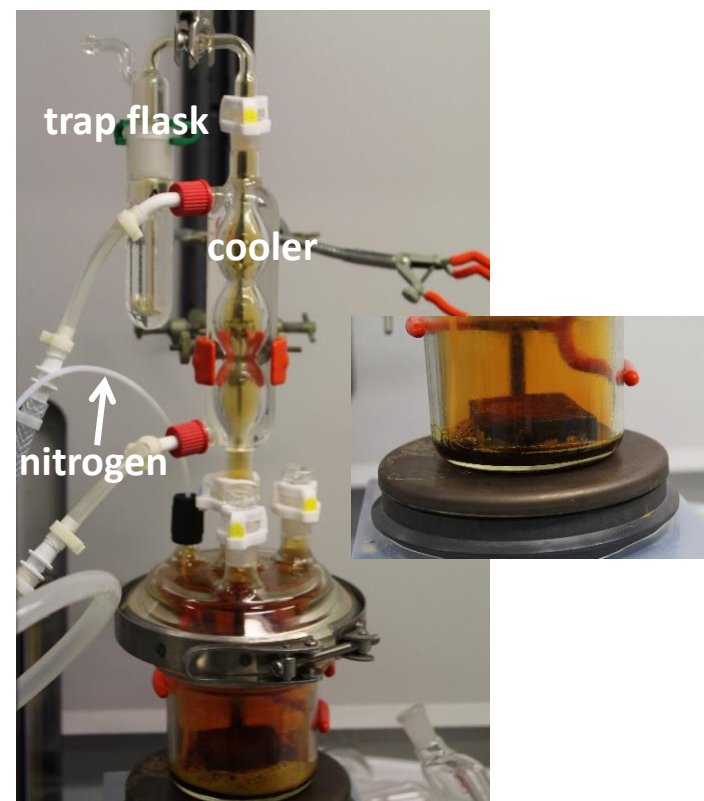
- Soft leaching in open reactor to remove only the contamination layers: adaptation of the reactor (flat bottom) to treat large blocks
- Application of digital autoradiography technique to monitor the decontamination steps



Radiosensitive phosphor screen

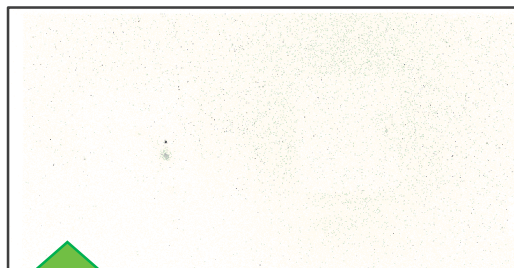


Scanner

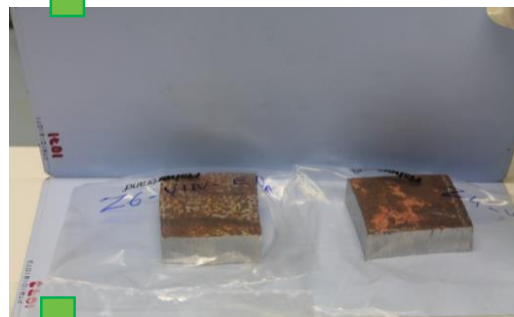


► Example 1: steel blocks with surface contamination

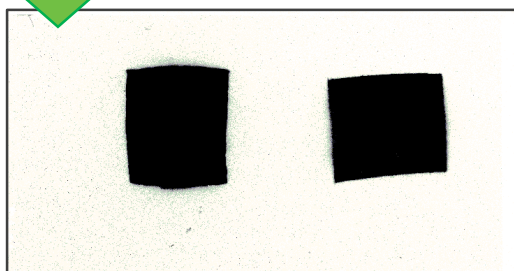
- Application of digital autoradiography technique to monitor the decontamination steps



Top screen



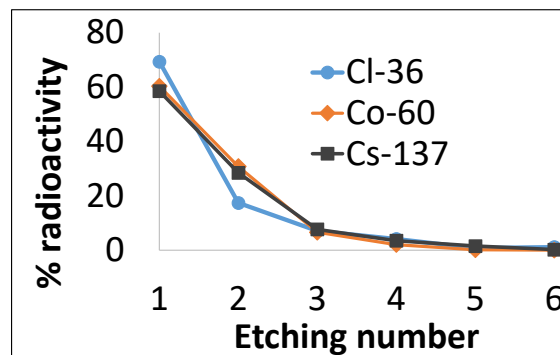
Only one side
contaminated to treat



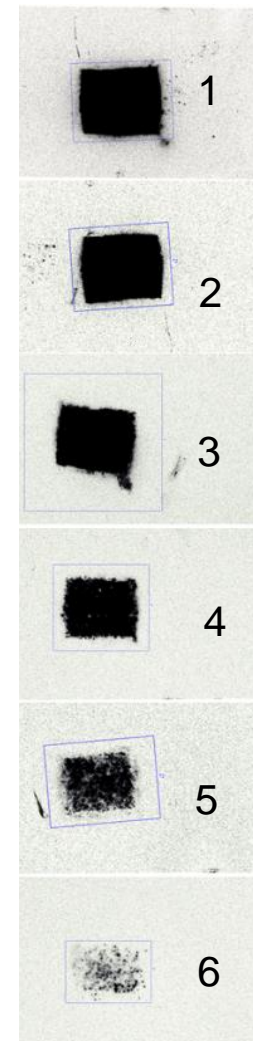
Bottom
screen



Sample after several etchings
($\approx 100\ \mu\text{m}$ thickness removed
at each etching)

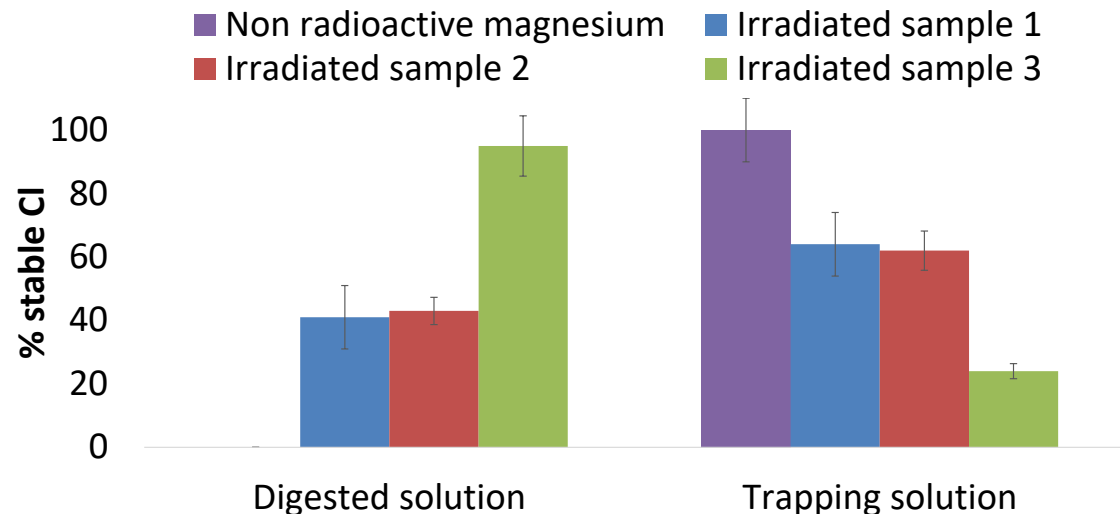


**Same
decontamination
profile for all RNs**



► 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

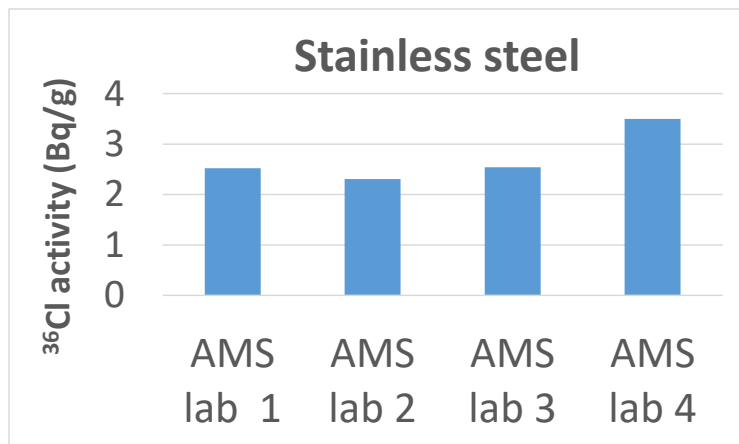
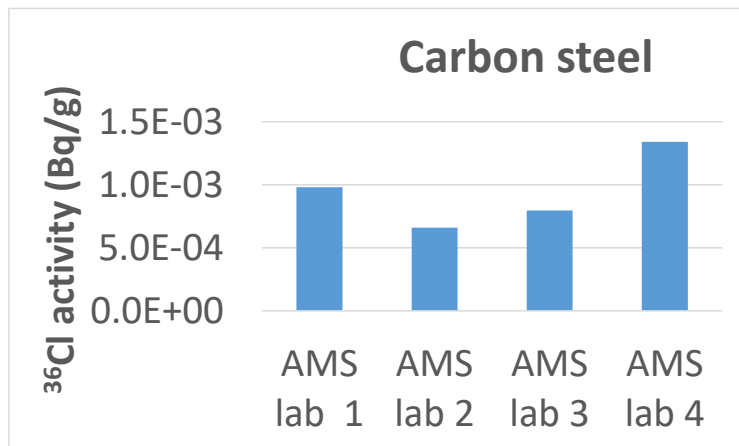
5

- 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

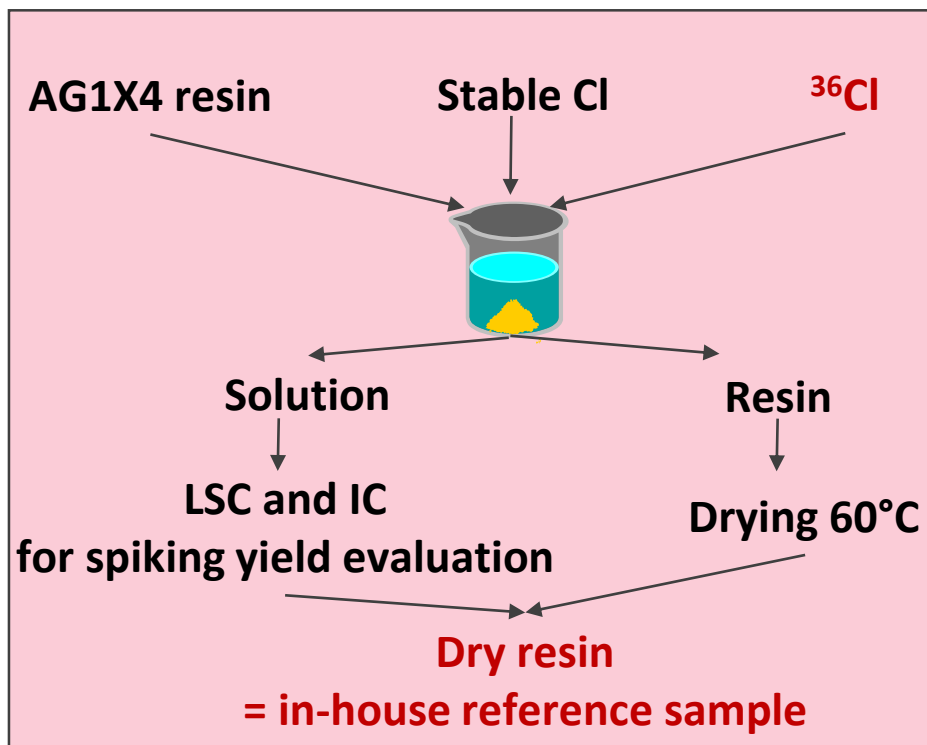


Validation of the developed radiochemical method

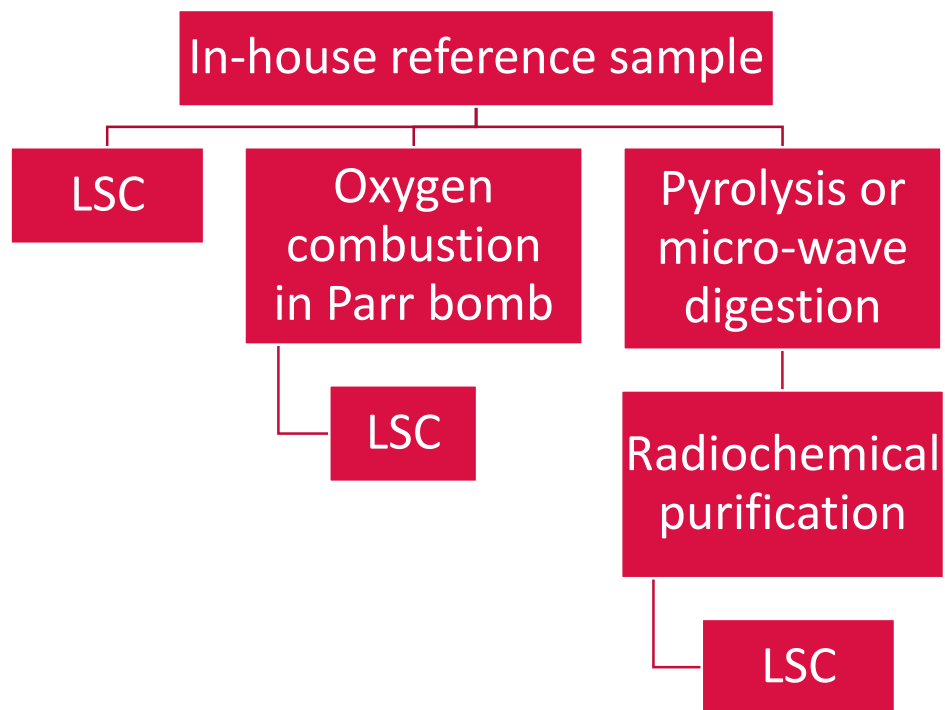
► Initial validation

- 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

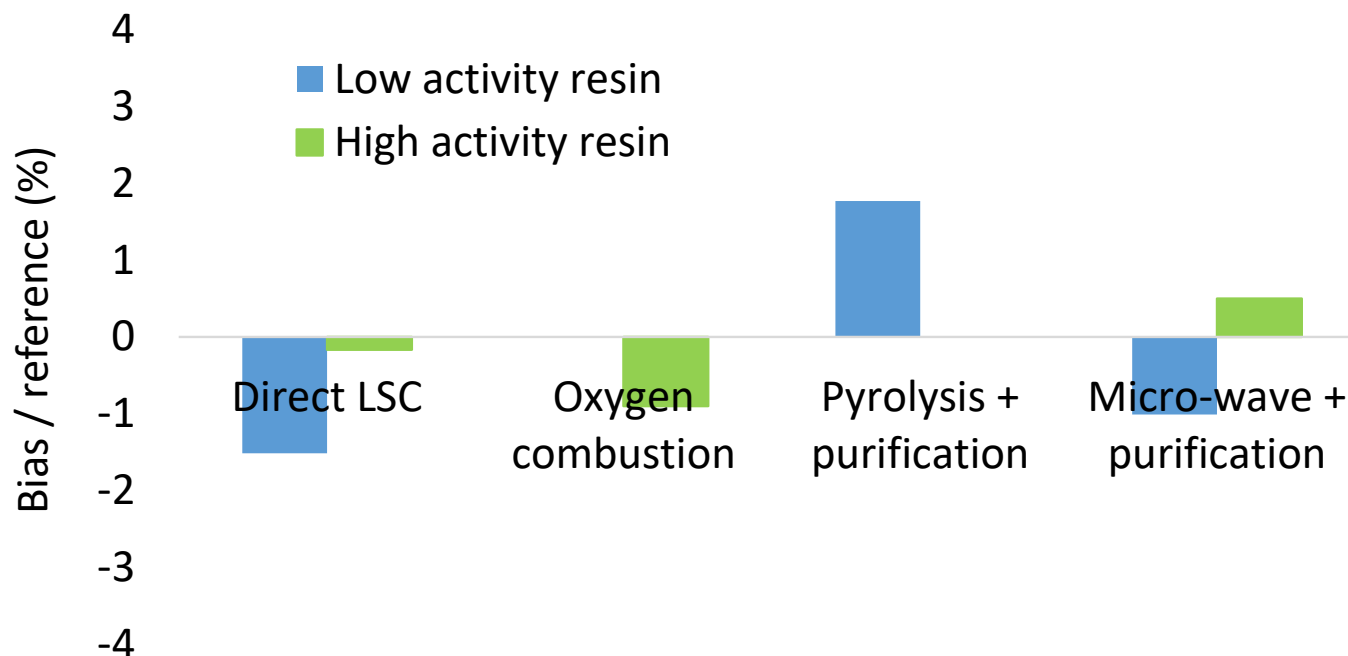


2. Comparisons of different methods



► Initial validation

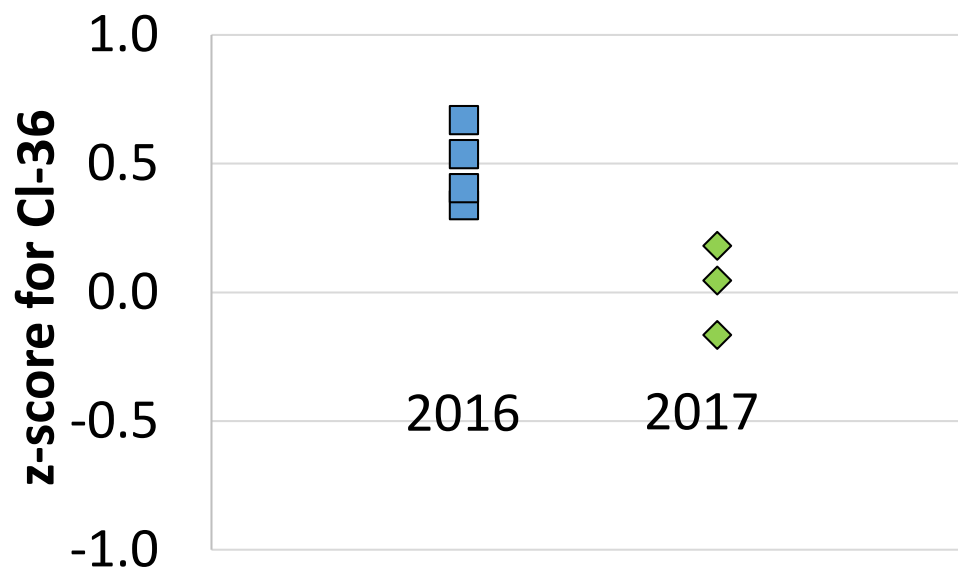
- Preparation of **two spiked resins** with low and high activities (40 and 3000 Bq/g)



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