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Characterization of Nuclear Waste by Accelerator Mass Spectrometry

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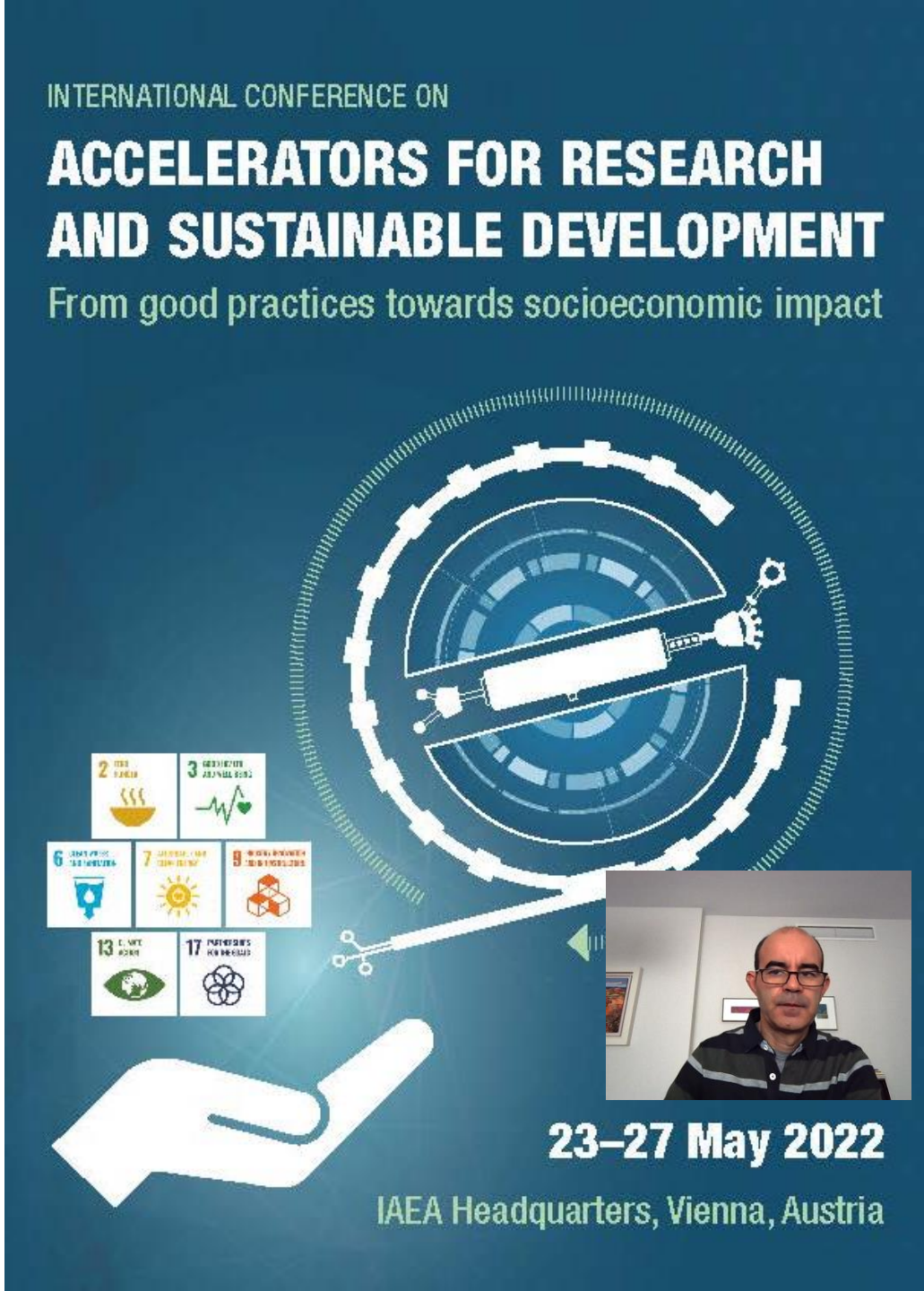
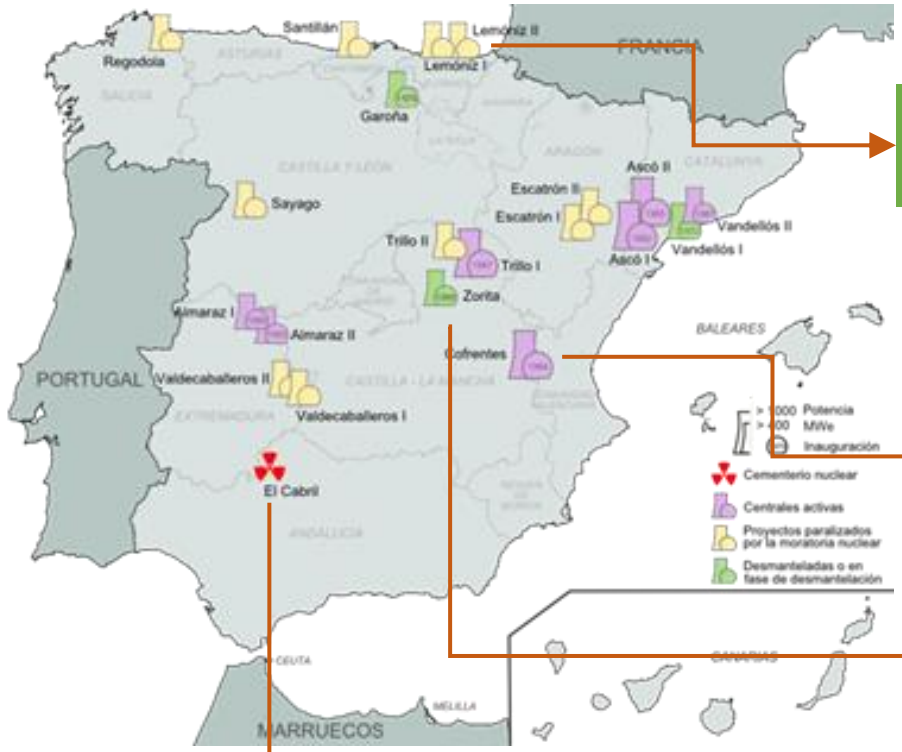


The problem

Nuclear facilities in Spain

- About 1300 radioactive facilities in Spain.
- They generate 30 m^3 of residues and 300 radioactive sources per year.

Nuclear power plants in Spain



El Cabril

- Situation on December 31st, 2020:
  - **19397 m^3** of very low activity residues stored.
  - **34927.19 m^3** of low and medium activity residues stored (**79.92%** of the total capacity).
- Physical and chemical methods used for volume reduction.

A better characterization of low level nuclear waste would allow to classify some residues as non or very little radioactive and treat them as standard residues.

How can we do it?

Low-level waste (LLW) conditions:	Low specific activity	Half-life under 30 years
	Beta-gamma emitters	Do not generate heat
	Alpha emitters at very low concentrations	**Long-lived radionuclides at very low concentrations**

Accelerator Mass Spectrometry (AMS) is a powerful tool for the detection of long-lived radioisotopes that can reduce strongly the detection limits reached for them with other techniques.

Long-lived radionuclides in residues must be evaluated in order to classify them as LLW.

Some of these radionuclides cannot easily be detected by radiometric methods.

In these cases, only detection limits are established as their activity value.

Accelerator Mass Spectrometry at CNA

Centro Nacional de Aceleradores (CNA) - Sevilla

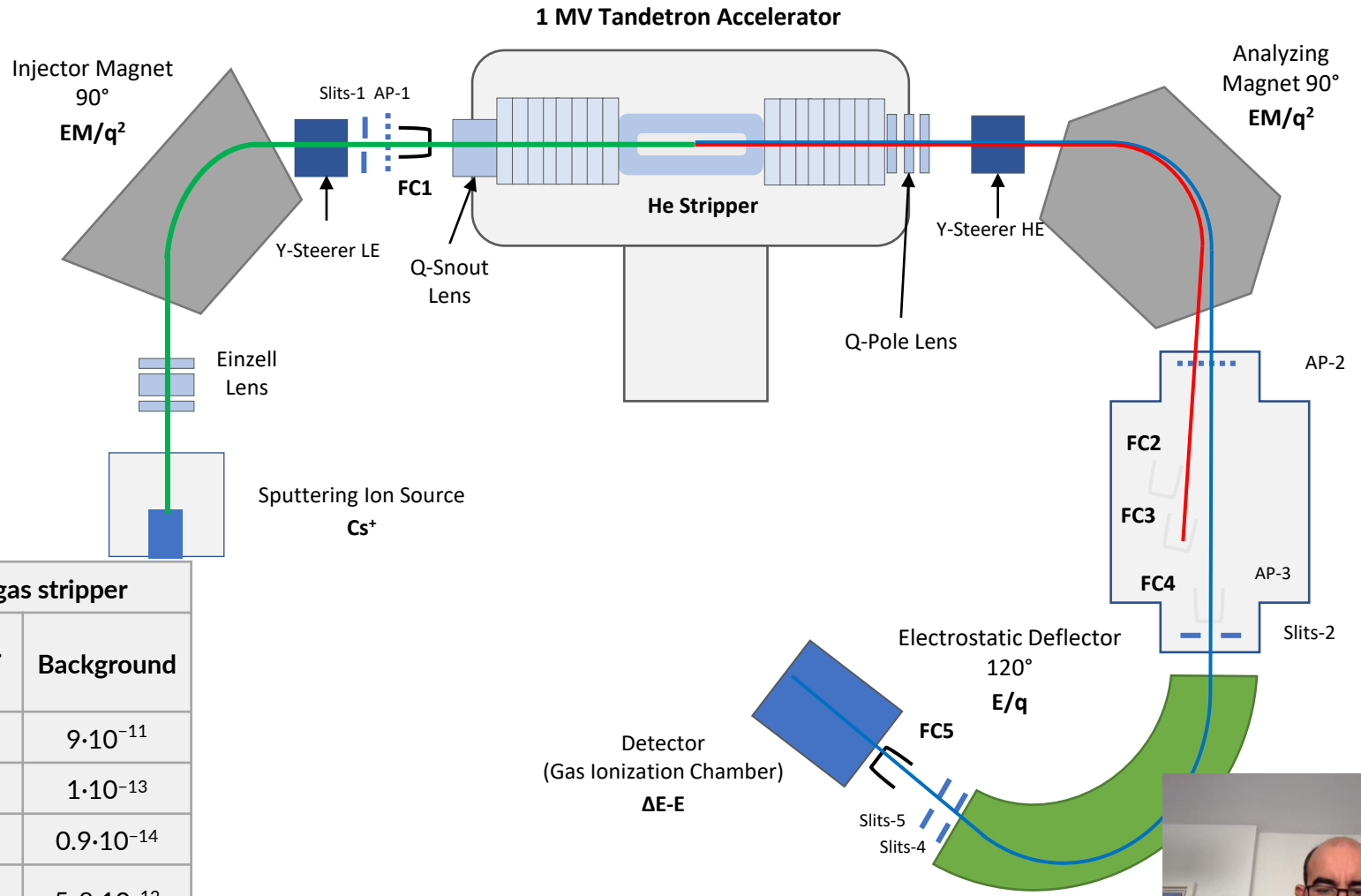
- Four accelerators:
  - 3 MV Tandem
  - 18 MeV protons and 9 MeV deuterons cyclotron
  - 1 MV Tandem for AMS
  - 200 kV Tandem for ^{14}C AMS
- Other facilities:
  - PET/CT Scanner for humans
  - ^{60}Co Irradiator

SARA (*Spanish Accelerator for Radionuclide Analysis*)

1 MV *Tandetron* Accelerator

High Voltage Engineering Europe (HVEE), Netherlands

2005



Isotope	Charge state	Terminal voltage (kV)	Energy (keV)	He gas stripper	
				Transm. (%)	Background
^{236}U	3+	650	2590	38	$9{\cdot}10^{-11}$
^{129}I	3+	1000	4000	25	$1{\cdot}10^{-13}$
	2+	700	2100	40	$0.9{\cdot}10^{-14}$
^{14}Ca	2+	972	1700	45	$5\text{-}8{\cdot}10^{-12}$ (K correction)
	3+	1000	2400	28	

Some long-lived radionuclides measured by AMS

Isotope	Decay	$T_{1/2}$ (years)	Radiometric detection limit (mBq)	AMS detection limit
^{14}C	β^-	5730	17.14	10^{-4} mBq
^{36}Cl		3.01×10^5	4	10^{-6} mBq ($\leftrightarrow$ $^{36}Cl/Cl \sim 10^{-15}$)
^{41}Ca	EC	1.03×10^5	15.00	0.1 mBq
^{129}I	β^-	1.56×10^7	17.14	10^{-6} mBq
^{237}Np	α	1.54×10^5	0.1	10^{-4} mBq
^{239}Pu		2.41×10^4	0.05	5×10^{-4} mBq
^{240}Pu		6.5×10^3		10^{-3} mBq
^{236}U		2.34×10^7		10^{-6} mBq

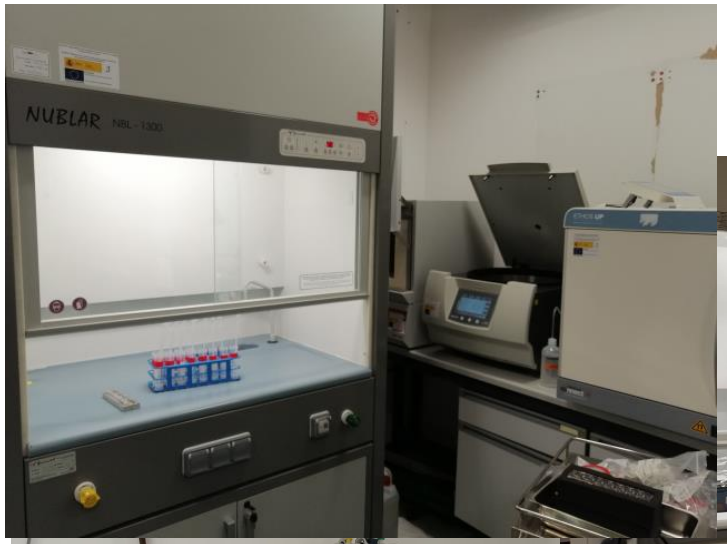
Xiaolin Hou, Per Roos, Analytica Chimica Acta 608 (2008) 105-139.
https://doi.org/10.1016/j.aca.2007.12.012.

Where are some these residues produced?

LLW samples from normal operation	
	Origin
Evaporator concentrate	Decontamination of liquids by evaporation
Resins	Cleaning of the reactor refrigeration water and other liquids
Dry sludge	Drying of the wet residues in containers or sinks
LLW samples from plants in decommissioning process	
	Origin
Smears	Control of surface contamination in different materials
Concrete	Demolition of buildings

Relatively high activities expected!

New exclusive lab set up



It is necessary to develop:

- Radiochemical methodology
- Measurement technique

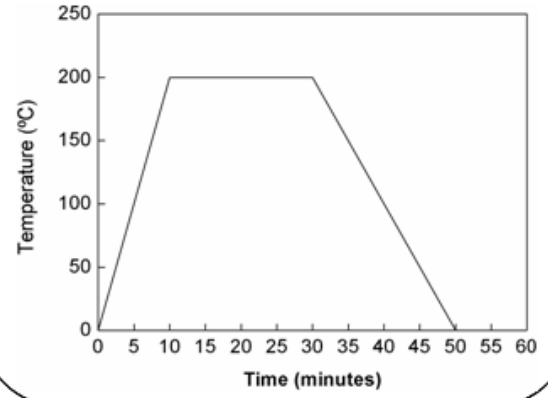
Some results

^{129}I ($T_{1/2}$ = 15.6 × 10^6 y) in operation and decommissioning residues

Acid microwave digestion

0.5 g sample
I Carrier
5 ml HNO_3

Microwave digestion:

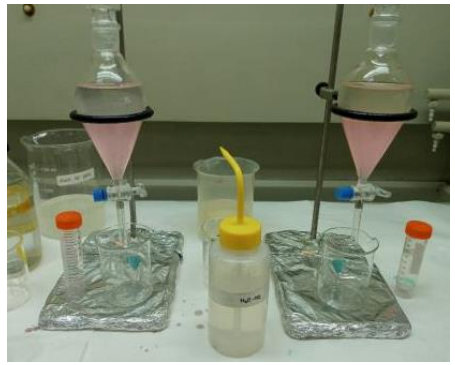


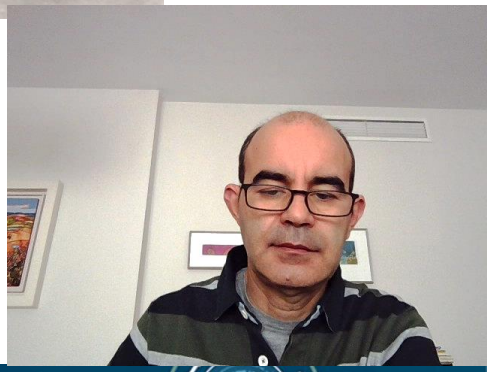
Extraction into $CHCl_3$

Back-extraction into water

Precipitation of AgI by $AgNO_3$

AMS targets, AgI + Nb





^{129}I in operation and decommissioning residues. Results.

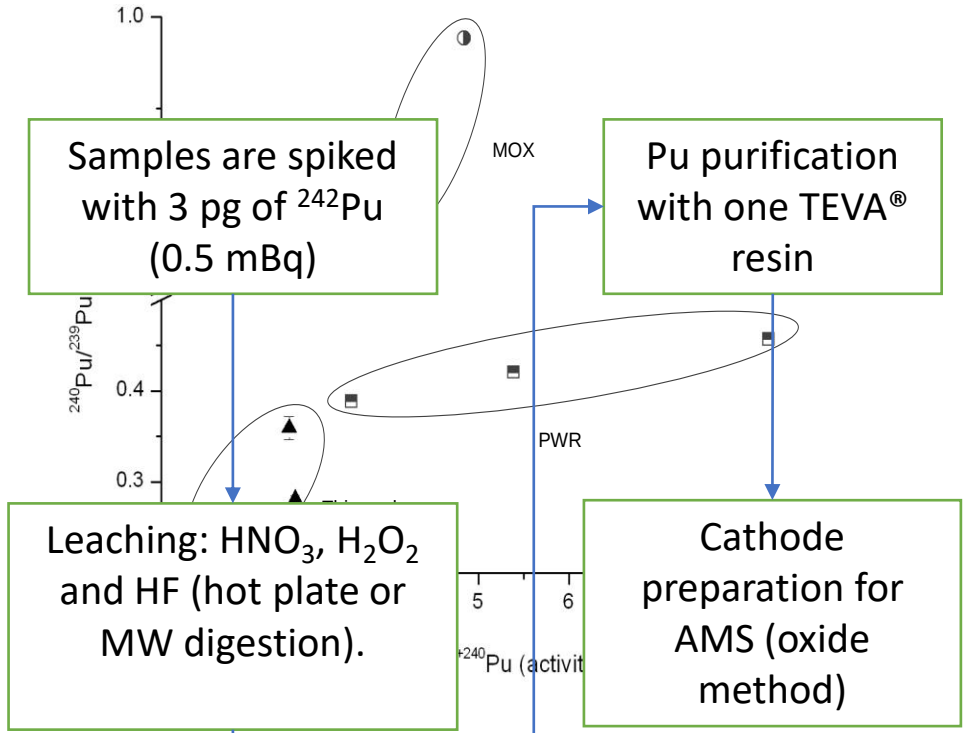
Sample	Type	Average ^{129}I activity (µBq/g)	Standard deviation(1)
R-AS-07-04	Resin	**210.0**	**54.2%**
R-AS-08-01	Resin	**42.7**	**88.2%**
VD-10-01	Resin	**4.63**	**51.6%**
R-VD-9-01(2)	Resin	**40.3**	6.7%
R-VD-9-02(2)	Dry sludge	**27.6**	11.5%
R-VD-9-03(2)	Dry sludge	**18.2**	11.2%
Concrete from NPP	Concrete	**0.010 - 5.73**	
IAEA-375	Env. Soil	**1.69**	7.8%

Large standard deviations for resins

In many cases, values are not much higher tan environmental levels

López-Gutiérrez, J.M. Gómez-Guzmán, E. Chamizo, J.I. Peruchena, M. García-León, Long-lived radionuclides in residues from operation and decommissioning of nuclear power plants, Nuclear Instruments and Methods B 294 (2013) 647-651. https://doi.org/10.1016/j.nimb.2012.07.046.

^{239}Pu and ^{240}Pu in operation residues



Samples are spiked with 3 pg of ^{242}Pu (0.5 mBq)

Pu purification with one TEVA® resin

Leaching: HNO_3, H_2O_2 and HF (hot plate or MW digestion).

Cathode preparation for AMS (oxide method)

Supernatant: Pu adjustment to Pu(IV) with Fe(II) and $NaNO_2$.

Sample	Type	Average (^{239}Pu + ^{240}Pu) activity (mBq/g)	Standard deviation	Average ^{240}Pu/^{239}Pu	Standard deviation
R-AS-07-04	Resin	**35.8**	**29.4%**	**0.246**	0.4%
R-AS-08-01	Resin	**8.9**	**71.3%**	**0.225**	8.4%
AS-06-03	Resin	**46.9**	**48.6%**	**0.355**	1.1%
R-CO-09-05	Resin	**1235.5**	13.1%	**0.359**	3.5%
VD-10-01	Resin	**7.9**	10.8%	**0.281**	6.2%
R-TR-08-02	Dry sludge	**7.06 (10)**	-	**0.1059 (32)**	-

- The ^{240}Pu/^{239}Pu ratio gives unambiguous information on the type of reactor.
- ortant tool to detect the
- sed Pu in the

Large standard deviations for resins

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^{243}Am and ^{241}Am in nuclear residues

Digestion
Hot plate with HNO_3 8M and H_2O_2.

Supernatant filtered and divided in twin aliquots

Aliquot A (~30%):
- Traced with ^{243}Am for ^{241}Am determination by alpha spectrometry

Aliquot B (~70%):
-Not traced for ^{243}Am determination by AMS.
-Traced with ^{242}Pu for ^{239}Pu and ^{240}Pu determination by AMS.

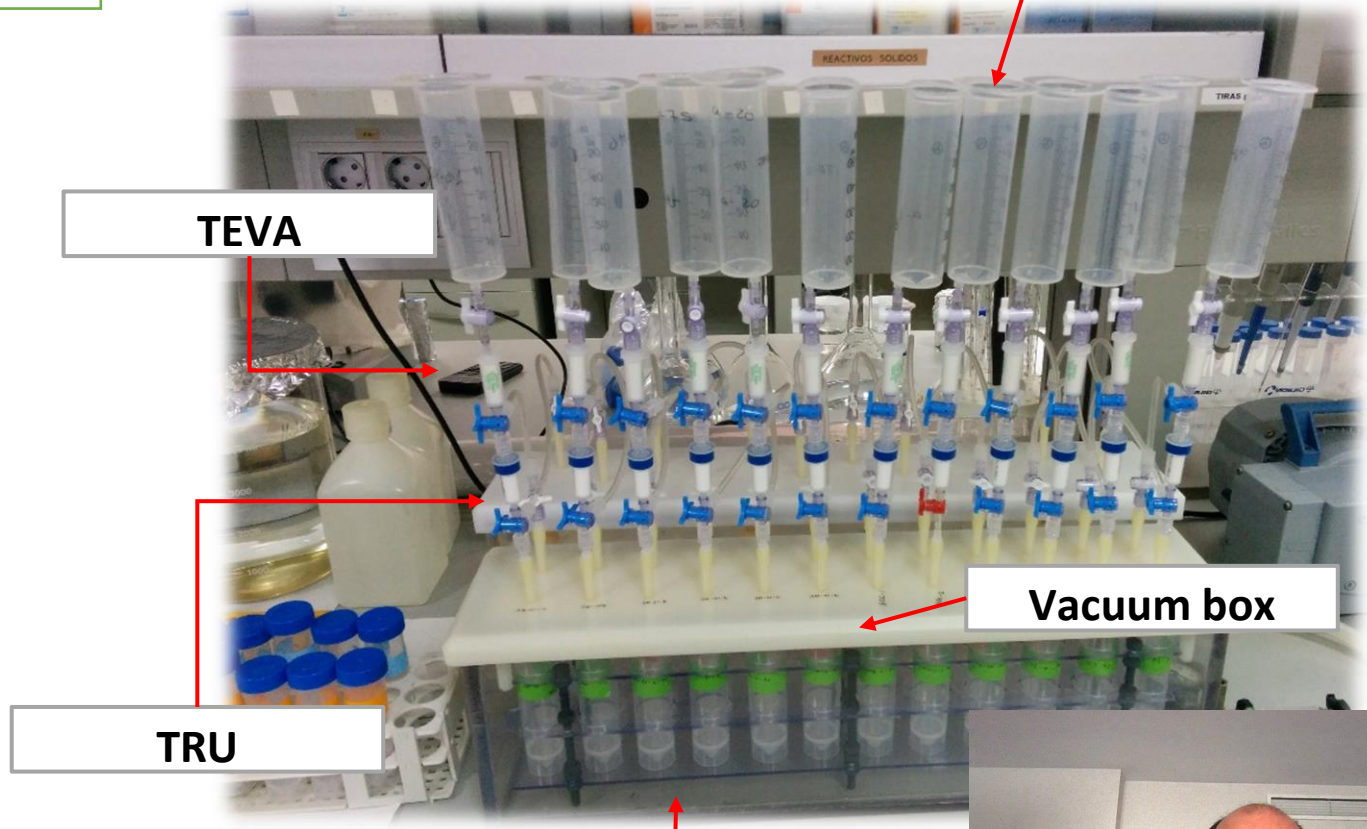
TEVA Column
Pu separation.

TEVA Column
Pu separation

TRU Column
Am extraction

TRU Column
Am extraction

Am^{3+}



^{243}Am and ^{241}Am in nuclear residues

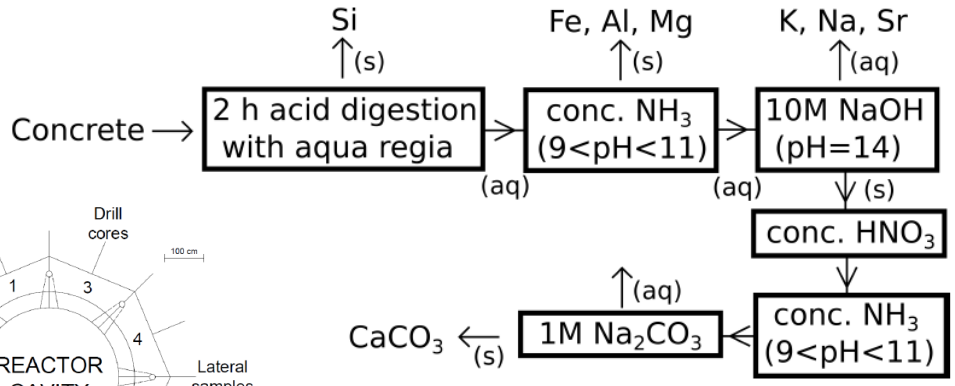
Very good agreement for isotopic ratio

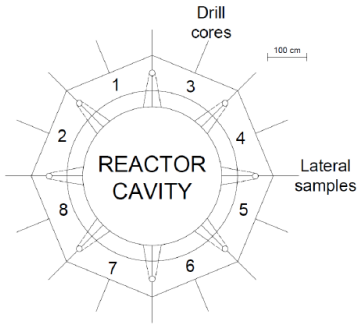
NPP/sample	Aliquot	^{241}Am (pg/g)	Error(^{241}Am) (pg/g)	^{243}Am (pg/g)	Error(^{243}Am) (pg/g)	^{243}Am/^{241}Am	Error
Cofrentes/0509	1	12.32	0.17	1.418	0.019	0.1151	0.0022
Vandellós/0212	1	0.4767	0.0041	0.05885	0.00051	0.1235	0.0015
	2	1.573	0.012	0.2081	0.0016	0.1323	0.0014
Garoña/1614	1	3.658	0.040	0.1596	0.0018	0.04363	0.00069
	2	2.064	0.023	0.07834	0.00087	0.03796	0.00060
Almaraz/0315	1	0.1432	0.0012	0.01459	0.00012	0.1019	0.0012
Ascó/0115	1	6.714	0.060	0.6186	0.0056	0.0921	0.0012
	2	6.902	0.067	0.6469	0.0063	0.0937	0.0013

Differences between aliquots for ^{243}Am concentration

^{243}Am/^{241}Am can be a good indicator of the origin of residues

^{41}Ca in concrete samples





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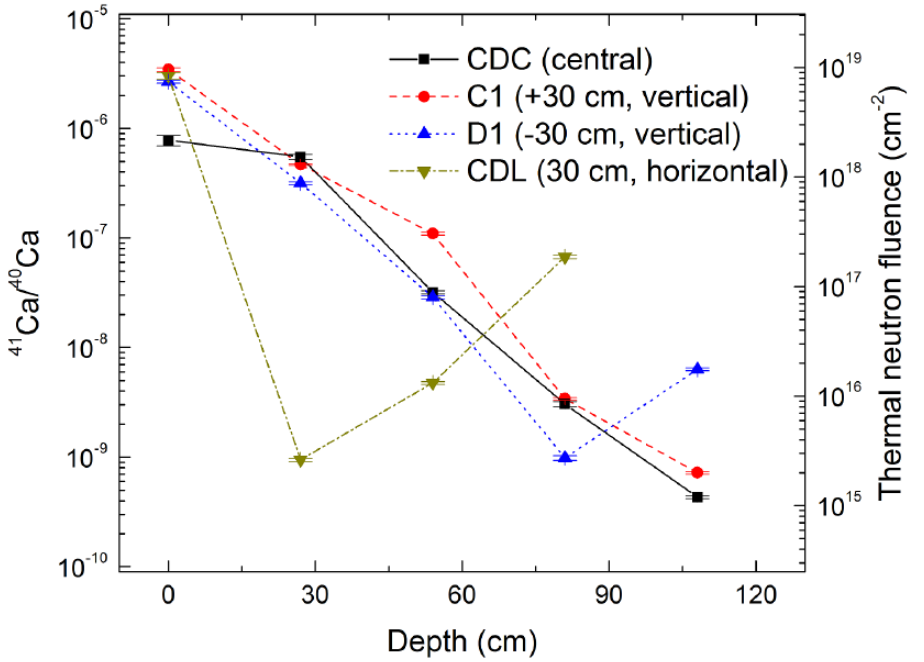

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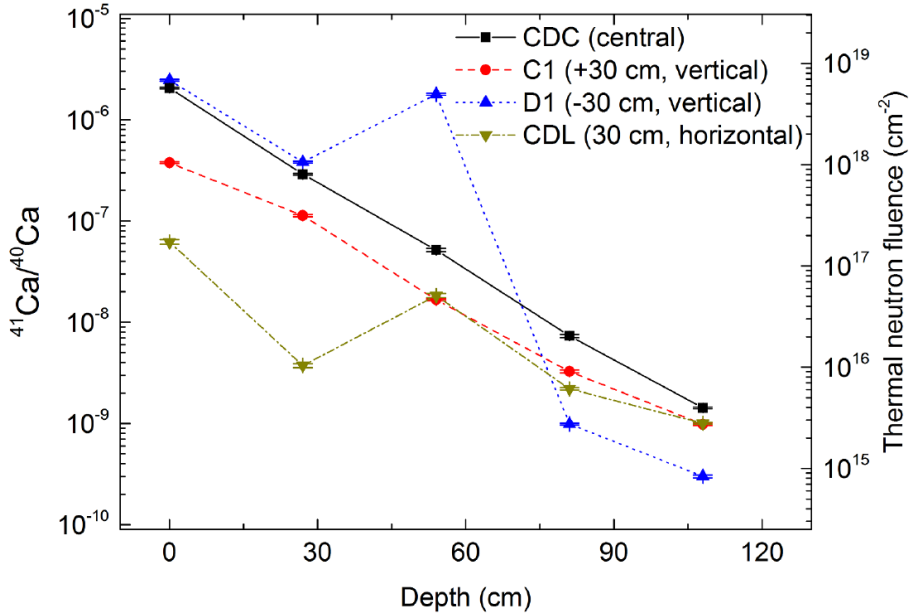
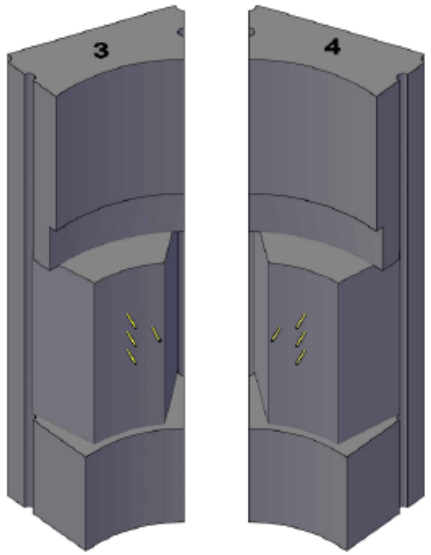
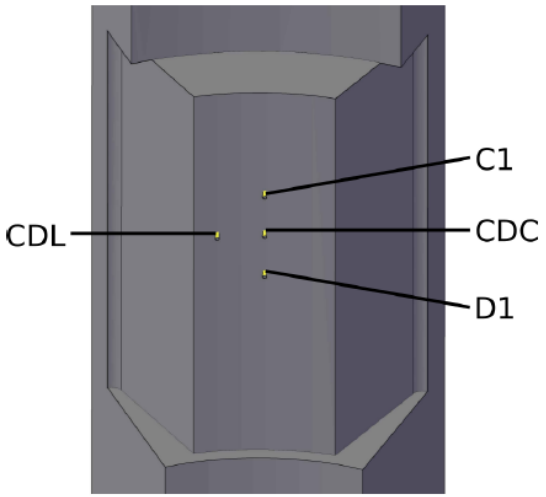


José Cabrera NPP





Conclusion

AMS is a powerful tool for the characterization of normal operation and decommissioning LLW from nuclear facilities, as it can determine the activity of long-lived radionuclides which must be under certain levels in these materials.

Thanks for your attention!

This project is founded by ENRESA

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