Advances, uncertainties and pitfalls in measurement for decommissioning waste classification

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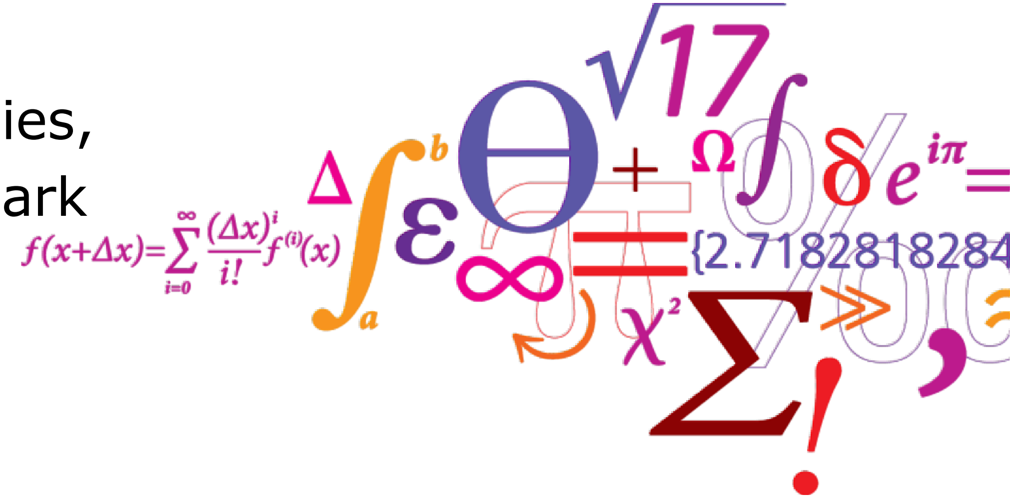
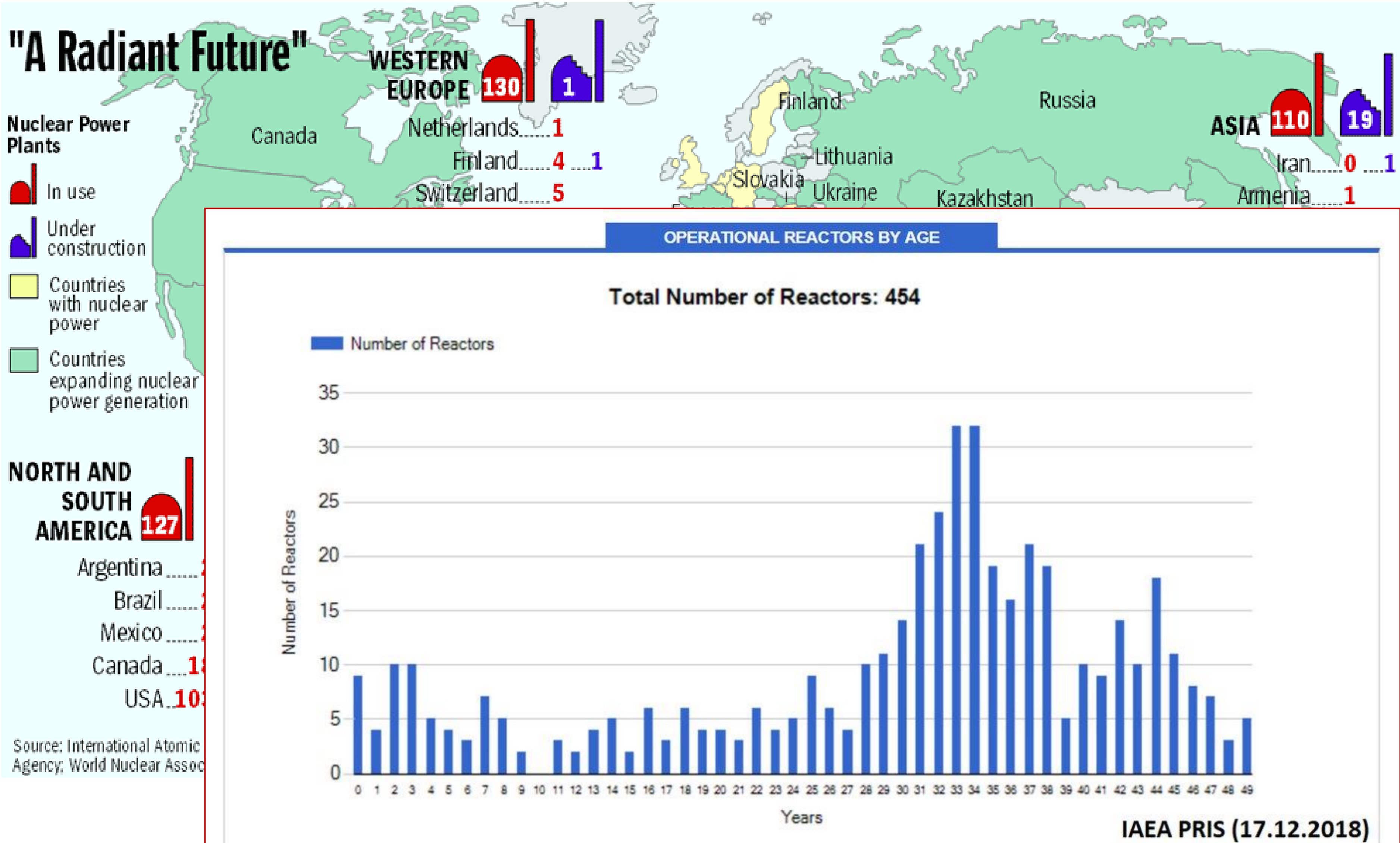
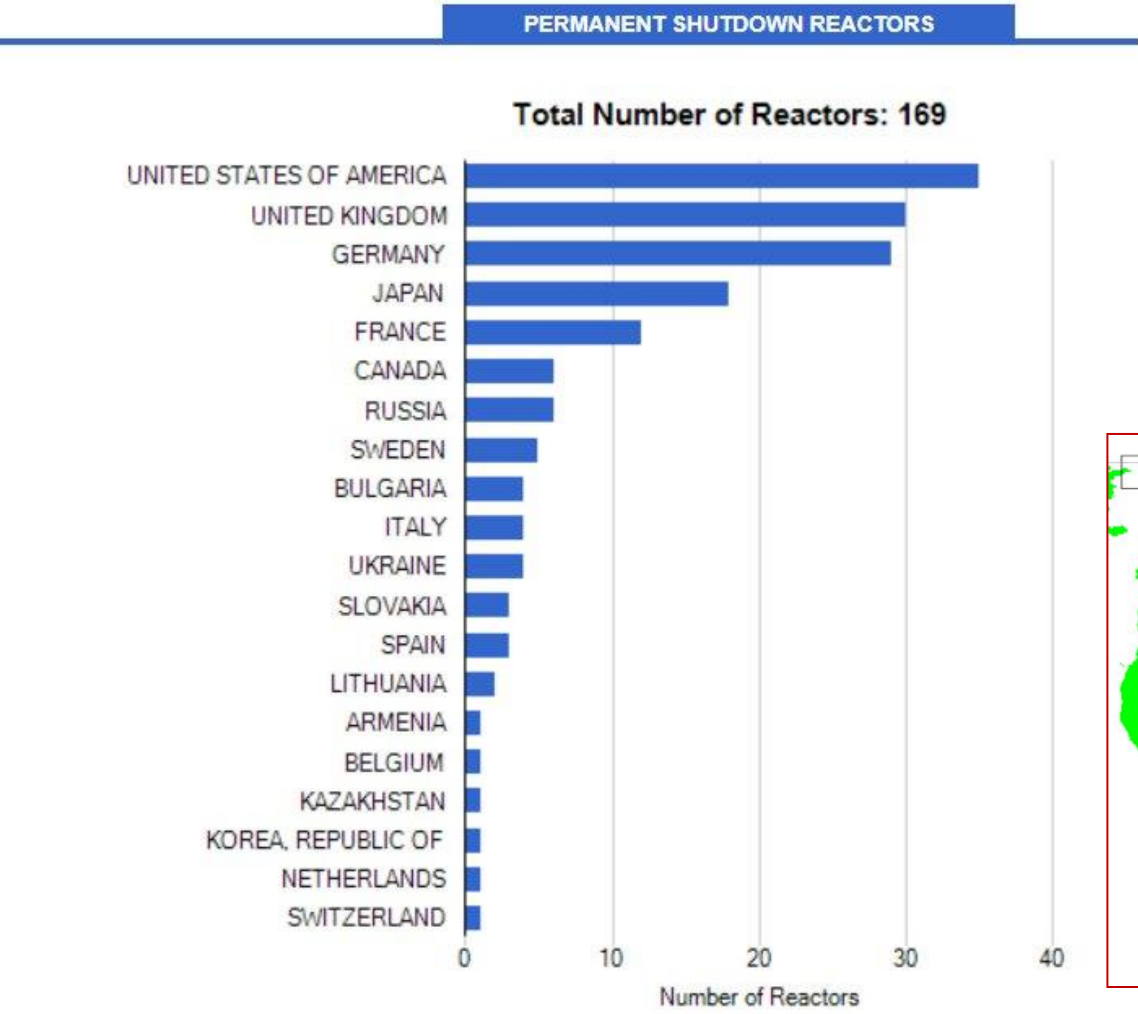


World-wide status about decommissioning

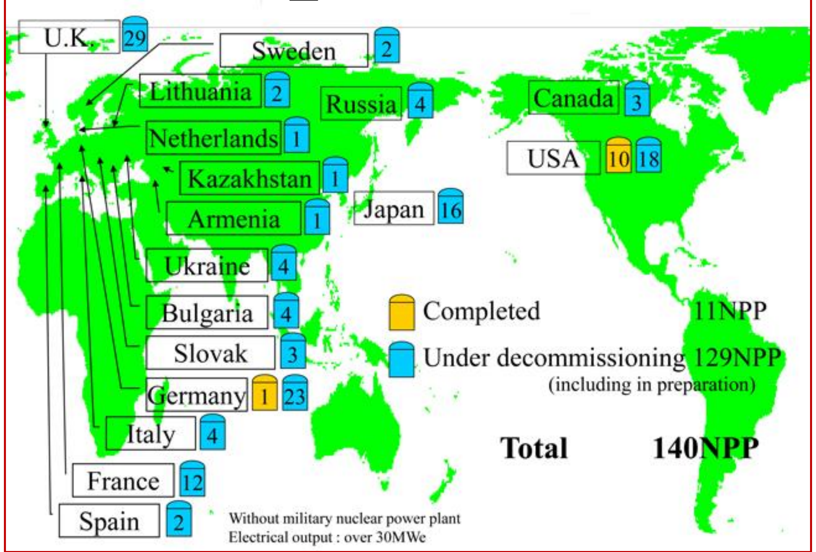


World-wide status about decommissioning



The total Number of Reactors includes also 2 reactors in Taiwan, China

IAEA PRIS, 15.11.2018



http://www.japc.co.jp, updated by 2016

NKS-B Radworkshop 2018

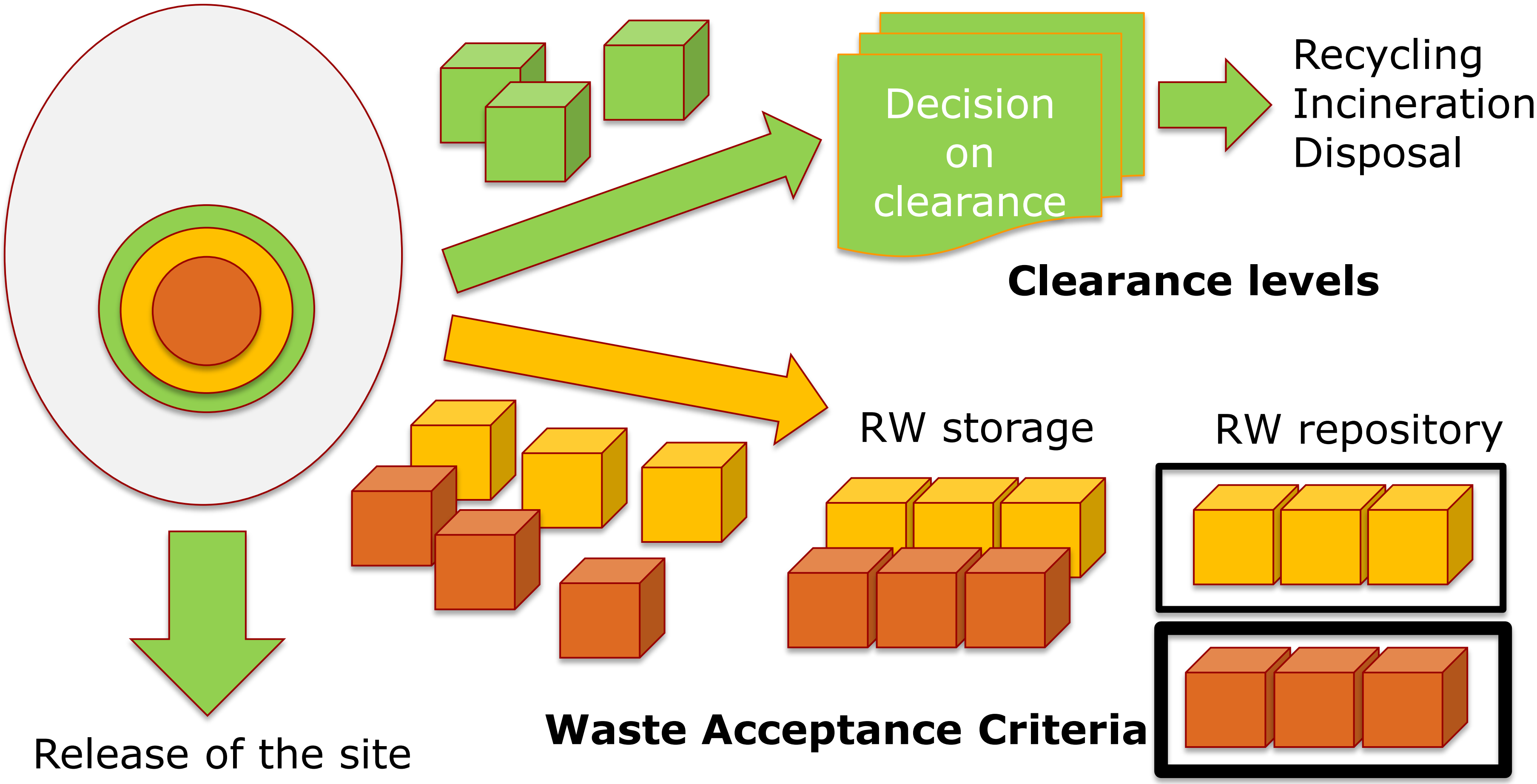
NKS-B Radworkshop

Radioanalytical Chemistry for Nuclear Decommissioning and Waste Management

8-12 OCTOBER 2018

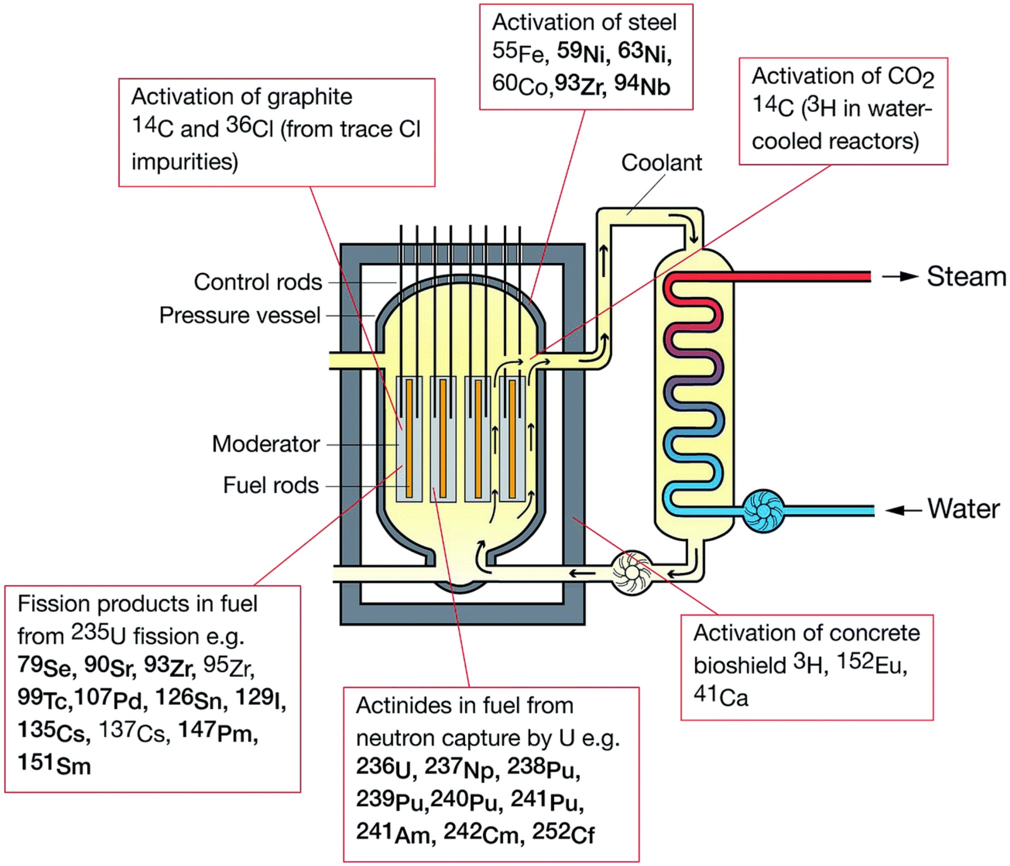
DTU Risø Campus, Denmark

The mission in decommissioning



Stages in nuclear decommisioning		Involvement of radioanalysis
Preparation	Background measurement around the facility →	Characterization!
Cleanout	Removal of most radioactive components e.g., spend fuel, reactor internals and vessels →	Characterization!
Decontamination	Removal of surfaces contamination by chemical or mechanical methods →	Characterization!
Dismantling and Demolition	Equipments dismantled and buildings demolished →	……
Waste storage/disposal	Radioactive wastes removed to storage or disposal →	

Sample types relevant for decommissioning



I. W. Croudace, et al. *J. Anal. At. Spectrom.*, 2016, DOI: 10.1039/C6JA00334F

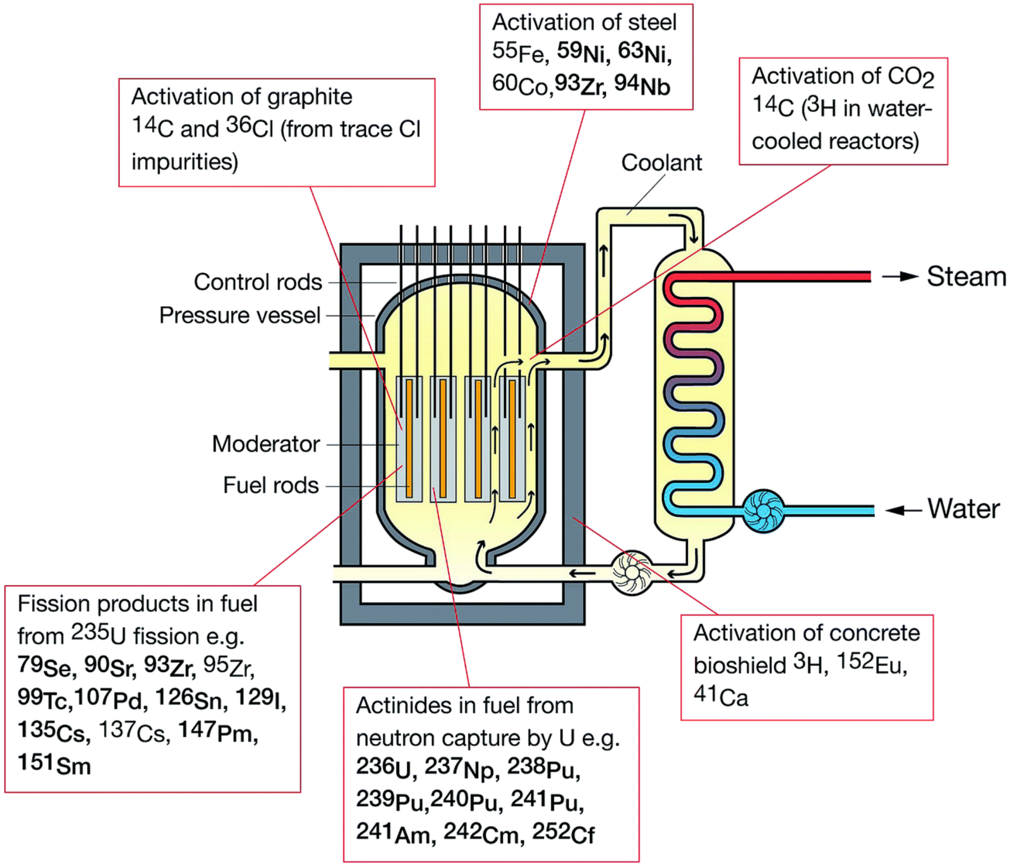
Large volume and common waste

- Concrete (normal or heavy)
- Graphite (reactor)
- Steel/stainless steel
- Evaporator concentrate
- Ion exchange resin

Unconventional waste

- Non-ferrous metals (Al, Pb, Cu)
- Zirconium and its alloy
- Mercury
- Plastics (PCB, PE, etc.)
- Oil
- Desiccant (silica gel, CaO, etc.)

Radionuclides relevant for decommissioning



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Easy-to-measure radionuclides

- **γ- radionuclides**

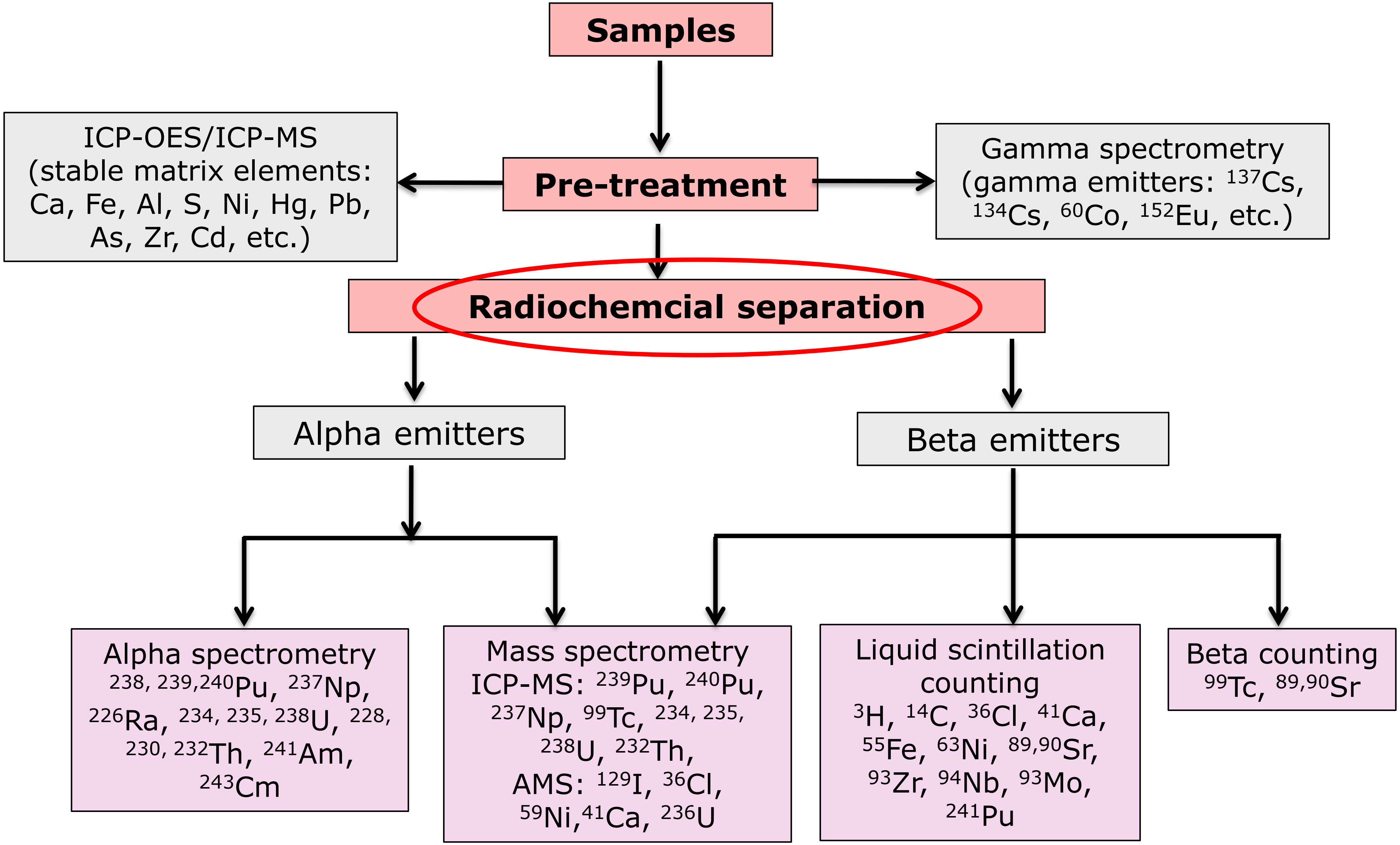
  ^{60}Co, ^{133}Ba, ^{137}Cs, ^{134}Cs, ^{106}Ru, ^{152,154,155}Eu, ^{58}Co, ^{54}Mn, ^{59}Fe, ^{110m}Ag, ^{94}Nb.

Hard-to-measure radionuclides

- **β- Emitter**
  - **^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}, ^{59}Ni, ^{93}Zr, ^{93}Mo, ^{90}Sr, ^{99}Tc, ^{129}I, ^{241}Pu, etc.**

- **α- emitter (actinides)**
  - **$^{238-240}$Pu, ^{241}Am, ^{243,244}Cm, ^{237}Np, etc.**

Scheme for characterization of radioactive wastes



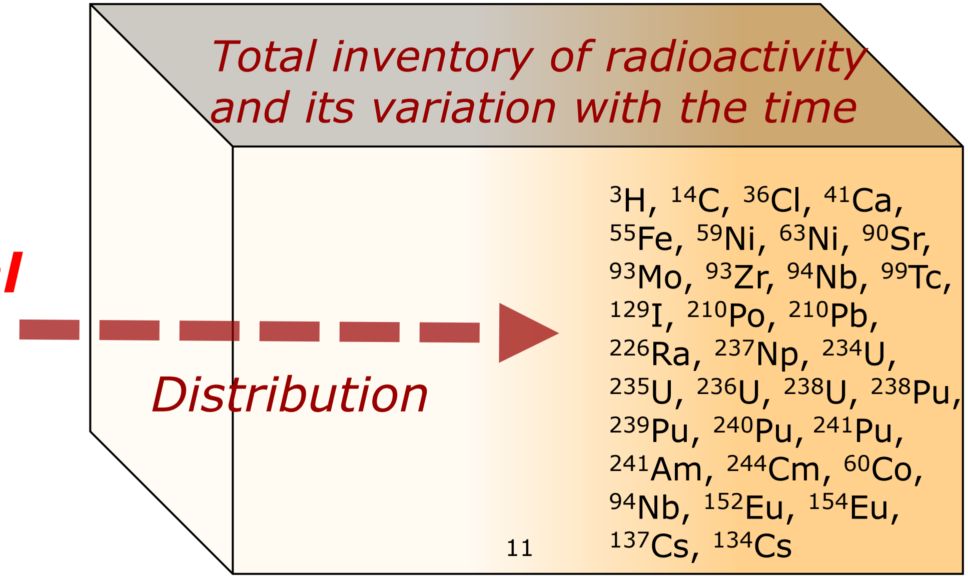
Radioanalytical methods at DTU Nutech

Radionuclides	Chemical Analyses	LSC	Total Beta Counting	Gamma Spec	Alpha Spec	ICPMS	AMS
Gamma emitters				X			
^{3}H	X	X					
^{14}C	X	X					
^{36}Cl	X	X					
^{41}Ca	X	X					
^{59}Fe	X	X					
^{63}Ni	X	X					
^{79}Se	X					X	
^{90}Sr	X	X	X				
^{93}Mo	X	X					
^{93}Zr	X					X	
^{94}Nb	X			X			
^{99}Tc	X		X			X	
^{126}Sn	X					X	
^{129}I	X						X
^{135}Cs	X			X		X	
^{137}Cs	X			X			
^{210}Pb				X			
^{210}Po	X				X		
^{226}Ra	X	X		X			
^{230}Th	X				X		
^{232}Th	X				X	X	
^{234}U, ^{238}U	X				X	X	
^{236}U	X						X
^{237}Np	X					X	
^{239}Pu, ^{240}Pu	X					X	
$^{239+240}Pu$	X	X			X		
^{241}Am	X			X	X		

Scientific advice (Commercial service)

- **Analytical work under accreditation (ISO/IEC 17025:2005)**
- **Surveillance and waste characterization for Danish Decommissioning**
- **Commercial analysis for nuclear decommissioning abroad, industry (import/export) and other research institutes**
- **Training on radiochemical analysis**
- **Consultancy in radiation protection, analytical method development, environmental monitoring, etc.**

DTU Nutech has long-term experience on radiochemical analyses for nuclear decommissioning



Challenges in waste characterization

- ✓ Matrix effect - Reliability and robustness
- ✓ Interferences, standard availability - accuracy and precision
- ✓ Time and lab intensity - cost and sample throughput
- ✓ Detection limit, radioactive level - sensitivity and applicability
- ✓ Sampling, preservation, treatment - representativeness
- ✓ Lack of documentation, experience, staff, infrastructure

Risø hot cell paint alpha/beta emitters analyses

Challenges

- Steel liner coated with epoxy paint, which is resistant to alkalines and organic solvents
- Contains PCB's and lead

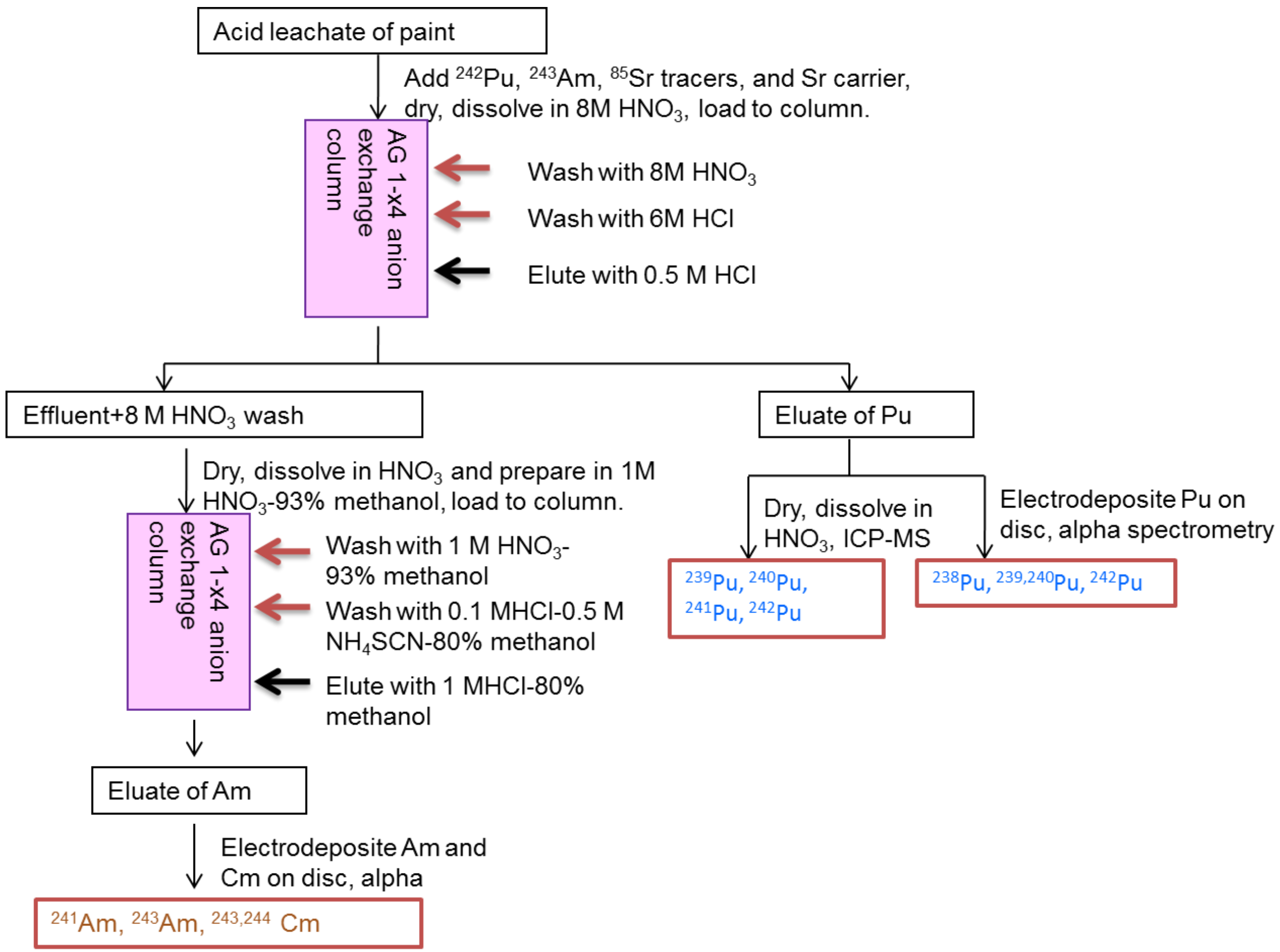
Approach

- Acid leaching with combined gamma measurements of ^{137}Cs and ^{241}Am as a marker

Sample ID	Weight, mg	Leaching rate, %	
		^{137}Cs	^{241}Am
1A	29.5	92.1	98.7
1B	39.1	95.3	99.1
2	9.2	98.8	99.2
3	19.5	97.8	98.7
4	85.7	78.8	97.5
5	130.3	91.0	95.0

Risø hot cell paint alpha/beta emitters analyses

Analytical procedure applied for Risø Hot Cells



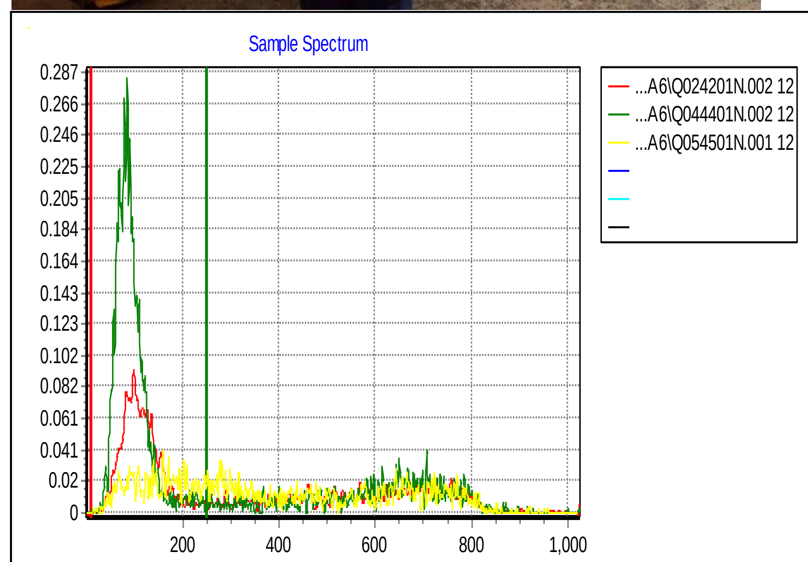
Determination of ^{41}Ca in heavy concrete

Challenges

- Heavey concrete (containing lead and baryte) is very difficult to dissolve
- Contains many interferences

Approach

- Decomposition of heavy concrete by alkali fussion, leaching Ca by acids
- Separation from active metals (^{60}Co, ^{152}Eu, ^{55}Fe, ^{63}Ni, ^{65}Zn, ^{54}Mn, ^{51}Cr) by $Fe(OH)_3$ precipitationat pH9
- Separation from other alkaline metals (^{133}Ba, ^{226}Ra and ^{90}Sr) by $Ca(OH)_2$ precipitation in NaOH solution



Hou X.L., Radiochim Acta, 2005

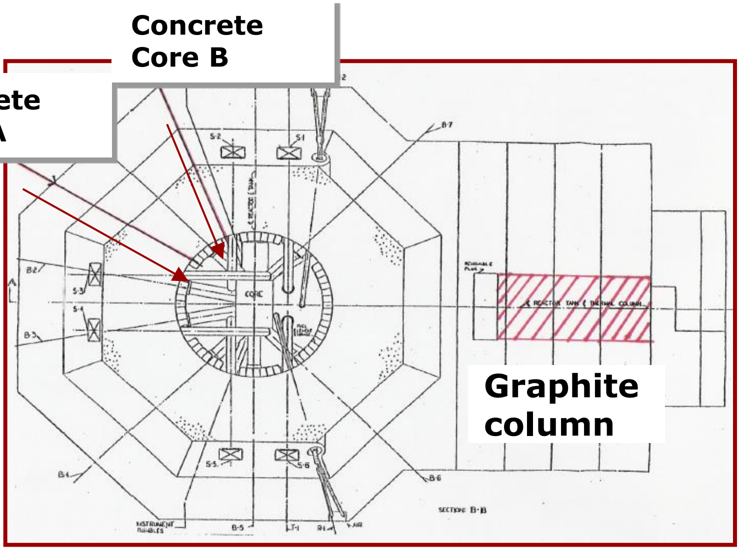
Analyses of ^{14}C and ^{3}H in graphite and concrete

Challenges

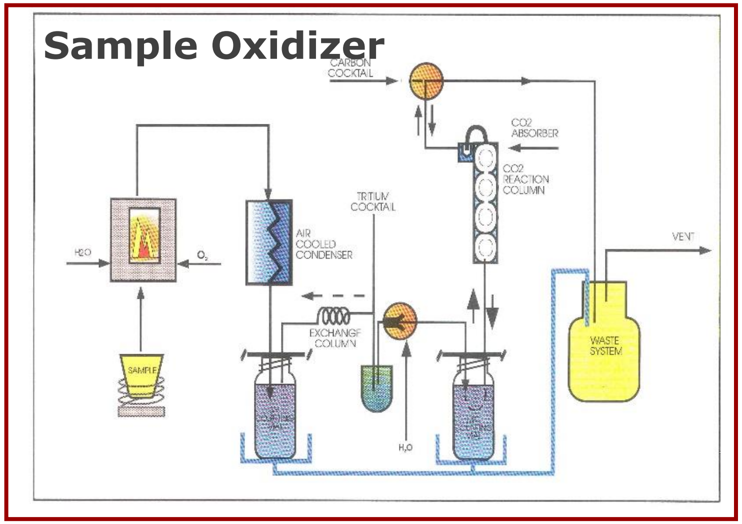
- *Graphite analyses:* time consuming, large volumes of alkalines and acids
- *Concrete analyses:* special equipment and chemicals (e.g. HF) needed, non-decomposable Ba_2SO_4 in heavy concrete

New approach and advantages

- Decomposition at high temperatures using sample oxidizer
- Oxidizer method more accurate than acid digestion
- Reduced sample processing time

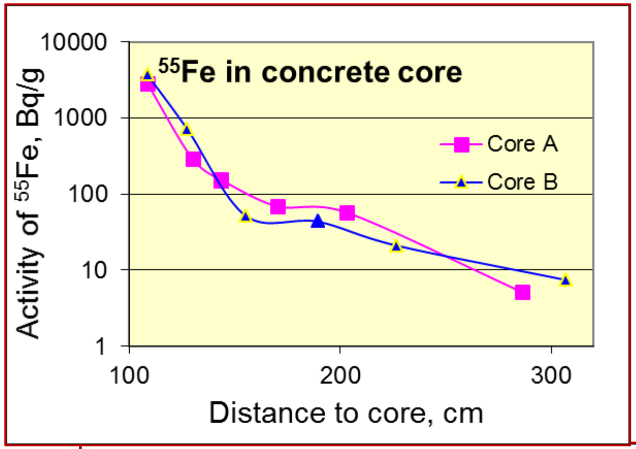


Schematic view of reactor DR-2 and sampling location



Hou X.L., Applied Radiation and Isotope, 2005

Distribution of radioactivity in nuclear waste

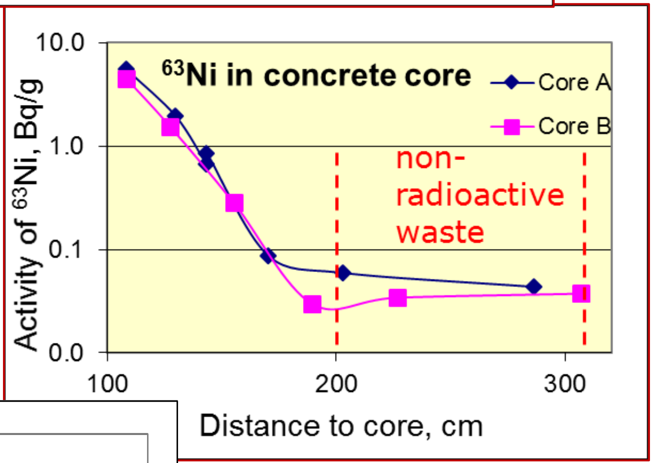


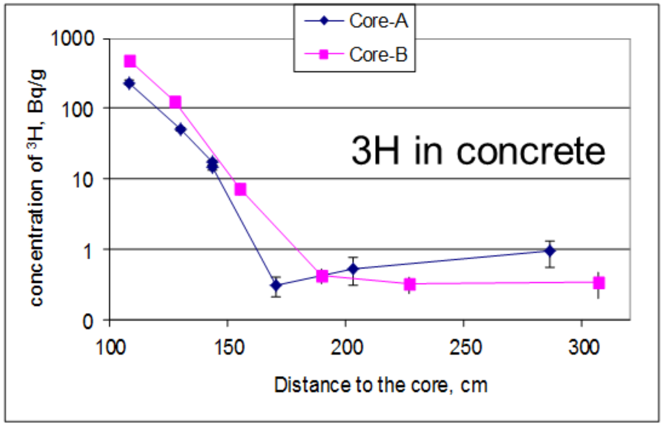
Challenge

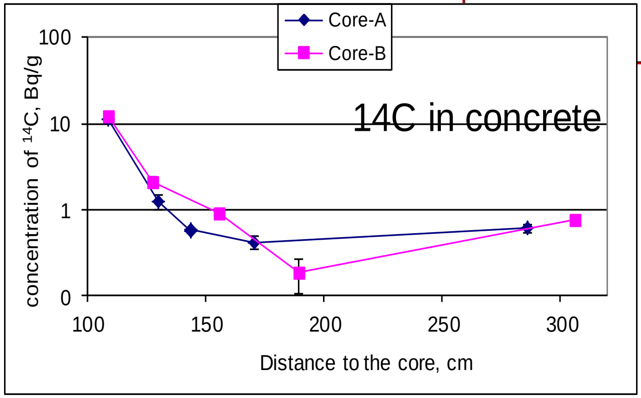
- Large amount of waste, high cost

Approach

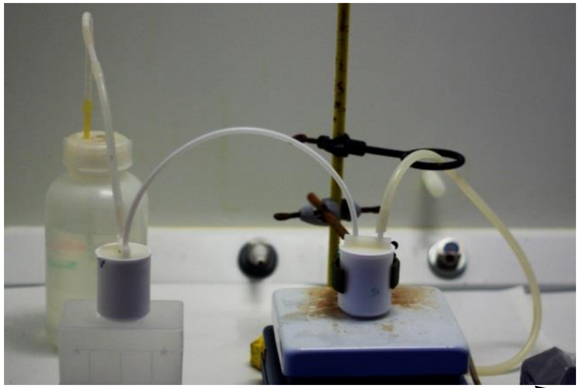
- Analysis depth profile of concrete core
- Radionuclides concentrations decrease exponentially with distance to the reactor
- 60% of the concrete (200-300 cm) can be treated as non-radioactive waste



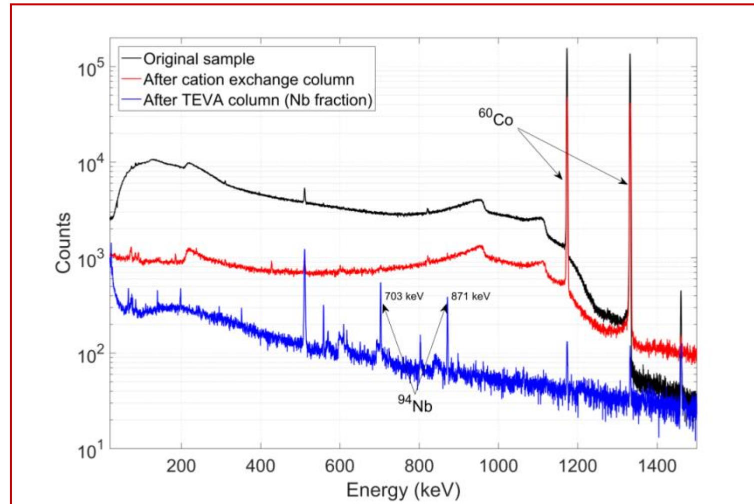


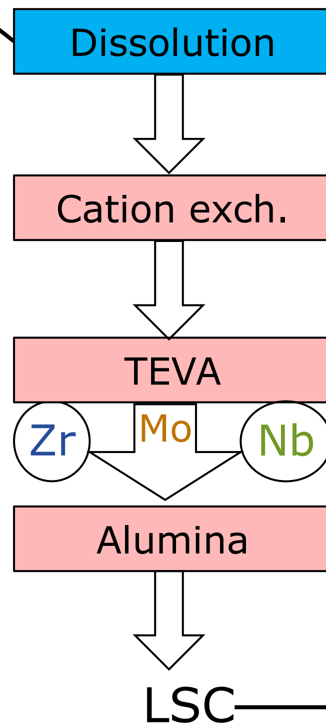


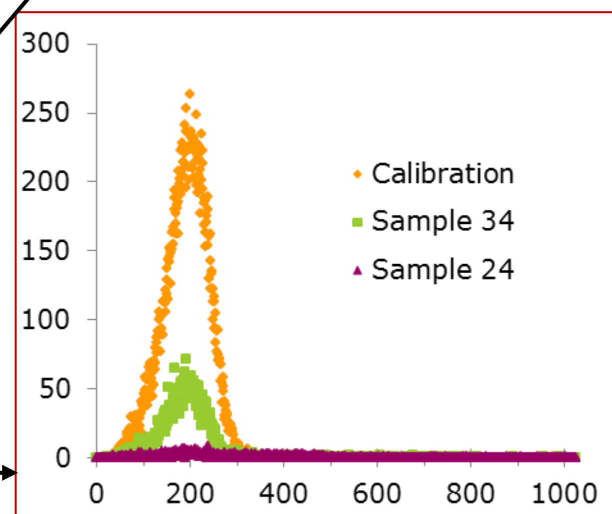
Determination of ^{93}Mo and ^{94}Nb



- Dissolution and repeated evaporation using aqua regia and HF



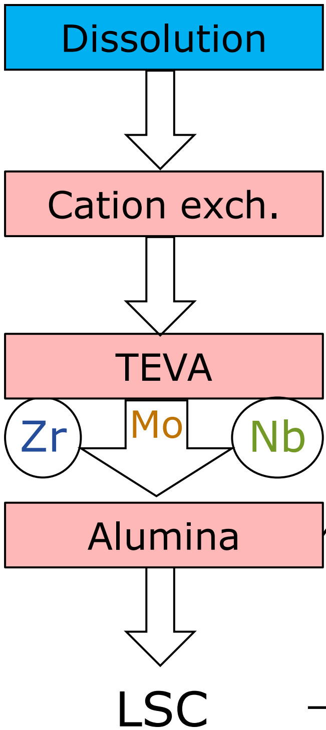




Challenge

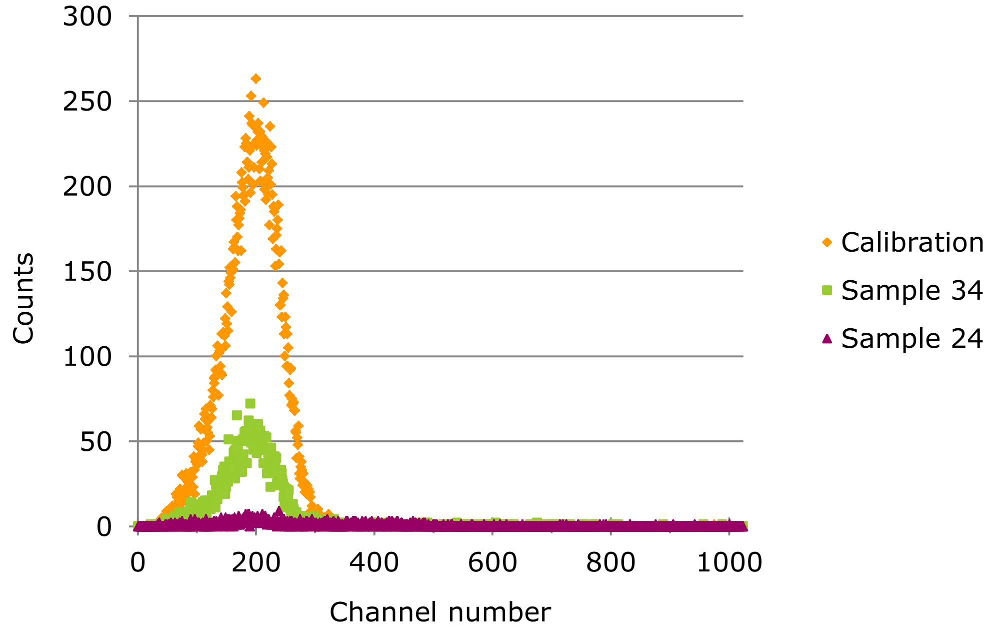
- Difficult to dissolve
- No Mo-93 standard avaliable
- No reference material

Determination of ^{93}Mo and ^{94}Nb



- Load & rinse: 1 M HNO_3
- Wash: 0.1 M HNO_3, H_2O and 0.01 M NH_3, respectively
- Mo strip: ≥1 M NH_3

Other metals pass mainly through



Outlook and conclusion

- **Decommissioning and waste management is an on-going challenging task**
- **Continuous methods development for effective radiochemical analyses is necessary**
- **Automation development could be helpful**
- **International collaboration is important**

Thank you!

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