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PREDIS Final Conference - WP4 Innovations in metallic radioactive waste management

A. ABDELOUAS
ON BEHALF OF WP4 CONSORTIUM

05 JUNE 2024

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

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FACULTAD DE CIENCIAS
UNIVERSIDAD AUTÓNOMA DE MADRID

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Irène Joliot-Curie
Laboratoire de Physique des 2 Infinis

Galson SCIENCES LTD

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Social Organization for Radioecological Cleanliness

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Presentations

- Summary (Abdesselam Abdelouas – IMT Atlantique)
- Scientific presentations:
  - Developing and optimizing decontamination processes (T. Suzuki, MT Atlantique)
  - Optimization of characterization and waste minimization techniques (A. Savidou, NCSRD)
  - Advances in encapsulation of materials in magnesium phosphate cement-based matrices (C. Cannes, IJCLab)
- Students presentations:
  - A non-destructive gamma spectrometry set-up for characterization of metallic waste (D. Mavrikis, NCSRD)
  - Decontamination of radioactive effluents (M. Robin, IMT Atlantique)

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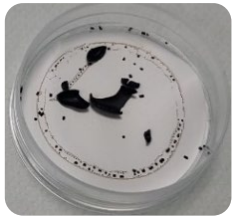
WP Objectives



- **Optimisation** and **innovation** for the management of large volumes of metallic waste (maintenance, dismantlement, etc…)
- **Characterisation techniques**
  - Non destructive control: classification & clearance
  - Difficult to measure radionuclides (RN): clearance

- **Decontamination techniques** mainly for recycling & clearance
- **Conditioning** of reactive metallic waste using innovative Magnesium Phosphate Cement (MPC) (Disposal)

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WP Expected Impacts

- Making problematic metallic waste management routes (from storage to disposal) **safer** and more **economically efficient**.
- Contributing to repository use optimization, by allowing a more efficient use of the available disposal volumes (**recycling**).
- Reduction of waste management and disposal cost by valorization of part of the waste stream (**declassification**, **recycling**, **minimization**)

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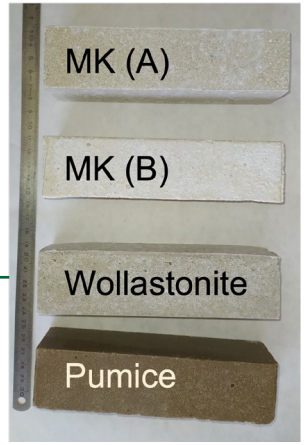
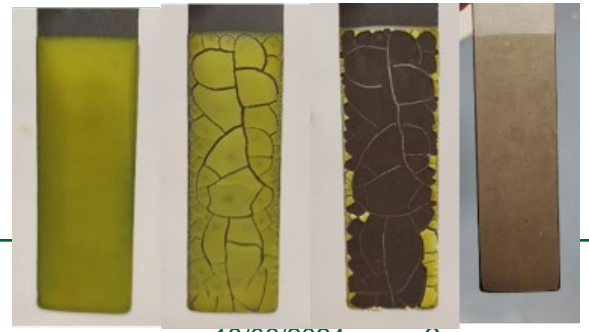
Work Package 4 Structure



- Task 4.1 WP management (IMTA)
- Task 4.2 GAP analyses (IMTA, all)
- Task 4.3 Defining Europe-wide Needs and Opportunities for Management of Metallic Waste Streams (GSL)
- Task 4.4 Development and optimisation of decontamination processes (IMTA)
- Task 4.5 Optimisation of metallic waste characterisation and procedures for waste minimisation and recycling (NCSRD)
- Task 4.6 Encapsulation of reactive metals in magnesium phosphate cement-based matrices (CNRS)
- Task 4.7 Dissemination (IMTA)



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WP Major Achievements, Task 4.4 Development and optimization of decontamination processes

- **Optimization** of the CORD (Chemical Oxidation Reduction Decontamination) process.

- **COREMIX** (Chemical Oxidation Reduction using nitric permanganate and oxalic acid MIXture)

Aditya Rivonkar (2023) Optimization of chemical decontamination methods for radioactive metals. PhD Thesis, IMT Atlantique (France).

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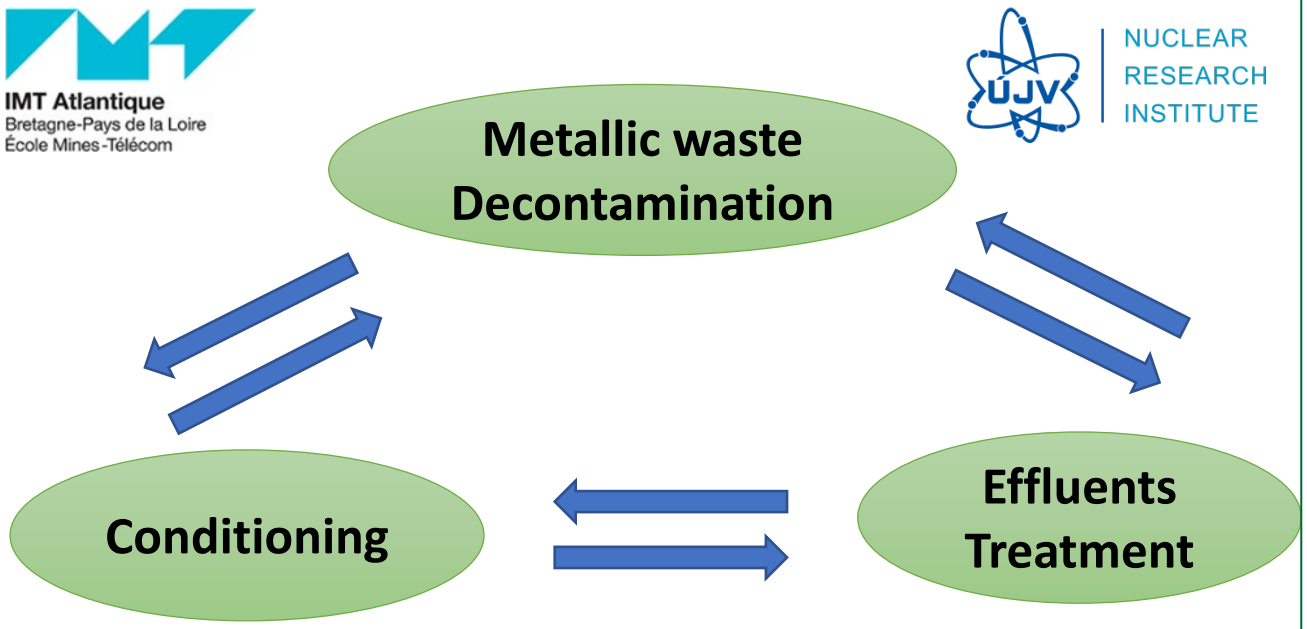
WP Major Achievements, Task 4.4 optimization: COREMIX process



- Less complex process for industrial application: no UV light treatment for oxalic acid destruction. Safer, environmentally friendly & more economic !
  - Oxalic acid destruction by H_2O_2 & heating. LCA/LCC approach helped optimizing the process by reducing energy consumption & CO_2 production.
- Replacement of toxic and unstable permanganic acid ($HMnO_4$) by a mixture of $KMnO_4$ + HNO_3. $HMnO_4$ must be prepared onsite and requires expensive acid cation resins.
  - Safer, more environmentally friendly and more economic.
- Reduction of treatment time (less contact cycles) by 50%.
  - Safer, more environmentally friendly and more economic.
- The chemicals involved are compatible with the effluent treatment step as well as with the WAC for the conditioning/storage steps.
  - Use of chemical precipitation processes allowing the transformation of m^3 of waste effluents into a few 100g of residues compatible with cement/geopolymer matrices (WP4 & WP5)

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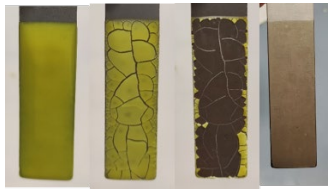
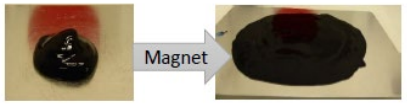
WP Major Achievements, Task 4.4 innovation: magnetic gel decontamination

Metallic waste Gel Decontamination

Gel preparation & testing



Oxidized metal preparation
Gel preparation & testing



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COREMIX process testing

Oxidized metal preparation

- Development of gel formulations for “dry” decontamination
  - After drying the gel can be collected with the extracted contamination. No effluents: Safer, more environmentally friendly and more economic.
- Optimization of chemical parameters of the gel (e.g. COREMIX testing with gel).
  - Efficient for metals with small oxidized layer.
- Innovative formulation to decontaminate hardly accessible surfaces.
  - Gel application and removal using remotely a magnet.

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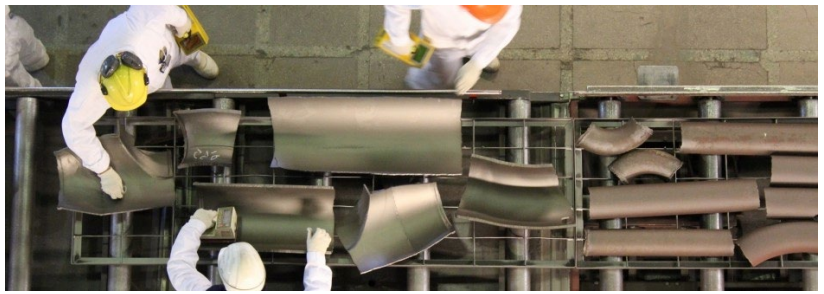
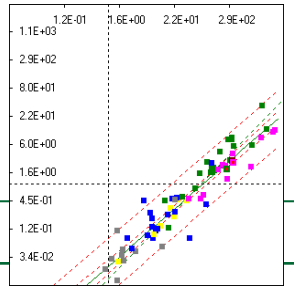
WP Major Achievements, Task 4.5 Optimization: radiological characterization



- Better determination of the waste management route
- Minimization of waste volume & increase of recycling

- Optimization of NDC using gamma spectrometry by reducing uncertainties.
  - Geometry of segment ; activity inhomogeneity ; measurement efficiency ; pipe direction
  - The method allows determination of activities of Cs-137 and Co-60 at the level of clearance in 1-2 min (amount of metallic waste about 100 kg)
  - Determination of activities in activated and / or contaminated metallic waste
- Optimization of sorting of metallic waste.
  - Scaling Factor.
- Development of procedures for DTM measurement.
  - Ni-59, Ni63, Mo-93, Ca-41, Zr-93
  - Validation will be held by an intercomparison exercise in 2024



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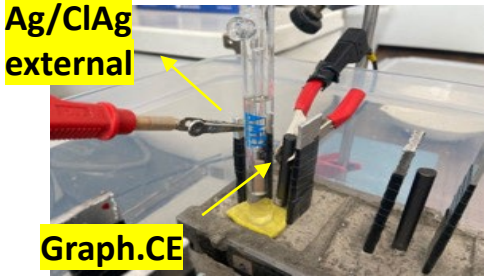
WP Major Achievements, Task 4.6 Optimization: MPC formulations for reactive metallic waste encapsulation

- Development of magnesium phosphate cement formulations based on WAC and economical considerations.

- Development of MPC formulations
  - Testing new alternative fillers to replace fly ash (volcanic ash, wollastonite)
- Optimization of cost production
  - Replacement of dead burned MgO by reactive MgO + retarder. MPC price reduction by 15%.
  - Lowering the volume of cement and increase the volume of aggregates
- Qualification of the developed MPC formulations
  - Corrosion, irradiation of MPC-Al, MPC-carbon steel, beryllium

B0T5
5% thiosulfate

B2T3
2% boric acid +
3% thiosulfate



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Industrial support

- Fruitful exchange with industrial partners
  - EDF, ORANO, ENRESA, ANDRA, Triskem…:
    - providing raw materials such as fly ash, metals (Ni-Alloy), resins
    - Advises in terms of suitable applications and processes, WAC, experimental conditions

Task 4.5

Task 4.6

Task 4.4

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Students involvement & Dissemination

- Number of PhD theses supported: **15**
  - Task 4: **8** (A. Rivonkar, M. Robin, T. Prasek, K. Fenclova, D. Barton, H. Lane, A. Santi, O. Ileri)
  - Task 5: **4** (A. Markopoulos, D. Mavrikis, E. Ntalla)
  - Task 6: **3** (M. Dieguez, I. Moschetti, C. Fernandez)

  - MSc students: **8**
- Number of open access publications: Achieved: **9** ; Submitted: **6**
- Number of participation to workshops / conferences: **31**
- Number of Patent submitted: **1**
- Number of processes with TRL increase: **4**

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WP4 Innovations in metallic treatment and conditioning

Task4.4: Development and optimization of decontamination processes

TOMO SUZUKI-MURESAN & ALL MEMBERS OF THE TASK4.4

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 945098.

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Context & Objectives

- Multiple origins of metallic wastes
  - Nuclear power plants: maintenance, dismantling, decommissioning
  - Nuclear facilities for retreatment and reprocessing
- Dismantling and decommissioning
  - Very large volumes of waste: Metallic components one of the main contributor of the inventory

  ⇒ may over-saturate the capacity of waste disposal repository.
- Typical metals studied in this task include Ni-alloys and stainless steels.
- Objectives:
  - Developing and optimizing decontamination procedure
  - Minimizing secondary effluent wastes

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Approaches & Methodologies

Sample preparation → Treatment of metallic wastes → Secondary waste treatment

Oxidized samples representing NPP and reprocessing facility

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HNO_3 Permanganate Oxalic acid (COREMIX)

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Preparation of decontamination loop by APOX optimization

cea

Vacuumable decontamination gels

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Electrochemical gel decontamination (EASD)

Precipitation
Electrocoagulation

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Presentation M. Robin

Ionic Liquid decontamination

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Electrochemical deposition from ionic liquids

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Interaction with WP2 LCC/LCA

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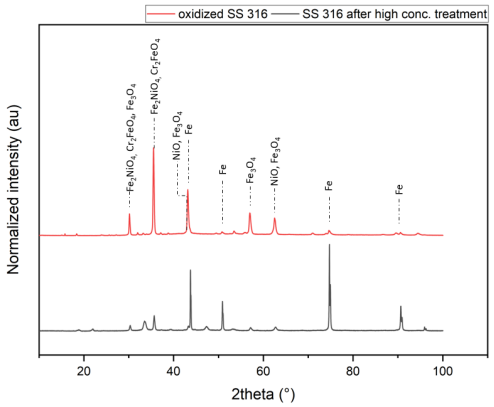
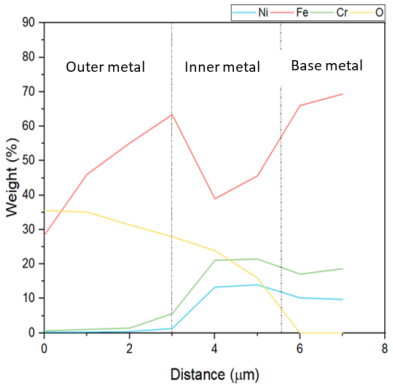
Sample preparation with contaminants and characterisation

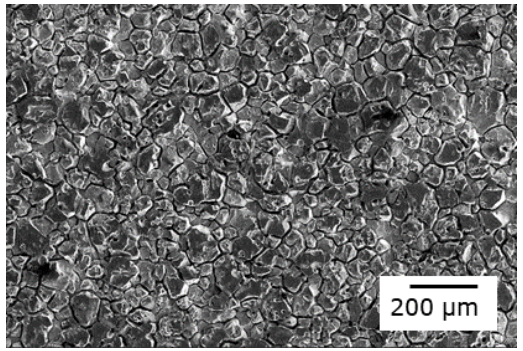
Metal heated up via induction and water vapour is used to form oxide layer

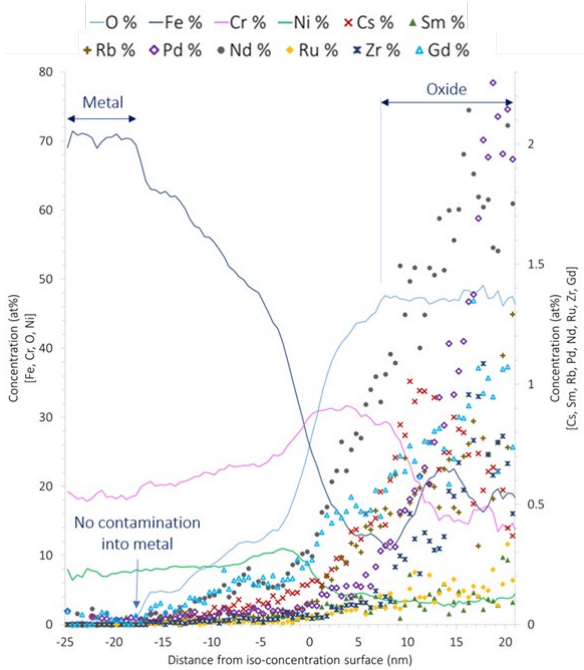


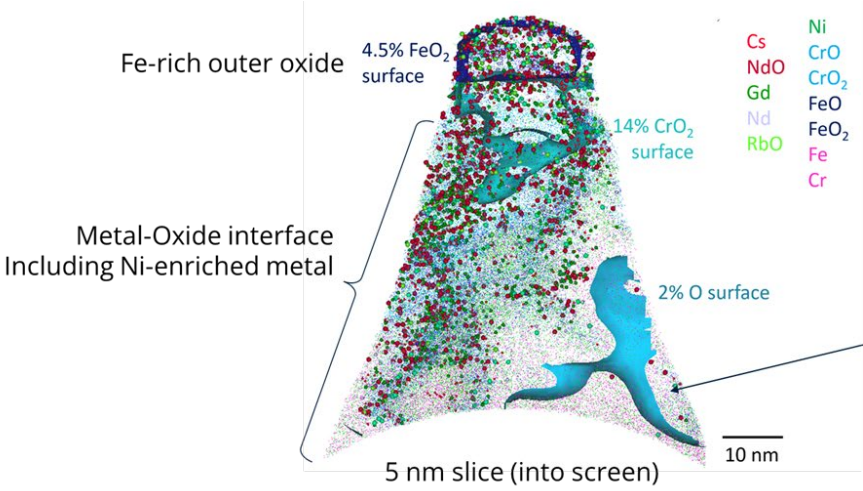


Multilayer oxide representative of the primary circuit and consisting of various oxides of Fe, Ni and Cr.

Successful 3D characterization of the contaminated oxide layer
Stainless steel boiled in 8M HNO_3 and contaminants







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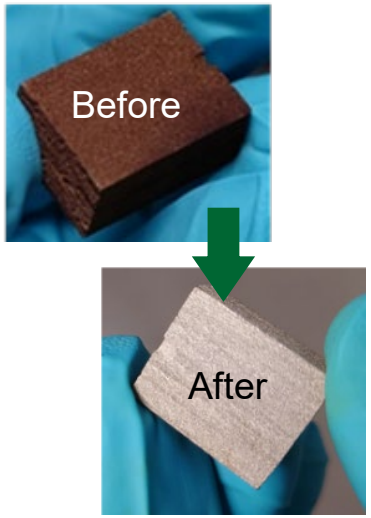
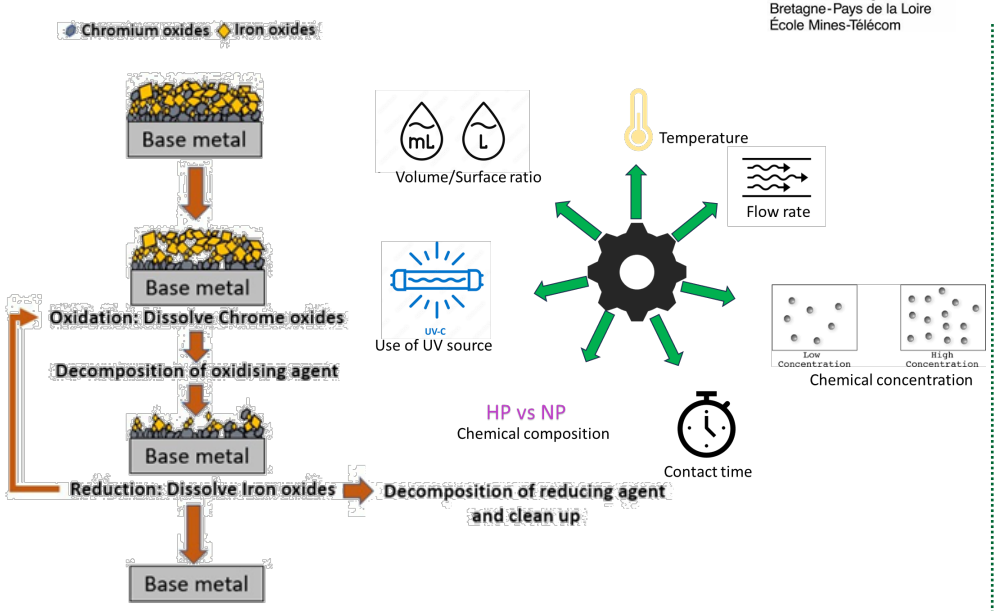
Optimizing chemical decontamination using Oxidation Reduction Decontamination Process

COREMIX





- Alternating steps of $HNO_3/KMnO_4$ and $H_2C_2O_4$
  → no additional clean-up required
- Process found to be optimal on SS and Ni-alloys from NPPs and reprocessing plants

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APOX

- Optimizing and upscaling existing process using decontamination loop
- Ready for further testing

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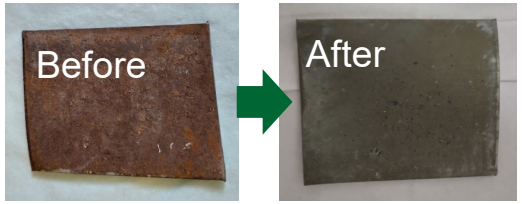

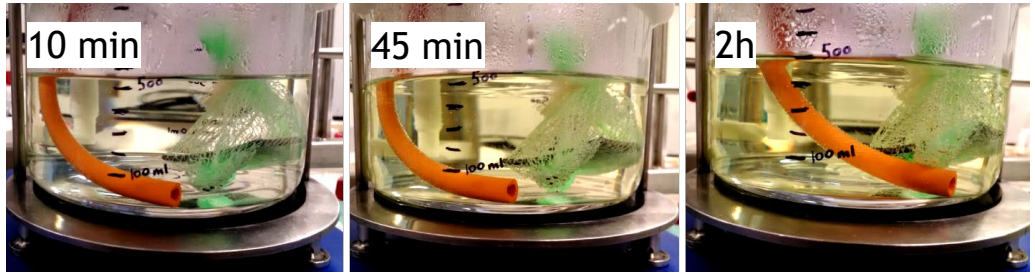

Coloration of the solution during leaching

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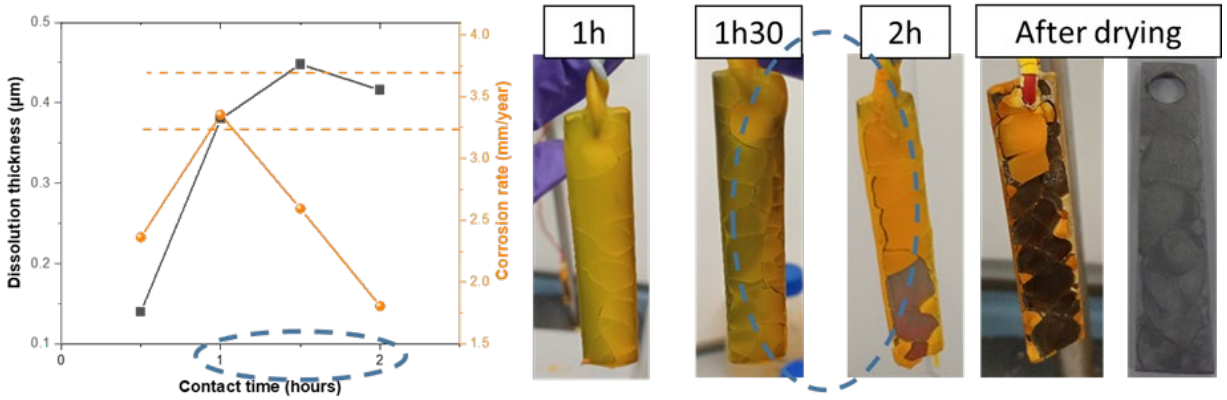
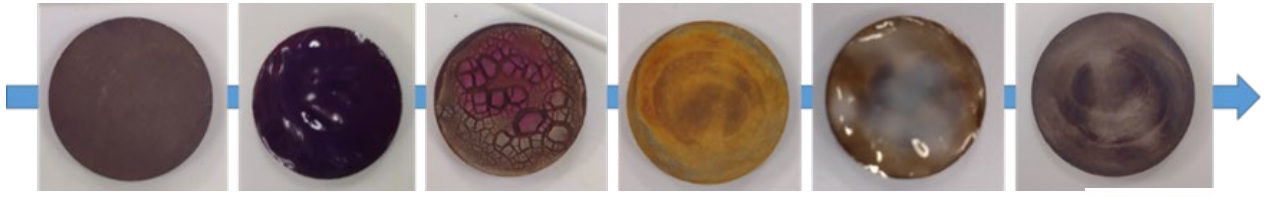
Decontamination of metallic waste using inorganic gels

Model system : Gel HNO_3 + Ce(IV) on non-oxidized SS



- **Adhesion on surfaces without flowing**
  ➔ contact between surface and solution
- **Smooth corrosion** (≈ µm) and absorption of the contamination
- **No secondary effluent, only solid waste**

New gel formulations based on the COREMIX process



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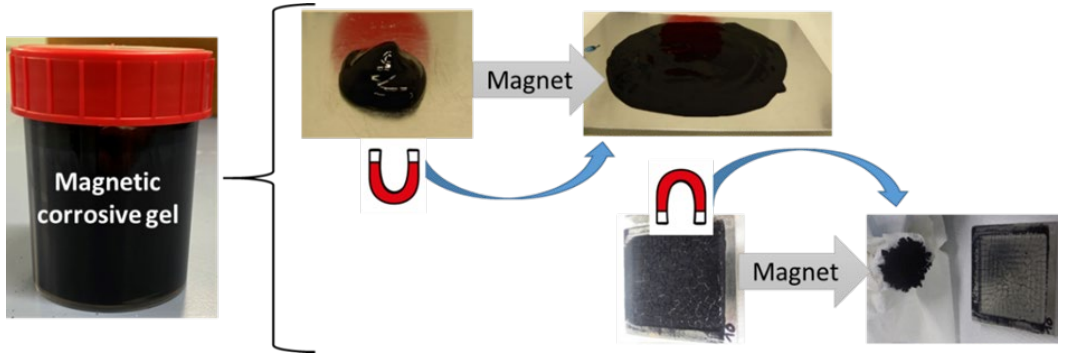
New gel formulation integrating magnetic particles to be remotely applied with a magnet (for hardly accessible surfaces)



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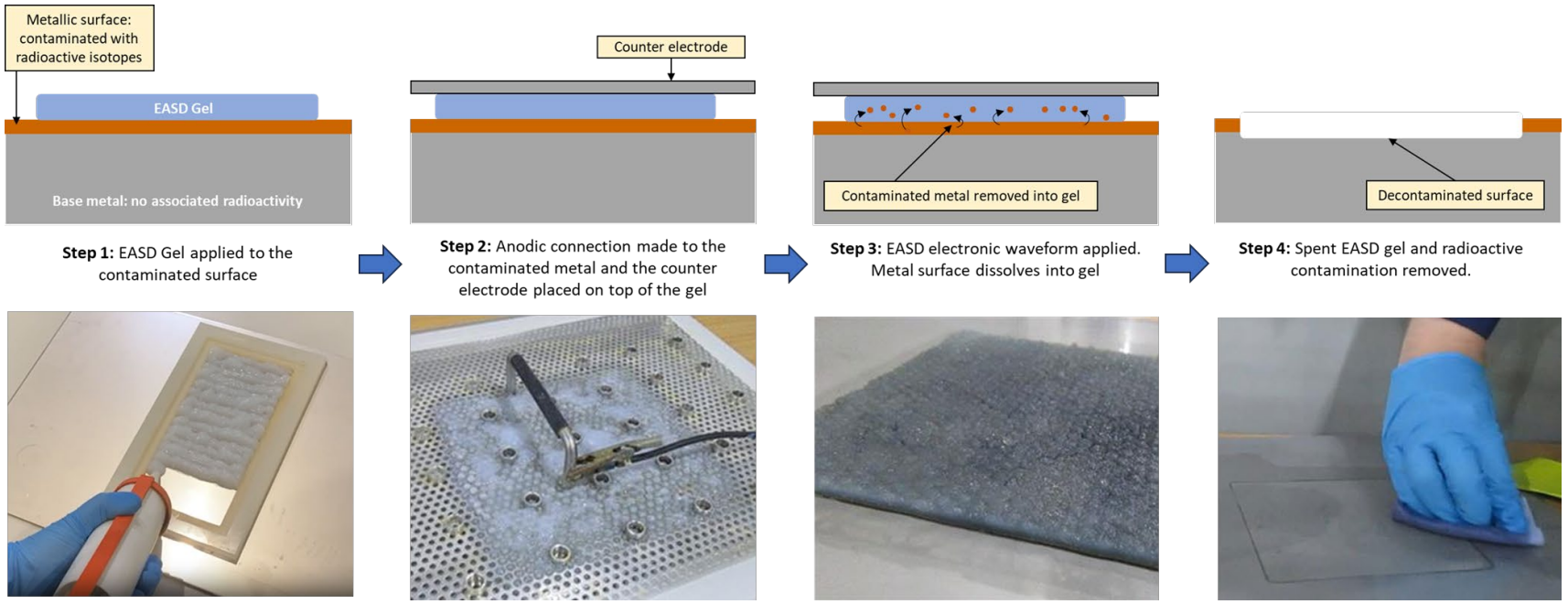
Gossard et al. *Progress in Nuclear Energy*, 149 (2022) 104255
Pochat-Cottiloux et al. Environmental Technology & Innovation, 35 (2024) 103688

Electrochemical gel decontamination (EASD)



Step 1: EASD Gel applied to the contaminated surface

Step 2: Anodic connection made to the contaminated metal and the counter electrode placed on top of the gel

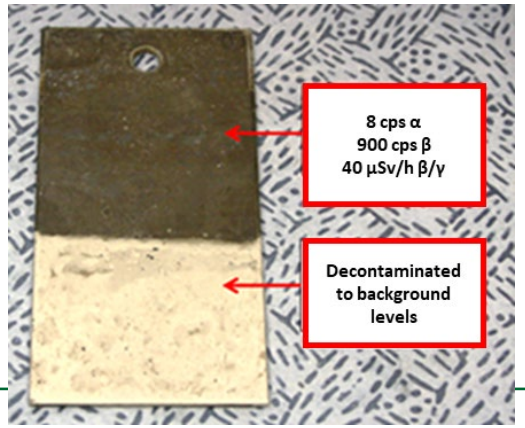
Step 3: EASD electronic waveform applied. Metal surface dissolves into gel

Step 4: Spent EASD gel and radioactive contamination removed.

Step-by-step process

Key Benefits:

- No aggressive chemicals, only electricity
- Simple secondary waste form
- Treatment is fast (~0.5µm/min removal for stainless steel)
- High DF's achievable
- Can be deployed in-situ to target radiation hot spots



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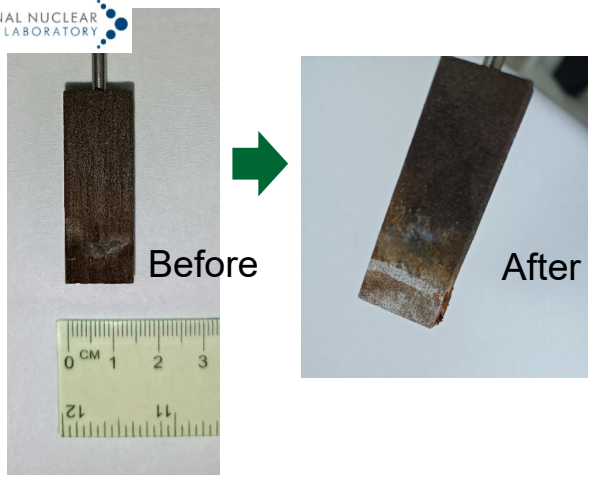
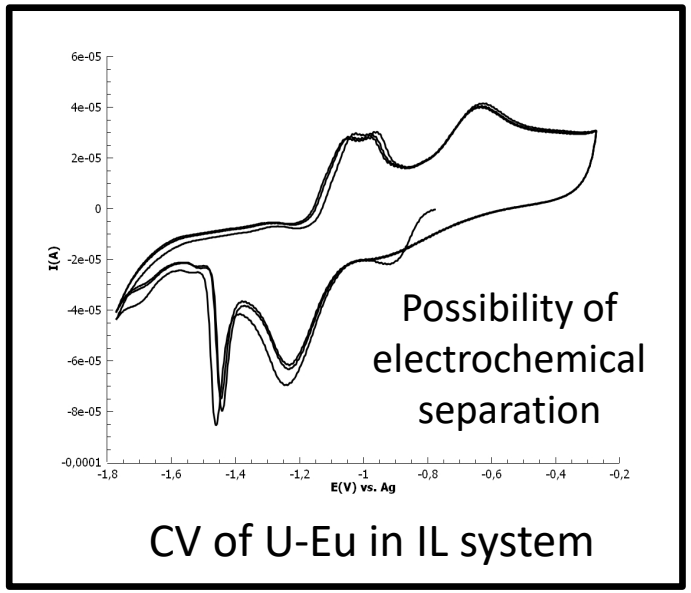
Coupling anodic dissolution and electrodeposition

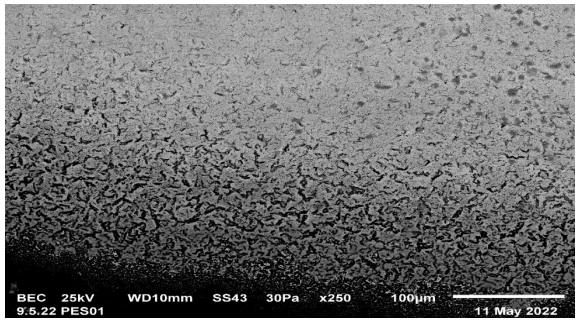
Waste Stream → Anodic dissolution : transfer of elements of interest into ionic liquid → Electrochemical deposition on solid electrode → IL, re-usable

Electrochemical deposition on solid electrode → Deposited element of interest

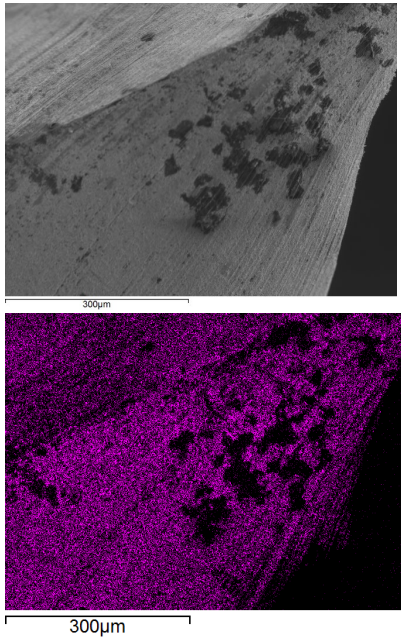




CV of U-Eu in IL system



Mixed deposit incl. Nd, Sm, Eu, Gd leading to clean IL



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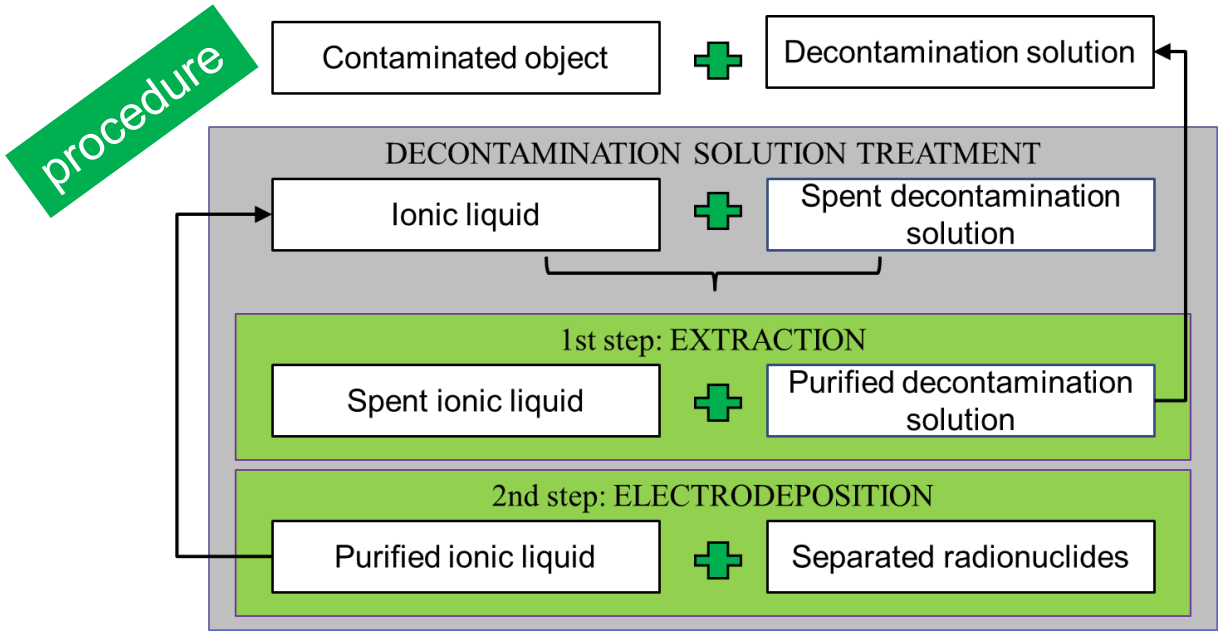
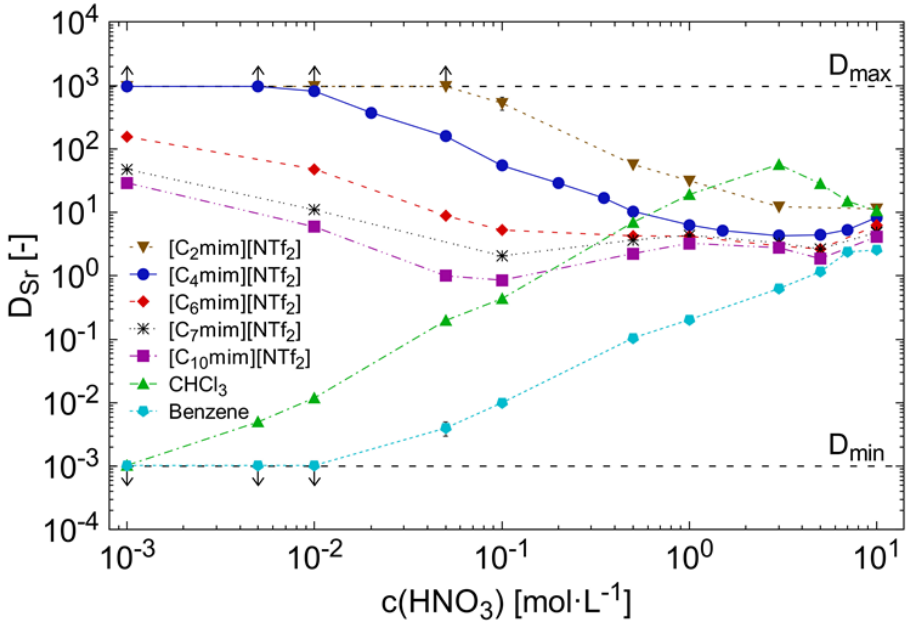
Coupling liquid/liquid extraction and electrodeposition



- Extraction of radionuclides from model decontamination solution → Possiblity to regenerate solution
- Regeneration of spent ionic liquid by electrochemical treatment.

- Ionic liquid extraction
  - Activation products (Co, Fe)
  - Fission products (Sr, Mo, Tc)



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New Skills and Collaborations

Training School at La Hague, France

NNL, UK

IMT Atlantique, France

Mobility program

PREDIS workshop, Belgium (2023)

Guest seminar presentations

This proje aining programme 2019-2020 under grant agreement No 945098.

PREDIS New Scientific Knowledge

Applied Radiation and Isotopes
Volume 181, March 2022, 110073
https://doi.org/10.1016/j.apradiso.2021.110073

Tafel-analysis of the AP-CITROX decontamination technology of Inconel alloy 690

R. Katona [a], A. Rivonkar [b], R. Locskai [a], G. Bátor [c], A. Abdelouas [b], J. Somlai [c], T. Kovács [a c]

Progress in Nuclear Energy
Volume 149, July 2022, 104255
https://doi.org/10.1016/j.pnucene.2022.104255

Review

Gels, coatings and foams for radioactive surface decontamination: State of the art and challenges for the nuclear industry

Alban Gossard [a], Audrey Lilin [b], Sylvain Faure [a]

Optimisation of the chemical oxidation reduction process (CORD) on surrogate stainless steel in regards to its efficiency and secondary wastes

https://doi.org/10.3389/fnuen.2022.1080954

Aditya Rivonkar[1]*, Richárd Katona[2,3], Mathurin Robin[1], Tomo Suzuki-Muresan[1], Abdessalam Abdelouas[1], Marcel Mokili[1], Gergő Bátor[2,3], Tibor Kovács[2,3]

Journal of Radioanalytical and Nuclear Chemistry
https://doi.org/10.1007/s10967-023-09293-6
https://link.springer.com/article/10.1007/s10967-023-09293-6

Liquid–liquid extraction of strontium from acidic solutions into ionic liquids using crown ethers

Jan Houzar[1] · Katerina Cubova[1] · Miroslava Semelova[1] · Mojmir Nemec[1]

Progress in Nuclear Energy
Volume 159, May 2023, 104637
https://doi.org/10.1016/j.pnucene.2023.104637

Review

A review of contamination of metallic surfaces within aqueous nuclear waste streams

Daniel N.T. Barton [a], Thomas Johnson [a], Anne Callow [b], Thomas Carey [b], Sarah E. Bibby [c], Simon Watson [a], Dirk L. Engelberg [d], Clint A. Sharrad [a]

Environmental Technology & Innovation
Volume 35, August 2024, 103688
https://doi.org/10.1016/j.eti.2024.103688

Colloidal magnetic gels for the decontamination of limited access metallic surfaces

Hippolyte Pochat-Cottilloux [a], Fabien Frances [a], Luc Girard [b], Aditya Rivonkar [c], Alban Gossard [a]

Methods for the destruction of oxalic acid decontamination effluents

Jessica Blenkinsop[1]*, Aditya Rivonkar[2], Mathurin Robin[2], Thomas Carey[1], Barbara Dunnett[1], Tomo Suzuki-Muresan[2], Cavit Percin[2], Abdesselam Abdelouas[2], Jonathan Street[3]

https://doi.org/10.3389/fnuen.2024.1347322

Optimized precipitation process for the treatment of radioactive effluents from Ni-alloy decontamination using a Chemical Oxidation Reduction process

Provisionally Accepted

https://doi.org/10.3389/fnuen.2024.1396821

Mathurin Robin[1]*, Aditya Rivonkar[1], Tomo Suzuki-Muresan[1], Abdesselam Abdelouas[1], Marcel Mokili[2]

Caesium and strontium contamination on NAG 18/10L stainless steel following corrosion in simulated nitric acid reprocessing liquor

Anne Callow[1,2*], Dean Connor[1,3], Thomas Carey[1,4], Kim Summers[1], Christina Hofer[2], Kerstin Jurkschat[2], Jonathan Street[5], Sarah Bibby[5]

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Manuscript currently under review, Corrosion Science

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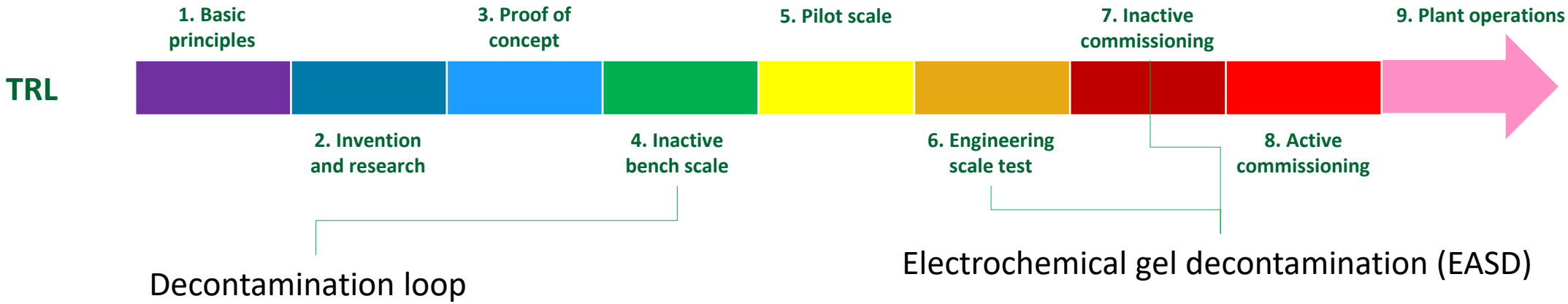
Achievements and Perspectives

- HNO_3 Permanganate Oxalic acid (COREMIX)
- Precipitation, Electrocoagulation
- Magnetic and COREMIX decontamination gels
- Electrochemical deposition from ionic liquids

⇒ Upscaling liquid effluent treatment
⇒ Upscaling magnetic gel technology
⇒ Innovation for matrix conditioning

Contributions in EURAD2
- WP STREAM
- WP LOPERA

Vacuumable decontamination gels



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

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Contributions

Alban Gossard, Fabien Frances, Hippolyte Pochat-Cottilloux, Gabriella Lucena

Kateřina Čubová, Mojmir Nemec

Aditya Rivonkar, Mathurin Robin, Abdesselam Abdelouas, Marcel Mokili

Thomas Carey, Anne Callow, Jess Blenkinsop, Rhianna Jobson, Moya Hay

Richard Katona, Gergő Bátor, Tibor Kovács

Martin Straka

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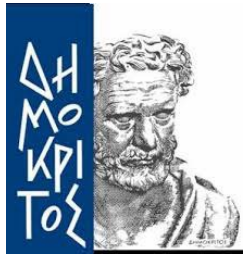
T4.5 Optimization of characterization techniques and waste minimization



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Necessity for optimization of metallic waste characterization & procedures for minimization and recycling

Radioactive metallic waste from decommissioning

(≈10^3 Mg for a 1 GW(e) PWR*)

- Historical information
- Installation simulation
- Destructive Analysis
- Non Destructive Analysis

RW classification (Exempt, VLLW, LLW, …)

Higher classification implies Higher management costs

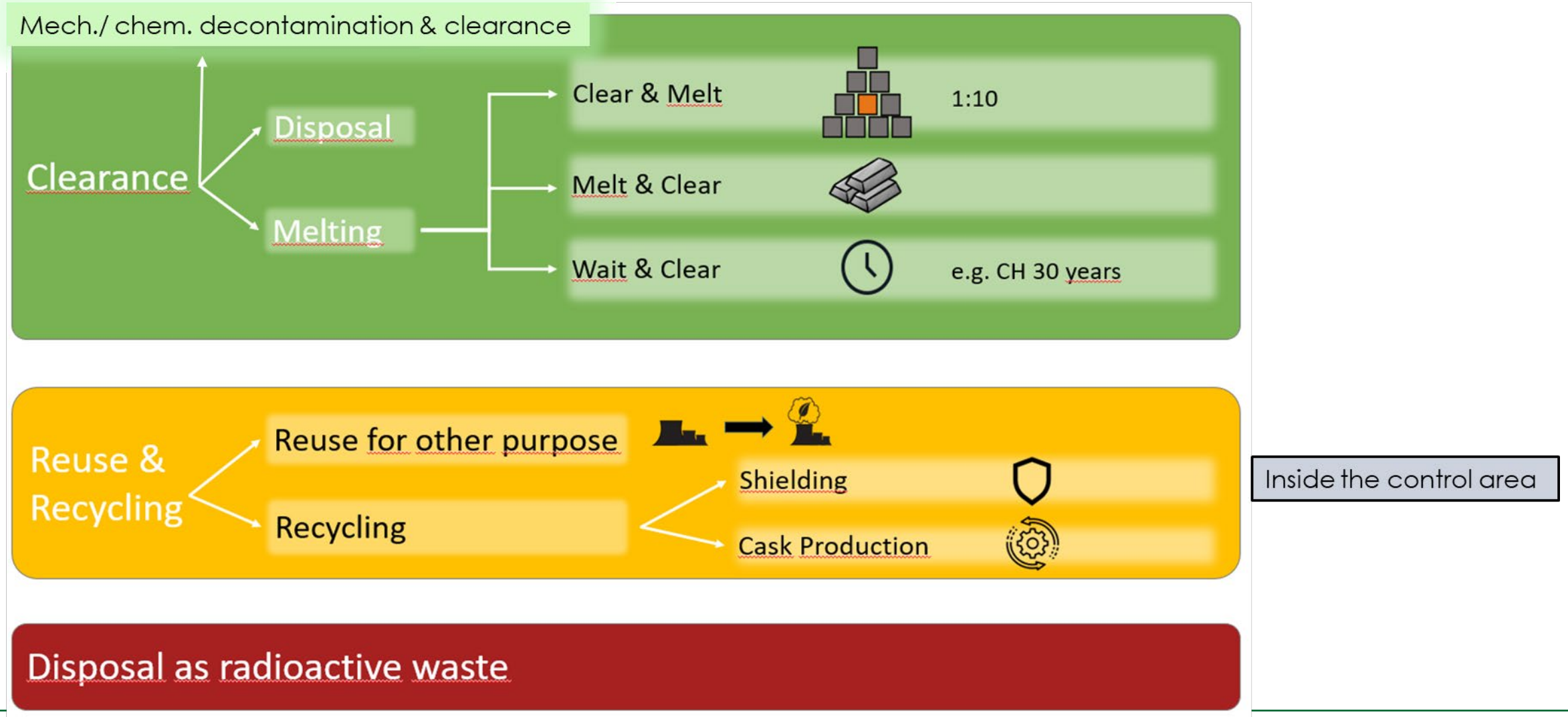
Optimized measurement setup (time, mass) → Less measurements and time

Improved assay accuracy and/ or precision → Less conservatism in RW inventory & low measurement uncertainty

*IAEA, TECHNICAL REPORTS SERIES No. 401

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Metallic waste management routes



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Classification of the waste streams (1)

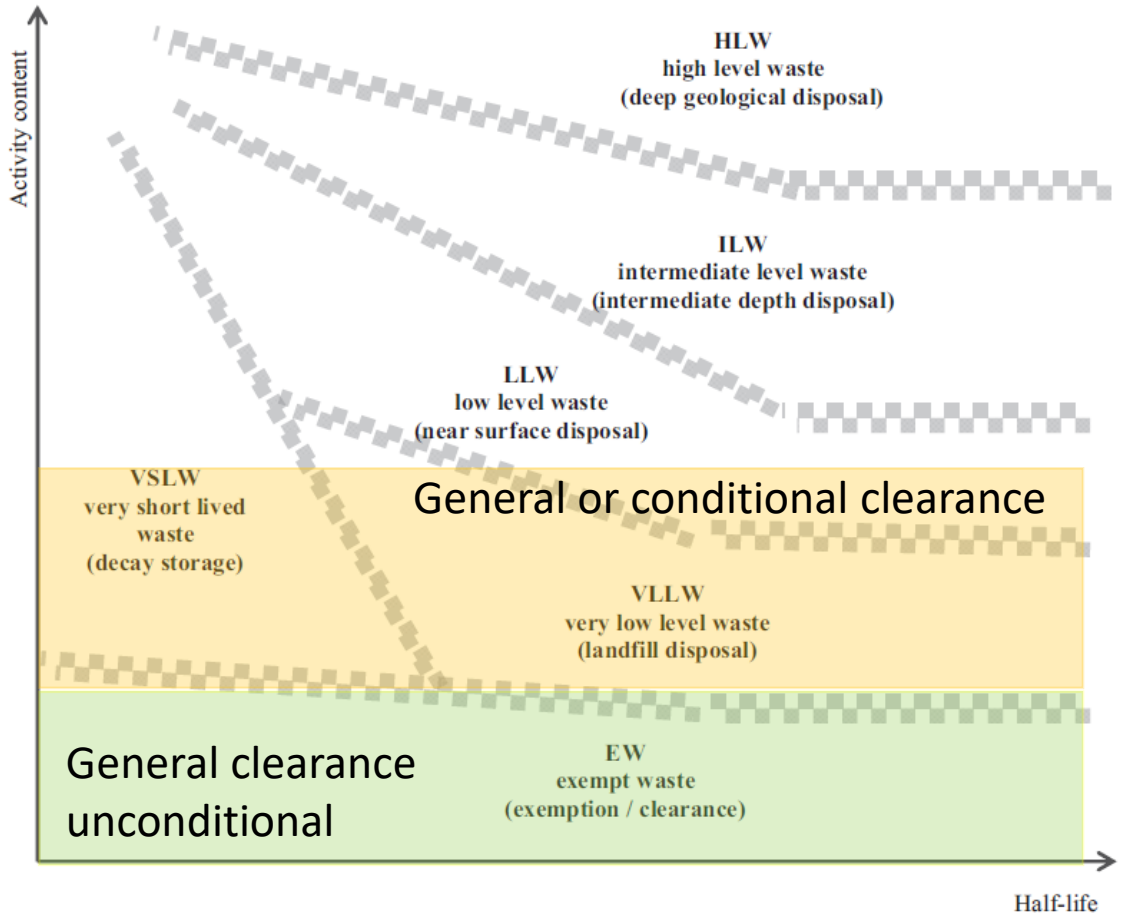


FIG. 1. Conceptual illustration of the waste classification scheme. (according to IAEA)

CLASSIFICATION: Quantification of specified radionuclides to comply with management route requirements or disposal site performance objectives.

The aim of classification of the metallic radioactive waste is changing together with the activity:

- HLW & ILW for radiation protection and best packaging concept
- LLW to demonstrate compliance with the WAC for engineered near surface facilities or near surface landfill
- VLLW to demonstrate compliance with the WAC for near surface landfill or
  to decide decontamination & clearance/ declassification

Optimization of sorting

(The largest volumes of waste from the dismantling of nuclear installations are EW, VLLW and LLW)

Classification of the waste streams (2)

Similar for all nuclear reactors:

- Reactor operation generates fission, activation & corrosion products
- ETM & DTM radionuclides
- Methodology for classification of reactor components (neutron calculations, scaling factors)
- Scaling factors and Nuclide Vector methodology

Different for nuclear reactors:

- Composition of different nuclear reactors metallic components
- Neutron energy distribution & fluence
- Time after reactor shutdown
- Extent & activity of long-lived neutron activation products
- Extent & activity of neutron activated, fission & corrosion products released to reactor coolant

VOLUME AND ACTIVITY OF LILW GENERATED ANNUALLY BY 1 GWe NUCLEAR POWER PLANT *(according to IAEA-TECDOC-1591)*

Reactor type	Volume (m^3)	Activity (TBq)
ABWR	500*	500*
AGR	650	600*
BWR	500	500
FBR	500*	500*
GCR	5000	1000*
LWGR (RBMK)	1500	1000*
PHWR	200	100*
PWR	250	100
WWER	600	600

* Values marked with an asterisk, were not taken from references, and are estimates, pending the availability of reliable information.

Pre-dismantling classification using a modeling approach & the scaling factors methodology allows sorting of metallic waste with regard to the level of activity and radionuclides presented in **waste streams**

Scaling Factors (1)

Finding correlation between Difficult to Measure isotopes, DTM, and Easy to Measure, ETM (Key Nuclides)

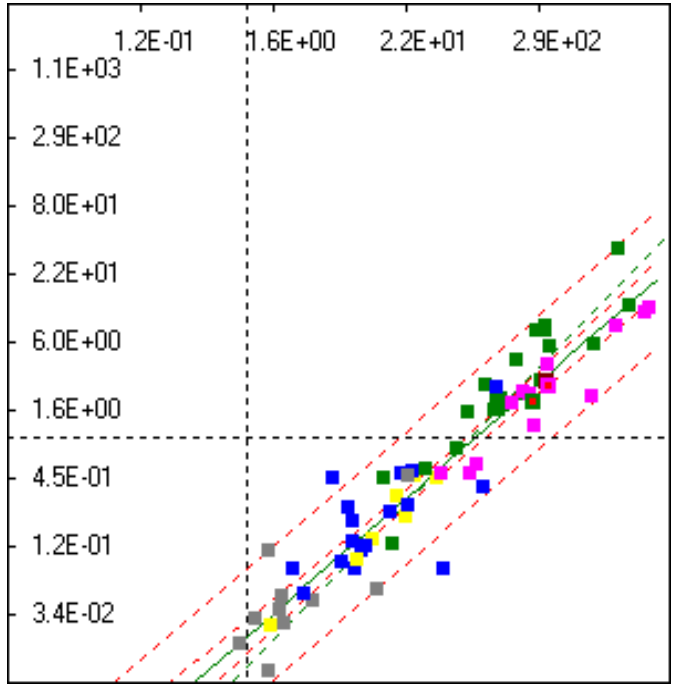
Key Nuclides (K.N.):

- **Gamma emitter easily detected for any gamma spectrometry**
- **Relatively long lived (^{60}Co and ^{137}Cs)**

Difficult to Measure Isotopes and K.N.:

- **Activation Products (AP), or Fission Products (FP)**
- **Similar solubility**
- **Similar transport process**

1) ISO 21238 “Scaling factor method to determine the radioactivity of low and intermediate-level radioactive waste packages generated at nuclear power plants”
2) IAEA TECDOC NW-T-1.18 “Determination and Use of Scaling Factors for Waste Characterization in Nuclear Power Plants”



- **Geometric Mean, Arithmetic Mean, Log-Linear Regression**
- **Collection of samples, time Consuming, High budget**
- **Manner of sampling as critical aspect**

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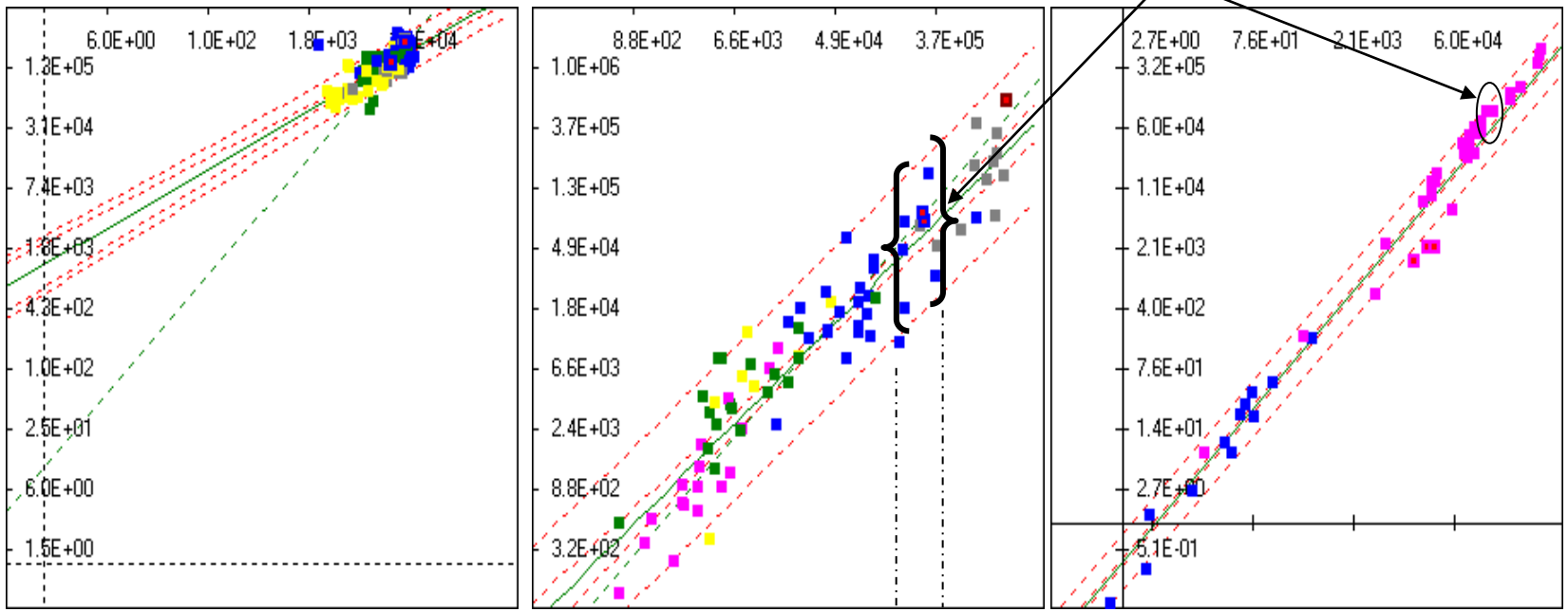
Scaling Factors (2)

CHARACTERIZATION DESIGN PLANNED IN ORDER TO OBTAIN REPREENTATIVE SCALING FACTORS

Intermediate Level Waste (ILW)
Low Level Waste (LLW)
Very Low Level Waste (VLLW)
Clearance purposes

REPRESENTATIVENESS OF SCALING FACTORS

Composite samples. Lower number of samples for radiochemical analyses



Increasing accuracy

Decreasing uncertainty

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Possibilities of surface and volume activity determination in metallic waste

by using experimental & MCNP modelling of γ-spectra

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Innovative Technique for metals characterization – Materials & Methods

A non-destructive γ-spectrometry technique for interpretation of γ-ray spectra of activated and/or contaminated components.

EXPERIMENT

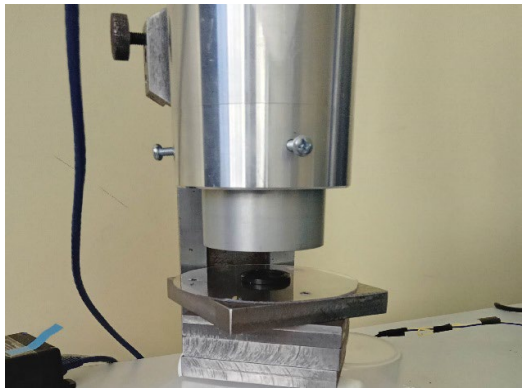
HPGe detector

$CeBr_3$ detector

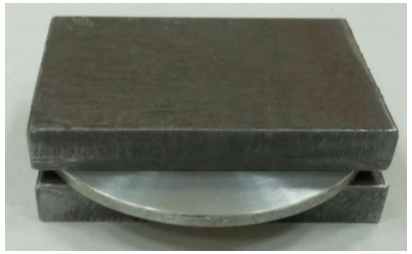
MCNP MODELLING

Experimental spectra have been compared to the modelled ones

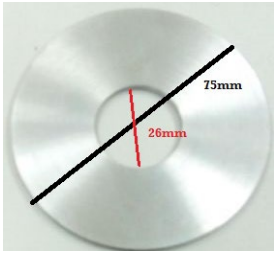
HPGe spectrometer
with Pb and steel based protection shield



$CeBr_3$ spectrometer
with metal plates and point source



The point source placed between two metal plates in the hole of Al disk.



Dimensions of Al disk

The activity of point sources:
^{137}Cs (60.4±2.0) kBq

^{60}Co (1.02±0.03) kBq

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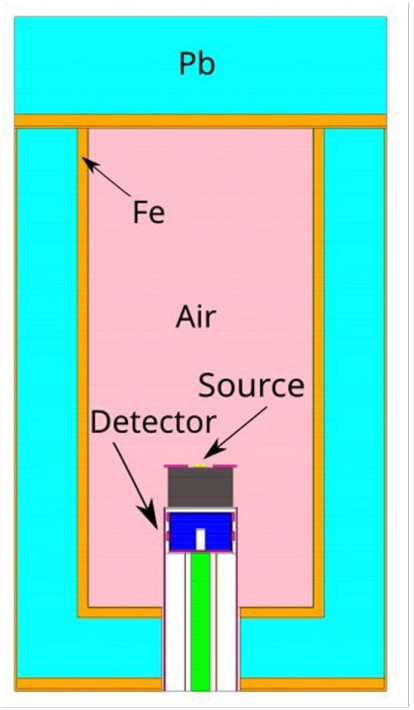
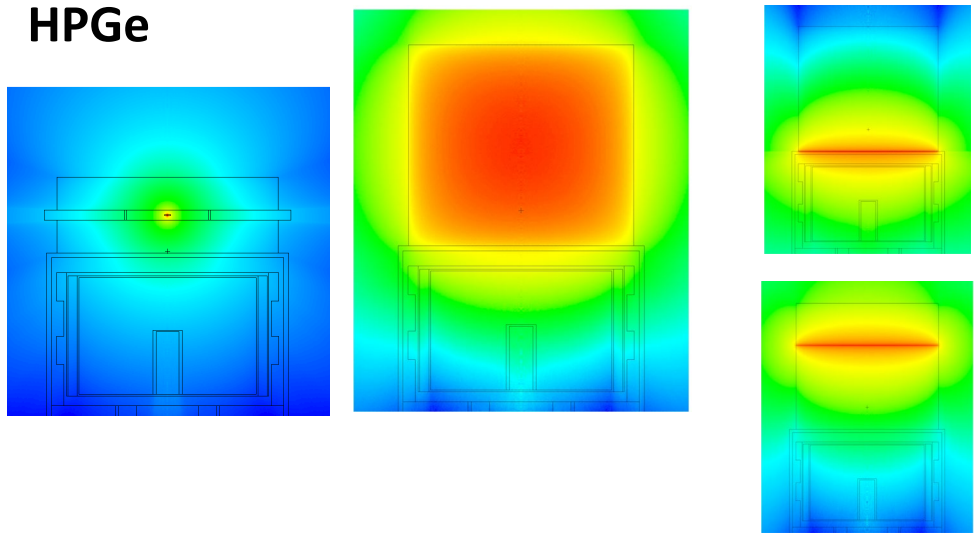
MCNP modelling of γ-ray spectra of metallic model samples measured by HPGe detector





a) b) c)

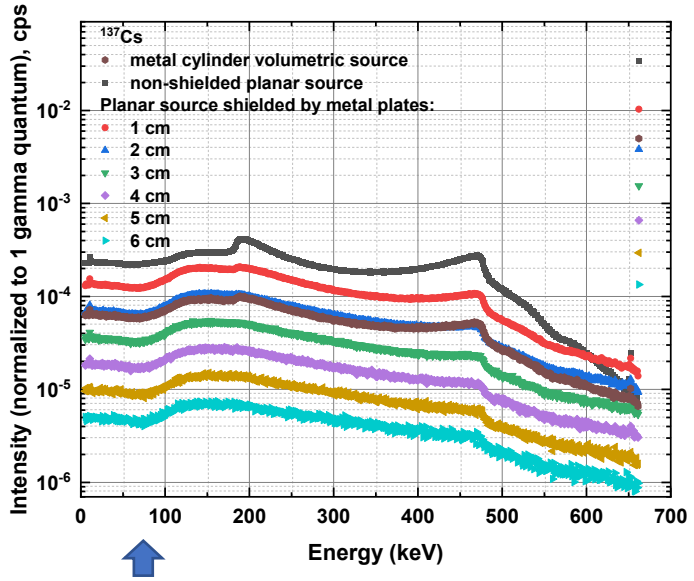
Modelled HPGe detector and ^{137}Cs photon flux for different geometry "metallic model samples":

(a) HPGe and point source between metal plates in the Al disk (as shown in previous slide),

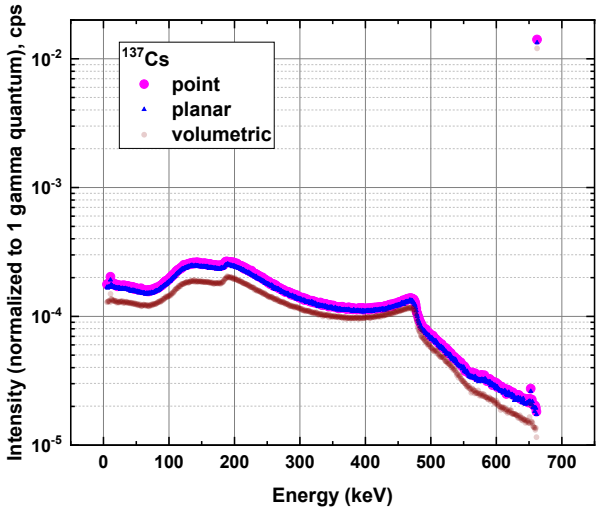
(b) HPGe and volume source,

(c) HPGe planar sources (top picture) 2 cm depth and 4 cm depth (bottom picture) in the metal sample

Comparison of modelled ^{137}Cs γ-spectra in HPGe for different source cases



Extended volume sample (distributed homogeneously in the h=6 cm r=3.36 cm metal cylinder) and planar sample shielded with metal plates of different thickness (1-6cm)



Taking into account both *intensity of the photopeak* and *Compton backscatter /peak ratio* of γ-spectra one could separate different shielding or volumetric samples

Point and planar sources shielded by 2 cm metal plate and volumetric source for comparison.

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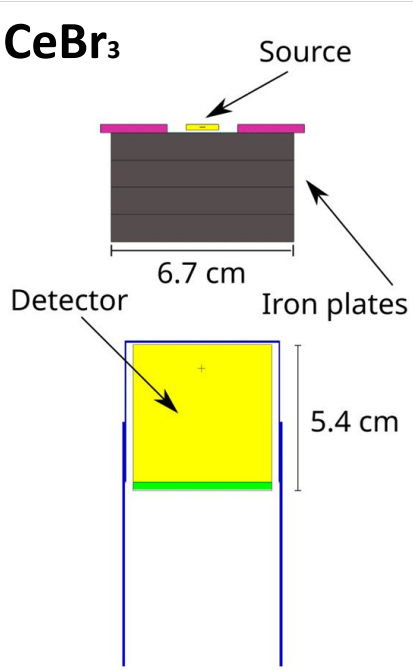
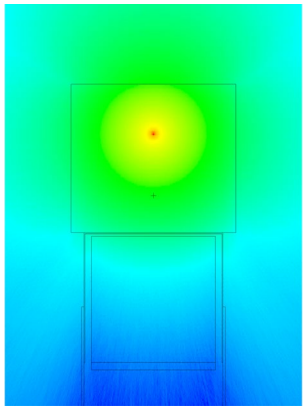
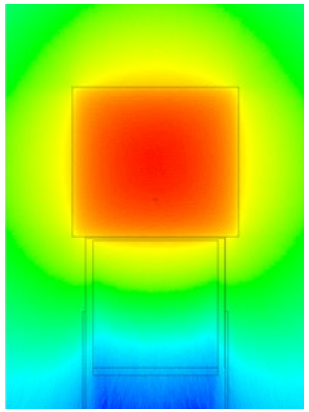
MCNP modelling of γ-ray spectra of metallic model samples measured by $CeBr_3$ detector

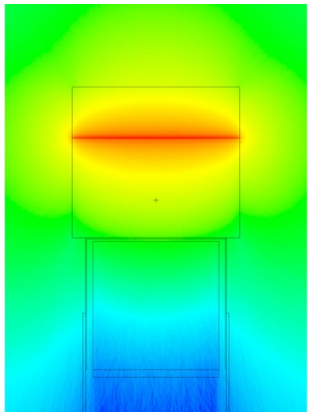




d)



e)



f)

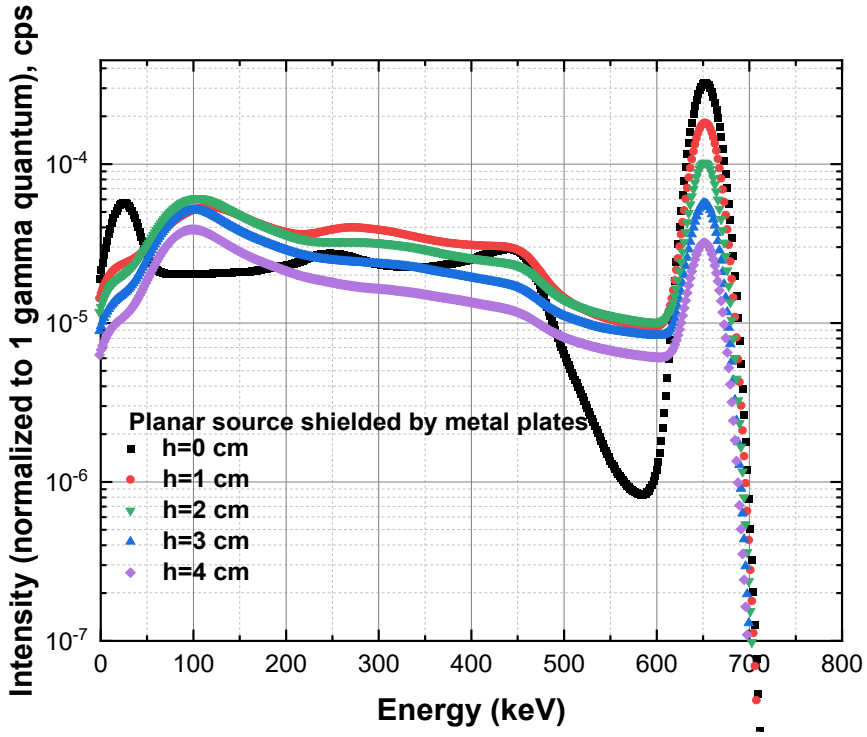
Modelled $CeBr_3$ detector and ^{137}Cs photon flux for different geometry "metallic model samples":

(d) $CeBr_3$ detector and point source at 4 cm depth in the metal sample,

(e) $CeBr_3$ detector and volume source

(f) $CeBr_3$ detector and planar source at 4 cm depth in the metal sample (stack of metal plates)

Modelled ^{137}Cs γ-spectra in $CeBr_3$ detector for planar source shielded with metal plates of different thickness.



Taking into account both *intensity of the photopeak* and *Compton backscatter /peak ratio* of γ-spectra measured by $CeBr_3$ one could separate different shielded planar, point or volumetric sources

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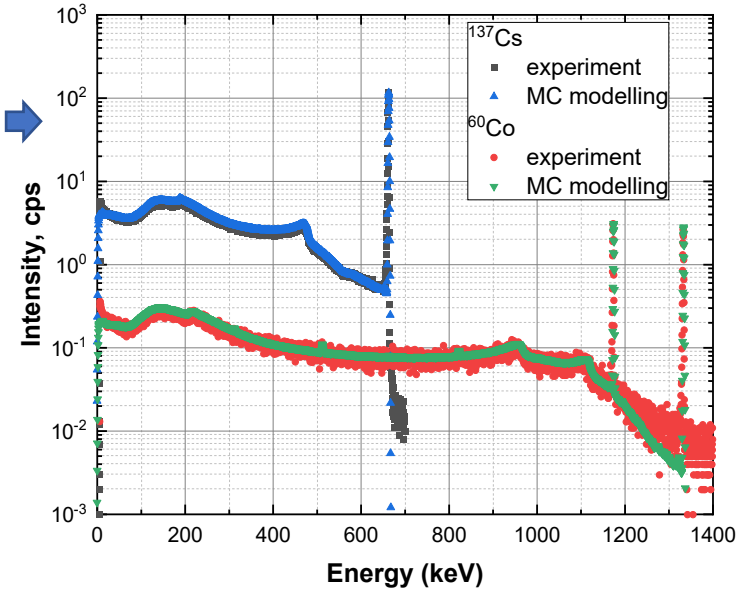
Validation of surface/ volume activity determination in metallic waste samples by using HPGe and $CeBr_3$ detectors and MCNP modelling of γ-ray spectra

HPGe

A comparison of acquired by the HPGe detector and modelled with MCNP γ-spectra of ^{60}Co and ^{137}Cs point sources shielded by 1cm thickness iron plates.

The agreement of HPGe γ-spectra experimental and modelled results is good for different ^{60}Co and ^{137}Cs point sources cases



Comparison of simulated and experimental Compton (backscatter)- to-Peak ratios of ^{137}Cs and ^{60}Co point sources obtained with HPGe detector.

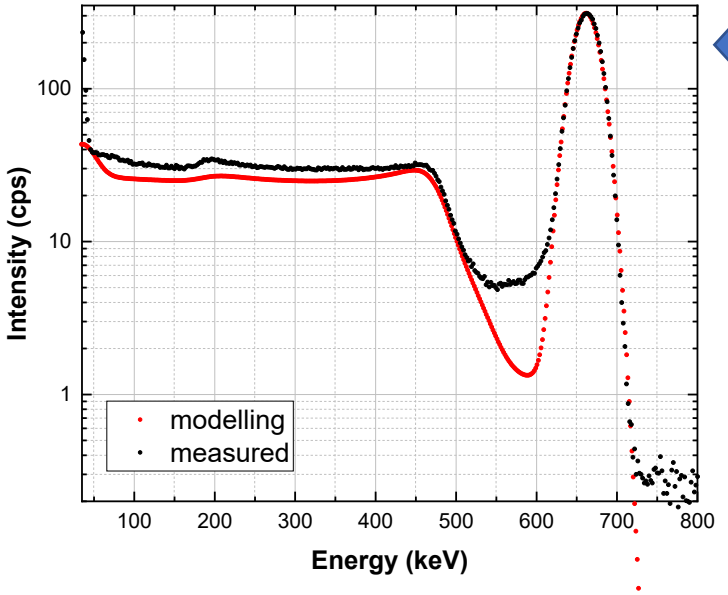
Thickness, cm	Modelled ^{137}Cs (661.6 keV)	Experimental ^{137}Cs (661.6 keV)	Modelled ^{60}Co (1173.2 keV)	Experimental ^{60}Co (1173.2 keV)
0	0.021±0.001	0.018±0.002	0.033±0.005	0.03±0.01
1	0.054±0.003	0.042±0.005	0.09±0.01	0.09±0.03
2	0.091±0.007	0.07±0.02	0.15±0.02	0.16±0.08
3	0.13±0.01	0.10±0.02	0.21±0.03	0.22±0.15
4	0.19±0.02	0.17±0.04	0.28±0.04	0.29±0.15

$CeBr_3$

Comparison of simulated and experimental Compton (backscatter)- to-Peak ratios of ^{137}Cs point source obtained with $CeBr_3$ detector.

** experiment in the open air/ no laboratory environment*

Thickness, cm	Modelled ^{137}Cs (661.6 keV)	Experimental ^{137}Cs (661.6 keV)
0*	0.20±0.01	0.19±0.02
0	0.5±0.2	0.5±0.04
1	0.7±0.2	0.9±0.1
2	0.9±0.2	1.3±0.2
3	1.1 ±0.3	1.8±0.3
4	1.2±0.4	2.4±0.4



Inter-comparison of γ-spectra of ^{137}Cs acquired by the $CeBr_3$ detector and modelled in case of point source on the surface of metal plate (no laboratory environment).

The agreement of experimental and modelled results for ^{137}Cs point source C/P ratio obtained with $CeBr_3$ detector is not very good because of not enough accurate modelling of laboratory environment (shielding thickness h=0 cm to h=4 cm cases). Environments significantly influences shape of Compton region.

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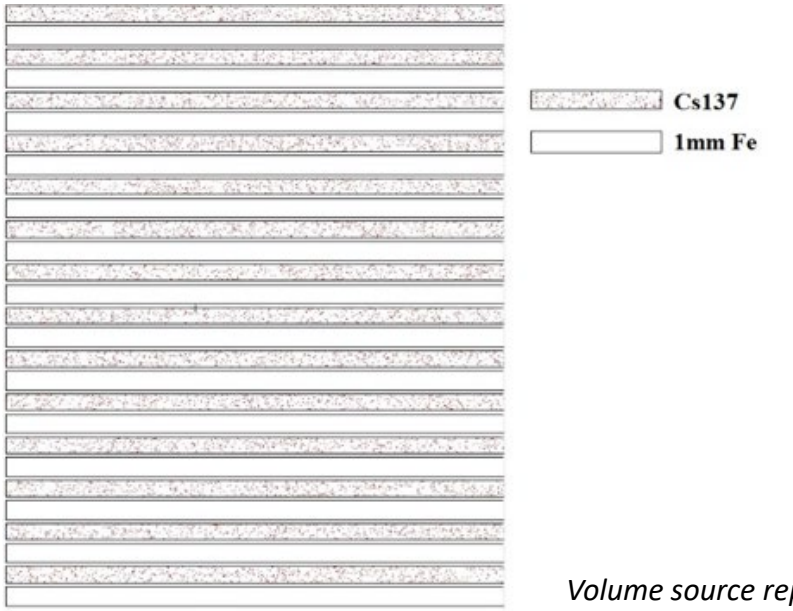
This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Determination of activities on the surface and in the volume

- Volume source representing the activated metallic slab with ^{137}Cs (instead of ^{60}Co) as well as the contamination on the surface with ^{137}Cs were prepared at the Radioactive Waste and Material Laboratory in the NCSRD.
- Filter paper was subdivided into squares of 9 cm^2 each and 0.05ml of ^{137}Cs acid solution (2M HNO_3) of 170 $\pm$ 17 Bq/ ml in the centre of each square. The total surface of the contaminated with ^{137}Cs filter paper was 5940 cm^2. The total surface was subdivided into 18 sheets of 33 $\times$ 10 cm^2. Hence, the activity for each one of the 18 contaminated sheets was 304 $\pm$ 30 Bq. (0.92 Bq/cm^2)



Volume source representing the activated slab for validation of MCNP6.1 models (VisedX_24E)

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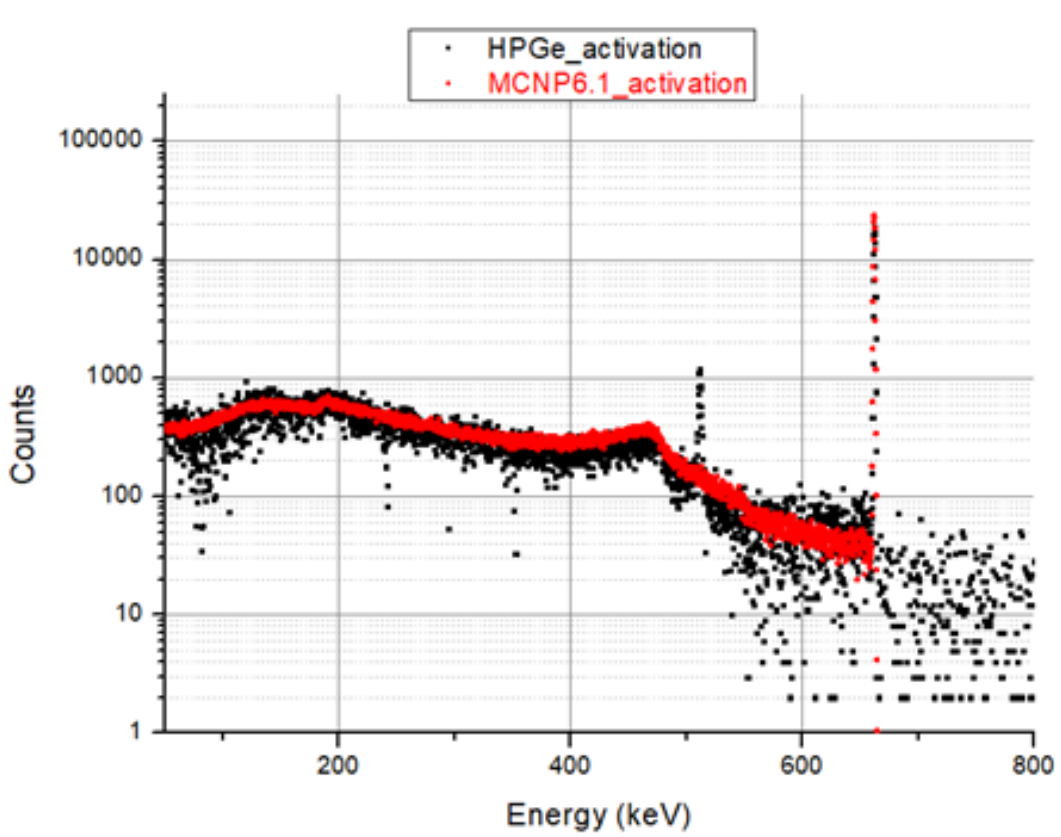
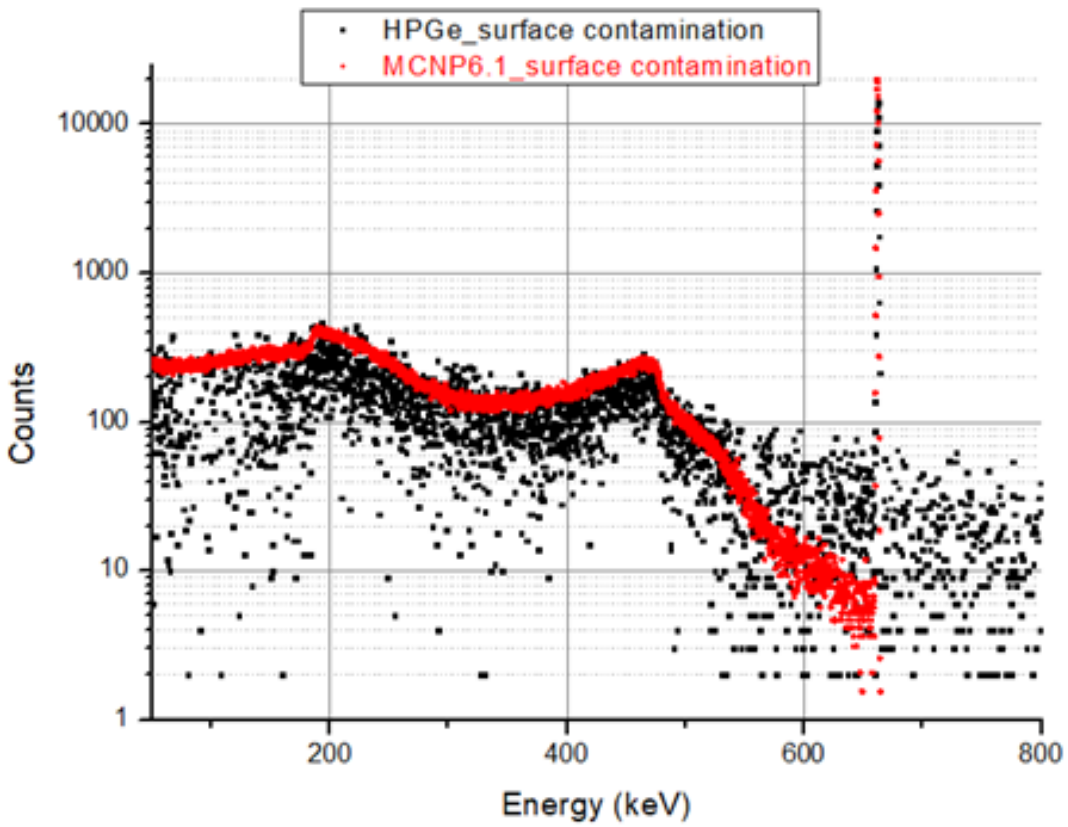




Comparing simulated and real spectra of volume sources representing a) the activated (^{137}Cs was used instead of ^{60}Co) and b) contaminated metallic slab

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Distinguishing activation and surface contamination (HPGe)

$$\#Counts\ of\ the\ photopeak\ for\ activated\ slab\ with\ surface\ contamination = \lambda_1 \times A(b) + \lambda_1' \times A'(b)$$

$$\#Counts\ of\ the\ \text{Compton edge}\ for\ activated\ slab\ with\ surface\ contamination = \lambda_2 \times A(b) + \lambda_2' \times A'(b)$$

Where:

$$\lambda_1 = \frac{\#\ Counts\ of\ the\ photopeak\ in\ the\ activated\ metallic\ slab}{A(a)}$$

$$\lambda_1' = \frac{\#\ Counts\ of\ the\ Compton\ edge\ in\ the\ activated\ metallic\ slab}{A(a)}$$

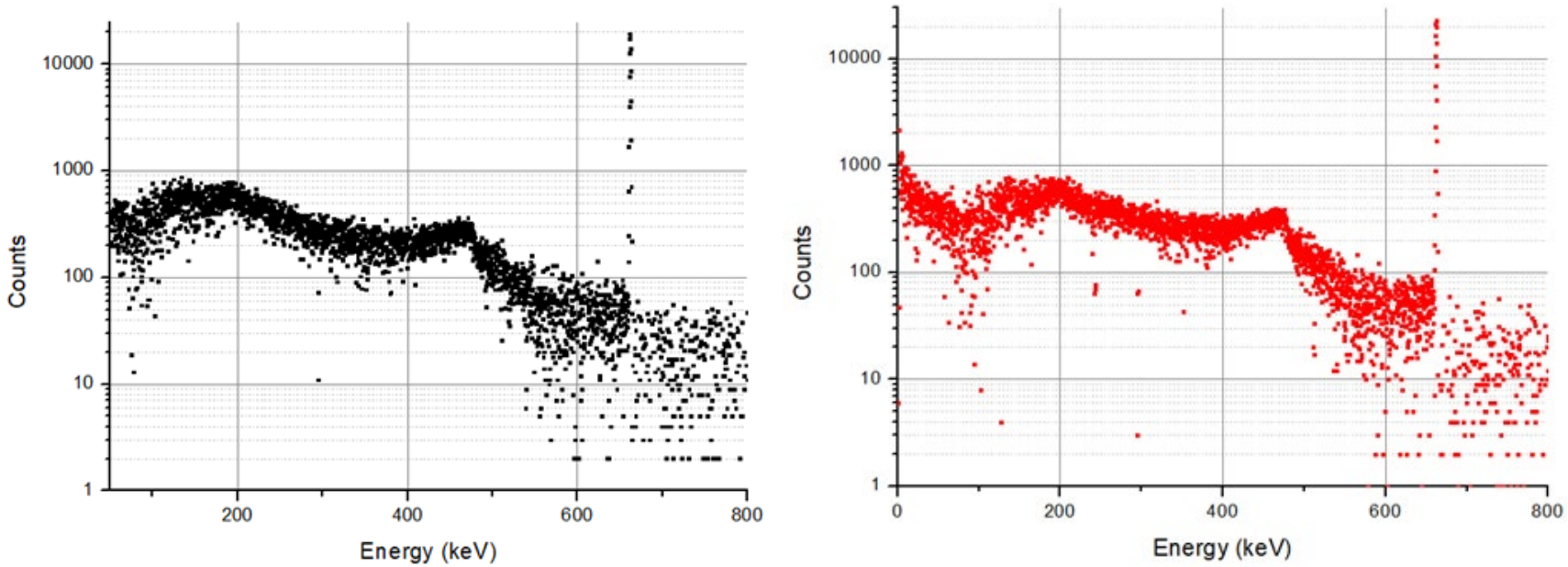
$$\lambda_2 = \frac{\#\ Counts\ of\ the\ photopeak\ of\ the\ surface\ contamination\ for\ the\ metallic\ slab}{A(c)}$$

$$\lambda_2' = \frac{\#\ Counts\ of\ the\ Compton\ edge\ of\ the\ surface\ contamination\ for\ the\ metallic\ slab}{A(c)}$$

$A(a)$: $known\ activity\ of\ activated\ metallic\ slab$

$A(c)$: $known\ activity\ of\ surface\ contaminated\ metallic\ slab$

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.



HPGe spectra from two different unknown sources representing the activated slab with surface contamination

	Volume activity $A(b)$	Surface activity $A'(b)$
Nominal 1	4900 ± 500	610 ± 60
Experimental 1	4300 ± 700	300 ± 200
Nominal 2	2400 ± 200	1500 ± 150
Experimental 2	2500 ± 300	1000 ± 200

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Conclusions

- The quantitative **agreement between the simulated and experimental spectrums** justifies the validity of the simulation method procedure for spectra production.
- The simulating spectra show that not only the gamma peaks are characteristic but also the continuum is representative for each source.
- Combination of gamma spectrometry measurements and MCNP simulation **allows distinguishing surface contamination from volume activation by the shape/ intensity or peak/ Compton ratio** of γ-spectra (of key nuclides ^{137}Cs and ^{60}Co) analysis. This was checked by using $CeBr_3$ and HPGe detectors for different known activity laboratory-made samples.
- The proposed method can be used for radiological characterization on activated reactor components.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

A non-destructive gamma spectrometry set-up designed for accurately characterizing low-activity metallic segments

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Scope/ objective of the proposed set-up

scope

- The aim of this work is to crucially reduce the measurement uncertainty (less than 30 %), for measuring time comparable to that of the existing methods (i.e. 100kg, 2 min).
- To achieve adequate sensitivity (i.e. 0.1 Bq/g) for the key radionuclides (Co-60, Cs-137) for acceptable measuring time

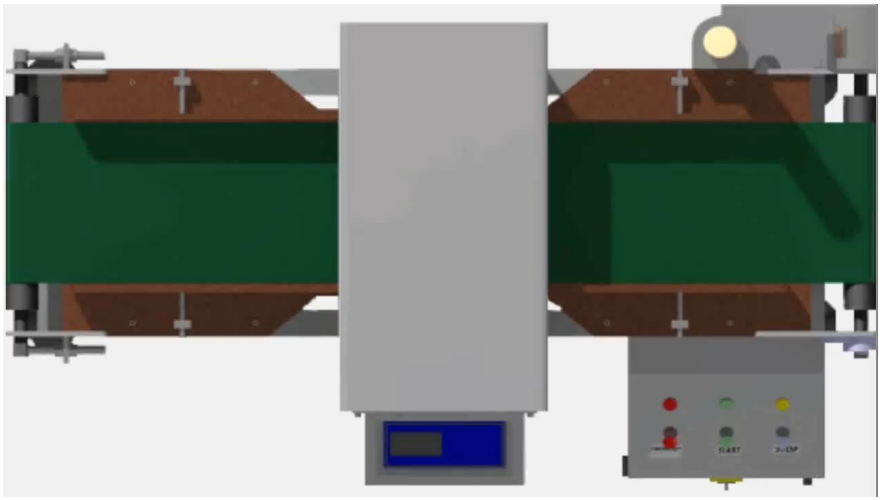
objective

Measurement of low activity metallic waste at the stage after dismantling and cutting of components into segments to:

- decide if decontamination is worth
- select the appropriate decontamination techniques
- select the clearance methodology

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

The proposed measurement set-up



The metallic segments are put on a square shallow box.

Segments geometry	Total weight in the shallow box 1.2×1.2 m^2 (kg)
12 steel pipes of 0.1 m diameter, 0.002 m wall thickness, 1.2 m length	70
12 steel pipes of 0.1 m diameter, 0.003 m wall thickness, 1.2 m length	104
6 steel pipes of 0.2 m diameter, 0.003 m thickness, 1.2 m length	105
4 steel pipes of 0.3 m diameter, 0.003 m thickness, 1.2 m length	106
4 steel pipes of 0.3 m diameter, 0.004 m thickness, 1.2 m length	140
4 steel pipes of 0.3 m diameter, 0.01 m thickness, 1.2 m length	344
steel slab 1.2x1.2x0.02 m^3	227
segments of small dimensions, homogeneous density of 4 Mg/m^3, layer of 0.05 m thickness	291

total weight of steel segments of specific geometries

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Development of new radiochemical procedures for DTM radionuclides

SUB-TASK 4.5.3

ANUMAIJA LESKINEN (VTT), MOJMÍR NĚMEC (CTU), TOMO SUZUKI (IMTA)

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

PREDIS

Radiochemical approach

- Difficulty to measure directly **pure beta emitters** :
  - destructive method generally used.
- DTMs characterized by their **low energy emission**
- Evaluation of the activities by **scaling factors** to determine the activity level

- Development of a **radiochemical procedure** for the optimal detection and measurement in metallic sample
- **Highly selective** and efficient separation and purification
- Development of **sensitive** to **ultra-sensitive** method of measurement, depending on the radionuclide

→ **^{59,63}Ni, ^{41}Ca, ^{93}Zr, ^{93}Mo**

- **Sample**
  - *Synthetic*: prepared in laboratory from chemical reagents
  - From *solid* containing the radionuclide source
  - *Surrogate* to simulate the radionuclide due to limited quantity or availability
- **Separation / Purification**
  - Purification by *chromatographic resins* to recover the radionuclide of interest
  - *Electrodeposition*
- **Conditioning**
  - Sample preparation for measurements
  - Liquid form or deposition on filters or on plates
- **Measurement**
  - Selection of an adapted analytical technique
  - Optimization of detection efficiency

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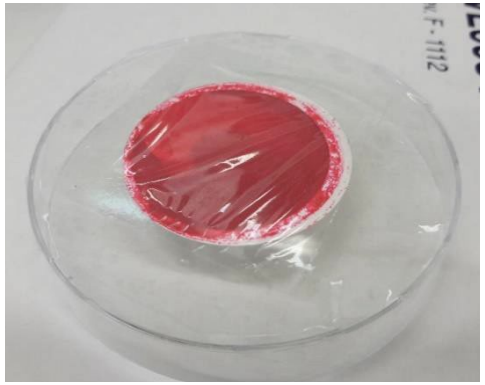
PREDIS

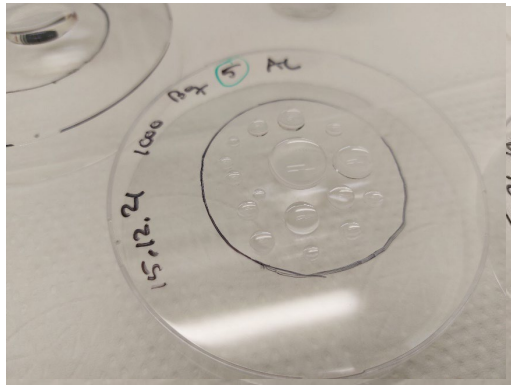
Innovation in sample preparation

^{59,63}Ni ⇒ BEGe gamma spectrometry



Ni-DMG precipitate

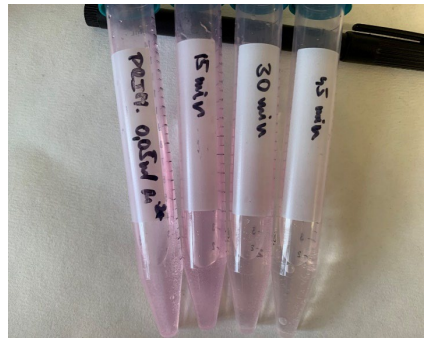
Direct evaporation on a membrane filter



Direct evaporation on a petri dish

$^{(59)+63}$Ni ⇒ liquid scintillation (+ LE gamma)

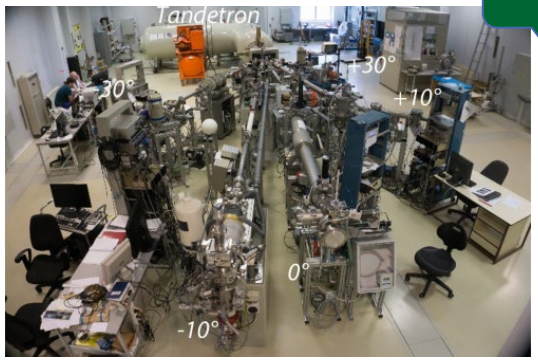
Electrodeposition



^{93}Zr ⇒ liquid scintillation

Acid digestion of surrogate metallic samples

^{41}Ca ⇒ AMS



CaF_2 + PbF_2 mixed sample preparation + ion mass selection

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PREDIS

Main challenges achieved

- Standard curves and calibration
  - Use of ^{55}Fe standard for the measurements of ^{59}Ni by BEGe spectrometry
    - Lowering the detection limits up to 20 Bq
    - Evaluation of ^{60}Co effect as contaminant on ^{55}Fe response: effect starting for activities at 200Bq of ^{55}Fe
  - Use of ^{63}Ni standard for the measurements of ^{93}Zr by liquid scintillation
    - Coupling chemical theory approach with experimental data
  - Selection of $[CaF_3]^-$ and $[CaF_4]^-$ ions for ^{41}Ca assessment by MILEA AMS
- Optimization in sample preparations
  - Separation and purification of Ni and Zr using chromatographic resins from a complex solution (surrogate, radioactive)
  - Conditions achieved for efficient electrodeposition of Ni (Ni-63 with carrier) on planchette
- Validation in the MoNi intercomparison exercise 2024 (coordination VTT) with a high activity steel

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Intercomparison exercise on ^{59}Ni and ^{93}Mo analysis

- Collaboration with Nordic Nuclear Safety Research Program started in January 2024
  - Nordic and Non-Nordic partners
  - Project content: ^{59}Ni and ^{93}Mo analysis in highly activated steel. Other DTMs of interest ^{55}Fe, ^{63}Ni, ^{93}Zr, ^{94}Nb. 2025 plan to focus on volatile DTMs e.g. ^{14}C, ^{36}Cl, ^{79}Se.

- Partners so far

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Thank you for your attention

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

PREDIS

WP4: Innovations in metallic materials treatment and conditioning

T6 : Advances in encapsulation of materials in magnesium phosphate cements based matrices

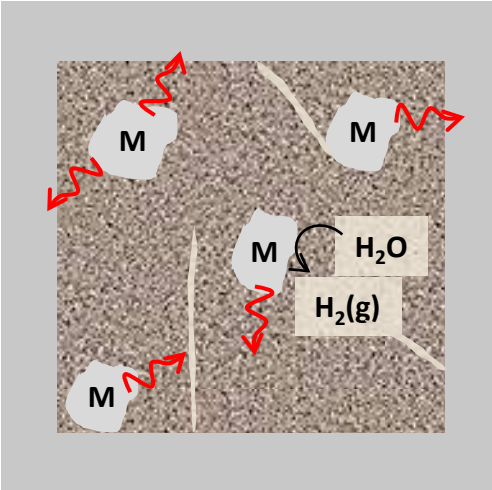
Céline Cannes (CNRS)

Contributors:

CEA, CNRS, CSIC, ENRESA, FZJ, IMT, KIPT, ORANO, POLIMI, RATEN, SCK CEN,UAM

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Context



- M: Low- or intermediate-level metal radioactive waste
- Conditioning in a cementitious matrix
- Container: steel or concrete

Main way to manage the low and intermediate level metallic waste:

Encapsulation in cementitious matrices with a container made of steel or concrete.

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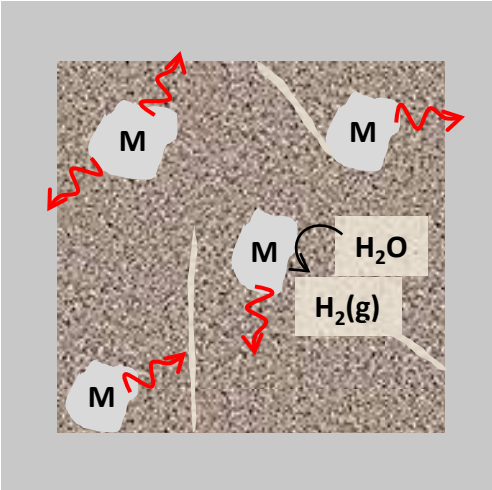
Context



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Encapsulation in cementitious matrices with a container made of steel or concrete.

conventional cementitious matrices:
based on Portland cement or composite cements

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Context

conventional cementitious matrices: Portland cement or composite cements

Benefits

Low cost, easy supply

Process implemented at room temperature, no gas treatment

Good mechanical strength and self-shielding

Compatibility with aqueous waste

Good stability of well-designed cement matrices over time

Pore solution with a high pH allowing the precipitation of many radionuclides as hydroxides

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Drawbacks

Pore solution with a high pH causing the corrosion of some metallic radioactive waste (Al, Be)

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Drawbacks

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Need to define an acceptable alternative to calcium silicate cements for specific metal waste

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Objectives

Al radioactive waste

Produced during the dismantling of old reactors.

Highly corroded in basic media.

Be radioactive waste

Material of the Belgian Reactor 2 heart and in the ITER fusion facility.

Lack of data on the Be reactivity in cementitious media.

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Steel

Material of the primary package drum.

More stable at basic pH than

In neutral pH media.

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Lack of data on the Be reactivity in cementitious media.

Steel

Material of the primary package drum.

More stable at basic pH than

In neutral pH media.

To fill an important gap for the management of LL and IL metallic radioactive waste (having high reactivity at high pH) by proposing magnesium phosphate cements (MPC) as alternative systems to conventional systems using Portland.

To control that the steel drum is not corroded in contact to the MPC.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Guidelines of the study

Magnesium phosphate cements (MPC)

New cement under consideration for conditioning radioactive metallic waste (having high reactivity at basic pH)

- Define MPC formulation based on WAC and economical considerations.
- Determine the behavior of MPC under leaching or irradiation.
- Study the corrosion of Al, Be (radioactive metal wastes) and steel (material of the primary package) in MPC.

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ST6-1 MPC formulations

Objective: To optimize the MPC formulation

- Influence of MgO (hard-burned and reactive)
- Influence of the Mg/P ratio
- Influence of the water/($MgO + KH_2PO_4$) ratio.
- Influence of the filler nature and the filler/($MgO + KH_2PO_4$) ratio.
- Influence of MPC curing conditions
- Determination of the physical, chemical and mineralogical properties of the different MPCs

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ST6-1 MPC formulations

Increasing the MgO content increases the pH but, improves the mechanical strength and mitigates efflorescence.

A Mg/P molar ratio = 2 is recommended to improve mechanical properties and reduce the efflorescence.

Adding filler materials increased the amount of inert solid, can improve the workability and the mechanical strength.

Fillers are less expensive than MgO and KH_2PO_4. Their use can decrease the global cost of the material.

Volcanic ash shows good characteristics to be incorporated into MPC. However, its distribution and its homogeneity is not guaranteed.

The formulation should include the minimum amount of water (water/solid mass ratio 0.25) to generate K-struvite as the main product.

Absence of retarder leads to a rapid exothermic reaction, fast setting, and efflorescence. It is thus recommended to add a retarder. The type of retarder influences the fluidity of MPC.

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ST6-1 MPC formulations

Higher moisture content in the MPC allows higher instability due to the rapid dissolution of the phosphates excess at 1M M/P ratio.

The formation of K-struvite is complete under high moisture condition. The main ions content in the pore solution decreases to the formation of the main mineral phases, increasing the pore pH over time.

S ions were observed in pore solution (attributed to the FA). The presence of this ions leads to an increase of the pore pH.

In endogenous or isolated curing, the reaction does not progress completely due to the lack of water, with more dissolved ions in the pore solution and more unreacted products, showing more near neutral pH values.

Better pore network is observed at higher moisture content showing more capillary pores than in isolated condition, which improve the MPC stability.

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ST6-2 MPC cost optimization

Raw materials (MgO, KH_2PO_4, retarder, filler): high purity or from few providers

High cost of MPC = barrier to a larger industrial use

Objective: To decrease the MPC cost

- MgO source
- Retarder
- Filler

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ST6-2 MPC cost optimization

Reactive MgO can be used to prepare MPC by using thiosulphate retarder alone (5 wt%) or in addition of boric acid (3wt% T + 2wt% HB) as retarders.

The setting time and the compressive strength values of these LC-MPC are in good agreement with the WAC.

The best compressive strength (53 MPa for a reactive MgO with 2wt.% HB and 3wt.% T) was obtained for a W/C of 0.5.

The hydration of MgO is enhanced, which leads to a better use of the raw material.

There is less efflorescence and the durability is better, as the depletion of KH_2PO_4 is enhanced by the total hydration of high specific surface of reactive MgO.

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ST6-2 MPC cost optimization

When the filler FA is replaced by BFS, the content of K-struvite practically does not change.

MPC-BFS samples demonstrate the highest compressive strength compared to MPC-FA and MPC-FA-BFS samples.

The increased compressive strength values are explained by the presence of a denser structure of the MPC-BFS samples, in contrast to the structure of the MPC-FA and MPC-FA-BFS samples. This is due to the fact that BFS particles are more reactive compared to FA.

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ST6-3 leaching behavior of MPC

MPC: under consideration for radiaoctive metal waste immobilisation

⟶ It si primordial to study the leaching behavior of MPC

- Assess the behavior of MPC pastes/mortars under leaching by demineralized water (reference) and by an alkaline solution representative of the pore solution of conventional concrete placed in the near field of the cemented waste packages.
- Understand and model the degradation processes of the MPC matrix under well-controlled leaching conditions.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

ST6-3 leaching behavior of MPC

Following ANS 16.1 standard, leaching tests were carried out on MPC mortars prepared with different fillers, FA, BFS, or FA-BFS (50-50).

The leachability indices and diffusivities were calculated from their cumulative concentrations in the leachates. Whatever the filler, the leachability indices of K, Mg, P and B (LI>9) largely exceeded the LI index of 6 defined by the US Nuclear Regulatory Commission.

BFS was shown to be an interesting filler, leading to denser materials than FA, and thus allowing to slow down the release of elements in the leachates.

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ST6-3 leaching behavior of MPC

Leaching tests were performed on MPC (with FA) under semi-dynamic and well-controlled conditions (pH at 7 or 13.2, renewal of the leaching solution, N_2 atmosphere, and at 25°C).

At pH 7, leaching is mainly governed by diffusion of dissolved species through the pore network of the paste. An interface retreat of the solid is observed. K-struvite is fully dissolved close to the exposed surface of the samples. Then, in an intermediate zone, K-struvite coexists with cattiite.

At pH 13.2, a layer of Ca-deficient hydroxyapatite (CDHA) rapidly forms on the surfaces and its thickness increases with the leaching duration. However, it is not sufficient to clog the porosity and protect the samples from further degradation. K-struvite dissolves near the exposed surface. In the intermediate zone, it mainly coexisted with brucite, CDHA and an hydrotalcite-like phase.

A first modeling approach based on reactive transport was proposed. Despite the simplified composition of the paste used for calculations, the model succeeded to reproduce the main mineralogical changes observed experimentally.

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ST6-4 Irradiation behaviour of MPC

MPC: under consideration for radiaoctive metal waste immobilisation

⟶ It si primordial to study the irradiation behavior of MPC

- Gamma irradiation: up to 200 kGy ^{137}Cs, 400 Gy/h (IMT) and up to 1000 kGy ^{60}Co 2.5 kGy/h (POLIMI)
- H_2 production by micro-gas chromatography
- Compression tests
- Mineralogical and microstructural characterization (XRD, SEM-EDX and μCT)
- Leaching behavior of samples and leachate analysis
  (pH, conductivity, ion Chromatography and ICP)

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

ST6-4 Irradiation behaviour of MPC

- ✓ No remarkable deterioration or changes were observed for cumulative doses up to 1000 kGy.
- ✓ Results show the good resistance of fresh matrix to irradiation.
- ✓ The WACs are respected regarding leaching and compression tests for MPC samples after irradiation.
- ✓ The MPC matrix characterisation supports experimental evidences.

Magnesium phosphate cement represents a promising immobilisation matrix for radioactive reactive metal wastes.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

ST6-5 Al corrosion in MPC

4 < pH or pH > 9: high corrosion of Al

$2\ Al + 6\ H^+ \rightarrow 2\ Al^{3+} + 3\ H_{2(g)}$ or $2\ Al + 2\ OH^- + 2\ H_2O \rightarrow 2\ AlO_2^- + 3\ H_{2(g)}$

4 < pH < 9 : passivation of Al by solid phase

$2\ Al + 3\ H_2O \rightarrow Al_2O_3 + 3\ H_2(g)$

High risk of Al corrosion in OPC (pH>12.6) with H_2 release.

Risk of radionucleides release and matrix degradation

Test of MPC and alternative Portland binders to condition Al radiaoctice waste

- Study the Al corrosion in MPC and comparison with the corrosion in CEM I.
- Determine the volume of H_2 released.
- Determine the effect of resaturation of the mortars on the Al reactivity.

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ST6-5 Al corrosion in MPC

The Al corrosion is the lowest in MPC and acceptable in CEM I + Silica fume. They both constitute good alternatives to CEM I.

The lowest Al corrosion was measured in MPC with a MgO/KH_2PO_4 ratio around 2M (pore pH 7 - 9).

The pore moisture content does affect the Al corrosion kinetic.

The alkalisation of MPC matrix reactivate the Al corrosion by increasing the pore water solution pH.

Al is less corroded in low-cost MPC prepared with reactive MgO and thiosulphate: lower H_2 release was measured.

LPR & EIS method gave similar H_2 assessment values. These results confirm the possibility to use both methods to study the corrosion of a metal encapsulated in a cementitious matrix.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

ST6-6 Steel corrosion in MPC

MPC: good alternative for Al radioactive waste immobilisation by reducing the pH of the pore water solution.

What about the reactivity of C-steel, material used as the primary waste package?

- Study the C-steel corrosion in MPC and comparison with the corrosion in CEM I.
- Determine the volume of H_2 released.
- Determine the effect of MPC formulation.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

ST6-6 Steel corrosion in MPC

The reactivity of C-steel in MPC is similar to that in OPC with the only difference that initially the corrosion rate is higher in MPC and towards the end of the test it decreased while in OPC it is the opposite.

C-steel is significantly corroded in low cost MPC compared to the reference MPC. Differences of reactivity in the LC-MPC prepared with only thiosulphate as retarder (B0T5) or with a mixture of thiosulphate and boric acid (B2T3) are minimal. However, the overall impedance of LC-MKPC formulations increases with prolonged exposure, suggesting a potential enhancement in corrosion resistance.

To overcome the higher corrosion of steel, concrete drums cam be used for Al embedding in low cost MPC. In cases the steel corrosion in the presence of thiosulphate exhibits linear kinetic corrosion, the consideration of concrete drums over steel ones could be warranted. The decrease in the cost of cement manufacturing could offset the high cost of concrete drums compared to steel drums.

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ST6-7 Be corrosion in MPC

Acid or high basic pH: high corrosion of Be

$Be + 2H^+ \rightarrow Be^{2+} + H_{2(g)}$

$Be + OH^- + 2H_2O \rightarrow Be(OH)_3^- + H_{2(g)}$

$Be + 2OH^- + 2H_2O \rightarrow Be(OH)_4^{2-} + H_{2(g)}$

Neutral pH: passivation of Be by a solid phase

$Be + 2\,H_2O \rightarrow Be(OH)_2 + H_2(g)$

High risk of Be corrosion at high basic pH with H_2 release.

Risk of radionucleides release and matrix degradation

Be corrosion (rate and mechanism) in MPC and comparison with Portland cement based matrix

- Electrochemical measurements.
- H_2 volume measurement by gas chromatography.
- Gravimetry.
- Scanning electron microscopy and X-ray diffraction.

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

ST6-7 Be corrosion in MPC

In high basic pH solutions (pH 12.5-14), the corrosion rate increases exponentially with pH. At pH ~13.5, the corrosion rate reaches ~2 µm/y after 120 to 365 days of immersion. The Be surface reveals pitting corrosion and a thin corrosion product layer. Mechanical defects on the initial Be surface acts as the initiation places for pitting corrosion.

In near neutral pH solutions, pure beryllium corrodes slower (0.04 to 1.4 µm/y) than the S-200-F grade (~12 µm/y). The addition of boric acid helps decreasing the corrosion rate. SEM analysis reveals the presence of $KBePO_4 \cdot H_2O$ crystals at the surface of both metal grade after corrosion in MPC solution.

The corrosion rates are lower in matrices than in solutions: 0.1 µm/y in OPC and 0.05 µm/y in MPC.

The comparison of the corrosion of Be embedded in MPC and LC-MPC was difficult as the results obtained in LC-MPC were not reproducible. Extra tests are therefore needed to better understand the results.

SEM analysis confirms the little corrosion rate as no corrosion product layer was observed. However, needle-like particles were observed in the OPC close to the Be surface.

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Thanks for your attention!

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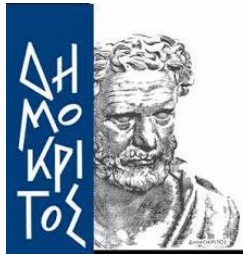
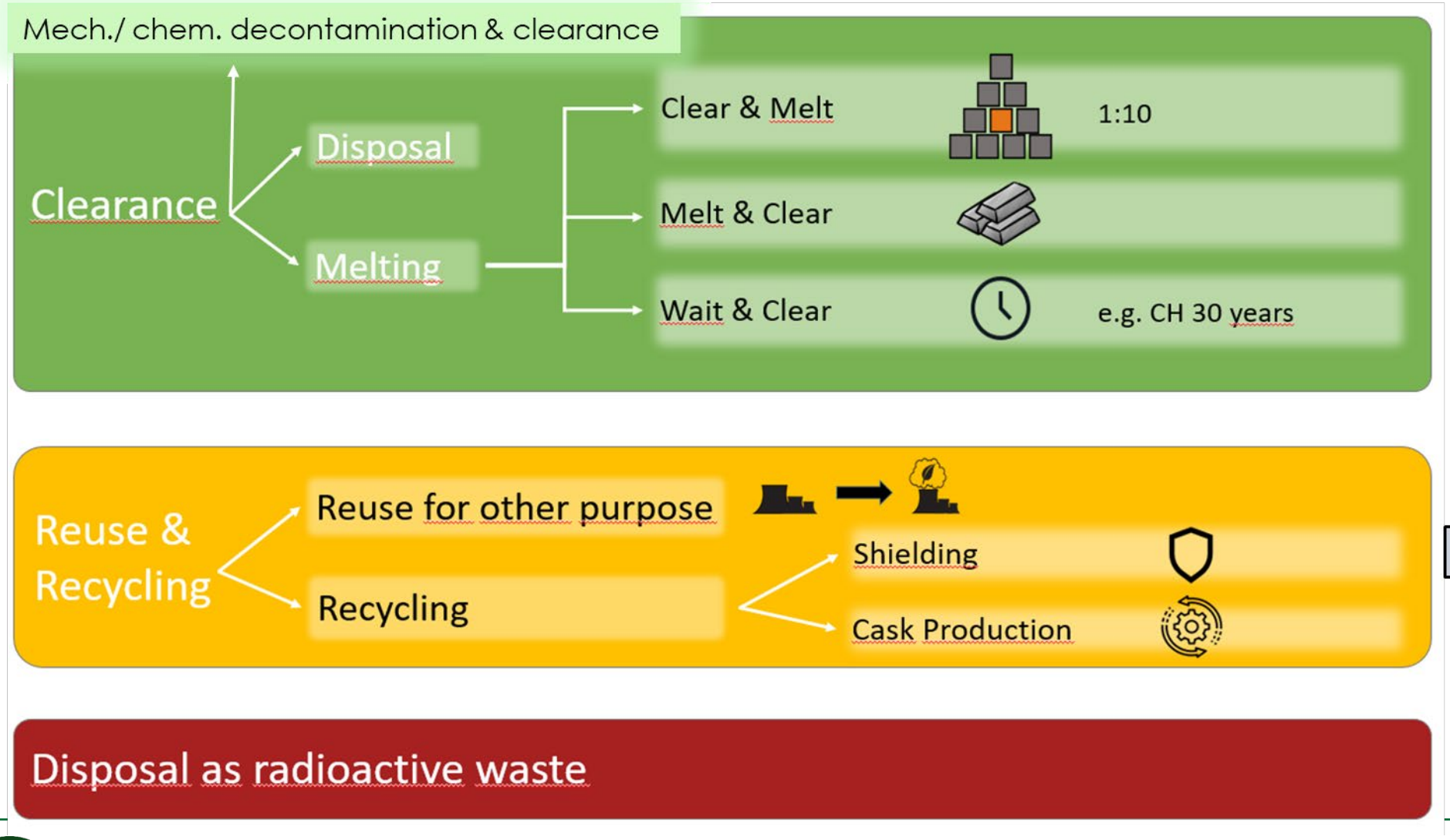
PREDIS

A non-destructive gamma spectrometry set-up for characterization of low activity metallic waste



D. Mavrikis and A. Savidou,
NCSRD

Metallic waste management routes



Inside the control area

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Scope/ objective of the proposed set-up

scope

- The aim of this work is to crucially reduce the measurement uncertainty (less than 30 %), for measuring time comparable to that of the existing methods (i.e. 100kg, 2 min).
- To achieve adequate sensitivity (i.e. 0.1 Bq/g) for the key radionuclides (Co-60, Cs-137) for acceptable measuring time

objective

Measurement of low activity metallic waste at the stage after dismantling and cutting of components into segments to:

- decide if decontamination is worth
- select the appropriate decontamination techniques
- select the clearance methodology

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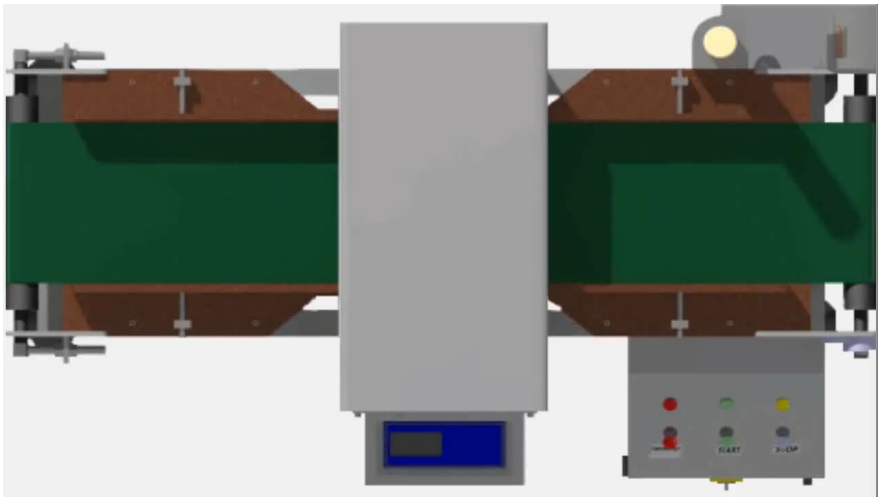
The proposed measurement set-up



The metallic segments are put on a square shallow box.

Segments geometry	Total weight in the shallow box 1.2×1.2 m^2 (kg)
12 steel pipes of 0.1 m diameter, 0.002 m wall thickness, 1.2 m length	70
12 steel pipes of 0.1 m diameter, 0.003 m wall thickness, 1.2 m length	104
6 steel pipes of 0.2 m diameter, 0.003 m thickness, 1.2 m length	105
4 steel pipes of 0.3 m diameter, 0.003 m thickness, 1.2 m length	106
4 steel pipes of 0.3 m diameter, 0.004 m thickness, 1.2 m length	140
4 steel pipes of 0.3 m diameter, 0.01 m thickness, 1.2 m length	344
steel slab 1.2x1.2x0.02 m^3	227
segments of small dimensions, homogeneous density of 4 Mg/m^3, layer of 0.05 m thickness	291

total weight of steel segments of specific geometries

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The proposed measurement set-up

- MCNPX simulations were carried out for source-detector configuration and the models were validated by using volume sources
- 3”×3” NaI(Tl) (reference detector) & HPGe detector (20%) were simulated

- Volume sources representing metallic segments of pipes and slabs with ^{137}Cs contamination were prepared and used for validation of the MCNPX models
- Surface contamination of the volume sources was 0.94 ± 0.09 Bq/cm^2

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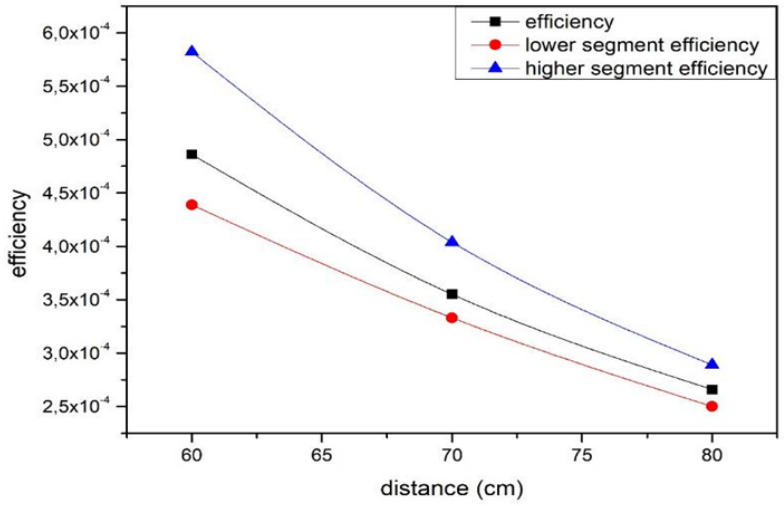
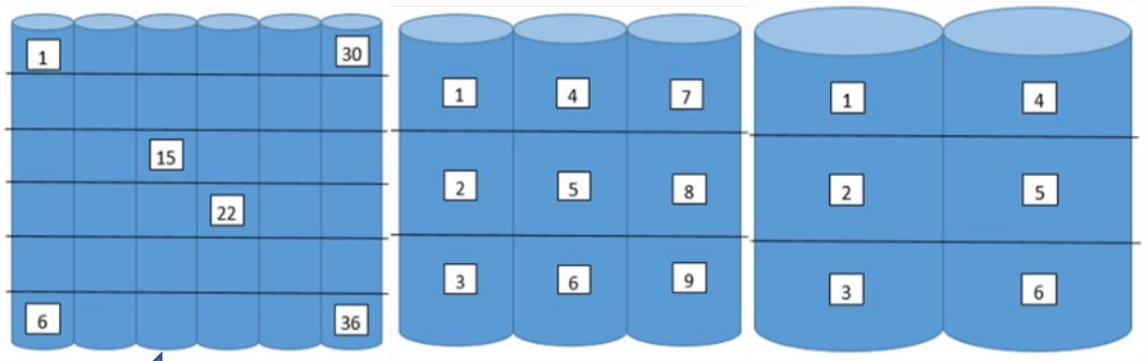
Optimum measurement distance

Pipes – NaI(Tl) detector

- *20 cm diameter*
- *^{137}Cs internal contamination*

- *detection efficiency for homogeneous activity distribution*
- *Study of activity inhomogeneity. Lower and the higher efficiency segment*





bias due to the activity inhomogeneity is lower when the distance of detector from the bottom of the shallow box is greater

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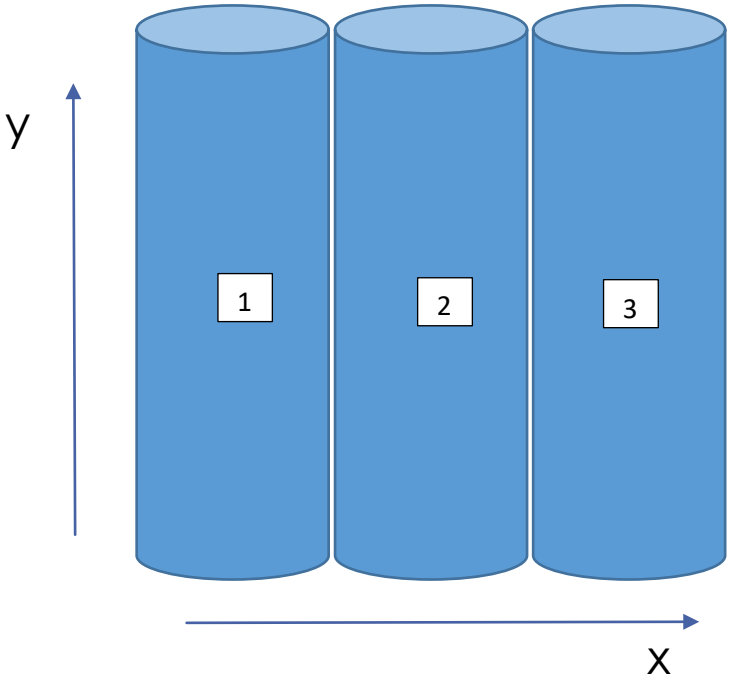
Missing segments (half-full box)



Pipe diameter = 20 cm
Pipe thickness = 0.3 cm
Pipe Length = 60 cm

CASE I

a) pipes 1 and 3 are homogeneously contaminated, pipe 2 is not contaminated
b) pipes 1 and 3 are homogeneously contaminated, pipe 2 is missing

CASE II

a) pipes 1 and 2 are homogeneously contaminated, pipe 3 is not contaminated
b) pipes 1 and 2 are homogeneously contaminated, pipe 3 is missing

	Efficiency (a)	Efficiency (b)	Efficiency (three pipes)
CASE I	2.63×10^{-4}	2.62×10^{-4}	2.66×10^{-4}
CASE II	2.67×10^{-4}	2.68×10^{-4}	

Missing segments has no significant effect to the measurement efficiency

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Detection efficiency and expected MDA

Pipes – HPGe detector

- homogeneous contamination on the internal surface of steel pipes,
- Efficiency of each HpGe detector 20%

Pipes diameter (cm)	Total weight (kg)	Efficiency	MDA ^{137}Cs in Bq/g area of low background		
			2 min	5 min	8 min
10	26.00	5.0×10^{-5}	0.08	0.05	**0.04**
20	26.25	5.59×10^{-5}	0.07	0.05	**0.04**
30	26.50	6.48×10^{-5}	0.06	0.04	**0.03**

MCNPX detection efficiencies for homogeneous activity distribution of ^{137}Cs as well as the expected MDA

Pipes diameter (cm)	Total weight (kg)	Efficiency	MDA ^{60}Co in Bq/g area of low background		
			2 min	5 min	8 min
10	26.00	1.7×10^{-5}	0.21	0.13	**0.10**
20	26.25	1.88×10^{-5}	0.19	0.11	**0.09**
30	26.50	2.17×10^{-5}	0.16	0.10	**0.08**

MCNPX detection efficiencies for homogeneous activity distribution of ^{60}Co as well as the expected MDA

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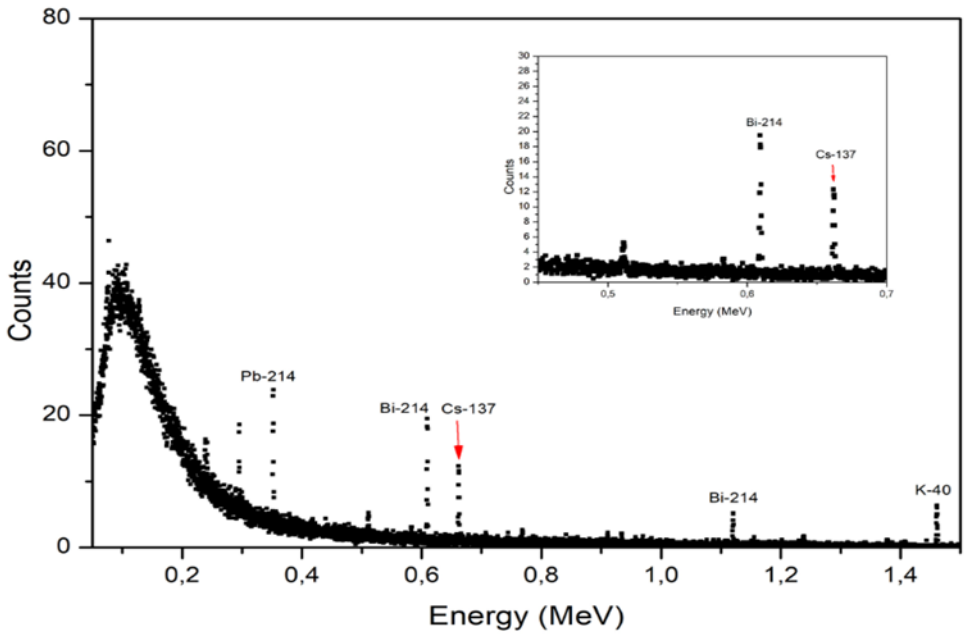
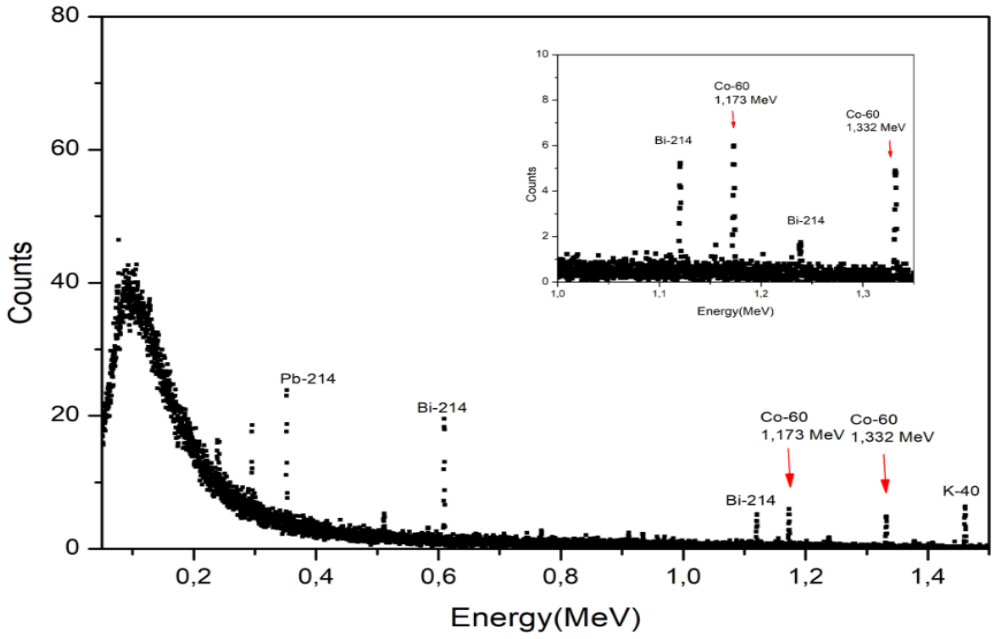
Simulating spectra



^{137}Cs



^{60}Co

The spectrum resulting from the summation of:

- *4 MCNPX spectra (4 HPGe detectors 20%), popes of 10 cm diameter with 0.1 Bq/g homogeneous activity, measured for 2 min simultaneously*
- *the background spectrum for 8 min at area of low background.*

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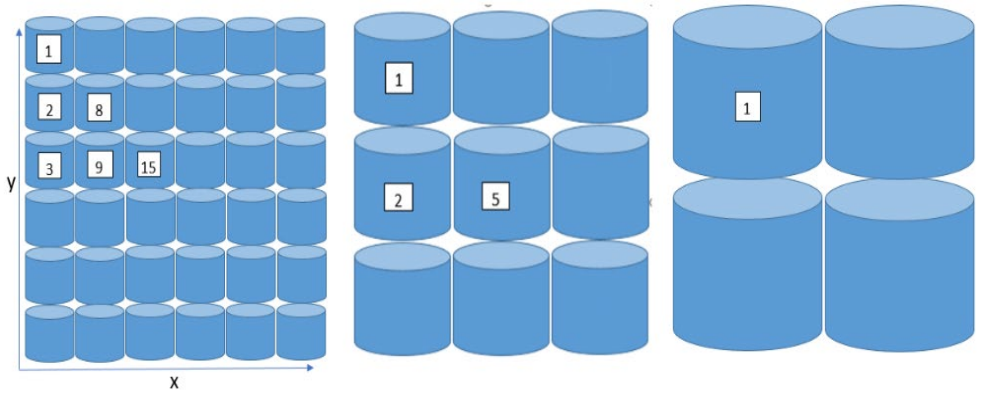
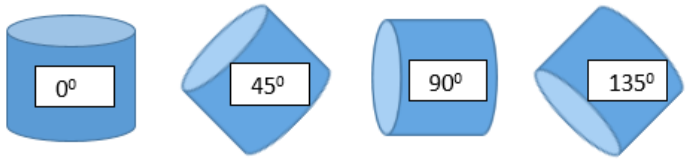
Direction of segments (convex pipes)





- *HPGe*
- rotations of 0º, 45º, 90º, 135º with respect to (x, y)

Diameter (cm)	Efficiency	Bias (act. inhomog.)	Bias (act. inhomog. & direction)
10	5.00×10^{-5}	-12% to +11%	-13% to +11%
20	5.60×10^{-5}	-6% to + 14%	-6% to +14%
30	6.49×10^{-5}	-3% to +9%	-3% to +9%

homogeneous activity distribution ^{137}Cs

Diameter (cm)	Efficiency	Bias (act. inhomog.)	Bias (act. inhomog. & direction)
10	1.70×10^{-5}	-14% to +13%	-15% to +14%
20	1.88×10^{-5}	-3% to + 14%	-5% to +14%
30	2.18×10^{-5}	-2% to +10%	-2% to +10%

homogeneous activity distribution ^{60}Co (1.17MeV)

Direction of segments has no significant effect to the measurement efficiency

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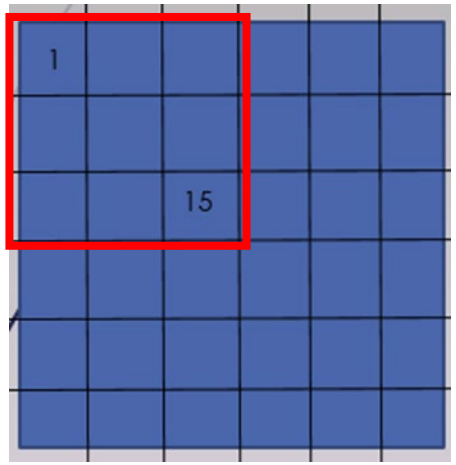
Slabs

- HPGe detector 20% metallic square slab of 60 cm side
- ^{137}Cs & ^{60}Co homogeneous surface contamination



36 square segments to study the activity inhomogeneity

	Efficiency homog.	Bias
^{137}Cs	6.0×10^{-5}	-10% to 10%
^{60}Co (1.17 MeV)	1.89×10^{-5}	-12% to 10%

overall detection efficiency and the respective bias (segment 1 & 15)

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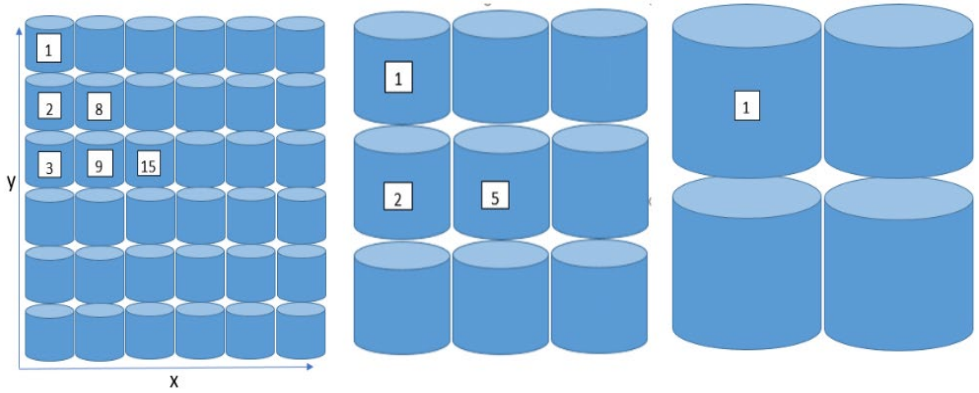
Validation of the MCNP models



Pipes of 10,20,30 cm diameter & numbered segments

Experimental verification of evaluated by MCNPX detection efficiencies

Object of measurement	Detector	Efficiency by MCNP	Efficiency by measurement	
pipe of 20 cm diameter: segments 1,2,3	HPGe 20%	5.47×10^{-5}	5.43×10^{-5}, 4%	-0.7%
pipe of 30 cm diameter, segments 1,2	HPGe 20%	6.45×10^{-5}	5.87×10^{-5}, 4%	-9 %
pipe of 30 cm diameter, segments 1	HPGe 20%	6.45×10^{-5}	6.33×10^{-5}, 6%	-2%
pipe of 30 cm diameter, segments 1	HPGe 20%	6.45×10^{-5}	5.75×10^{-5}, 6%	-11%
pipe of 10 cm diameter, segments 1-6	HPGe 20%	4.78×10^{-5}	5.06×10^{-5}, 4%	+6%
pipe of 20 cm diameter, segments 4,5,6	3×3 NaI(Tl)	2.72×10^{-4}	2.82×10^{-4}	+4%
pipe of 30 cm diameter, segments 1,2	3×3 NaI(Tl)	3.10×10^{-4}	2.85×10^{-4}	-8%
slab 0.6x0.6 m^2	3×3 NaI(Tl)	2.80×10^{-4}	3.00×10^{-4}	+7%

Evaluated by MCNPX detection efficiencies for 3”×3” NaI(Tl) & HPGe 20% detectors for specific metallic segments are compared with the respective experimentally determined efficiencies

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Conclusions

The results showed that by the proposed set-up based on HPGe 20% detectors:

- crucial reduction of the measurement uncertainty (less than 25%) of metallic waste can be achieved
- sufficient measurement sensitivity (determination of 0.1 Bq/g of the key radionuclides ^{137}Cs and ^{60}Co in metallic waste of total mass more than 100 kg can be achieved in less than 2 min).

the proposed set-up for measurement of metallic waste after decommissioning can be used to select the management route as well as the decontamination and clearance procedure

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Thank you!!

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cnrs NUCLÉAIRE & PARTICULES

Subatech

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Nantes Métropole

Development of decontamination process for metallic radioactive effluents

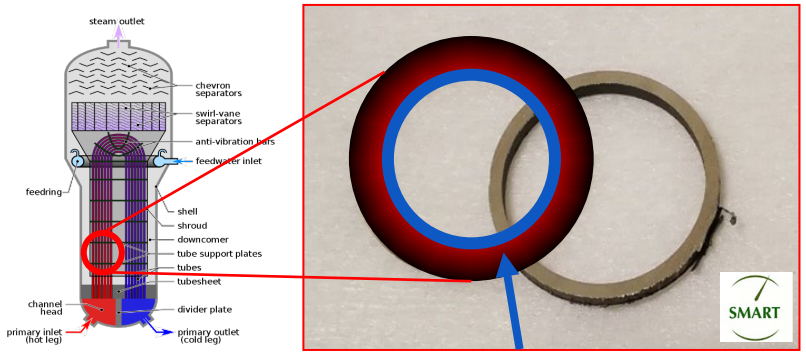
MATHURIN ROBIN

TOMO SUZUKI, ABDESSELAM ABDELOUAS, MARCEL MOKILI

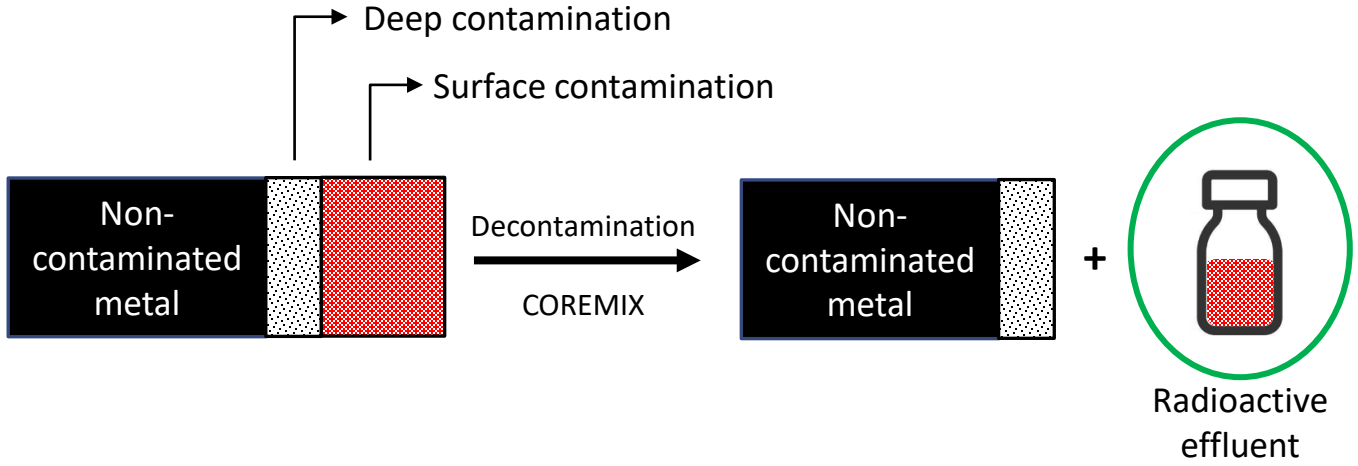
This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Introduction

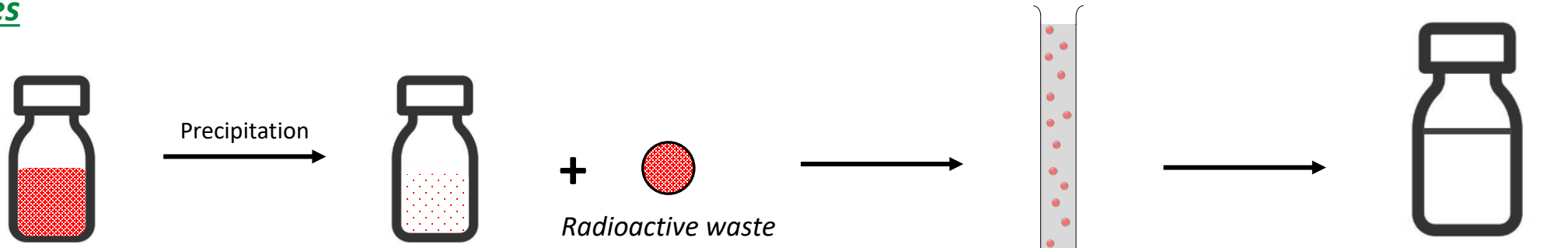
Context



Deposition of radionuclides from primary circuit



Objectives



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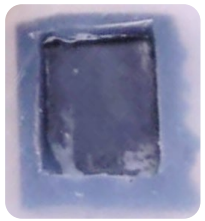
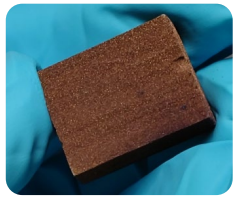
COREMIX process

Stainless Steel 316





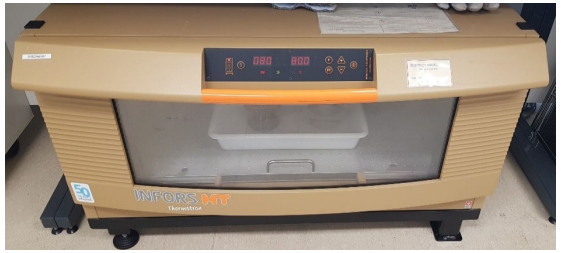
Ni-alloy 600

$KMnO_4$ step
15 mM / 80°C / 3h

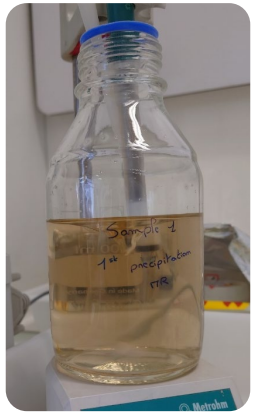
$H_2C_2O_4$ step
18.5 mM / 80°C / 3h

Radioactive effluent

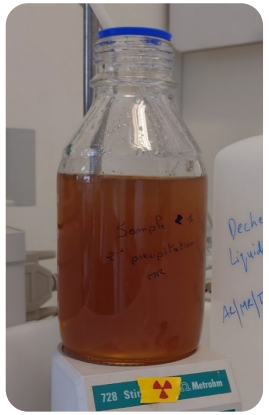
Precipitation process



Oxalic acid destruction step
0.1 M H_2O_2 / 80°C / 24h



1st precipitation
pH 8.5



2nd precipitation
pH 12

Filtration

Decontaminated effluent

Contaminated sludge

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Results

- Decontamination by COREMIX process
  - 4 cycles
  - 350 mL of effluents
  - Total activity of 24.5 ± 1.4 kBq/g

- Activity mainly coming from ^{55}Fe, ^{60}Co and ^{63}Ni (24h counting time)

- Initial activity ≈ 28 000 Bq/L
- Final activity ≈ 36 Bq/L

✓ **DF ≈ 800**

	Activity before treatment (Bq/L)	*Activity after treatment (Bq/L)*	*DF*
^{54}Mn	73 ± 29	< 0.7*	> 60
^{55}Fe	5 200 ± 1200	28 ± 8	190 ± 100
^{60}Co	15 300 ± 1 100	4.8 ± 0.7	3 200 ± 700
^{63}Ni	7 300 ± 1 800	< 0.8*	> 6 900
^{99}Tc	124 ± 44	< 0.3*	> 270
^{125}Sb	94 ± 38	< 1.8*	> 32
Total :	**28 100 ± 4 200**	**36 ± 9**	**780 ± 310**

*The measured values are below the detection limit of the equipment.

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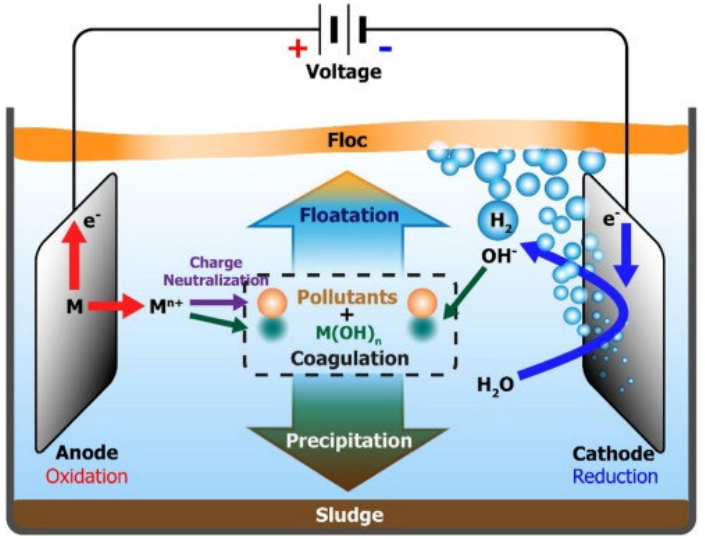
Summary

- ***Optimisation of the precipitation process***
  - pH
  - Oxalic acid destruction
  - Time of contact
  - Reagents -> NaOH / Na_2S / Na_3PO_4

- ***Characterisation***
  - pH 8.5 -> $Fe(OH)_3$ / FeO(OH)
  - pH 12 -> Mn_3O_4

- ***Application***
  - Functional on SS316 and A600 effluent
  - Effective on more than 20 elements
  - DF of 800
  - 99% less resin required

- ***Precipitation by electrocoagulation***
  - Avoid the use of precipitant
  - Increasing efficiency
  - Reduce the amount of salts in the effluent



Picture taken from :
Chunjiang. A, **2017**

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