Chemical decontamination of metallic waste and measurement of radionuclides

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cnrs NUCLÉAIRE & PARTICULES

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Subatech

General introduction

Decomissioning waste

Solid

- Steel
- Aluminium
- Concrete
- Graphite
- Resins
- …

Liquid

- Aqueous
- Solvents
- Complexants
- Oil
- LSC

Emitters

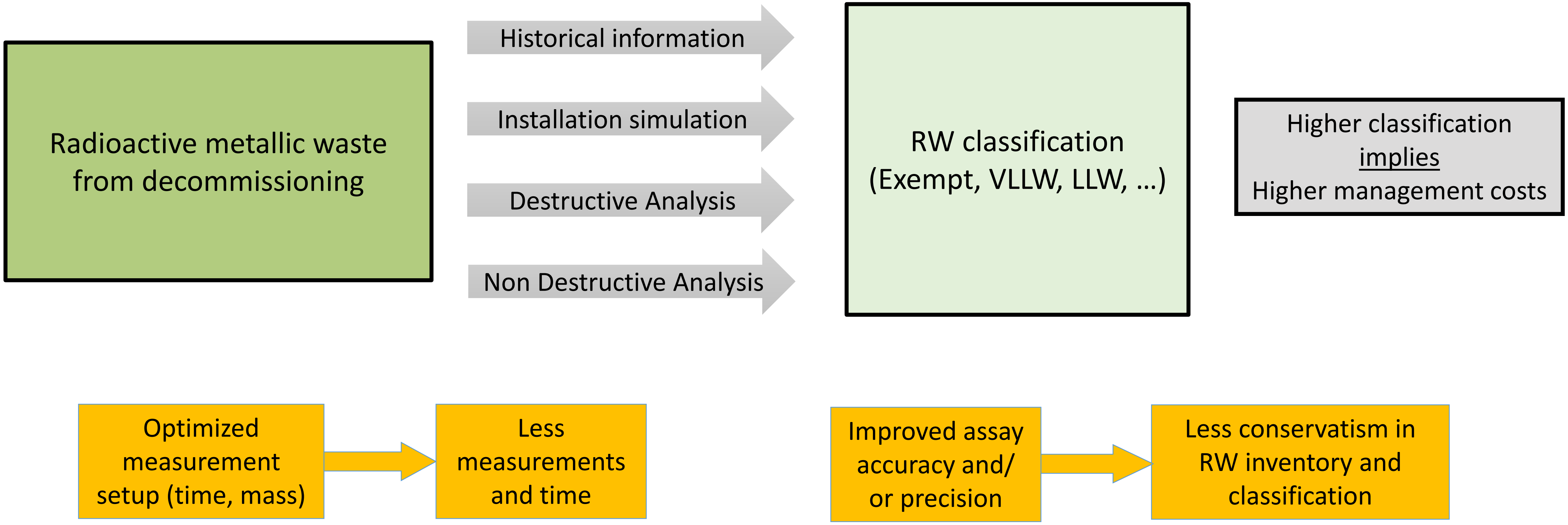
- Alpha
- Beta
- Gamma

Context, issues, challenges

- ❑ 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.
  - About 500 000 tons of metallic wastes expected
  - Including about 130 000 tons from steam generators

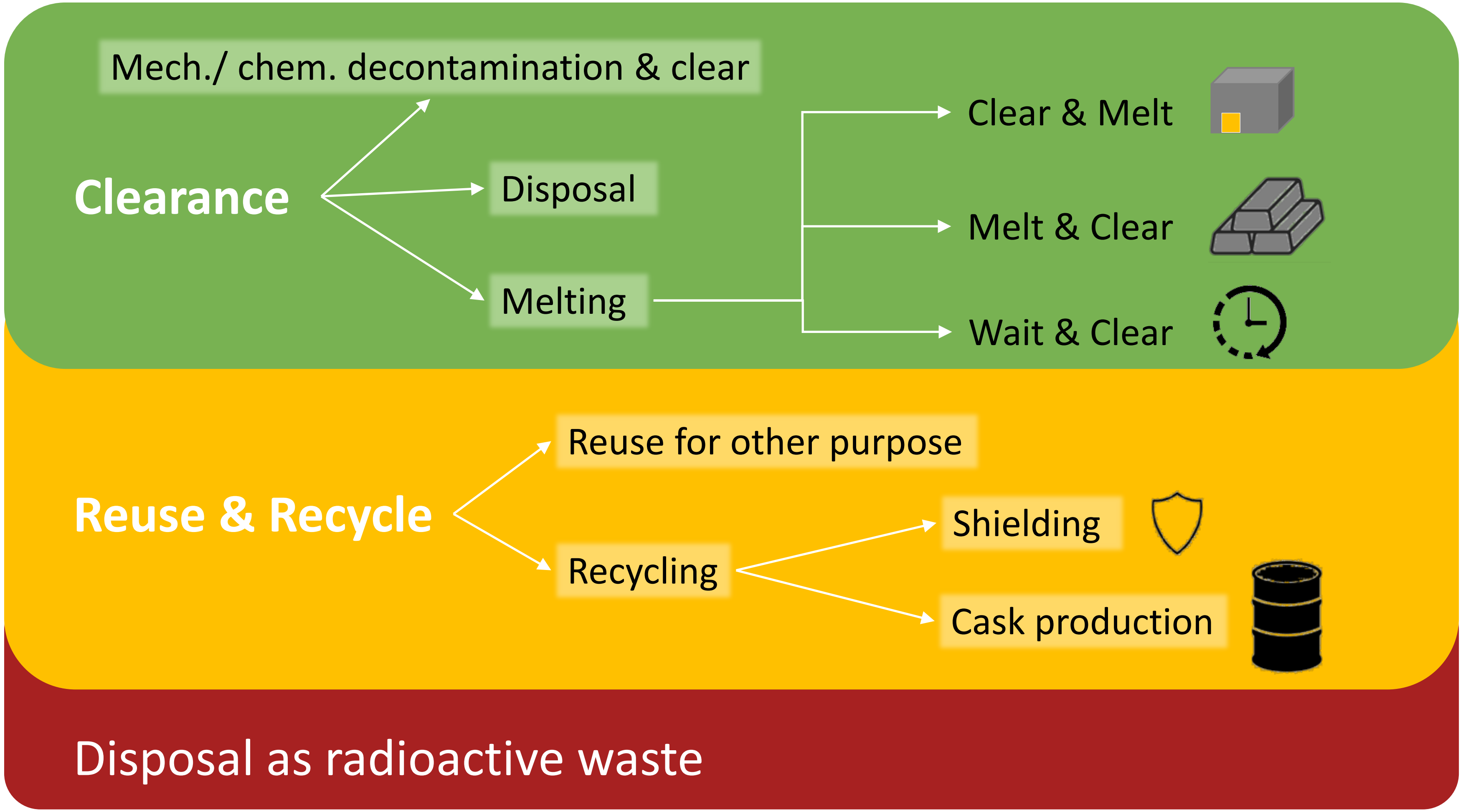
ASN REPORT on the state of nuclear safety andradiation protection in France. May 2022

Necessity for optimizing metallic waste characterization & procedures for minimization and recycling



From A. Savidou and R. Plukienė, Predis project, WP4, Task5

Metallic Waste Management



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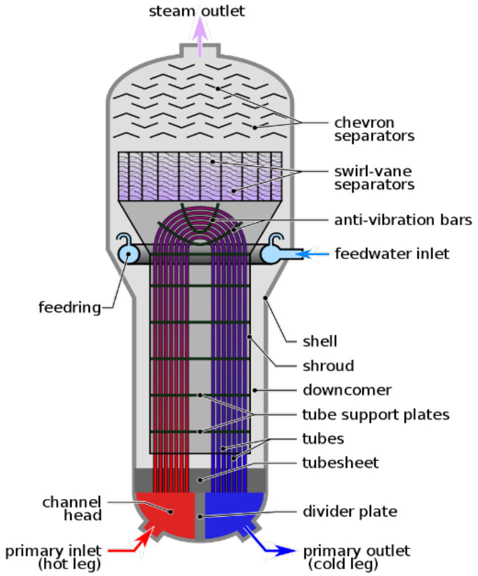
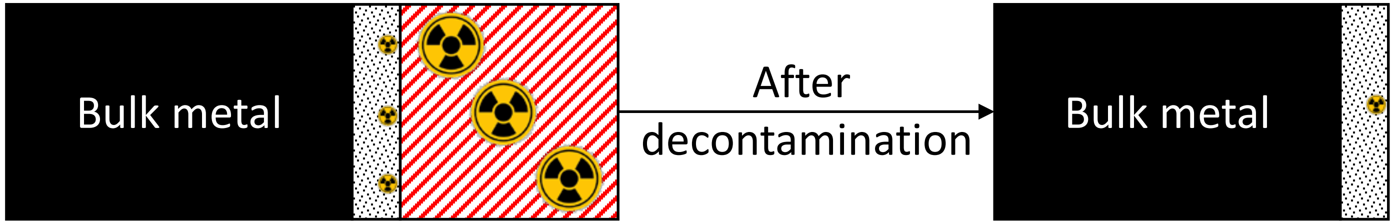
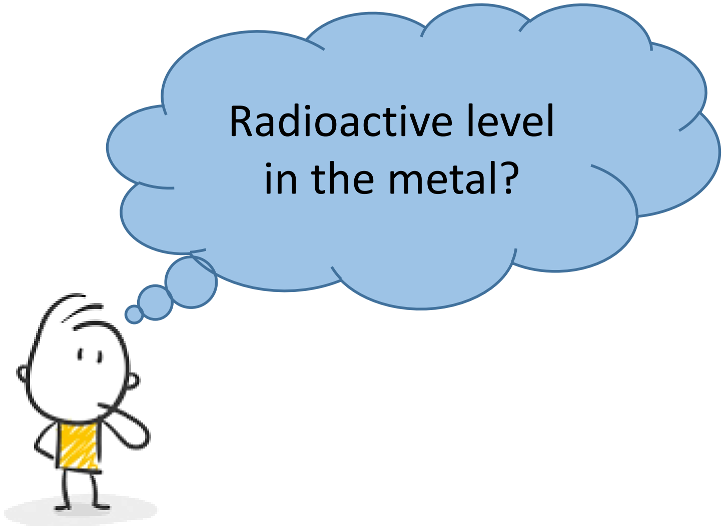
Decontamination

- ❑ Characterization
  - oxidized metal matrices, radiochemical contamination
- ❑ Decontamination methods:
  - chemical, mechanical, thermal, etc.
- ❑ Taking into account
  - waste acceptance criteria from the waste management agency prior to decontamination
  - difficulty of certain matrices to be decontaminated: e.g. tubes vs. pumps, pipe obstructions, etc.
- ❑ Industrial conditions: segmentation, fusion, in situ or ex situ







M.E. Pick, 1989, Decontamination and decommissioning of nuclear facilities, IAEA; Décret 2013/59/EURATOM; CORDIS website

Characterization & Measurements

Measurements/characterization of decontaminated metal waste

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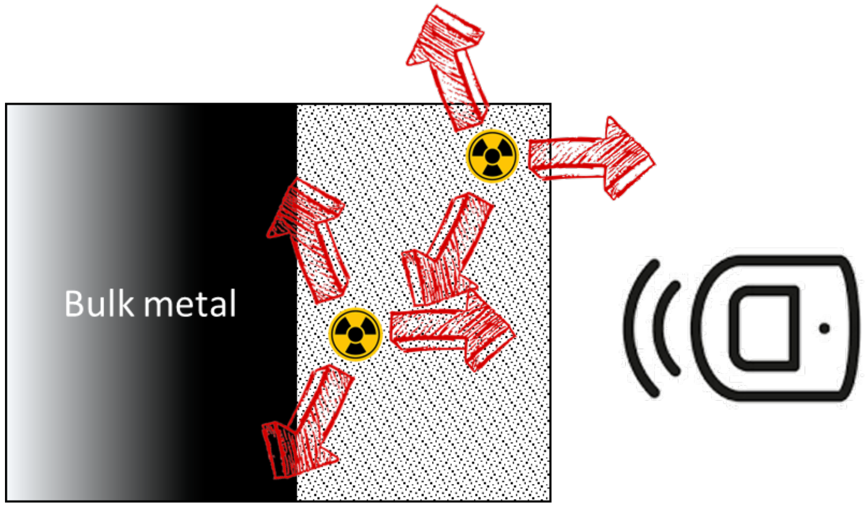
Radioactivity level < release threshold ?

↓

Radioactivity level of radionuclides difficult to measure



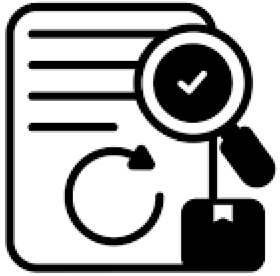
Radionuclide	Activity (kBq/cm²) [1]
^{60}Co	250-1000
^{54}Mn	4-30
^{58}Co	150-500
^{57}Co	0-2
^{65}Zn	2-6

Radionuclide	release threshold (solid) [2]
^{14}C	1 Bq/g
^{36}Cl	1 Bq/g
^{54}Mn	0.1 Bq/g
^{55}Fe	1000 Bq/g
^{58}Co	1 Bq/g
^{60}Co	0.1 Bq/g
^{63}Ni	100 Bq/g
^{65}Zn	0.1 Bq/g
^{93}Zr	10 Bq/g
^{106}Ru	0.1 Bq/g
^{125}Sb	0.1 Bq/g
^{129}I	0.01 Bq/g

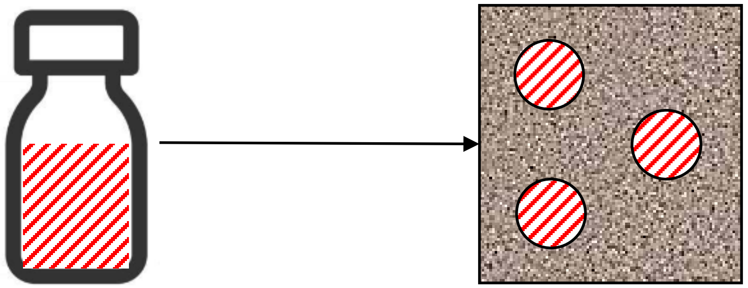
[1] M.E. Pick, 1989, Decontamination and decommissioning of nuclear facilities, IAEA

[2] Décret 2013/59/EURATOM

Waste acceptance criteria

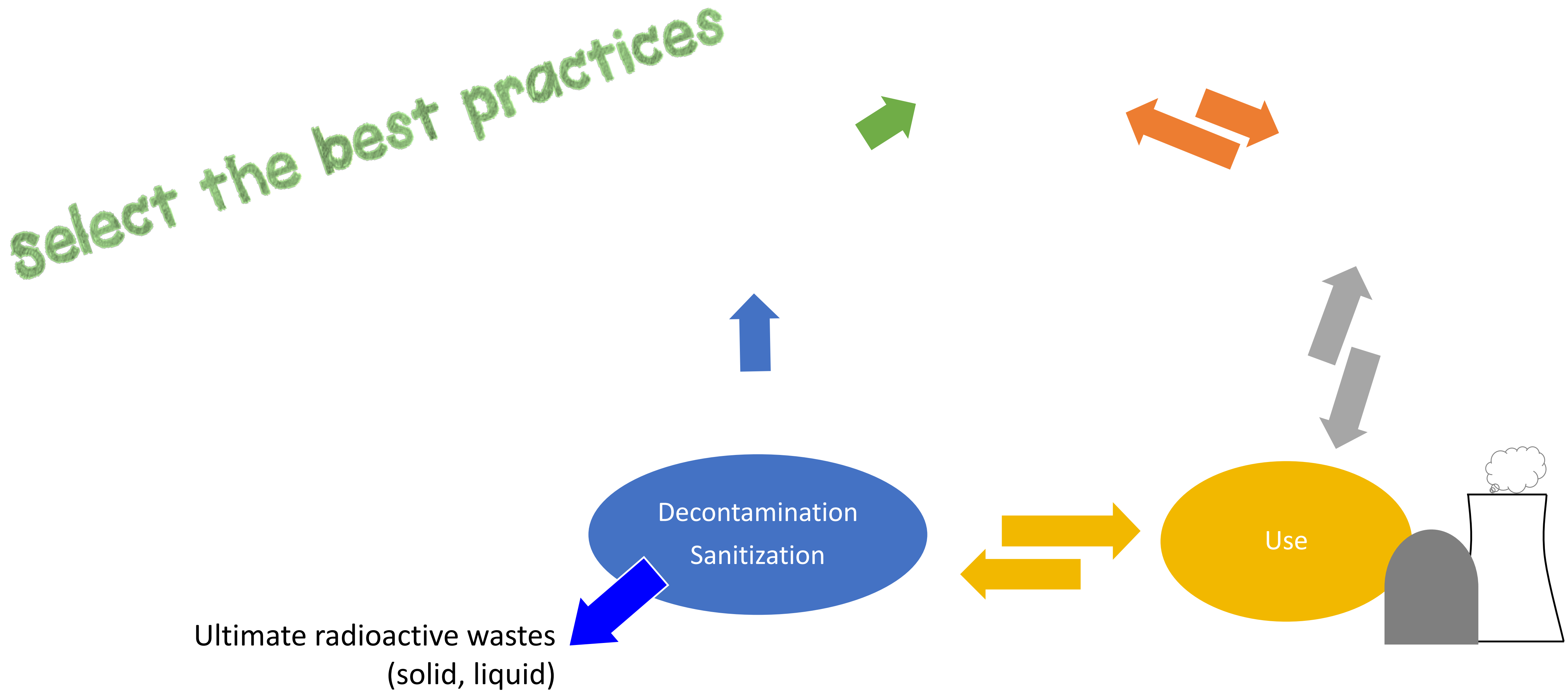


- **Radiological** parameters
  - Total activity level, dose rate, half-life, type of emitters
  - Avoid fissile materials (guarantee under-critic conditions)
- **Chemical** parameters: stabilization of the waste matrices
  - Attention on the chemical reactivity, avoid metallic reactive wastes
  - Limitations on complexing agents, accelerators of leaching processes (Cl, F…), organic substances (EDTA, NTA…), pyrophoric, flammable, explosive, corrosive or oxidizing
  - Toxic chemical species are controlled
  - Avoid liquid form, biologically active waste are forbidden
- **Mechanical** parameters:
  - Compression resistance, void limitation, swelling
  - Confinement of RN to limit the diffusivity and leachability
- Other parameters
  - H_2 production, integrity and homogeneity of the waste form

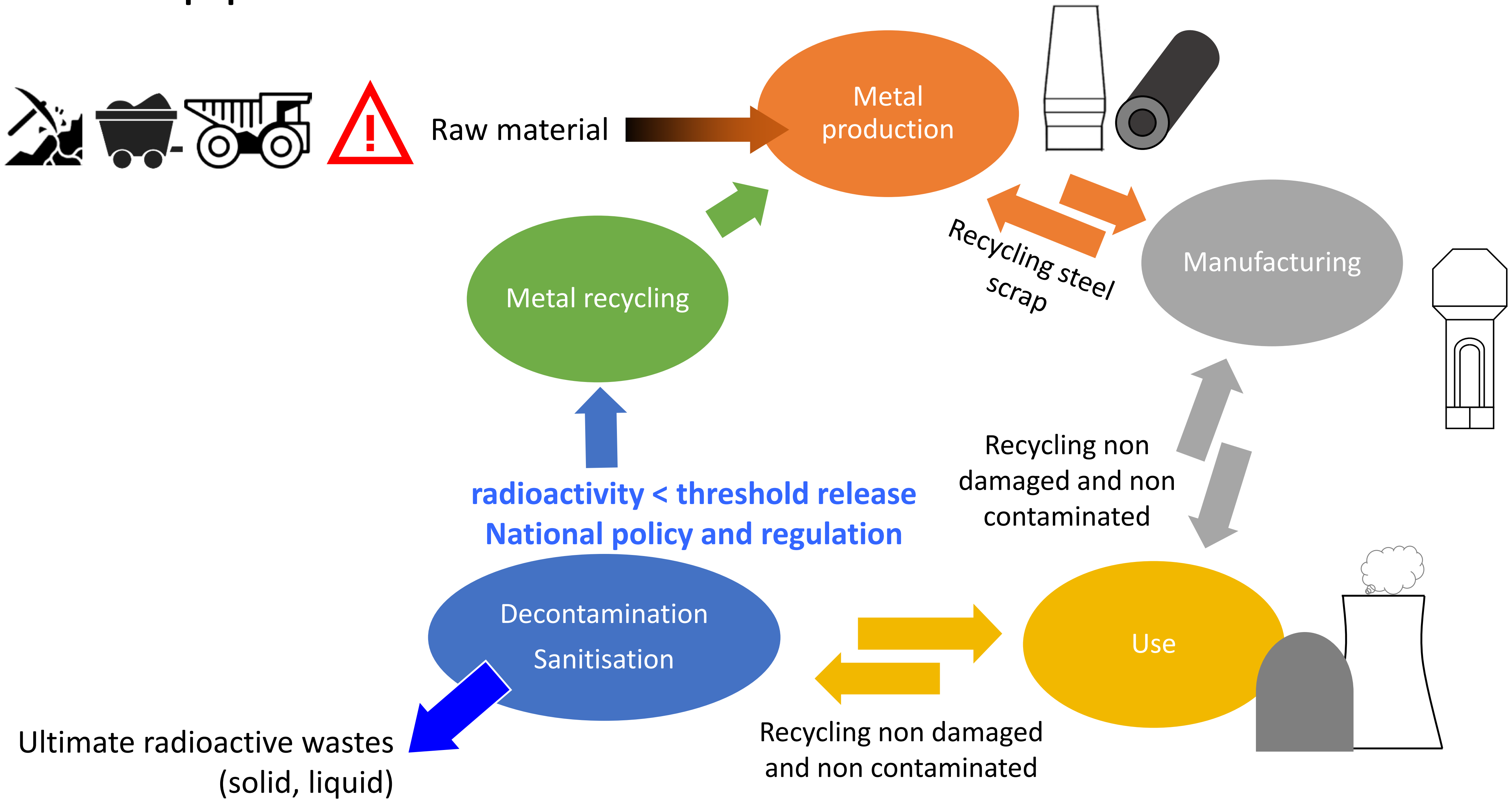


From C. Bucur, CHANCE project, PREDIS webinars 2021

Life Cycle Assessment (LCA) and Life Cycle Costing (LCC)



LCC / LCA approach



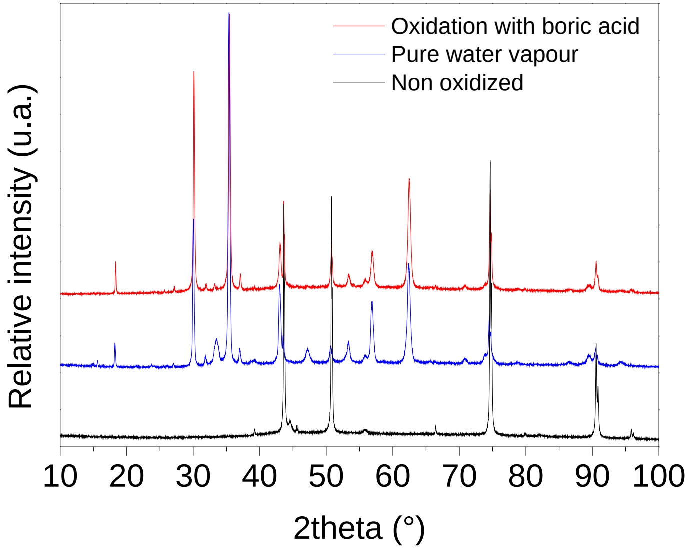
Content

- Metal decontamination
- Secondary waste treatment
- Difficult to measure radionuclide

Chemical metal decontamination

Approach and Methodology

Sample preparation → Characterization



Treatment of decontamination

- Chemical, mechanical, electrochemistry, laser, …
- Temperature, frequency…

Secondary waste treatment

- Precipitation, ion exchange resins, liquid/liquid extraction….
- Evaporation, incineration, ….

A Rivonkar et. al. (2022) Frontiers in Nuclear Engineering-Radioactive Waste Management. *doi:10.3389/fnuen.2022.1080954)*

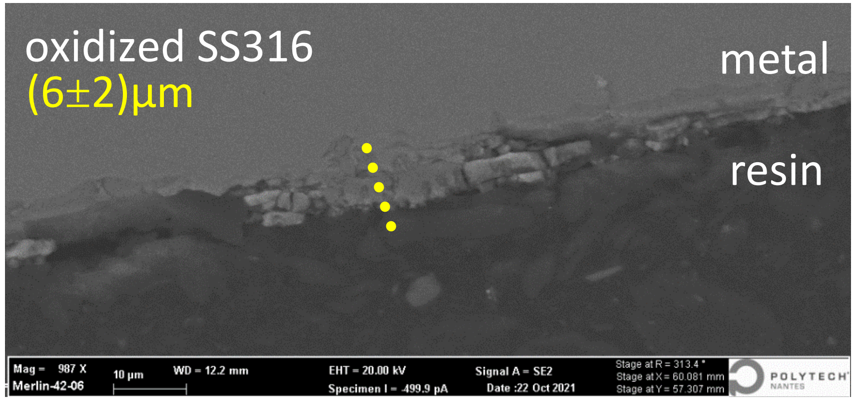
PhD A. Rivonkar

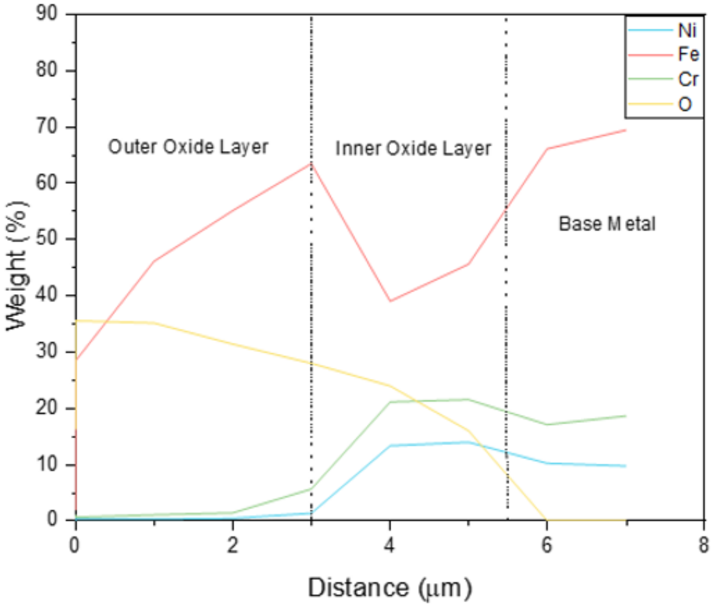
Chemical decontamination

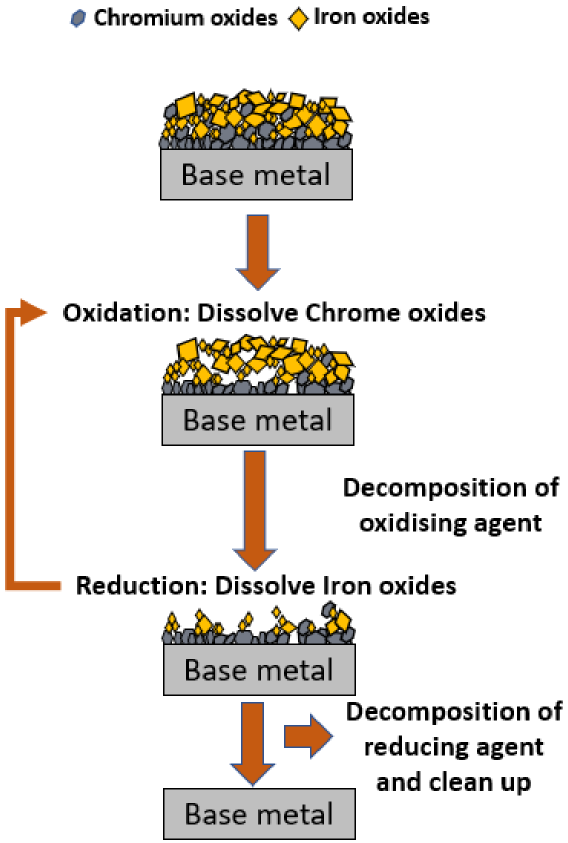
- **COREMIX process :** Chemical Oxidation Reduction Decontamination
- Consecutive multi-step process:
  - 1/ Pre-oxidation of the Cr oxide layer in the presence of permanganate
  - 2/ oxidative dissolution of Fe oxides in the presence of oxalic acid

$$Cr_2O_3 + 2MnO_4^- + H_2O \rightarrow 2HCrO_4^- + 2MnO_{2(s)}$$

$$Fe_3O_4 + 4H_2C_2O_4 \rightarrow 3FeC_2O_4 + 2CO_2 + 4H_2O$$

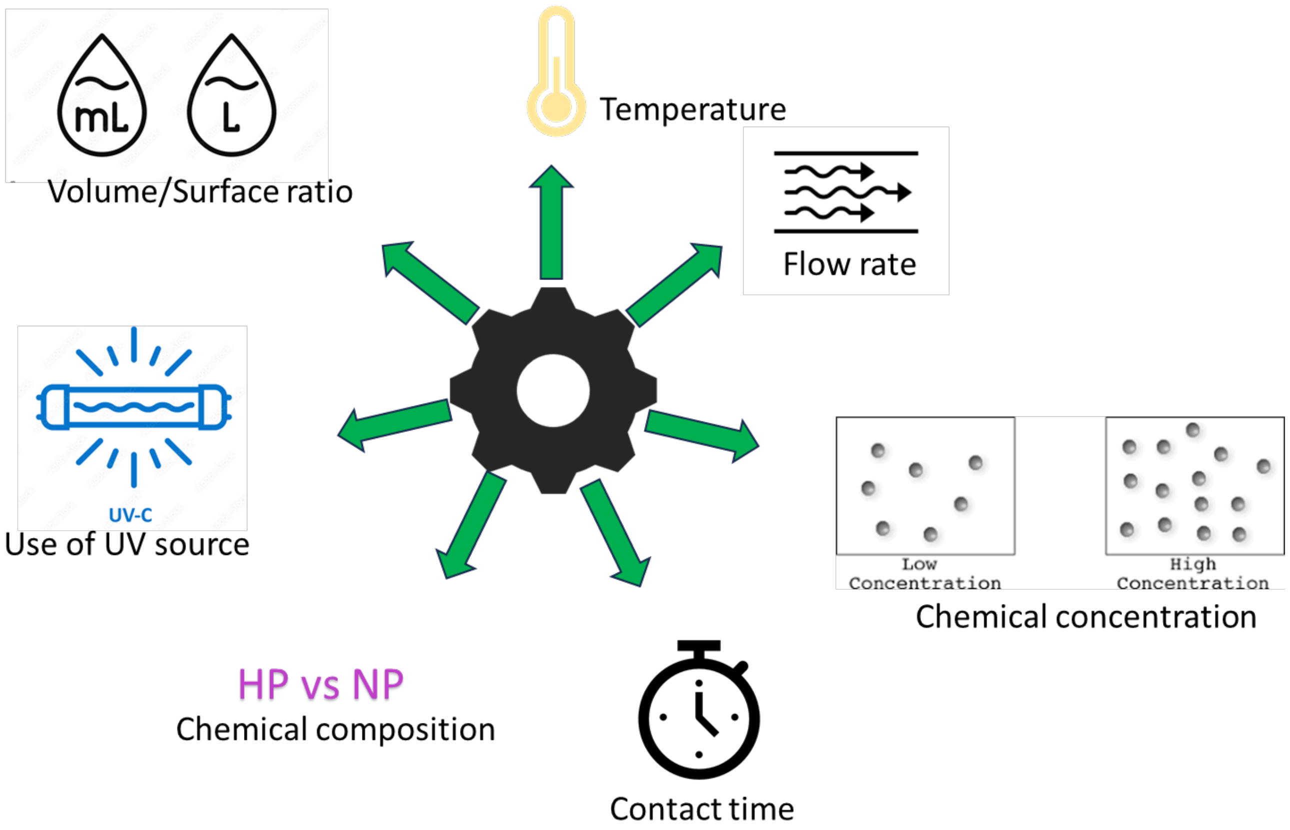






V.M. Efremenkov et al. 1998, New methods and techniques for decontamination in maintenance or decommissioning operations, IAEA

Parameters evaluated



Non radioactive sample

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Radioactive sample

Effect of chemical concentrations

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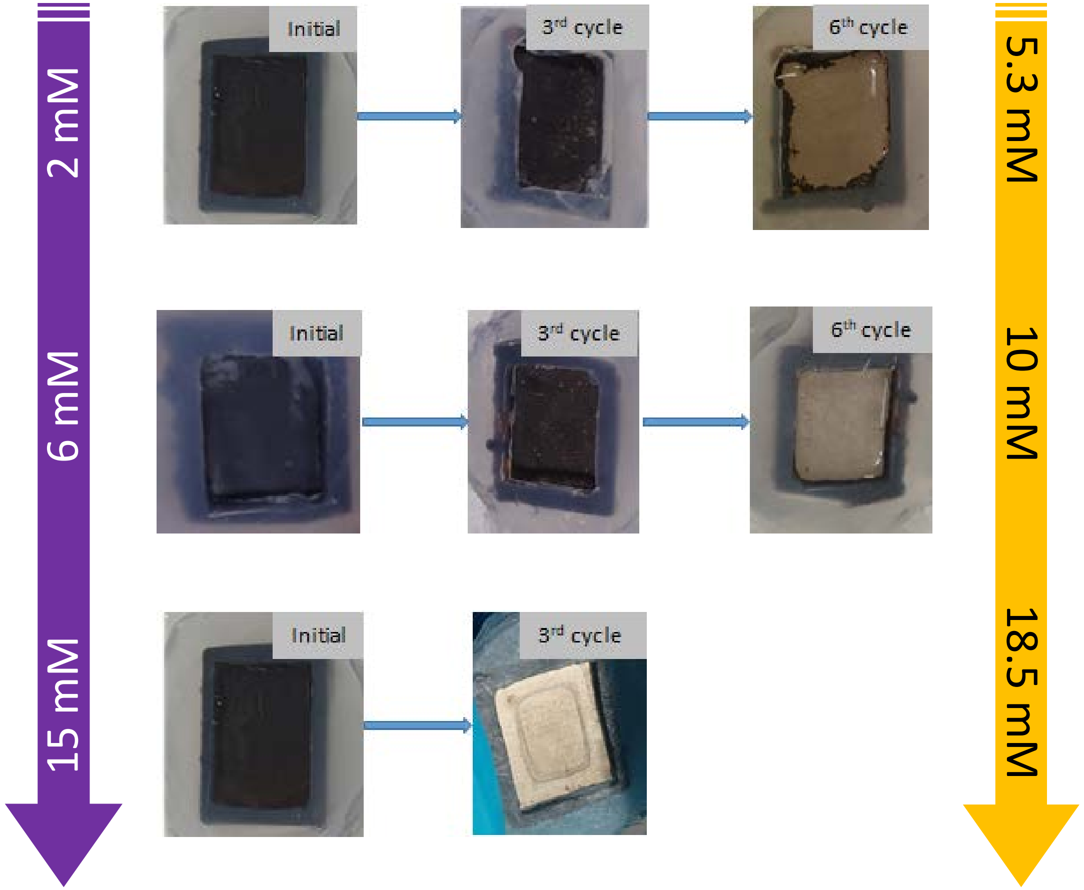
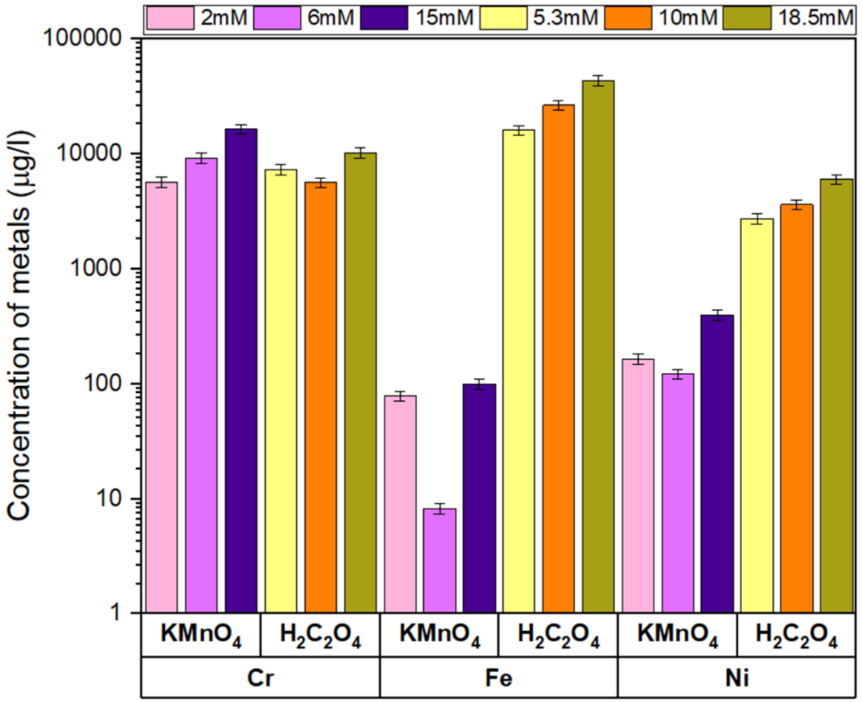


[$KMnO_4$]
+ 3mM HNO_3

$H_2C_2O_4$]

Each step applied at 80°C for 4 hours



- **Increasing concentration leads to reduction in number of cycles to 3**

Rivonkar A. et.al., in Frontiers in Nuclear Engineering 1 (2022)

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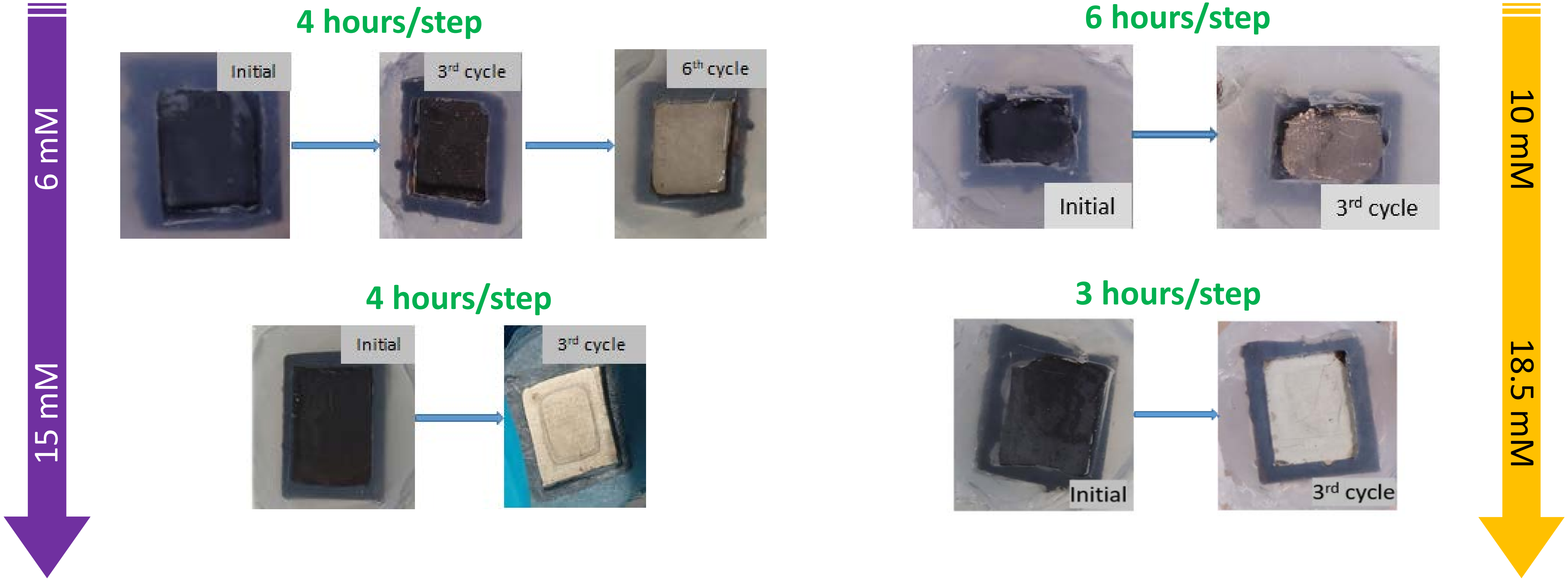
Effect of contact time



$[KMnO_4]$
+ 3mM HNO_3

$[H_2C_2O_4]$

- **Increasing concentration leads to reduction in contact time to 3 hours**

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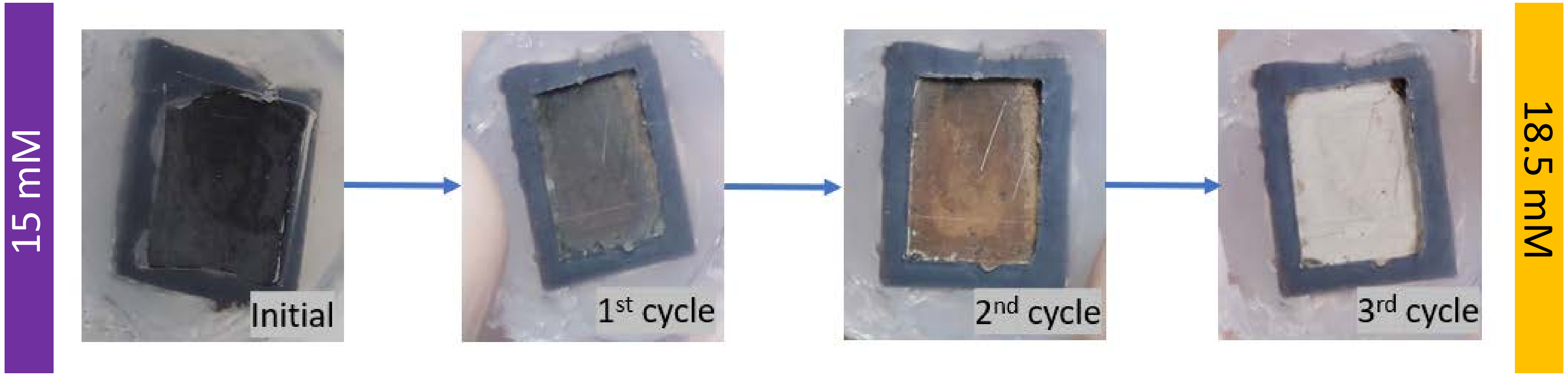
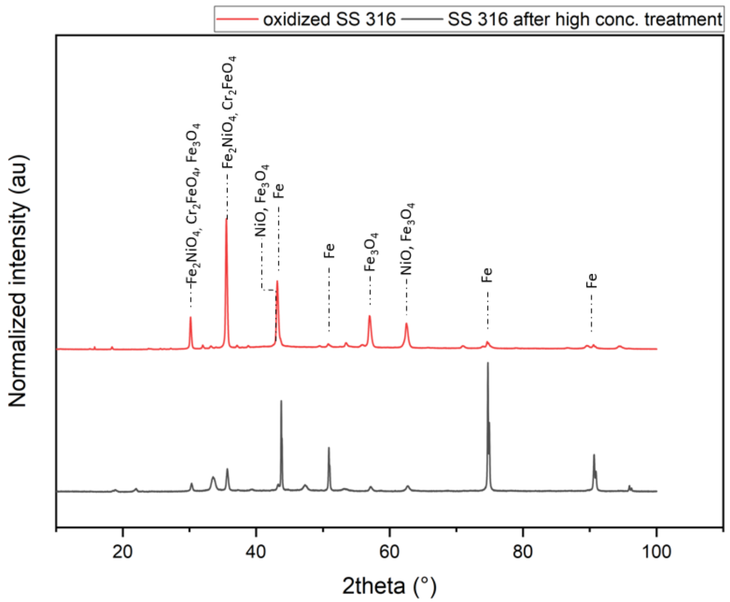
Evolution of sample surface

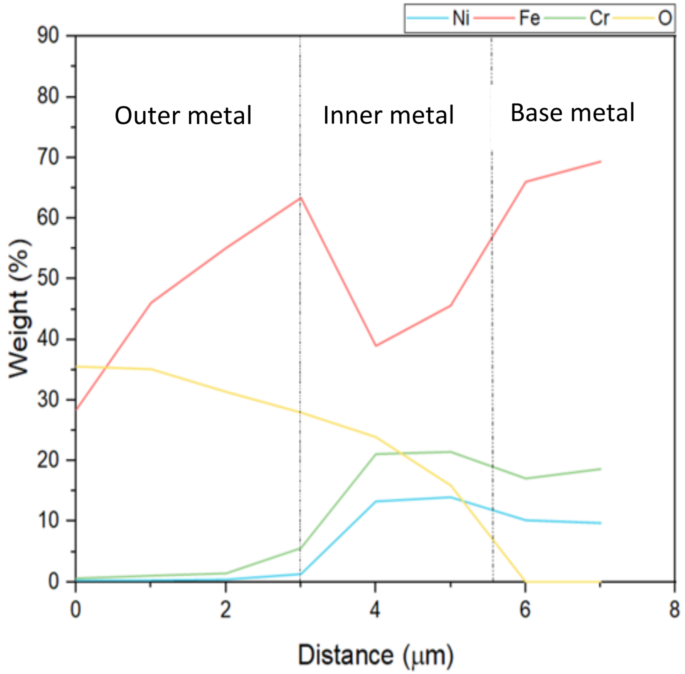


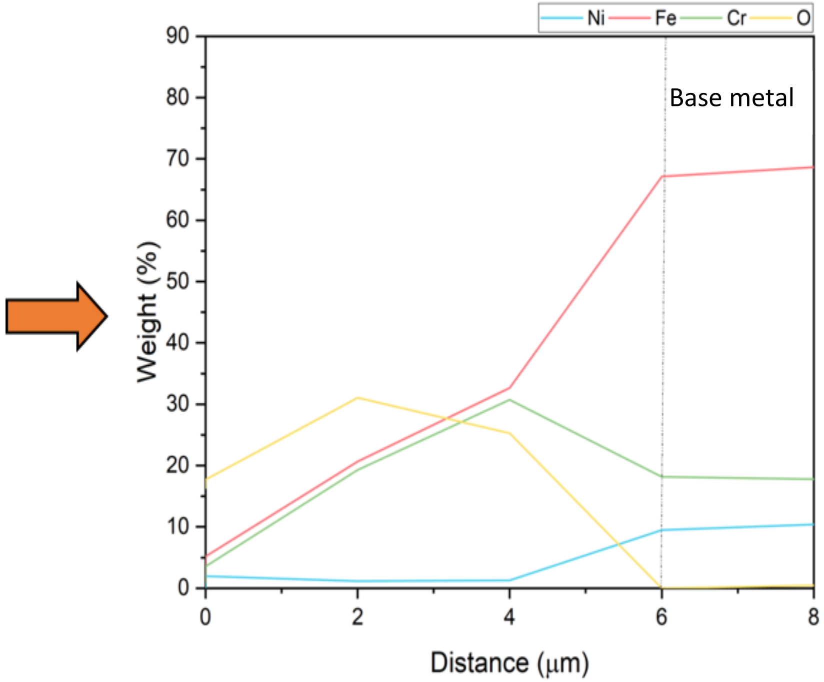
$[KMnO_4]$
$+ 3mM\ HNO_3$

$[H_2C_2O_4]$

- **Gradual dissolution of the oxide layer**







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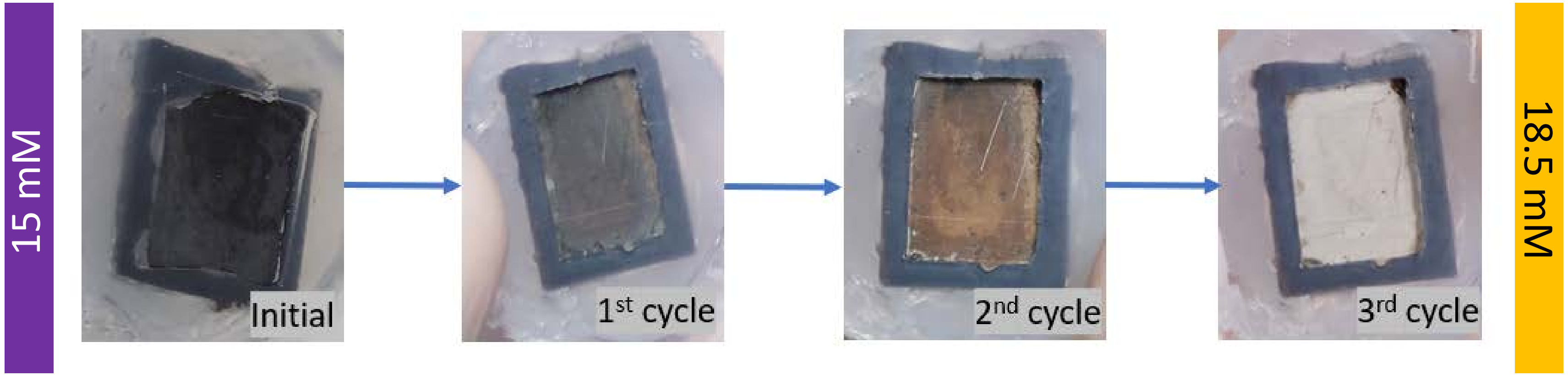
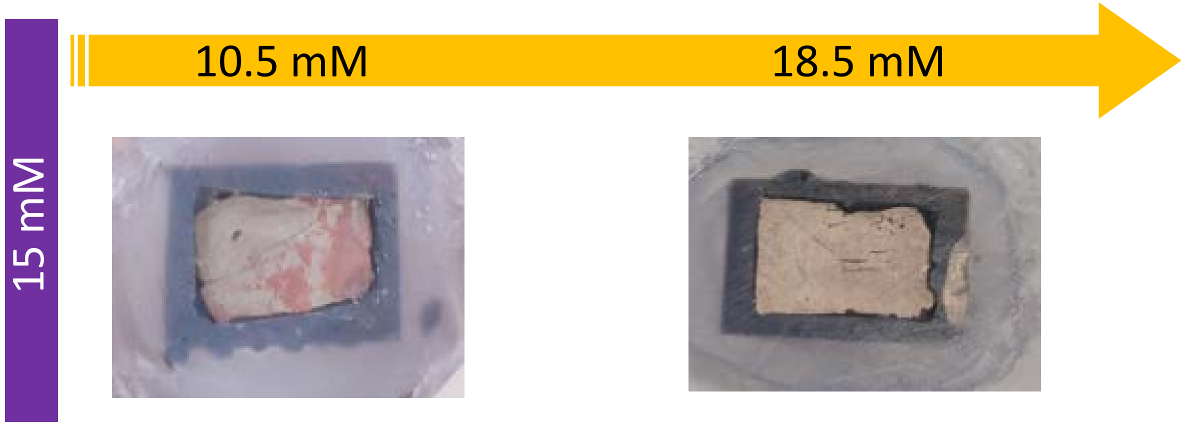
Evolution of sample surface



$[KMnO_4]$
$+ 3mM\ HNO_3$

$[H_2C_2O_4]$

- **Gradual dissolution of the oxide layer**



$[H_2C_2O_4]$

$[KMnO_4]$
$+ 3mM\ HNO_3$

- **Oxalic acid critical to oxide dissolution**

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Treatment of secondary wastes

Liquid wastes from COREMIX process

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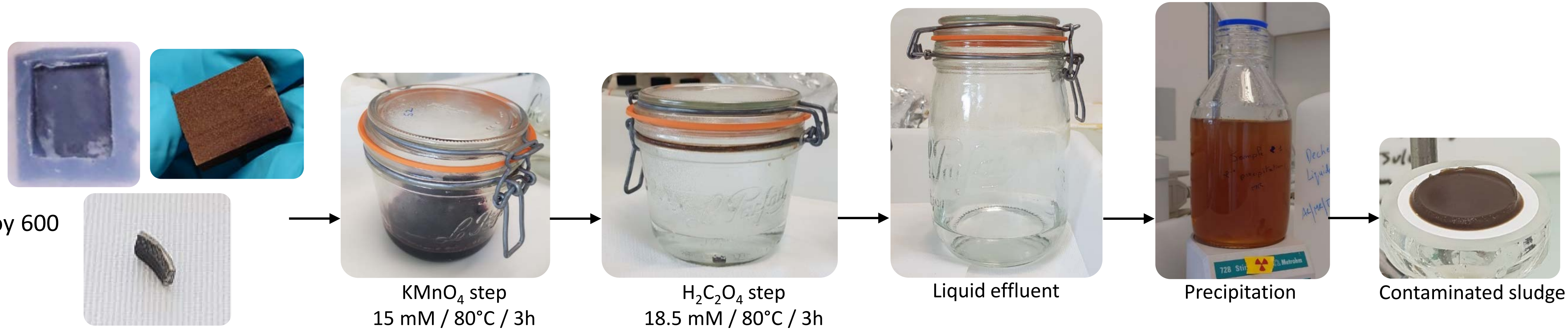
From metal waste to liquid waste

Stainless Steel

Ni-alloy 600



$KMnO_4$ step
15 mM / 80°C / 3h

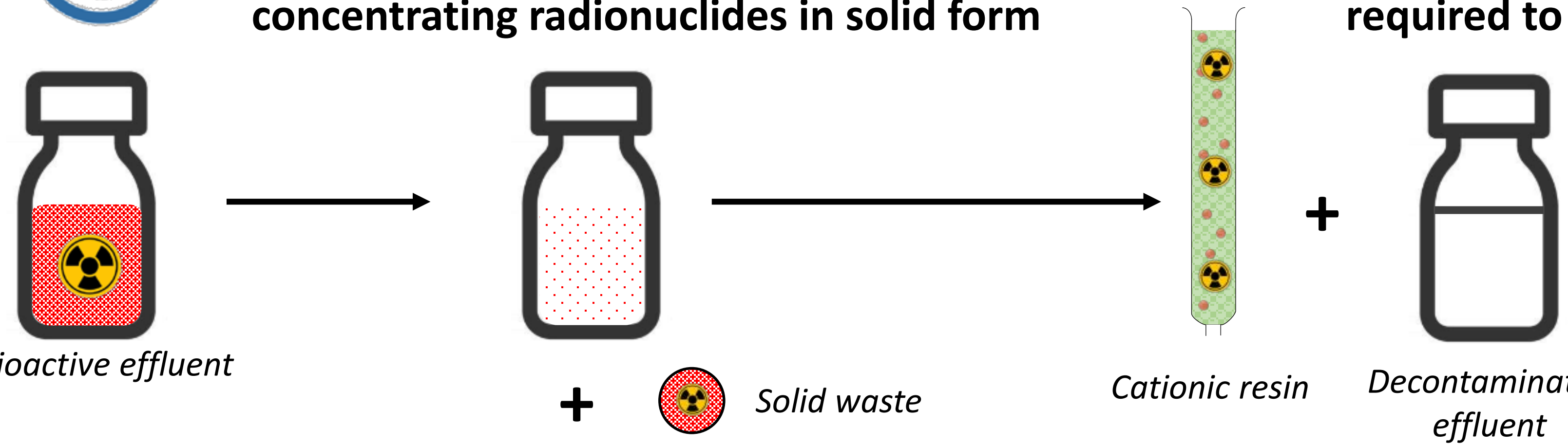
$H_2C_2O_4$ step
18.5 mM / 80°C / 3h

Liquid effluent

Precipitation

Contaminated sludge

- **Reduction of secondary effluent volume by concentrating radionuclides in solid form**
- **Reduction in the amount of cationic resin required to remove residual radionuclides**



Radioactive effluent

\+ *Solid waste*

Cationic resin

\+ *Decontaminated effluent*

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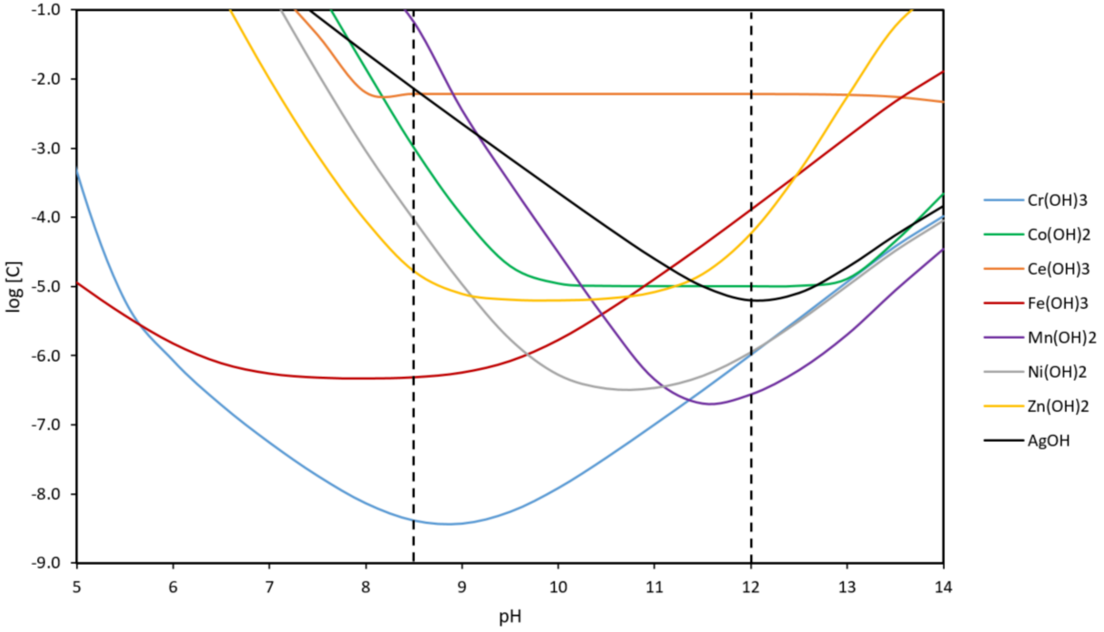
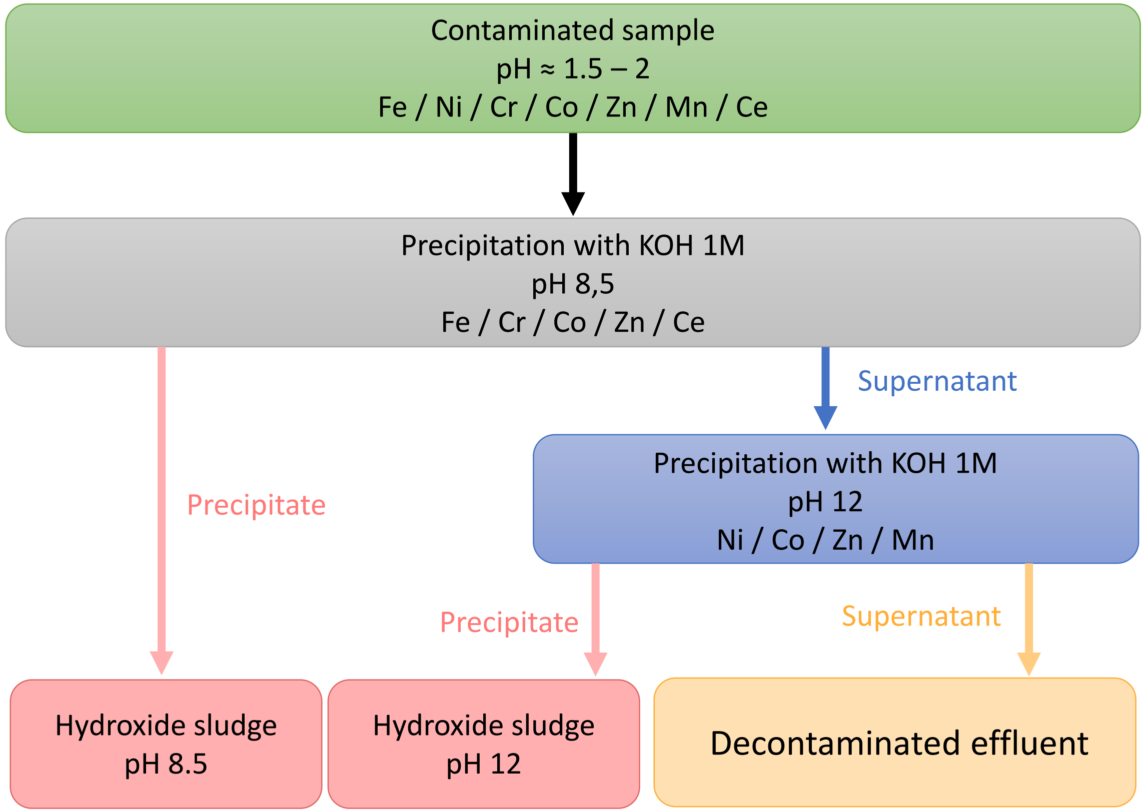
Precipitation protocol



✕ **Hydroxide precipitates are pH dependant**



<u>Several types of precipitates are possible</u> :

- Oxide
- Hydroxide
- Sulphide
- Phosphate
- Chloride
- Fluoride

✓ **Cheap reagent, fine for WAC and safe**
✓ **Environmentally friendly**
✓ **Adaptable at large scale**

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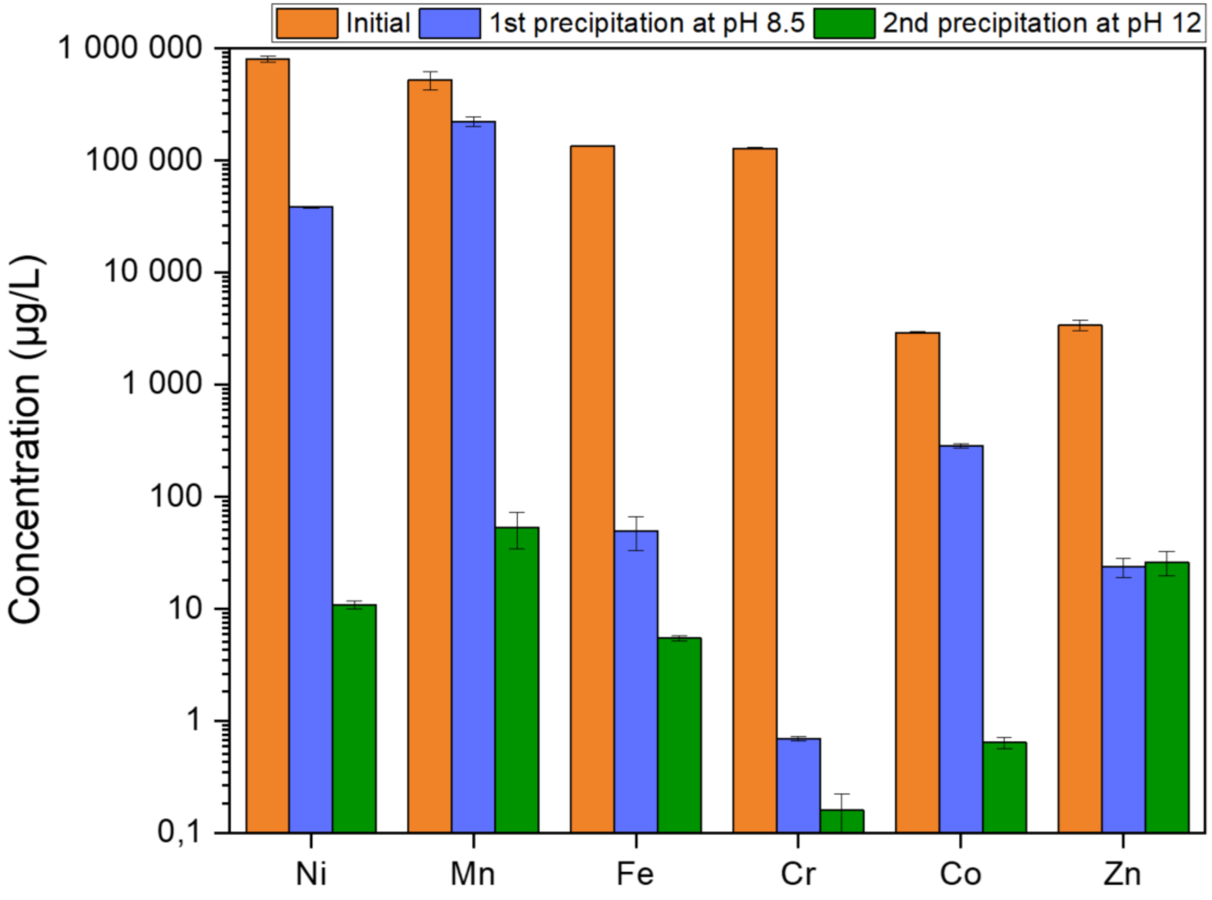
Test on synthetic solution



Elements	***% precipitated pH 8.5***	***% precipitated pH 12***
^{52}Cr	100.0	100.0
^{55}Mn	48.4	100.0
^{56}Fe	100.0	100.0
^{59}Co	76.8	100.0
^{60}Ni	84.3	100.0
^{66}Zn	99.2	99.9
Total efficiency	**77.0**	**100.0**

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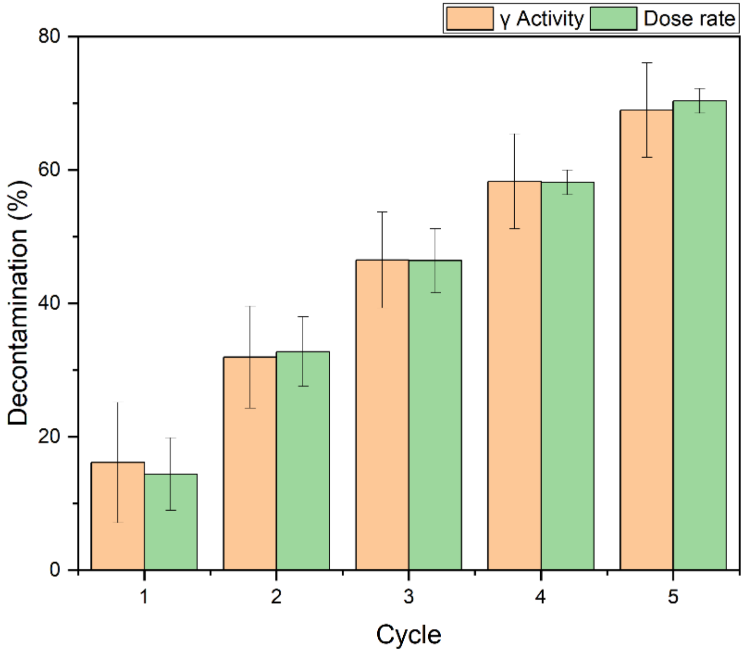
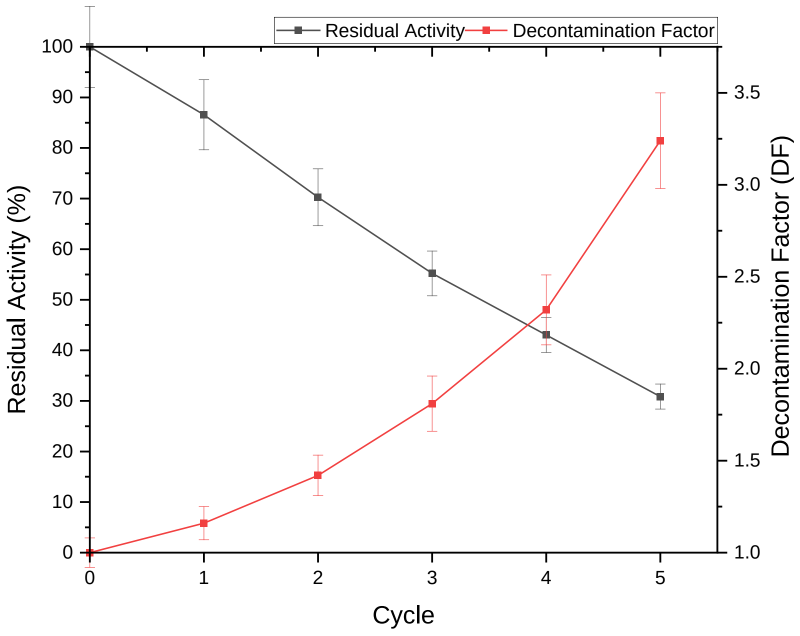
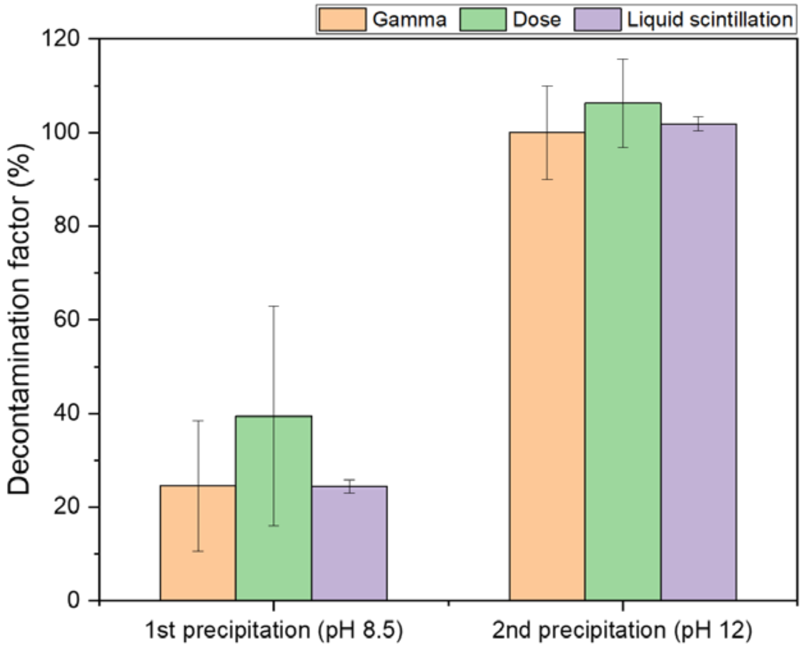
COREMIX process applied on A600







- **Metal** decontamination
  - 12%–14% decontamination per cycle ⇒ total of 8-9 cycles required for complete decontamination.
  - About 60%–70% decontamination achieved in 30 h of treatment
- **Liquid** effluent decontamination
  - pH 8.5 : ~24% drop in total radioactivity ⇦ Mainly coming from ^{55}Fe removal
  - pH 12: ~100% of decontamination ⇦ Removal of ^{60}Co and ^{63}Ni

Robin M. et.al., Front. Nucl. Eng. 3:1396821 (2024)

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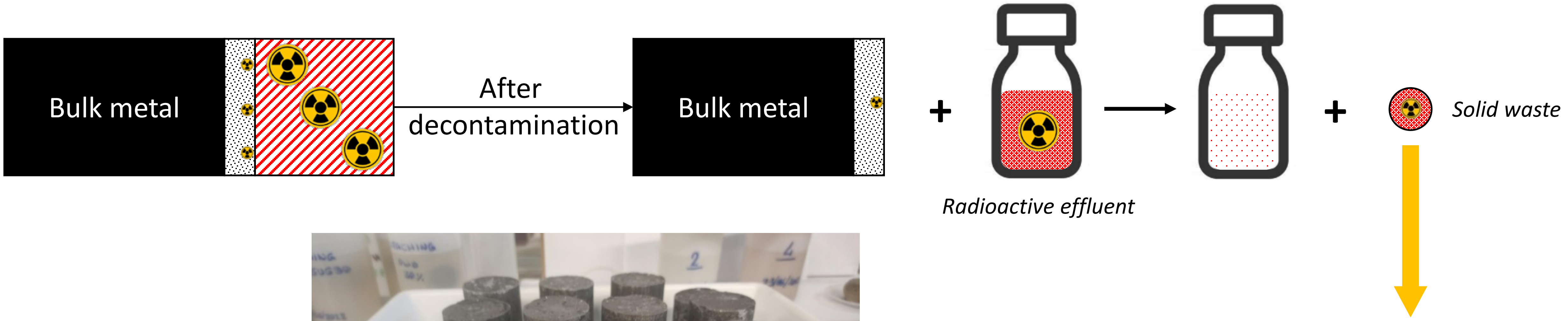
Conditioning secondary waste



- **Inovative matrixes**: geopolymers, magnesium cement phosphate, …

Difficult to measure radionuclides

DTM

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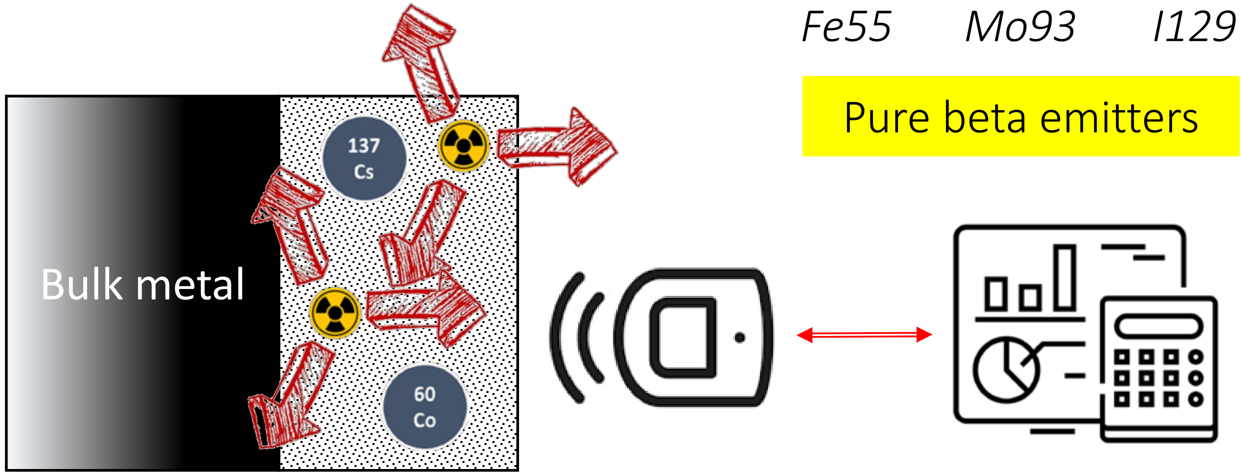
What is a DTM?

Be10	*Zr93*	*Ni59*
C14	*Nb94*	*Ni63*
Cl36	*Tc99*	*Se79*
Ca41	*Pd107*	*Sr90*
Fe55	*Mo93*	*I129*

Pure beta emitters

- ❑ DTMs characterized by their low energy emission, and/or low intensity of emission
- ❑ Evaluation of the activities by scaling factors to determine the activity level
  - Non destructive approach
- ❑ Difficulty to measure directly pure beta emitters :
  - destructive method generally used.
- ❑ Need of destructive approach to:
  - Direct measurement of radioactivity
  - Validation of scaling factor models
  - Minimization of uncertainties



⇨ 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

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Example: zirconium-93

- a long-lived RN (1.61×10^6 years)
  - Fission product of uranium and plutonium.
  - Neutron activation product of stable Zr in PWR nuclear fuel cladding.
  - Contribution to the total waste inventory: dominates after 1000 years with Tc-99.
- decays to stable Nb-93 by beta emission
  - but with a low energy : E_{max} 60Kev
  - E_{max} : 60.0 keV (73%) et 90.8 keV (27%)
  - Analyses by
    - LSC: require a very good chemical separation prior the measurement
    - ICP-MS: possible presence of isobaric interfering elements (Mo-93 and Nb-93)
- element to monitor
  - Decommissioning and characterization of nuclear sites
  - Release to the environment

⇨ no standard procedure, no standard source

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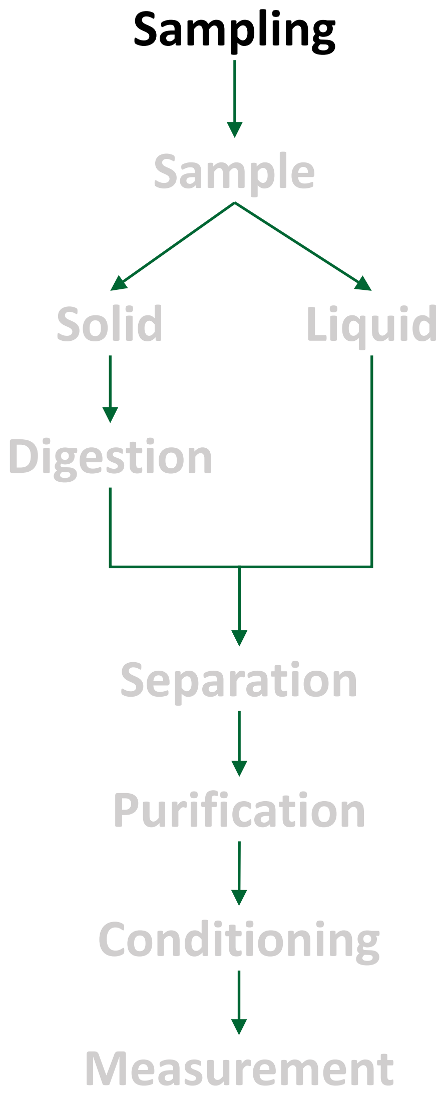
General methodology & Challenges



❑ Sampling

- Representative samples
  - mass/volume
  - high/low activity
  - heterogeneity/homogeneity
  - Location, access
- Selection of sampling technique
  - Drill, saw, cutter etc.
  - Geometry/form of the sample
- Cross contamination
  - What will be studied?
  - Contamination from the sampling technique?

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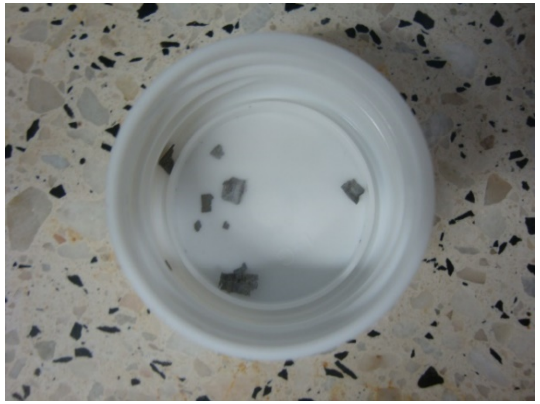
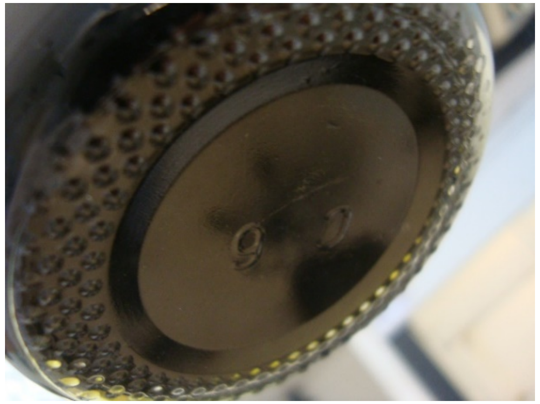
General methodology & Challenges

- ❑ **Sampling**
- ❑ **Sample preparation**
  - DTM extraction from metal: acid digestion, thermal oxidation, ….
  - Radionuclide specific restrictions: volatility, activity level
  - Chemical constrains: solubility, chemical composition….
  - Total digestion?
  - Synthetic solution, surrogate sample





Sampling
↓
Sample
↙ ↘
Solid **Liquid**
↓
Digestion
↓
Separation
↓
Purification
↓
Conditioning
↓
Measurement

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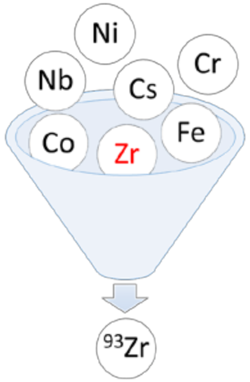
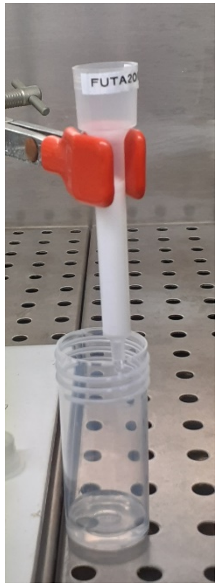
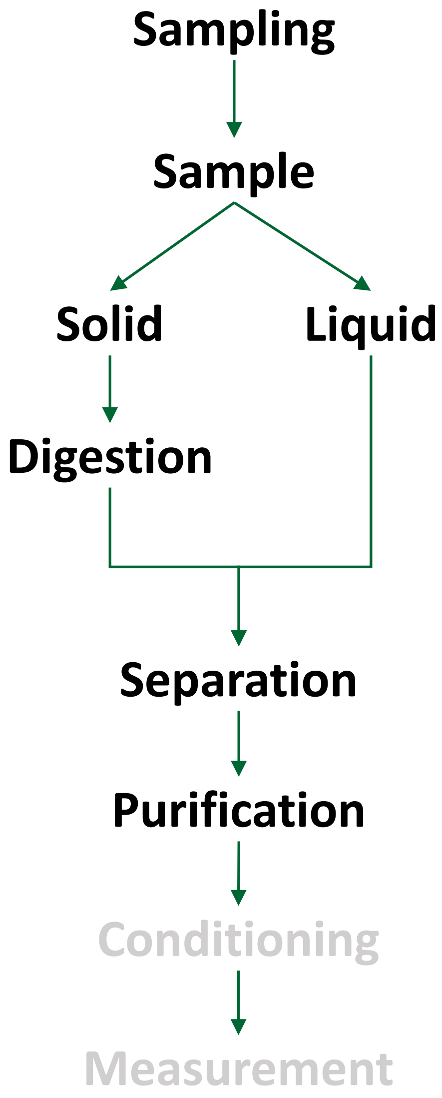
General methodology & Challenges

- **Sampling**
- **Sample preparation**
- **Separation – Purification**
  - Chromatographic resins
  - Liquid/liquid extraction
  - Consideration of interferences during purification process and detection







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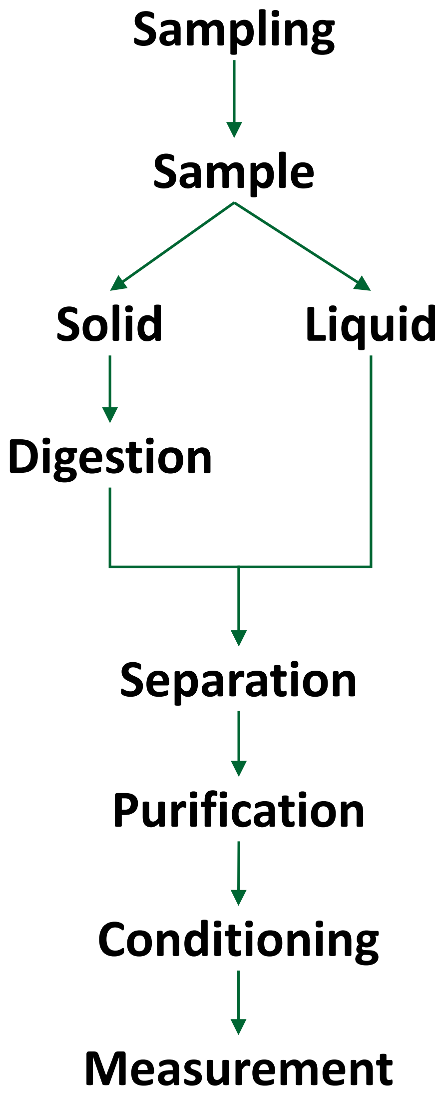
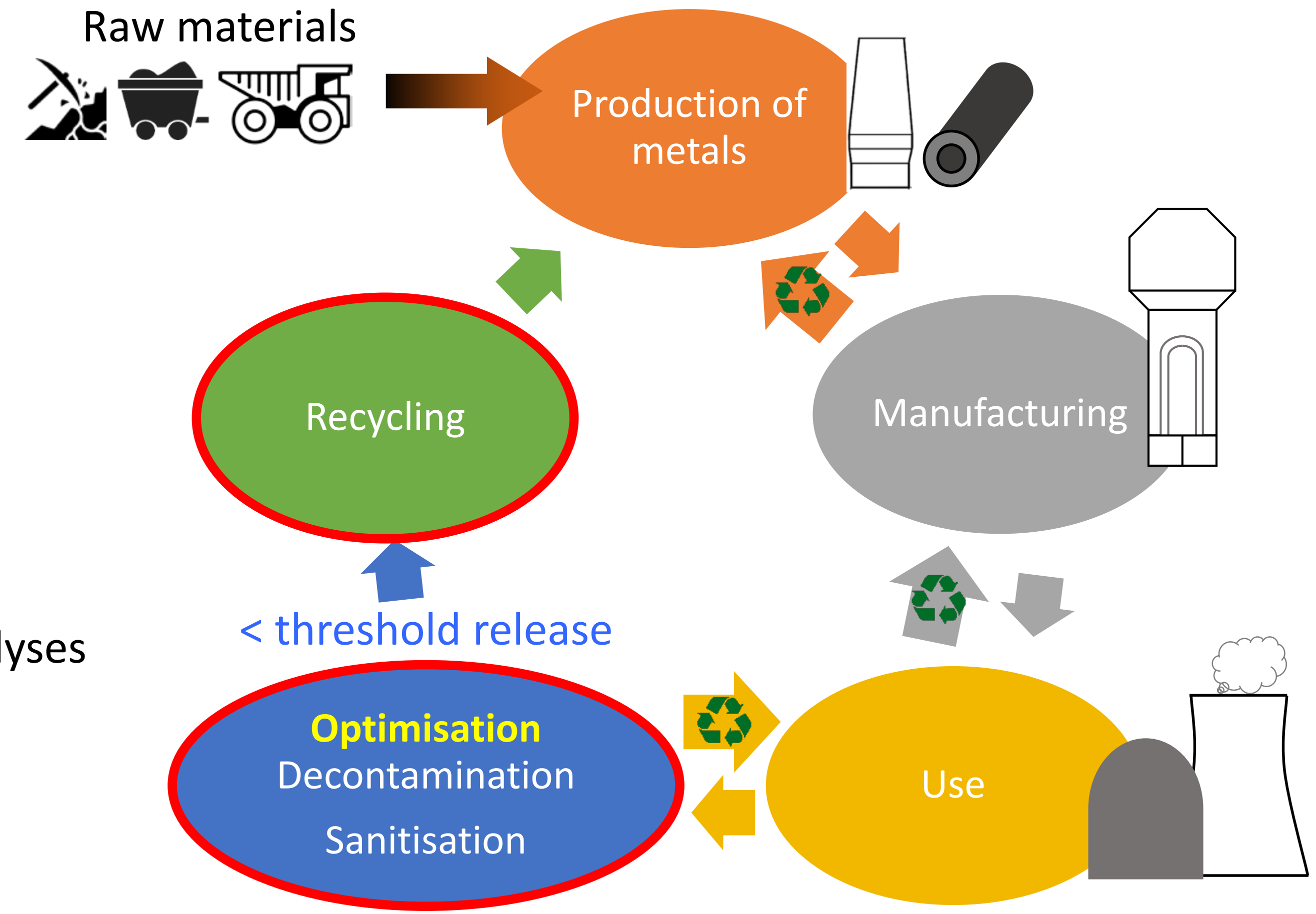
General methodology & Challenges



- **Sampling**
- **Sample preparation**
- **Separation – Purification**
- **Sample conditioning and measurement**
  - Liquid form or solid form
  - Selection of an adapted analytical technique for measurements
    - Liquid scintillation counting: quenching, contamination
    - X-ray: BEGe gamma spectrometer,
    - Mass spectrometry: ICP, AMS (limited), …
    - Lowering detection limits, optimization of detection efficiency

To summarize

- Reduction of volume waste
- Saving raw materials
- Developing innovative matrixes
- Developing new procedures for DTM analyses



Acknowlegements

- Subatech laboratory
  - Radiochemistry team
  - SMART team

- WP4 partners of PREDIS Project
  - VTT, NNL, SORC, CEA, UJV, CTU, POLIMI

- Triskem company