STUDY OF EXISTING CHEMICAL DECONTAMINATION METHODS OF RADIOACTIVE METALS WITH A VIEW ON THEIR OPTIMIZATION

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ABSTRACT

- Large volumes of low activity wastes including metallic wastes, made of stainless steel 316 and Ni-Alloy 600 following decommissioning and maintenance operations; make up majority of PWR primary circuit and undergo contamination or activation corrosion product.
- Multi oxide layered corrosion with a composition of: inner layer Cr; outer layer Fe/Ni
- Assessment and testing of Chemical Oxidation Reduction Decontamination (CORD) method and Metal Decontamination by Oxidation with Cerium (MEDOC).
- Tests carried out on surrogate inactive steel samples prepared by SORC
- Optimization of process for treatment of secondary liquid effluents.
- Process taking into consideration final geological disposal
  - Products acceptable by Waste Acceptance Criteria (WAC)

BACKGROUND/INTRODUCTION

- The activated corrosion products (CP) in the reactor may contaminate internal surface of the primary circuit by deposition. The CP can also diffuse into the oxide layer and sub-surface.
- Treatment of these wastes can lead to significant savings in space.
- Chemical decontamination is the method of choice mainly for complex geometries
- CORD : 2 step decontamination method [1]
  1) Oxidative dissolution of Cr-oxide layer by MnO_4^- ion
  2) Reductive dissolution of Ni/Fe-oxides layers by oxalic acid
- MEDOC: Regenerative single step method using Ce^{4+} to oxidize metal
- Spent Ce^{4+} is reduced into Ce^{3+}; regenerated using Ozone.
- Metallic ions captured by ion-exchange resins

CHALLENGES / METHODS / IMPLEMENTATION

Preparation of representative metallic samples

- Surrogate samples provided by Social Organization for Radioecological Cleanliness (SORC).
- Heated up to 800°C and exposed to water vapour, some with boric acid.
- Samples being characterized with XRD and SEM.

Decontamination tests using CORD on Stainless Steel (SS) 316 Samples

- Oxidation reaction with acidic $KMnO_4$ solution, concentration varying from 2mM to 15mM in 3mM HNO_3
- Reductive reaction carried out by respectively varying oxalic acid concentration from 5mM to 18mM with additional oxalic acid being added for the reduction of the MnO_4^- ion and MnO_2 formed during oxidation to Mn^{2+}.
- Tests carried out at 80°C for 3 hours in each step with agitation.

Fig 1. Raw and Surrogate SS 316 sample prepared by SORC

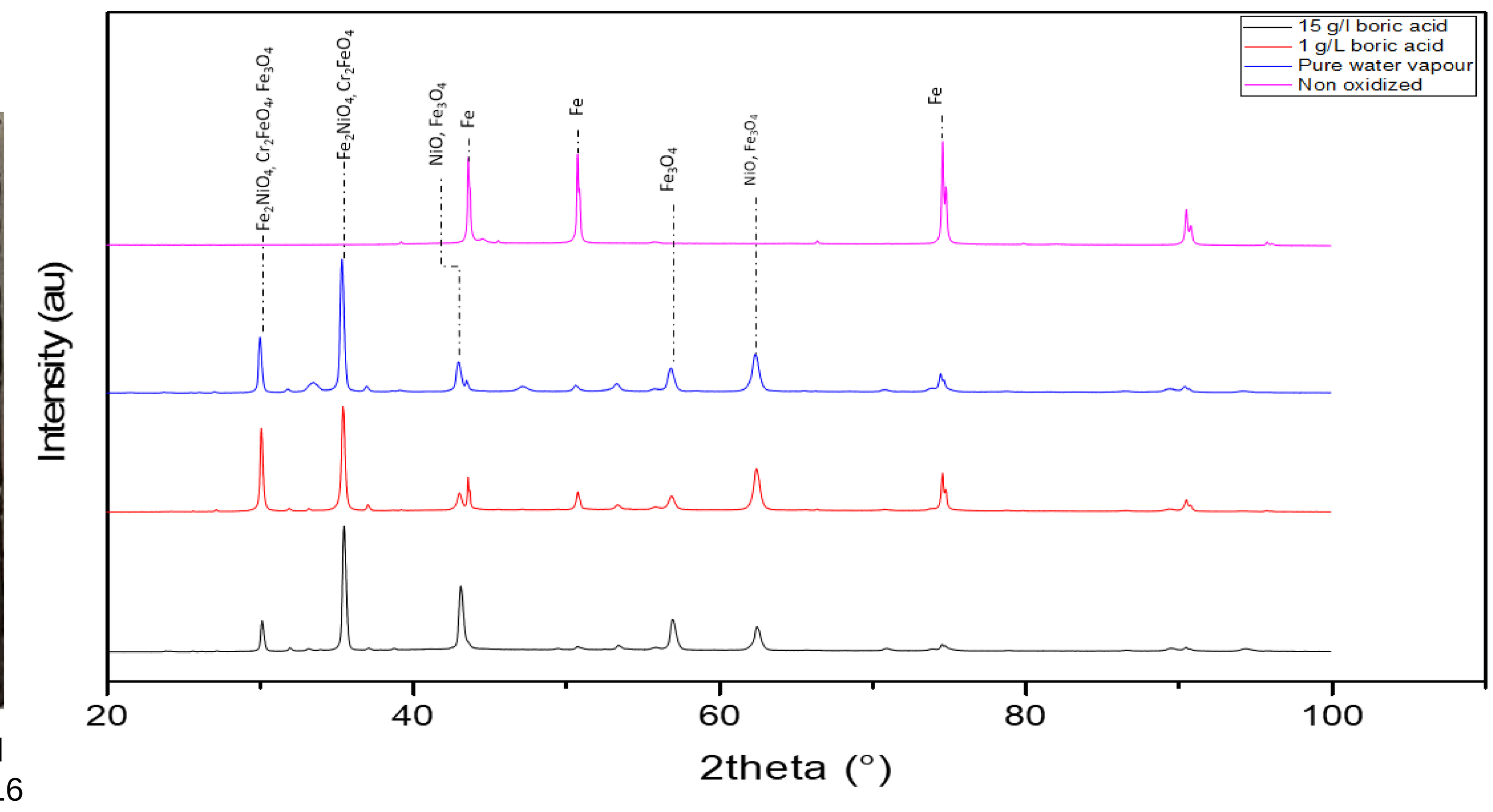

Fig 2. XRD patterns of SS 316 samples oxidized under different conditions

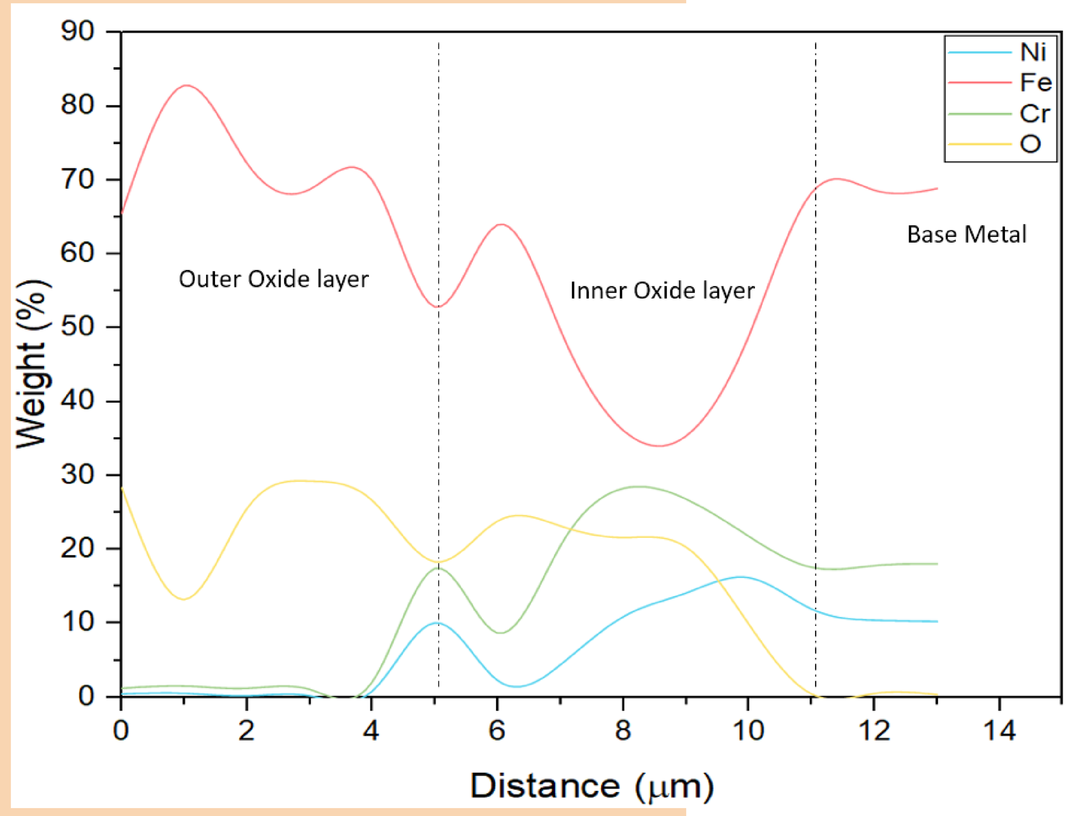

Fig 3. SEM-EDX analysis of SS 316 oxide layer

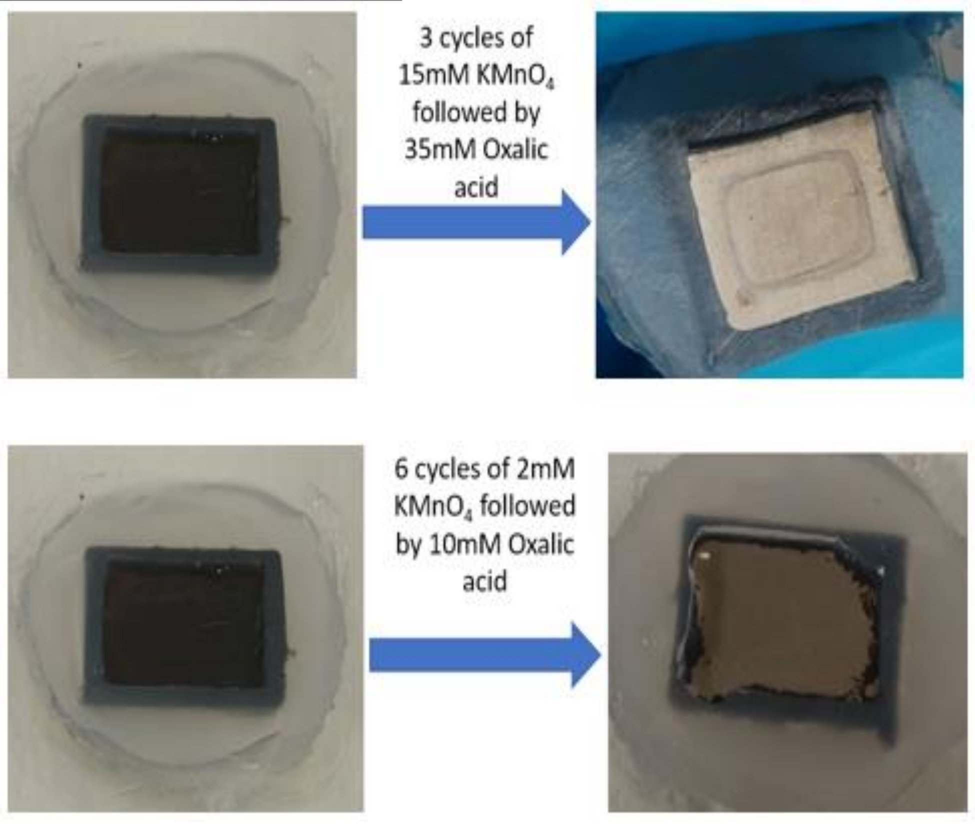

Fig 4. SS 316 samples before and after treatment at high (top) and low (bottom) concentrations

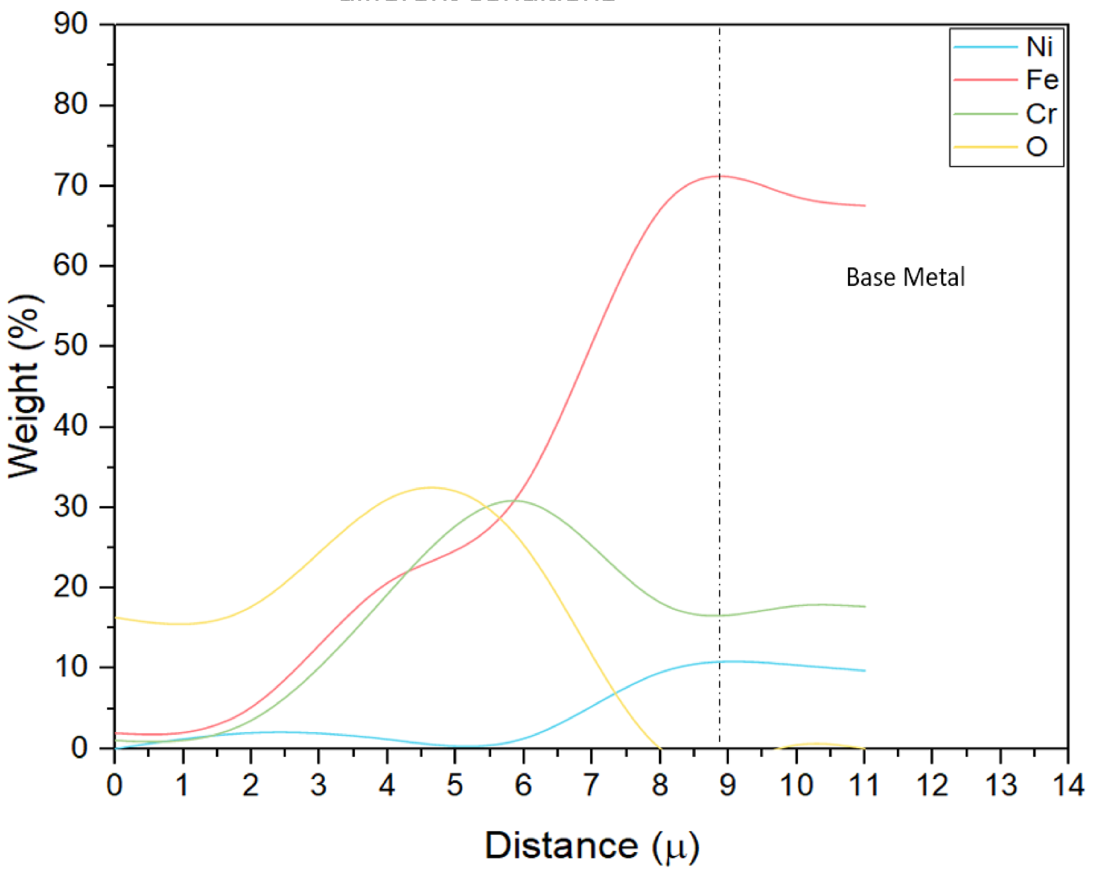

Fig 5. SEM-EDX analysis of SS 316 sample after CORD treatment

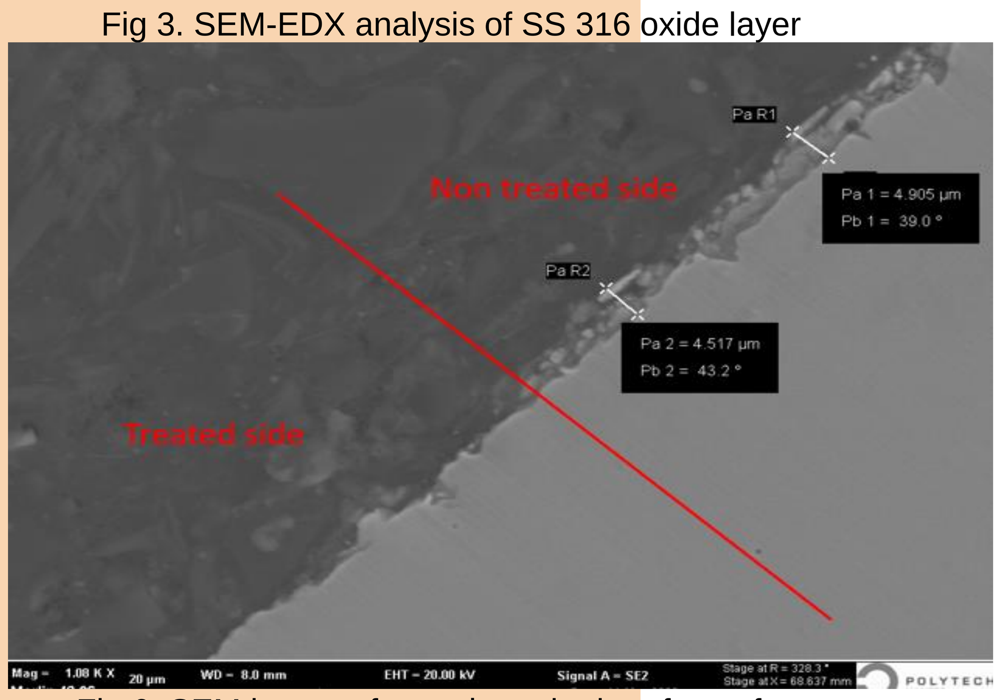

Fig 6. SEM image of sample at the interface of treatment showing no oxide layer after treatment

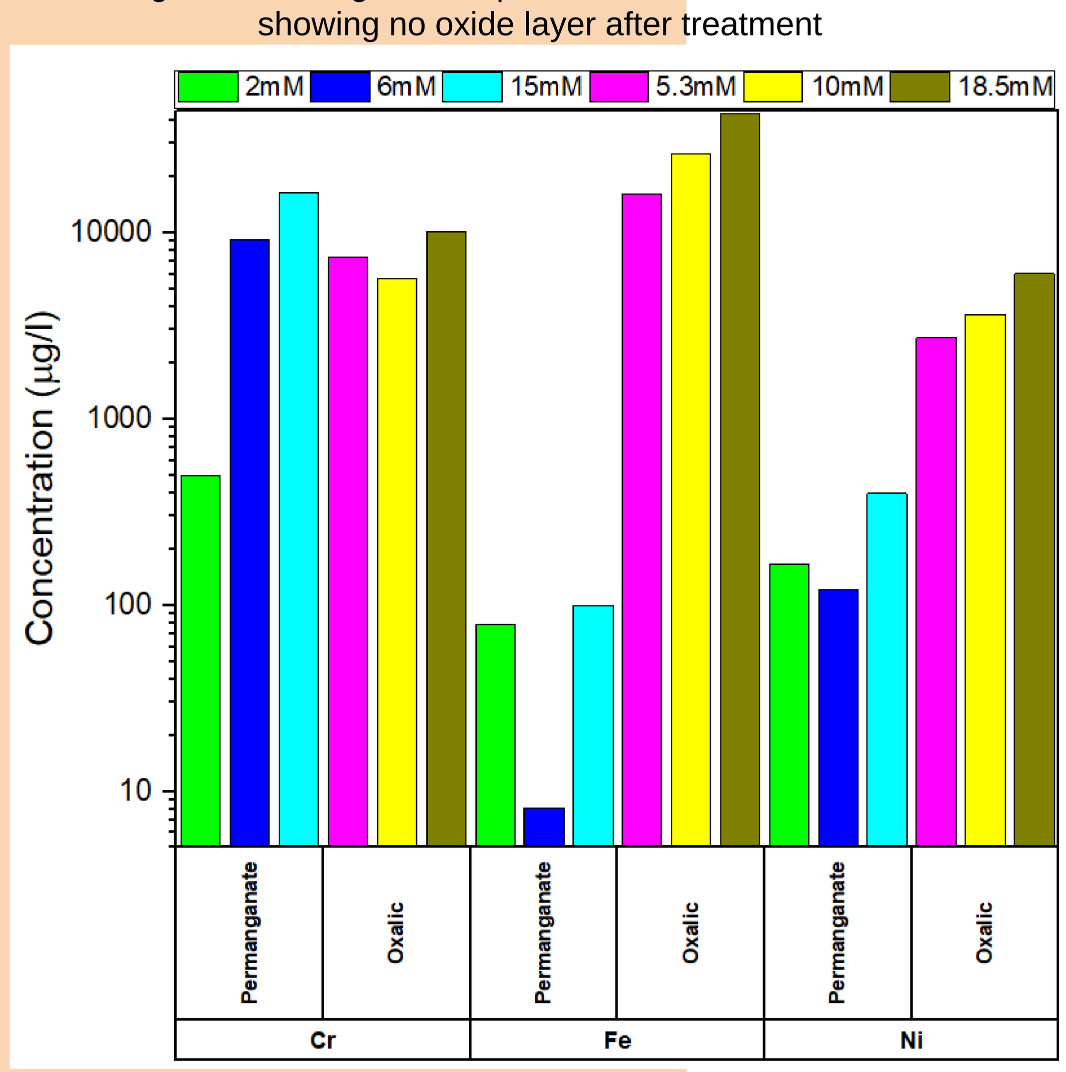

Fig 7. ICP-MS results depicting efficiency of permanganate and oxalic acid steps

OUTCOME/RESULTS

Characterization Results

- Multi-layered oxide layer seen: with a mean thickness of 8-10 µm.
  - Outer layer of mainly Fe-oxide with a mean thickness of 5-6 µm.
  - Inner layer is slightly enriched in Cr/Fe-oxide + Fe/Ni-oxide and a mean thickness of 3-5 µm.
  - Post decontamination shows no visible oxide layer and no oxides seen in EDX profile, with oxygen contribution coming mainly from resin material.

Decontamination tests using CORD on Stainless Steel (SS) 316 Samples

- Acidic $KMnO_4$ used for oxidation with concentration varying from 2mM to 15mM in 3mM HNO_3.
  - Dissolves mainly Cr-oxides as compared to Fe and Ni-Oxide
  - Efficiency increases with increased concentrations as seen in Fig 4.
- Reductive step carried out by respectively varying oxalic acid concentration from 5mM to 18mM
  - Dissolves Fe and Ni Oxides as compared to Cr oxides.
  - Increases efficiency at higher concentrations

CONCLUSION AND FUTURE ASPECTS

- CORD process shows efficiency in dissolution at low and high concentrations
- This process generates liquid effluents that contain dissolved metallic cations and oxalic acid.
- Oxalic acid destruction is being tested using H_2O_2 in the presence of UV and HNO_3
  - Precipitation / Co-precipitation of metals to reduce resin use (work of M. Robin); lower total volumes to be disposed geologically
- Evaluation requested to choose between low concentration and more cycles vs high concentration and few cycles.
- Oxalic acid destruction is viable and the entire process uses no chelating agents allowing for easier geological disposal of wastes.
- MEDOC process currently being tested.

ACKNOWLEDGMENTS/REFERENCES

A special thank you to Marion Allart, IMN for all her support and help to carry out SEM analysis.

[1] Decontamination Handbook, TR 112352, EPRI, Palo Alto, CA: (1999).

[2] Ponnet et al., Thorough Chemical Decontamination With the MEDOC Process: Batch Treatment of Dismantled Pieces or Loop Treatment of Large Components Such as the BR3 Steam Generator and Pressurizer; WM'03 Conference (2003)