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An innovative use of carbon brushes for the electrochemical decontamination of wastes

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Introduction

The ORANO la Hague plant (Manche) must be innovative in dismantling its old facilities.
In particularly, the dismantling HAO's cells (High Activities Oxides building) involves the clean-up of equipment in "904" cell that was used to shear and dissolve spent fuel.
The 904 clean-up operations require a very significant decontamination factor to be achieved to allow most of the metallic wastes from the dismantling of equipment, pipes and accessories can be compatible with surface waste disposal. Indeed, being located at the most contaminating level of the reprocessing process, the equipment has accumulated a large quantity of radioelements.

For all these reasons, it has seemed necessary to search for new technologies or improved existing technologies, which bring sustainability to the D&D operations while carrying a higher standard in terms of safety, easiness and economic value.

Issue

Electrochemical decontamination was extensively used in the pre-maintenance job decontamination for its high efficiency and innocuousness towards the components treated. It generates low amount of effluent, usually exhibit high decontamination factor as DF high as 1000 were commonly obtained.
Its ventures in the D&D areas were rare, because of the complex set-up.
Indeed, the different operating uses of this process used electrolysis in acid chemical baths or by pads (for in-situ large surfaces treatment) by applying an anodic polarization on the metal, resulting in an oxidation on its surface. Requiring rigid electrodes to be applied on the surface, electrochemical decontamination was limited to metallic regular surfaces.

Electrochemical decontamination by brush

Addressing a recurrent implementation issue, ORANO DS in collaboration with the manufacturer REUTER designs a simple solution to be able to use an electrochemical decontamination process by remote handling to treat all shapes of metal wastes.
Reuter GmbH had already developed a new electro-decontamination equipment by brush that makes all shapes of stainless-steel surfaces decontamination possible. The innovative characteristic is the use of a flexible electrode design that guarantee an effective decontamination to all points instead of a rigid electrode.

The purpose of this technical development in collaboration with REUTER GmbH is to adapt this new electrochemical equipment to allow its use in a specific nuclear environment: work in zone 4, where access is forbidden to humans and interventions are carried out by remote handling.

These particularities require many modifications to allow the reliability of the equipment in a remote use. Particularly, it requires:

- The modification of the electro chemical decontamination brush to make it compatible with the remote manipulators,

- The modification of the connectors for the connection of the equipment in zone 4 and the physical protection of the cables and hoses

Before detailing the new implementation, this technical paper also details the different possibilities considered and the reasons for choosing to use this new electro-decontamination implementation.

Historical implementations

The electrochemical decontamination mainly uses the principle of electrolysis by dissolving the metal surface polarized as anode (the metal to be decontaminated) in the electrolyte to remove the contaminants from the metal surface and then achieve decontamination. The main advantages of electrochemical decontamination are simple equipment, high decontamination efficiency, and a small number of chemical reagents. Therefore, the secondary waste produced is less than the general chemical reagent decontamination. Electrochemical decontamination eliminates metallic pollutants both on the surface and deep down. It is a widely used radioactive waste treatment method in the nuclear industry. According to the different methods of electrolytic decontamination, it can be divided mainly into immersion electrochemical decontamination and mobile electrochemical decontamination.

Immersed electrochemical decontamination:

Immersion electrochemical decontamination is the decontamination method in which the metal to be decontaminated is used as an anode, insoluble metal or inert conductor is used as a cathode, both of them are immersed in an electrolyte (nitric acid, phosphoric acid, sulfuric acid, etc.), and the anode is dissolved by direct current. This method is generally applicable to the decontamination of small polluted workpieces.

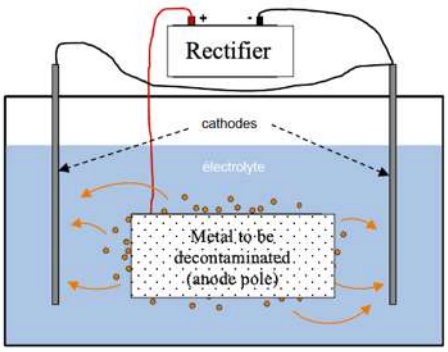


Figure 1 *:* Schematic diagram "immersed electrochemical decontamination"

Mobile electrochemical decontamination:

The principle of decontamination is to connect the anode of the DC power supply with the metal surface to be decontaminated, and the cathode with the decontamination head. The decontamination head is composed of a conductor metal (with or without cap) with electrolyte. Once the decontamination head contacts with the anode metal, a current loop is formed, which makes the electrons of the anode flow to the cathode, causing the elements Fe, Cr, Ni from the stainless steel to dissolve, thereby decontaminating the metal.

There are two types of decontamination head:

- The first one (cf figure 2) contains a cap soaked with electrolyte and allows in this case to move easily on the surface without electrolyte flowing,

- The second one (figure 3) is cap free but it is necessary in this case to keep it watertight by means of seals

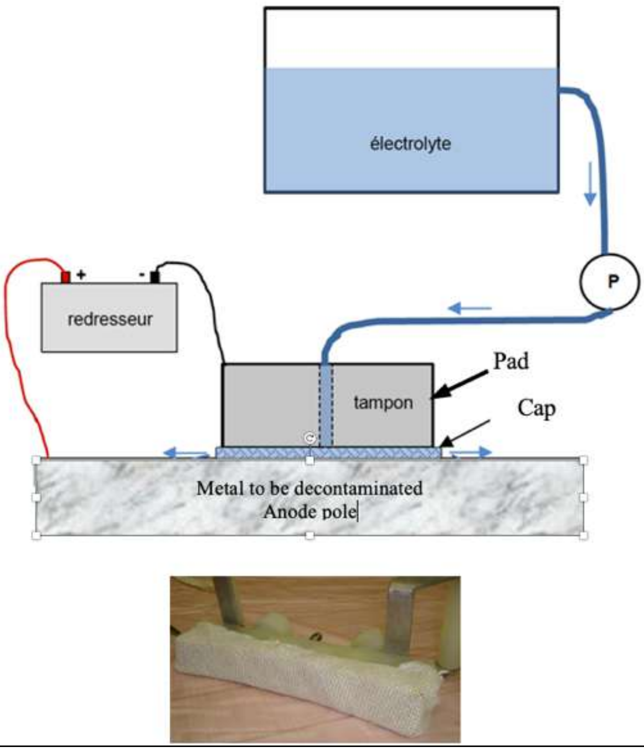


Figure 2 *:* Schematic diagram PAD + CAP - Picture of the PAD + CAP

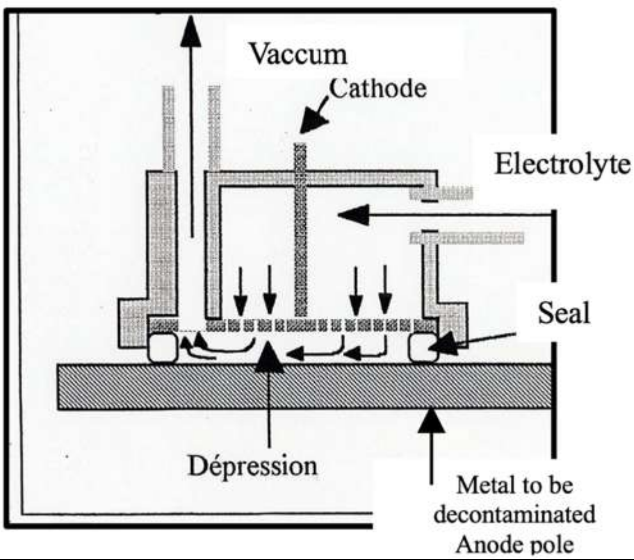


Figure 3 *:* Schematic diagram PAD + Seals

Background

904 Cell (HAO) had the function of shearing and dissolving fuel elements

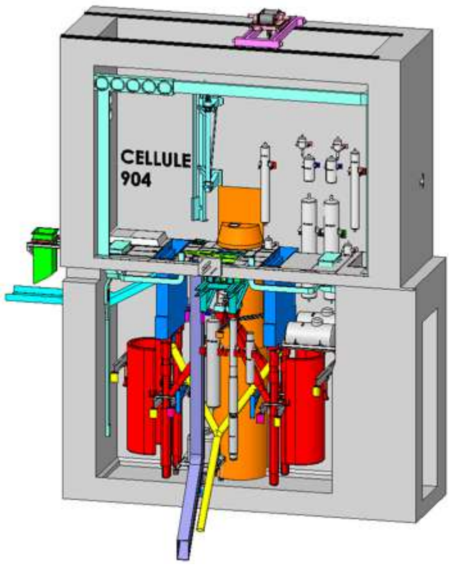


Figure 4 : 904 Cell (HAO: High Activities Oxides building)

The equipment in 904 cell is planned to be cut up and then decontaminated successively by:

- Vacuum and brushing,
- Dry ice

The fixed contamination of some waste is assumed to be too high to be compatible with Low Level and Medium Level activity wastes (3 m^3 type CBF-K). Treatment by electro-decontamination of this waste is therefore planned once it has been removed from 904 cell.

The implementation of the electro-decontamination process in the HAO (916 Cell) facility has the advantage of being able to treat the waste regardless of its level of contamination and without exposing the operators to an external dose during the decontamination operations.

New implementation – New equipment

A new electrolytic decontamination equipment using carbon brushes as conducting anode was investigated.

Indeed, since few years, Reuter GmbH has developed a new electrochemical decontamination implementation with a flexible electrode design (figures 6, 7) that guarantee an effective decontamination at all points as carbon fiber brush hug the shape of the work piece.

		
Figure 5: AC/DC Device (1500VA)	**Figure 6**: Auto-feed handle	**Figure 7**: Auto-feed carbon brush

Figure 8: Magic box (Autofeed system)

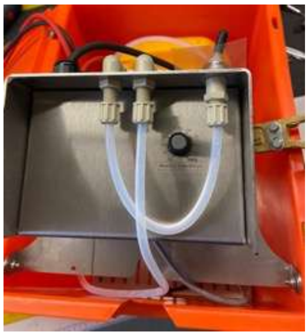


Figure 9: Potentiometer

Selection of the electro chemical decontamination equipment

The choice of the electro chemical decontamination method is conditioned by the elements to be treated (size, geometry). As waste pieces of equipment in cell 904 will have many sizes and geometries, it was difficult to use the immersion process and the mobile rigid head described above.

The decision to use the new implementation with brush was made due to the following main advantages:

- The newly developed carbon fiber brush (up to 2 million fibers are used per brush) conducts a high current to the work piece (current density up to 250 A/cm²) which induce the removal of few microns of base metal in a very short time,
- The carbon fiber brush can be automatically supplied with electrolyte,
- A microprocessor calculates the optimum amount of electrolyte fed directly into the carbon fiber brush,
- The carbon fiber brush adapts to the shape of the workpiece, allowing complex surfaces to be decontaminated,
- The new implementation allows to use it in remote conditions,
- Its portability also makes it easier to implement.

Adaptations – modifications

Choice of electrolyte and concentration of electrolyte

Choice of electrolyte

The electrochemical decontamination is used to decontaminate either in order to reduce the dose rate or to decategorize pieces to be dismantled. If the technique is applied on pieces to be reused, the innocuity of the surfaces must be guaranteed. The use of phosphoric acid more that 50% in weight allows not only to respect the innocuousness of the metal but also reduce its susceptibility to the incrustation of subsequent contamination, by reducing the roughness of the surface (electropolishing).

For pieces destined as scrap, surface finish is not at all important compared to the efficiency of the decontamination and the volume of secondary wastes produced are.

Thus, the different used processes distinguish themselves by the used electrolyte and the operational conditions.

In our case, as the pieces to decontaminate will be future wastes, nitric acid is chosen for its efficiency and its compatibility with the treatment of the effluents at La Hague plant.

The reduction of nitric acid is a complex process in which nitrogen (V) is reduced to the oxidation state (**III**) in the following overall electrochemical reaction [4].

$HNO_3 + 2\ H^+ + 2\ e^- = HNO_2 + H_2O$

This global equilibrium only reflects the change in the degree of oxidation of nitrogen and does not fully reflect the reality of the phenomenon. Thus, the reduction of nitric acid involves multiple reactions in solution or at the electrode, involving a large number of intermediate compounds.

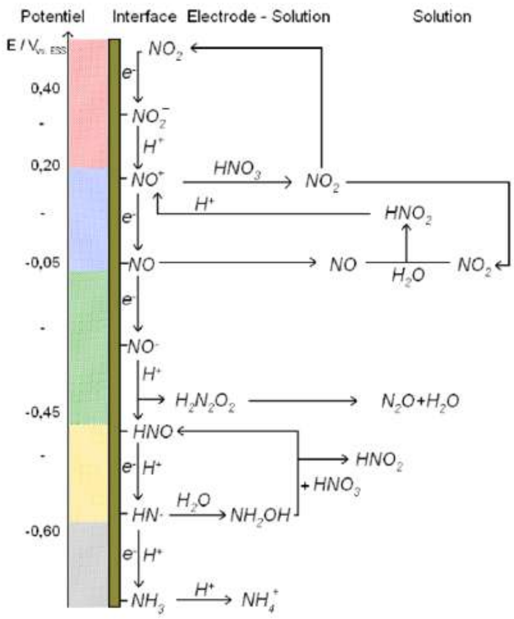


Figure 10 *:* Mechanisms of nitric acid reduction [4]

Concentration of electrolyte

The CEA developed an anodic dissolution process in drum in an HNO_3 environment for the treatment of plutonium contaminated metallic waste, ref [1-2-3]. The waste in bulk is placed in a titanium perforated reactor, polarized in anode and put in motion. The stainless-steel cathodes are placed parallel to the drum. Nitric acid is chosen for its compatibility with the treatment of the decontamination effluents and its reprocessing in case presence of PuO_2.

Figure 11: CEA Drum

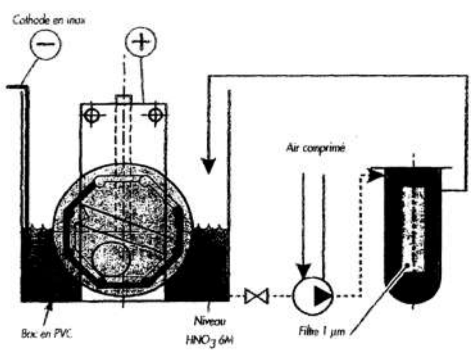


Figure 12: CEA Drum diagram [2]

Tests have shown that at constant current density, the erosion rate increases with acidity.

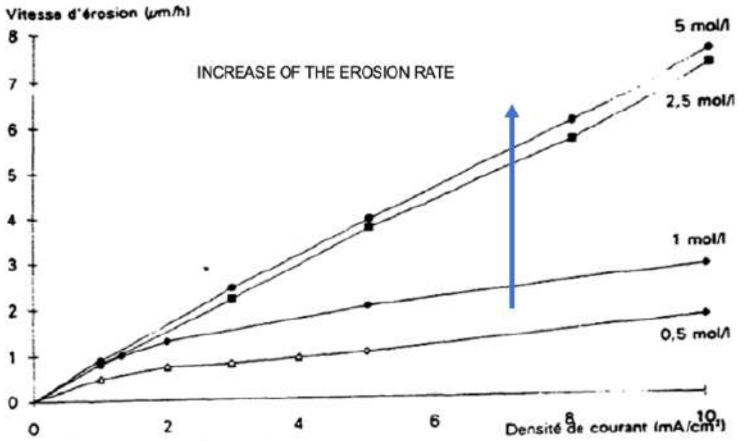


Figure 13 *:* Evolution of the erosion rate as a function of current density and nitric acid concentration [2]

As the REUTER equipment used has different parameters (U, I, current density), tests were carried out at different nitric acid concentrations from 1.5 to 6N for different voltages output. The device allows a voltage of between 6 and 12 Volts to be set, and the higher the output voltage, the higher the resulting current.

For test times of one minute, the thickness removed in µm was measured. Other parameters such as the electrolyte flow rate consumed, the surface temperature of the plate and the amount of vapor released were also recorded.

Adaptation for use in remote conditions

The purpose of this development is to adapt the existing new electrochemical decontamination equipment to allow its use in a zone where access is forbidden to humans and interventions are carried out by remote handling.

In order to represent the future use of the system, all the elements are represented in the figure 14.

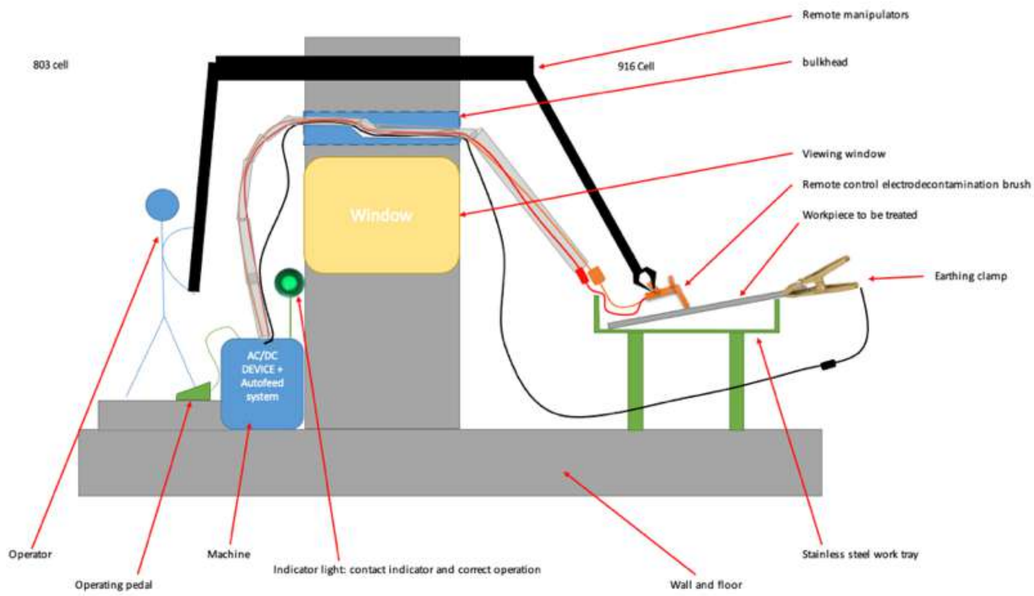


Figure 14 *: S*chematic diagram for adapting electrodecontamination to remote work

The electrochemical decontamination machine will be installed in areas accessible to humans, so preparation and adjustment operations can be carried out manually.

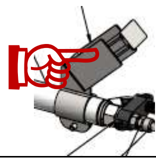
All the equipment is secured on a stainless-steel transport trolley (stainless steel 304L) at operator height equipped with castors to facilitate its handling.

	
Figure 15: Stainless-steel transport trolley (front side)	**Figure 16:** Stainless-steel transport trolley (back side)

The electro chemical decontamination brush holder will be located in zone 4 and will be in direct contact with the clamp of the remote manipulator. It must be adapted to this use.

The modifications done to the existing brush holder as seen on figure 14 concern the 3 points below:

- Increase in carbon fibre length from 60 mm to 85 mm (Figure 17)
- Teflon sleeve with « wings » to adapt its position according to the wear of the brush (Figure 18)
- Addition of gripping hoods (Figure 19)
- Specific fittings for quick change of the brush holder.

		
Figure 17: length of the carbon fibers	**Figure 18**: Teflon sleeve with « wings”	**Figure 19**: Addition of a gripping hood

It also needs to be possible to disconnect and reconnect all the power supply connections (cf Figure 20):

- In electrolyte (Staubli connector)
- Current (Jupiter connector)

Figure 20: Staubli and Jupiter connectors

Inactive conditions tests of the equipment to validate the feasibility of operations by remote manipulator

Tests were carried out in inactive conditions to validate the feasibility of using this new implementation with a remote manipulator. In particular, the following tests were carried out:

- Earth clamp connection (Figure 21)
- Change the length of the carbon fibers by turning the wings of the Teflon sleeve (Figure 22)
- Disconnecting/reconnecting the electrolyte supply connector (Staubli connector) (Figure 23)


Figure 21: Earth clamp grip test

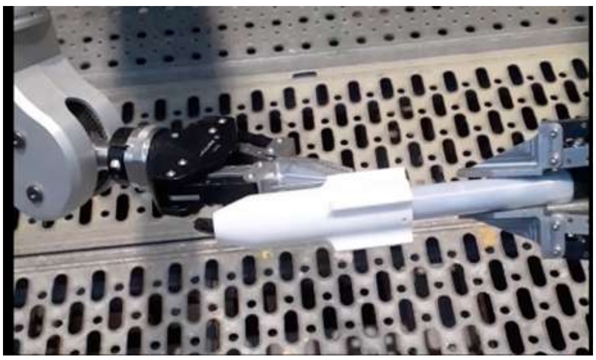


Figure 22: Fiber length modification tests

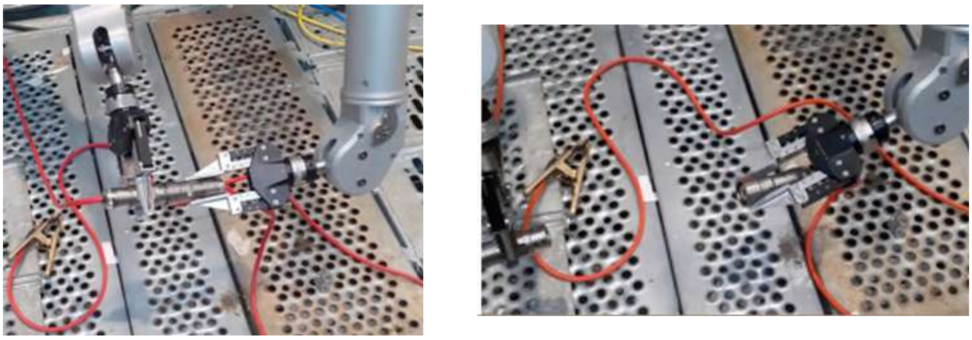


Figure 23: Disconnecting/reconnecting the electrolyte supply connector

Conclusion

The possibility to use carbon fibers instead of rigid electrodes, allow to deliver a very high current density, thus reducing the time required for the electro chemical decontamination operations. It allows to treat all shapes of metal wastes.

Its portability is also unique, making it easy to implement and a perfect partner for glovebox or cell equipment for waste clean-up.

This new implementation is not only useful as we have seen for decommissioning wastes, but it can also be used to remove hot spots or extensive decontamination of expensive or strategic parts to allow their maintenance and then their re-use.

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