

MOBILE MODULAR UNIT FOR ELECTROCHEMICAL DECONTAMINATION OF METAL SURFACES

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The article describes operation principle and design of a mobile modular unit for electrochemical decontamination of metal surfaces. It presents the experimental data on its testing which involved various real-world radioactively contaminated objects with corrosion products and layers of mechanical contamination present on their surfaces. The unit can be used to decontaminate large-size metal equipment of radiochemical plants (hot cells, glove boxes) without fragmentation, in semi-automatic mode with a minimum exposure time of personnel in the work area.

Keywords: *radioactive waste, electrochemical decontamination, radiochemical production, metal decontamination, decommissioning, hot cells.*

Dismantlement of large-sized equipment is seen as a most challenging issue in nuclear decommissioning. Commonly such equipment requires fragmentation which is seen as a laborious operation associated with radiation exposure risks involving certain releases of radioactive aerosols causing secondary radioactive contamination. Equipment decontamination at the pre-dismantlement stage can significantly increase the level of dismantlement safety.

In 2009–2017, an equipment package was developed by MosNPO RADON (hereinafter referred to as Radon) allowing in-situ electrochemical decontamination of metal surfaces with a number of installations manufactured based on this technology. This project was prompted by low efficiency and high laboriousness of operations commonly applied to decontaminate large-sized metal equipment, especially vertical and reverse horizontal surfaces. Electrochemical decontamination method was chosen

as the most effective and versatile, primarily for metal surface decontamination [1].

The decontamination method developed suggests the use of a purpose-designed tool: it is a cell held on the surface of the equipment subjected to decontamination while creating and continuously maintaining vacuum in its inner cavity. This design solution allows to decontaminate inclined, vertical and reverse horizontal surfaces with no latching devices required, which greatly simplifies the movement of the cell over the decontamination surface and significantly reduces the spills of decontamination solution. Cells of various shapes (curvatures) allow to decontaminate not only flat areas of equipment, but also cylindrically shaped ones, as well as corner joints being considered as most problematic in terms of their decontamination.

Electrolyte solution used during the process is supplied from the reservoir to a discharge area in the inner cavity of the cell fitted with an electrode

made of stainless steel 12X18H10T (if the cell is made of metal, its body serves as the electrode). Equipment subjected to decontamination is considered as the second electrode. Edges of the cell are fitted with a foam rubber gasket sealing its internal working cavity and providing electrical isolation from the equipment undergoing decontamination. This design enables reliable containment of decontamination solution inside the cavity preventing its spread during decontamination. Decontamination products (pickling sludge containing radionuclides, gases, emulsified organic contaminants) are removed together with spent decontamination solution through evacuation fitting. Figure 1 presents the layout of the cell. Figures 2 and 3 show the photographs of real cells.

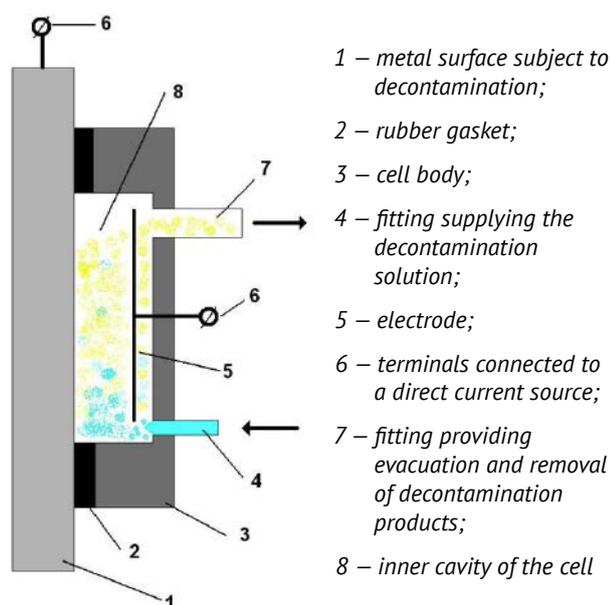


Figure 1. Layout of the cell



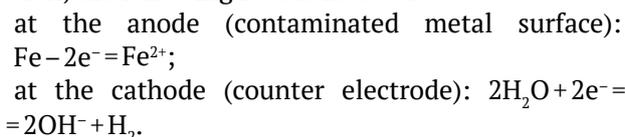
Figure 2. Stainless steel cells with an area of 0.4, 1 and 4.5 dm²



Figure 3. Cell with a 4 dm² caprolon body. In the background, a piece of metal decontaminated by this tool

Different decontamination solutions were used during the refinement of decontamination modes, namely, 1 M KNO₃, 0.5 M HNO₃, 1 % NaNO₃, 10 % NaNO₃, 1 % NaOH, 3 % Na₂CO₃. It was demonstrated that if no intense corrosion and contamination with organic substances is found on material surface subject to decontamination, neutral solution of sodium or potassium nitrate with a concentration of 0.5–1 M appears to be the best decontamination solution. Neutral solution reduces the requirements imposed on the structural materials of the installation itself, improves sanitary conditions for personnel and enables full recycling of the decontamination solution, which significantly reduces the volume of secondary RW. The specified decontamination solution can effectively remove radioactive contaminants from various metal surfaces: carbon and stainless steel, lead, aluminum. In case of surfaces with a significant organic contamination, it is advisable to use alkaline-carbonate solutions similar in their composition to those used in the industry to de-oil the metal parts [2].

Closed cycle for the decontamination solution is carried out as follows. When direct-current flow passes through sodium (potassium) nitrate solution, the following reactions occur:



In the inner cavity of the cell, interaction between anodic and cathodic half-reaction products occurs: $\text{Fe}^{2+} + 2\text{OH}^- = \text{Fe}(\text{OH})_2$. Further, under the action of anodic reaction and oxygen in the air, $\text{Fe}(\text{OH})_2$ is oxidized to $\text{Fe}(\text{OH})_3$, which actually has the composition of polymeric oxyhydroxide FeOOH [3]. Similar reactions proceed for nickel, lead and aluminum. Under the anodic process at operating

current densities (about 10 A/dm²), chromium (stainless steel component) can be oxidized to a chromium ion (directly or through chromium (III) hydroxide [4]).

Thus, sodium (potassium) nitrate is virtually not consumed at all, and the resulting sludge of insoluble metal hydroxides incorporates a significant number of radionuclides removed from the surface. Table 1 presents the distribution of various radionuclides between the pickling sludge of metal hydroxides obtained during the decontamination of 12Kh18N10T steel surface (actual part of a hot chamber) and a 0.5 M solution of potassium nitrate.

Table 1. Distribution of radionuclides between pickling sludge and reusable solution during the decontamination of steel 12Kh18N10T

Specific activity	Radionuclide				
	¹³⁷ Cs	²³⁹ Pu	²⁴¹ Am	⁶⁰ Co	¹⁵⁴ Eu
Solution, Bq/l	5.2·10 ⁴	Less than 140	Not detected	Not detected	Not detected
Sludge, Bq/kg	1.2·10 ⁶	1.5·10 ⁶	3.8·10 ⁵	8.2·10 ³	2.0·10 ⁴

After mechanical separation of hydroxide sludge by filtration or settling, the decontamination solution can be recycled. Additional treatment of the reusable decontamination solution from cesium radionuclides can be performed on a sorbent.

Under certain conditions, when the surface subject to decontamination is covered with a thick layer of corrosion products, soot, oil, etc., deactivation rate and efficiency increases if the process is carried out in a reverse mode, when the polarity of the electrodes changes cyclically. Under cathodic polarization, passivating anode films (on stainless steels) are destroyed, corrosion products and organic contaminants are mechanically detached by the evolved hydrogen bubbles, and oil and fat contaminants are emulsified [2, 5]. Duration of the cycles and the ratio of anodic and cathodic polarization times in the course of a cycle are selected experimentally depending on specific conditions. Thus, for example, to deactivate 12Kh18N10T steel surface at a current density of 10 A/dm², the following optimal ratio was selected: anodic polarization of the contaminated surface for 5 min+cathodic polarization for 1 min. Then the cycle was repeated until the required degree of decontamination was achieved. As shown by a number of experiments, as well as for reasons of electrical safety, the voltage between the cell electrode and the contaminated surface should be reduced to 12–15 V.

Figure 4 shows a simplified flowchart for a mobile electrochemical device providing closed solution cycle.

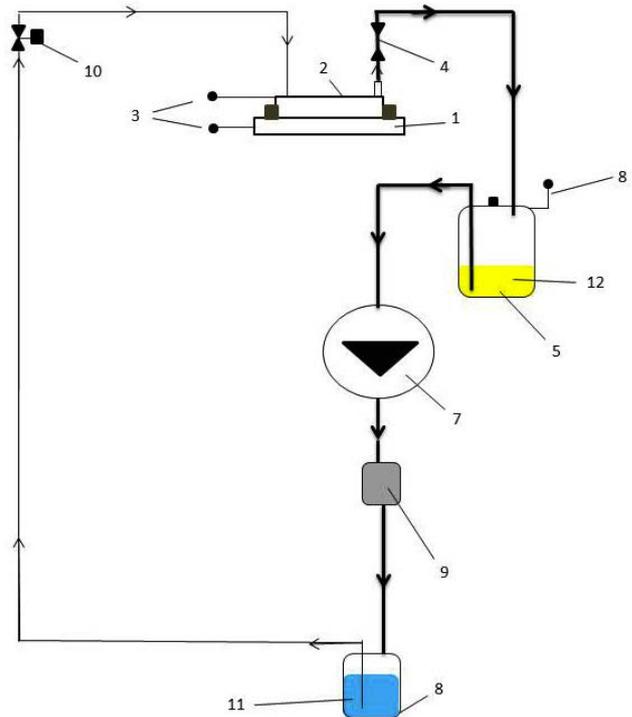


Figure 4. Flow chart according to a closed solution cycle:

- 1 – contaminated surface; 2 – cell; 3 – terminals;
- 4 – vacuum line valve; 5 – spent decontamination solution; 6 – vacuum gauge; 7 – vacuum pump; 8 – tank for decontamination solution; 9 – regeneration system for decontamination solution (mechanical and ion-exchange filters); 10 – valve supplying decontamination solution; 11 – treated decontamination solution; 12 – vacuum receiver

Closed cycle operation occurs in the following way. A pump is used to create vacuum in the vacuum receiver and after the required level is reached, the cell is installed on the contaminated surface area and, when the vacuum line valve is opened, is attached on it. The vacuum pump operates throughout the entire decontamination cycle: pump designs should provide the pumping of not only the air, but also of liquid-gas mixtures (industrial peristaltic pumps, for example, NP-25 type or foreign analogues comply with this requirement). After opening the supply valve, the decontamination solution automatically (under atmospheric pressure) flows into the working cavity of the cell. Voltage is applied to the deactivated part and the electrode of the installation supplied by a direct current source. Spent decontamination solution together with the pickling sludge and electrolysis gases is removed through a vacuum line into the receiver, from where it is pumped through a mechanical filter and ion-exchange column with a sorbent using the same pump. Treated decontamination solution enters the supply tank again.

Several options of the flowchart presented above were tested on various real-world objects:

Table 2. Decontamination results for various objects

Initial contamination	Decontamination mode	Residual contamination	Decontamination factor
Stainless steel sheet from the flue of RW incineration plant. The surface is covered with a continuous thick layer of soot			
36 β -particles/(cm ² ·min) 36 α -particles/(cm ² ·min)	Reversible. Length of anodic and cathodic periods – 5 minutes each. Total treatment time – 15 minutes. Solution flow rate – 0.37 l/min. Electric current density – 6-10 A/dm ²	2–3 β -particles/(cm ² ·min) 2–4 α -particles/(cm ² ·min)	15.7
Stainless steel sheet from a hot cell. The surface has a slight coating of corrosion products			
13 β -particles/(cm ² ·min) 125 α -particles/(cm ² ·min)	Anodic. Total treatment time – 30 minutes. Solution flow rate – 0.3 l/min. Electric current density – 10 A/dm ²	2–4 β -particles/(cm ² ·min) 2–3 α -particles/(cm ² ·min)	5.8 for β -emitters, 53.5 for α -emitters
Hot cell stainless steel sheet with small spots of brown corrosion products			
4500 α -particles/(cm ² ·min)	Reversible. Duration of anode period – 2 min, duration of cathode period – 1 min. Total treatment time – 15 minutes. Solution flow rate – 0.21 l/min. Electric current density – 10 A/dm ²	3–4.5 α -particles/(cm ² ·min)	1,216
Stainless steel sheet from a hot cell with small spots of brown corrosion products			
10000 α -particles/(cm ² ·min)	Reversible. Length of anode period – 2 min, duration of cathode period – 1 min. Total treatment time – 30 min. Solution flow rate – 0.2 l/min. Electric current density – 10 A/dm ²	5–8 α -particles/(cm ² ·min)	1,577
Hot cell stainless steel sheet. Approximately 40-50% of the area is covered with a thick layer of brown corrosion products			
3700 α -particles/(cm ² ·min)	Reversible. Length of anode period – 2 min, duration of cathode period – 1 min. Total treatment time – 5 minutes. Solution flow rate – 1.0 l/min. Electric current density – 10 A/dm ²	9–10 α -particles/(cm ² ·min)	368
Hot cell stainless steel sheet with deep “craters” on the surface with corrosion products			
5400 α -particles/(cm ² ·min)	Reversible. Length of anode period – 2 min, duration of cathode period – 1 min. Total treatment time – 30 min. Solution flow rate – 0.2–0.33 l/min. Electric current density – 10 A/m ²	11 α -particles/(cm ² ·min)	487
Hot cell stainless steel sheet having matt surface, light gray metal			
1900 α -particles/(cm ² ·min)	Reversible. Length of anode period – 2 min, duration of cathode period – 1 min. Total treatment time – 15 minutes. Solution flow rate – 0.33 l/min. Electric current density – 10 A/dm ²	5–7 α -particles/(cm ² ·min)	317
Hot cell stainless steel sheet having light gray matt surface			
340 α -particles/(cm ² ·min)	Reversible. Length of anode period ranging from 2 up to 4 min, length of cathode period – 1 min. Total treatment time – 24 min. Solution flow rate – 0.34–0.64 l/min. Electric current density – 10 A/dm ²	0.9 α -particles/(cm ² ·min)	378

contaminated parts of RW processing units, transport containers, inner surfaces of hot chambers and glove boxes operated in “hot” laboratories.

In many cases, mobile electrochemical unit showed high efficiency. For example, flat surfaces made of stainless steels (shelves of hot chambers) with an initial level of contamination of 4–12 thous. α -particles/(cm²·min) can be decontaminated to a level of 3–10 α -particles/(cm²·min) at a current density of 10 A/dm² in a reverse mode in one cycle lasting 5–45 min. The required treatment time depends on the initial state of the surface and the electrical current density. Repeated treatment of the same area can reduce the surface

contamination to less than 1 thous. α -particles/(cm²·min). Table 2 overviews some of the results obtained.

Figures 5–7 show the appearance of contaminated surfaces after decontamination.

Availability of non-conductive paint and varnish coatings, deep dents, thick layers of corrosion products on metal surfaces greatly reduces the decontamination efficiency (in the latter case, the treatment time of a section should be significantly increased). Metal surfaces with a continuous layer of mill scale (Fe₃O₄) are practically not amenable to electrochemical decontamination in a neutral electrolyte. However, such items are very uncommon.



Figure 5. Flue section of RW incineration unit with an area of 1 dm² cleaned from soot and radionuclides using a mobile unit. Gas duct is made of stainless steel 12X18H10T

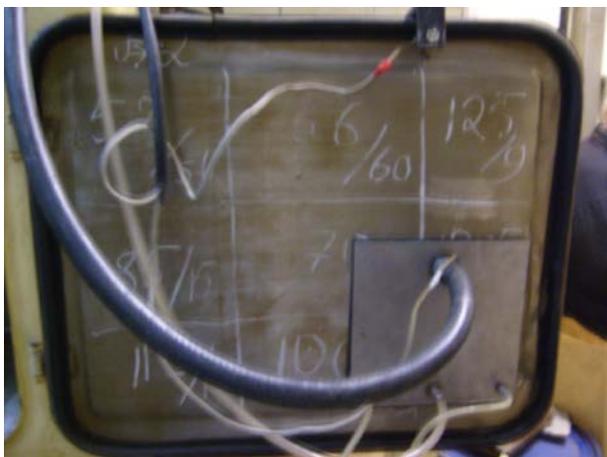


Figure 6. Cell on a glovebox door

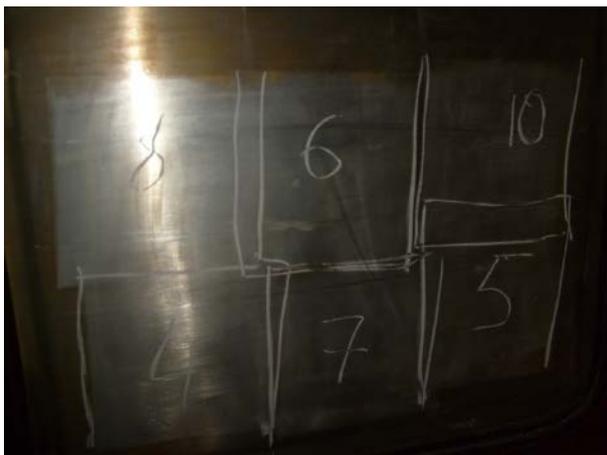


Figure 7. Sections marked on a glove box door that have been decontaminated using a mobile unit. The area of each section accounts for 4 dm²

Further refinement of this decontamination technology resulted in a mobile unit enabling the decontamination of flat horizontal, inclined, vertical surfaces, which operates in a closed cycle mode

providing solution treatment and recycling. The installation provides the decontamination of premises and equipment before their fragmentation to reduce radiation loads on personnel. It also allows to decontaminate the surfaces of existing equipment enabling its further safe use.



Figure 8. Modular unit for electrochemical decontamination (module box covers were removed)

The final design of the unit (Figure 8) involves a modular structure assembled on site using flexible rubber hoses with threaded fittings. Each module is a stainless-steel box, inside of which various installation units are located. Each box operates under a vacuum of at least 200 Pa excluding spillages of a radioactive solution in case of main equipment depressurization. Control panel displays the controls for the electric drives of the pump, the exhaust fan, gate valves and solenoid valves. It also displays readings of the temperature and decontamination solution levels in the tanks, vacuum in the vacuum system and the working space of the boxes, hydraulic resistance of filters and solution flow rate through the deactivation cell. The unit includes a direct current source of an original design equipped with an electronic timer providing operation according to a given program (including its operation in a reverse mode).

Unit designs have been patented [6, 7].

References

1. Ampelogova N. I., Simanovskiy Yu. M., Trapeznikov A. A. *Dezaktivatsiya v yadernoy energetike* [Decontamination in nuclear power]. Ed. by V. M. Sedov. Moscow, Energoizdat Publ., 1982. 256 p.
2. Belenkiy M. A., Ivanov A. F. *Elektroosazhdeniye metallicheskih pokrytiy* [Electrodeposition of metal coatings]. Handbook. Moscow, Metallurgiya Publ., 1985. 292 p.

3. Chalyy V. P. *Gidrookisi metallov (zakonomernosti obrazovaniya, sostav, struktura i svoystva)* [Metal hydroxides (patterns of formation, composition, structure and properties)]. Kiev, Naukova Dumka Publ., 1972. 160 p.

4. *Spravochnik po elektrokhemii* [Handbook on electrochemistry]. Ed. by prof. A. M. Sukhotin. Leningrad, Khimiya Publ., 1981. 488 p.

5. *Gal'vanotekhnika* [Electroplating technology]. Moscow, Metallurgiya Publ., 1987. 736 p.

6. Ustanovka dlya elektrokhimicheskoy dezaktivatsii metallicheskih poverkhnostey [Installation for electrochemical decontamination of metal surfaces]. Patent №2448380 Russian Federation,

IPC G21F 9/28. / Barinov A. S., Karlina O. K., Yurchenko A. Yu., Nikolaev A. N.; Applicant and patent holder — State Unitary Enterprise MosNPO Radon — No.2010142626/07; application date: 19.10.2010; publication date: 20.04.2012.

7. Ustanovka dlya elektrokhimicheskoy dezaktivatsii metallicheskih poverkhnostey [Installation for electrochemical decontamination of metal surfaces]. Patent №2453939 Russian Federation, IPC G21F 9/28. / Barinov A. S., Karlina O. K., Yurchenko A. Yu., Nikolaev A. N.; Applicant and patent holder — State Unitary Enterprise MosNPO Radon — No.2011106385/07; application date: 22.02.2011; publication date 20.06.2012.

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