

Experiments on rehabilitation of radioactive metallic waste (RMW) of reactor stainless steels of Siberian chemical plant

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Abstract. Stainless steel pipes, used to cool a reactor plant, have a high cost, and after taking a reactor out of service they must be buried together with other radioactive waste. Therefore, the relevant problem is the rinse of pipes from contamination, followed by returning to operation.

1. Introduction

The acuteness of the problem was how to deal with the pipes of the first cooling circuit of a reactor, taken out of service. Pipes made of expensive stainless steel (X18H9T) had a contamination of both external and internal surfaces. They could be buried as radioactive waste, or one could try to “rinse” them to acceptable values of β - and γ -activity, take them off the books and return them to the production cycle. The latter was more preferred.

2. Experiment

These were the so-called weakly fixed deposits. Whereas external contamination of pipes was formed by deposition of radioactive aerosols, the internal surface of the same pipes had a film with thickness of about 0.5 mm, formed due to the deposition of water impurities at temperatures less than 100 °C. Research of film composition has shown that it is composed of oxides of elements: 48-63% Al_2O_3 ; 17-21% Fe_2O_3 ; 6-17% MgO and CaO 14-21% SiO_2 ; less than 0.39% CrO_2 and NiO_2 and contaminated by radioactive isotopes ^{60}Co , ^{137}Cs , ^{152}Eu . Under certain conditions, a film of pipes of “cold” leg was easily removed and thus was weakly fixed. This could mean that it has no strong chemical or epitaxial substrate. In appearance, it had pale brown color and looked like a scale. By speculating about scale and how it is removed in steam boilers, we came to the conclusion that alkaline solutions NaOH (potash) can be used.

The advisor on this issue, Prof. N.A. Kolpakova proposed not to use ready alkali NaOH , but to obtain it in the process of electrolysis of NaCl solution. In this case, chemical effect of NaOH , formed at the cathode (of the rinsed surface) will be intensified by the flowing of current.

The next step was to select the material of anode. There were two possibilities: either stainless steel or graphite. The benefits of graphite were quickly revealed. The specific resistance of graphite is about 10 times higher than that of steel, so graphite caused higher voltage on the cathode surface and decomposition of NaCl . At the same time, when current densities are suitable for rinse, ($\sim 1000 \text{ A/m}^2$) a steel electrode, made of stainless steel, is exposed to partial electrodisolution of its components, and especially chromium, having a lower potential of electrodisolution than other stainless steel



components. Chromium is deposited on the rinsed surface in the form of crystals of deep black color, preventing the rinse.

Further, optimizing the process according to current density, concentrations of NaCl and time of electrolysis, the results, shown in Table 1 and the figure, were obtained.

Table 1. The results of electrolytic rinse when the concentration of salt is 40 g/l

Sample number	Electrolysis conditions		Contamination $\frac{\textit{before}}{\textit{after}}$		Note
	Current, A	Time, min	Beta, min^{-1}	Gamma, $\mu\text{R/hr}$	
1	30	20	$\frac{1200}{10}$	$\frac{170}{42}$	pH = 6.5
2	30	25	$\frac{580}{10}$	$\frac{724}{34}$	pH = 6.0
3	30	20	$\frac{220}{20}$	$\frac{247}{40}$	pH = 6.0
4	30	40	$\frac{1000}{30}$	$\frac{159}{45}$	pH = 6.0

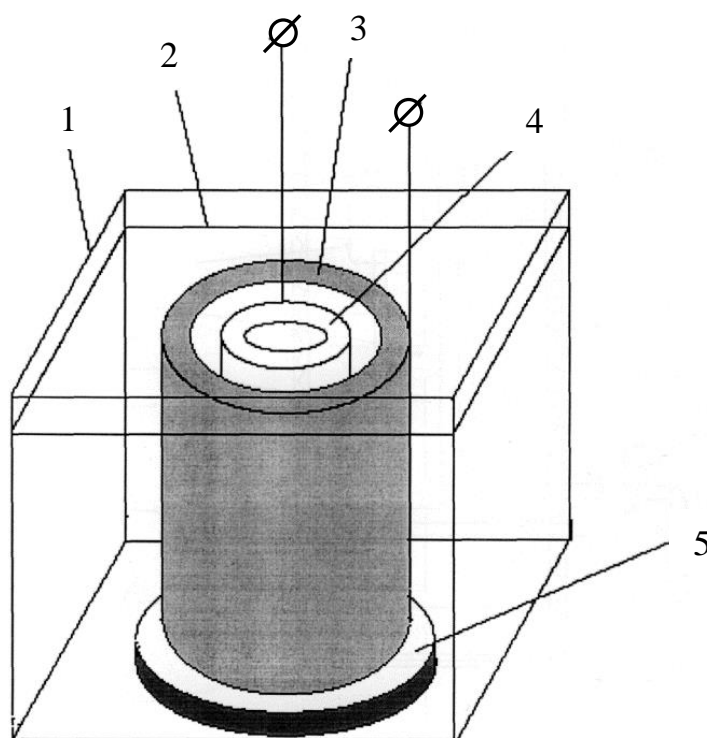


Figure 1. Installation diagram for deactivation: 1 – vessel with capacity of 9 liters; 2 – electrolyte level; 3 – rinsed pipe – first electrode; 4 – second electrode; 5 – rack-insulator for electrodes.

The analysis of obtained results led to the important conclusion that the porosity of a rinsed film has crucial importance for the process of rinse, if it is well wetted, due to good porosity, the process

goes successfully. In this case, long-term “soaking” of samples can help. The driving force of further process of electrolysis is the formation of H₂ bubbles at the film-substrate interface, whereby the oxide film is peeled off almost without dissolving, that reduces LRW. Experiments have also shown that the external contamination of pipes is removed when there is a simultaneous impact on internal contamination.

3. Results and discussion

Research [1, 2] has shown, that the composition of such a film is a mixture of oxides, formed as a result of both corrosion of the shells of fuel elements and circuit walls, and water impurities, Table 2.

Table 2. Composition of deposits on the internal surface of pipe samples of “hot” branch of cooling, wt. %

Substance	Data of authors [1]		Data of authors [2]
	Scale of light brown color	Scale of red-brown color	
Al ₂ O ₃	60.4	38.6	71.0-17.0
Fe ₂ O ₃	2.86	9.8	15.2-1.2
MgO, CaO	2.0	7.9	1.0-0.0
CuO	0.14	-	0.10-0.01
Cr ₂ O	0.2	0.16	0.6-0.0
NiO	0.06	0.22	2.19-0.03
SiO ₂	10.0	8.2	21.8-1.0
SO ₄ ⁺²	2.35	0.86	3.9-0.9
P ₂ O ₅	-	4.5	19.1-2.1

Such polyoxide deposition is firmly fixed, since it was formed at increased temperatures close to 200 °C. This was pointed out in [3, 4], in which, inter alia, it is stated that under conditions of operation of nuclear power plant with RBMK, a film is formed on steel OH18N10T. This film consists of maghemite and mixed spinels of iron, chromium and nickel of common composition [Fe, Ni]O[Fe, Cr]₂O₃. It is assumed that the film is formed and is growing both due to adsorption of oxygen on metal surface, and due to the solid-state diffusion mechanism. In this case, thin films are formed, with thickness of tens of angstroms, dense with low porosity, protecting metal.

Attempts to remove an oxide film in a single step electrolytically in solution of sodium chloride were unsuccessful. The result was not affected by the changes in external conditions: electrolyte concentration, its temperature, handling time, current density and change of electrode polarity. However, there was a partial reduction of radioactivity according to beta particles by 5-7 times, but it still remained unacceptably high: up to 50 or more particles (cm²·min).

From the previous experience it was concluded that the efficiency of the electrolytic method of deactivation in our case depends on the permeability of the film, i.e. on its porosity. This is indicated by the fact that pre-exposure of the samples in solution significantly improves the result of the electrolytic deactivation and reduces its time. The solution wets an oxide film, and the effect of the current destroys it. If the pre-exposure (i.e. chemical handling) is not performed, the oxide film is not removed, deactivation factor is negligible.

Special experiments were carried out to determine the porosity of polyoxide film. When carrying out experiments on the electrolytic removal of firmly fixed deposits, we used:

- many hours of “soaking” of samples in the background electrolytes;
- as background electrolyte we used acids, affecting the components of oxide film (NaCl, H₃PO₄, HNO₃, HCl), and the mixture of acids leading to formation of soluble complexes (30 g/l H₃PO₄ + 50 g/l HNO₃ + 20 g/l H₂C₂O₄).

The most successful experiences on rehabilitation were the experiments with sample №5.

Sample №5 was subjected to the rinse in anodic mode in solution of common salt, handling time is 30 minutes, current density is 100 mA/cm², exposure in nitric acid solution (60 g/l) is 96 hours, handling in anodic mode in solution of nitric acid (60 g/l). The anodic handling was performed in the acid solution under the following conditions: handling time is 1 minute, current density is 3000 mA/cm², the solution is boiling [5, 6].

Table 3. Deactivation results

Sample number	Radioactive contamination / dose rate of ionizing radiation			$\frac{frequency}{min \cdot cm^2} / \frac{\mu Sv}{hr}$	
5	internal	2600/4.60	490/3.2	40/0.31	natural background
	external	96/2.07	75/2.5	14/0.12	natural background
Note	Baseline characteristics	Handling in NaCl	Soaking in HNO ₃	Electrolysis HNO ₃	

4. Conclusion

1. A combined method to rinse stainless steel scrap from firmly fixed and weakly fixed polyoxide deposits saturated with radionuclides has been proposed.

2. The essence of the method lies in the combination of chemical and electrolytic methods of deactivation. The first step included a many-hours exposure of contaminated sample in alkali or acid solution (electrolyte), and the second step included short electrolytic handling in the same solution in the anodic mode.

3. The holding time in the first step depends on the porosity of deposit. The worse the porosity, the longer the exposure, which is determined experimentally.

4. The current density of electrolysis is low, 100-600 mA/cm², electrolysis time is up to 10 minutes, which provides the surface quality.

5. Unlike the method of chemical deactivation, the concentrations of solutions (electrolytes) refer to "soft" ones, not more than 2-3%.

6. The number of steps and the type of electrolyte depend on the number and type of oxide components, as well as their partial concentration (usually 15-17% or more).

7. The sequence of steps is the following: first, the alkaline electrolytes are applied and oxides are exposed, reacting in alkali, and then acid solutions are applied. At that, in the final step, a solution of the acid is used, which can react with metal and can remove its surface layer containing radioactive contamination.

References

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- [5] Patent № 241746 dated 27.04.2011.
- [6] Patent № 154091 dated 19.12.2014.