

HIGH-TEMPERATURE DECONTAMINATION OF METAL SCRAP

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ABSTRACT

Decontamination of radioactive waste metal scrap (RWMS) is of vital importance because of its ever growing amount and the lack of potential disposal sites.

Early in the 90s a technique was developed and tested for high-temperature decontaminating heavy RWMS from ship building. The research was suspended due to cutting off funding but resumed later by joint efforts of VNIINM and SIA "RADON". The adaptation of the technique for other RWMS, radionuclide loss mechanisms and choice of relevant equipment were the objectives. As a result, the high-temperature decontamination technique (HTDT) adapted to cleaning local contaminants away from metal surfaces has been improved.

HIGH-TEMPERATURE DECONTAMINATION TECHNIQUE

The radioactive bulk is known from numerous studies to be located within metal pores, essentially at the surface (to a depth of ~2-10 mkm). So metal surface descaling results in its cleaning. The challenge was in initiating a high-speed corrosion of the RWMS surface and in sticking radionuclides and a decontaminating agent together. Thus, the HTDT developed depends on a high-speed controlled corrosion of RWMS treated with decontaminants based on Cl-, F-, S- and P-bearing compounds as well as on the interaction between these agents and contaminants (Patent priority 95111176 of 10.01.96).

The HTDT process can be illustrated by the example of stainless steel. High-temperature heating results in oxidizing primarily Fe, Cr, Ni to form a solid oxide layers. The oxides developed interact with a decontaminant, with a subsequent destruction and scaling at the alloy body surface. In a suitable temperature range, the decontaminant enables the corrosion of the carbon alloy to proceed at a high speed in the liquid phase. The decontaminant reacts with radionuclides as well to form readily removable chemical compounds. On cooling, the cracked loose scale developed can be cleared out of the metal surface along with radionuclides adhered.

As for radionuclides which are volatile at low temperatures, the high-temperature decontamination can be implemented by two steps: the **first** - producing either poorly sublimated

strippable scales; second - volatile products with large molecules which are easily caught by filters in the effluent gas purification system.

An investigation into the effect of a variety of decontaminants, treatment temperature and time, the number of treatment cycles on the decontamination of three sets of RWMS has been performed by VNIINM.

The **first set** involved sheets 0.3 mm thick 20 mm long 10 mm wide which were cut out of nuclear reactor primary circuit stainless steel tubes contaminated primarily with Co-60 up to $3.9 \cdot 10^4$ - $4.9 \cdot 10^5$ Bq/sample. In this case the efficiency of various decontaminants applied at the same temperature for the same time was determined. The time dependence at optimum temperature was also studied.

The **second set** represented Rascig rings (20 by 40 by 1.5 mm) sampled from nuclear fuel reprocessing facilities, which had been in operation for many years. Spectroscopy evidenced the presence of Cs-137, Co-60, Sb-125 and small Pu-239 amounts. The total radioactivity was (1.5 - 4.3) 10^3 Bq/sample. The candidate decontaminants chosen in the first set experimentation were put to tests.

The **third set** samples were modeling stainless steel plates contaminated with volatile radionuclides such Cs-137 (2.3 - 4.5) 10^4 Bq/sample, Ru-106 (1.9-2.1) 10^4 Bq/sample and Pu-239 (6.4-7.5) 10^3 Bq/sample by artificial means. For this purpose the metal plates were contaminated to radionuclides nitrate solutions, air dried, treated with a decontaminant and heated in a muffle. On cooling, the loose scale developed was stripped from the sheet along with radionuclides adhered to the scale. If necessary, the cycle could be repeated until the decontamination was perfect. After each cycle variations in the sample weight and contamination level were measured.

The experiments made it possible to specify the optimum decontamination and descaling conditions, the best decontaminants, relevant equipment and a procedure for catching gaseous effluents.

An experimental HTDT facility consisted of a muffle, an air pipe cooler, a filter, a float-type flow meter and a backing pump. Temperature was measured with a Chromel-Alumel thermocouple. Alpha- beta- and gamma- activity was detected with scintillation detector. The cooling and descaling were performed under water.



Fig 1. The experimental HTDT facility

It follows from the experiments that:

- chosen decontaminants are adequate to yield as high decontamination factors as 8200-9500 for refractory radionuclides (the first RWMS set) and 310-880 for the second RWMS set;
- total decontamination requires two cycles of treatment;
- with special agents and conditions the HTDT is efficient in confining volatile radioactivity within the scale. About 86-97 % Cs-137 is trapped with the scale, the filter activity being at the background level. A single treatment of Ru-106 - contaminated metal surfaces yields their 96-98% decontamination, 60% Ru-106 confined within the scale, the rest on the filters in the effluent gas purification system. Also, the scale catches 90-92% Pu-239, its aerosol loss being very small.

It should be noted that the decontaminant composition and the treatment time have an essential effect on radioactive aerosol loss and decontamination levels. Chlorine-bearing agents are found to be the best in this respect. Besides, the longer is the process, the better results.

Metal losses in the HTDT process evidence small amounts of secondary solid waste (0.1% of the weight of materials treated). It is also evident from the experiments that with proper decontaminating agents and conditions the HTDT works well, irrespective of the contamination type and level.

Table I. The contamination distribution on samples depth.

<i>Thickness of remove layer, mm</i>	<i>Sample 1, Bq/sample</i>	<i>Sample 2, Bq/sample</i>
0	$3.0 \cdot 10^5$	$7.0 \cdot 10^5$
0.002	$2.0 \cdot 10^4$	$3.5 \cdot 10^4$
0.003	$2.5 \cdot 10^4$	$4.0 \cdot 10^4$
0.004	$1.5 \cdot 10^4$	$3.5 \cdot 10^4$
0.005	$1.6 \cdot 10^4$	$3.7 \cdot 10^4$
0.006	$1.5 \cdot 10^4$	$1.8 \cdot 10^4$
0.007	$0.9 \cdot 10^4$	$0.9 \cdot 10^4$
0.008	$0.8 \cdot 10^4$	$0.75 \cdot 10^4$
0.010	$0.8 \cdot 10^3$	$0.8 \cdot 10^3$
0.012	$0.6 \cdot 10^3$	$0.7 \cdot 10^3$
0.013	$0.2 \cdot 10^3$	$0.2 \cdot 10^3$
0.014	$0.1 \cdot 10^3$	$0.1 \cdot 10^3$

Descaling is an important part of the process. A variety of mechanical abrading procedures by various materials has been tested. Shot-blast cleaning is found to be also suitable. The abrasive and sand-blast treatments can replace aqueous descaling procedures resulting in secondary liquid and aerosol waste.

The HTDT offers:

- maximum removal of radioactivity from metal surfaces irrespective of the chemical composition of a metal to be cleaned and the isotopic composition of contaminants;
- small volume of secondary solid waste ;
- no liquid radwaste;
- no expensive equipment.

THE METHOD OF THERMOSORPTION DECONTAMINATION OF METAL

The method of thermosorption decontamination of metal was first proposed in SIA “Radon”. This method is realized by means of contact heating of the radionuclide contaminated surface of metal with help of exothermic metallic compositions (EMC) [1]. The heat combustion of EMC is about 25-27 MJ/kg. Temperatures from 300° to 1500° C and higher (depending on the composition of EMC) are overreached in the process of flameless combustion of EMC on the contaminated surface during 10 - 20 min. The radionuclides are desorbed from material due to heating after that they are adsorbed by colder layer of reacted products of combustion in the form of slag. The slag has porous structure with highly developed interface providing adsorption of radionuclides. After cooling the slag is removed mechanically jointly with contamination.

EMC represent highly metallised powder compositions with different additives, which provide ignition, burning, adsorption etc. [1-2]. Variation in composition as well as sort and amount of technological additives provide main parameters of decontamination process: temperature and duration of heating as well as adhesion strength between obtained slag and decontaminated surface.

The thermo-sorption decontamination of metals on the base of microthermocouples and microgravimetric measurements can be represented as a two stage process of EMC 1 combustion, which provides desorption of radionuclides from the surface of metals 2 and their fixation on the combustion products (slag) 3 (see Fig.2a).

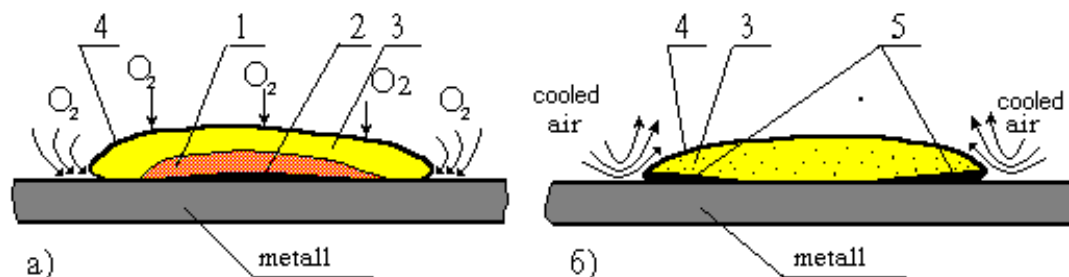


Figure 2. The scheme of thermo-sorption decontamination of metal surfaces.

The first stage of process represents a fast spreading of combustion wave (with linear velocity 1 cm/s) from the ignition point through whole area of EMC layer due to own oxidant (its fraction being 2-3%) and air oxygen. The first stage ends with the formation of a durable slag layer 4 with a few mm thickness on the surface of EMC, that consists mainly of metal oxides. During the second stage enough slow oxidation of EMC occurs (with the linear velocity about 1 mm/min) mainly due to air oxygen which diffuses downward through combustion products layer. Due to heat combustion release the temperature of metal increases up to 600° - 1000°C. At these temperatures the desorption of radionuclides occur from the surface of metal and their conversion into gaseous phase. The combustion of EMC occurs in diffusion regime. While the temperature of the metal grows up to 600°C and higher the permeability of slag layer 3 increases and the oxygen flux is provided due to peripheral inflow of air (Fig.2b) which retains radionuclides under the layer of burning EMC. Accordingly with our estimations the linear velocity of air is higher than 1 m/s. Since Peclet number $Pe \gg 1$ the convection diffusion is stronger than Brown diffusion. While the combustion process ends this convection flow decreases as well as the temperature of peripheral areas of slag carcass. The temperature of metal near the boundaries of the slag layer is higher than the temperature of slag carcass because high heat conductivity of metals. As a result radionuclides spread into the gap between slag and metal from the central part to peripheral areas where they are settled to the colder slag 5 due to thermophoresis which occurs in the gap between warm metal and cold slag. At temperature gradient about 100 K/cm the efficiency of thermo-precipitation reaches 99% at air flow velocities about 1 m/s [3]. Therefore the radionuclides release into environment not exceeds 1%.

Proposed model of decontamination process is confirmed by autoradiographical images of stainless steel surface contaminated by Cs-137 before and after decontamination as well as by autoradiograms of produced slag carcass (Fig.3).

The efficiency of decontamination of metal surfaces K was calculated by formula $K = [(A_0 - A_f)/A_0] * 100\%$, where A_0 - radioactivity of metal surface before decontamination, A_f - radioactivity of metal surface after decontamination.



Figure 3. Autoradiographical images of stainless steel surface contaminated by Cs-137 before (a) and after (b) decontamination and autoradiogram slag surface which contacted with contaminated metal(c).

The results of experiments showed that the efficiency of decontamination of carbon and stainless steel depends mainly on surface heating temperature (Fig.4).

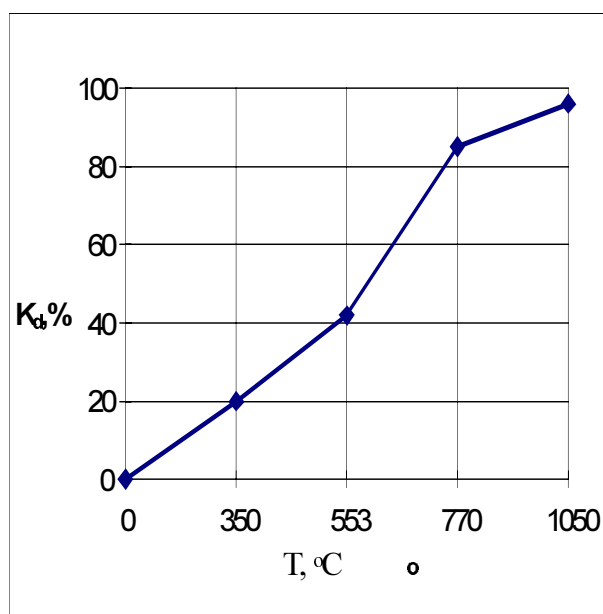


Figure 4. The dependence of efficiency of decontamination on surface heating temperature.

As one can see from this figure practical complete decontamination of steel can be achieved through one step of decontamination process if the temperature overreaches 1000° C.

Now SRC VNIINM and Moscow SIA “Radon” developed a combined high temperature decontamination technique, which use both earlier methods: additional oxidation of contaminated metals + high temperature action of burning EMC on surface. The new thermal decontamination technique consists of preliminary treatment of surface to be decontaminated by two layers. The first layer consists of reagents able at high temperatures to oxide metal to be decontaminated without oxygen. The second layer consists of an EMC which being burnt maintains necessary temperature during enough long period of time near the surface of metal. Application of new decontamination technique increase efficiency of decontamination of metals 3-5 times. Moreover by using new method it is possible to decontaminate metals which have enough deep contamination. Due to protective properties of slag produced after burning of EMC (e.g. sorption of radionuclides in slag layer) it is possible to carry out decontamination procedure without additional protective equipment. Main advantages of new decontamination technique are as follows:

- simple and inexpensive equipment,
- no liquid waste produced during decontamination,
- small amount of secondary waste (0,1% of total mass of scrap),
- high efficiency,
- no power consumption,
- on-site treatment of assembled parts,
- independence of heat source and no necessity of heating of materials,
- protective properties of slag produced after decontamination.

CONCLUSIONS

- It can be concluded from the study that the HTDT offers the following benefits:
- high efficiency for RWMS irrespective of the type and level of contamination;
- low radioactive aerosol loss due to the adhesion of their majority (85-97%) to corrosion-induced scale;
- small amount of secondary solid waste (no more than 0.1%).

LITERATURE

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