



^{137}Cs AND ^{90}Sr PHASE TRANSITIONS IN SURFACING OF RADIOACTIVELY CONTAMINATED METAL STRUCTURES

A.A. ENNAN¹, S.A. KIRO¹, M.V. OPRYA¹, V.E. KHAN², B.I. OGORODNIKOV², V.A. KRASNOV²,
A. de MEYER-VOROBETS³, L. DARCHUK³ and B. HOREMENCE³

¹Physical-Chemical Institute for Environmental and Human Protection, NASU, Odessa, Ukraine

²Institute for Problems of Nuclear Power Plants Safety, NASU, Chernobyl, Ukraine

³University of Antwerp, Antwerp, Belgium

The paper presents the results of investigation of phase transitions of ^{137}Cs and ^{90}Sr radionuclides from the surface of contaminated metal structures into the solid component of welding aerosol (SCWA), slag crust and deposited metal in metal surfacing with stick electrodes. It is shown that SCWA radioactivity is due to adsorption of thermolysis products of Cs_2CO_3 (Cs_2O , Cs_2O_2 , Cs), slag (its contamination by ^{90}Sr and ^{137}Cs), deposited metal surface (formation of cesium monoferrite (CsFeO_2) and/or polyferrites ($\text{Cs}_2\text{O}\cdot 6\text{Fe}_2\text{O}_3$ and $\text{CsFe}_{11}\text{O}_{17}$)). The established empirical dependence of specific activity of ^{137}Cs in SCWA composition on ^{137}Cs surface activity can be used in forecasting the radioactive contamination or air in the working zone and rating the need for personal protective gear for respiratory organs.

Keywords: arc surfacing, radioactively contaminated metal structures, welding aerosol, slag crust, deposited metal, activity of ^{137}Cs , ^{90}Sr radionuclides, phase transitions, object «Ukrytie»

Service experience of ChNPP object «Ukrytie» shows that despite the taken measures (monitoring and essential reduction of emissions of radioactive aerodispersed particles into the environment), its radioecological hazard remains high. A characteristic example of air contamination inside and outside object «Ukrytie» is formation of radioactive aerosols during performance of building-mounting operations, in particular, at cutting and repair of damaged and welding of new metal structures of shielding barriers and constructions [1].

In this connection investigations of the regularities and mechanism of phase transitions of radionuclides from the surface of contaminated metal structures are of theoretical and practical interest. It is obvious that for monitoring of radioactive situation in service of object «Ukrytie», and forecasting the effectiveness of application of personal and collective protective means for respiratory organs of personnel it is also important

Table 1. Initial surface activity of plates, Bq/cm²

Plate number	^{137}Cs	^{90}Sr
1	17	3
2	160	56
3	146	51
4	20	3.5
5	200	70
6	22	3.7
7	100	35

to know the intensity of formation, dispersion, as well as chemical composition of the forming SCWA [2, 3].

This work presents the results of investigation of phase transitions of ^{137}Cs and ^{90}Sr radionuclides into SCWA, slag crust and deposited metal in stick electrode arc surfacing of radioactively contaminated metal plates. 25 years after the accident in the 4th reactor of ChNPP the above-mentioned beta-emitting radionuclides are exactly the particles responsible for surface contamination of metal structures in the premises and local zone of object «Ukrytie».

Investigations were performed using plates of low-carbon steel St3 of $400 \times 150 \times 8$ mm size, on which single-pass surfacing was performed with 4 mm ANO-4 and UONI-13/45 electrodes applied for welding low-carbon and low-alloyed structural steels.

To simulate radioactive contamination of metal structures of object «Ukrytie», alkali-carbonate liquid radioactive wastes (LRW) taken from water accumulated in the premises at the lower marks of object «Ukrytie» (rooms 012/7 and 014/2) were uniformly applied onto the plate surface by dripping method. According to the current classification, LRW belong to the category of medium radioactive wastes, ^{137}Cs and ^{90}Sr isotopes making the greatest contribution to their radioactivity (furtheron referred to as activity). After LRW drying, a rust layer forms on the plate surface.

Data on the initial value of surface activity of plates, A_s , prepared for investigations, are given in Table 1.

Electrode metal deposition on the plates was performed in a cabinet of 0.7 m^3 volume (Figure 1, a) at two values of welding heat input E_i (electric power consumed per a unit of weld length $E_i = IU/v$, where I is the reverse polarity direct current; U is the voltage;



v is the electrode displacement speed): 0.8 kJ/mm ($I = 110$ A, $U = 24$ V, $v = 3.3$ mm/s) and 1.3 kJ/mm ($I = 200$ A, $U = 33$ V, $v = 5$ mm/s). Electrode position relative to the plate is vertical. SCWA plume was localized using a hood installed at 0.4 m above the arc. Here the rate of feeding gas-air mixture by a flexible hose (0.06 m diameter) into the sampling chamber (1.9 m high and 0.19 m in diameter) (Figure 1, *b*) was equal to 75 dm³/s.

Air flow velocity in the points of taking representative SCWA samples was equal to 2.7 ± 0.2 m/s, SCWA concentration in the chamber was changed in the range of 50–200 mg/m³, depending on the welding mode and grade of applied electrodes. Simultaneous selection of SCWA samples: respirable fraction (SCWA_{2.5}) – particles with less than 2.5 μm aerodynamic diameter, penetrating into and depositing in the lung alveoli, was performed using low-pressure single-stage impactor LPI 2.5/10 dm³/min (Air Diagnostic and Engineering Inc., USA), fitted with filter (Teflon membrane filter TK15-G3M); for particles of 0.005–20,000 μm size (SCWA_{tot}) impactor of the same grade but without the separating plate was used. Sampling time was varied in the range of 10–60 s, filter weighing before and after sampling was performed with the accuracy of $5 \cdot 10^{-6}$ g under similar conditions (not less than 48 h conditioning time, $T = 20 \pm 1$ °C, air humidity of 50 ± 5 %).

¹³⁷Cs activity in the samples was determined using gamma-spectrometer with germanium detector GL2020 with input beryllium window of 0.5 mm thickness with energy resolution of 1.6 keV for gamma-quantum energy of 1.33 MeV of ⁶⁰Co. Minimum detectable activity of ¹³⁷Cs was equal to 0.1 ± 0.02 Bq per sample. Geniu-200 program was used for spectra interpretation. ⁹⁰Sr activity in the samples was determined using beta-spectrometer SEB-01 and low-background (background of 0.03 ± 0.01 pulse/s) alpha- and beta-counter Tesla NRR-610.

Results of gamma-spectrometric investigations of SCWA_{2.5} and SCWA_{tot} samples are given in Figure 2. Intensity of formation of SCWA_{2.5} and SCWA_{tot} at $E_i = 1.3$ kJ/mm, $G_{2.5}$ and G_{tot} , respectively, was as follows, mg/s:

	ANO-4	UONI-13/45
$G_{2.5}$	10.2	12.5
G_{tot}	13.1	15.3

As follows from Figure 2, dependence of specific activity of ¹³⁷Cs A_{sp} in SCWA composition on surface activity A_s of the plates is best described by the following exponential dependence:

$$A_{sp} = N(A_s)^n \quad (1)$$

Specific activity of SCWA_{2.5} respirable fraction is by 20–30 % higher than that of SCWA_{tot}. The latter is quite explainable, considering that thermolysis of ¹³⁷Cs carbonate ($Cs_2CO_3 \rightarrow Cs_2O + CO_2$; $2Cs_2O \rightarrow$

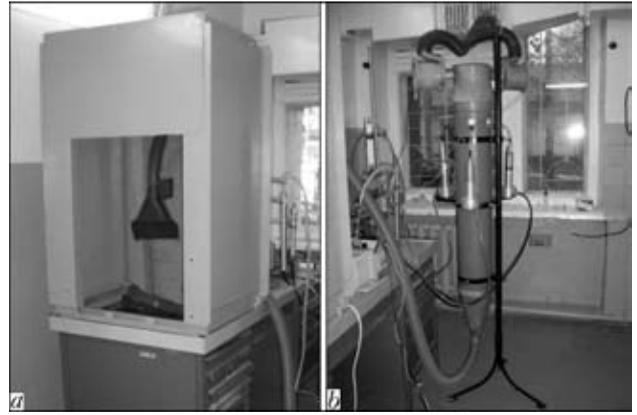


Figure 1. Experimental set up: *a* – welding cabinet with hood; *b* – sampling chamber fitted with impactors

$\rightarrow Cs_2O_2 + 2Cs$) occurs in an air atmosphere at $T \geq 880$ K, and in carbon dioxide gas atmosphere – at $T = 1065$ K it melts without noticeable decomposition, while its dissociation with CO₂ detachment occurs only at higher temperature [4], and assuming that the products of thermolysis of Cs₂CO₃ (Cs₂O, Cs₂O₂, Cs), evaporating from the plate area, where $T \geq T_{dis}$ of Cs₂CO₃ are sorbed by all the aerodispersed particles,

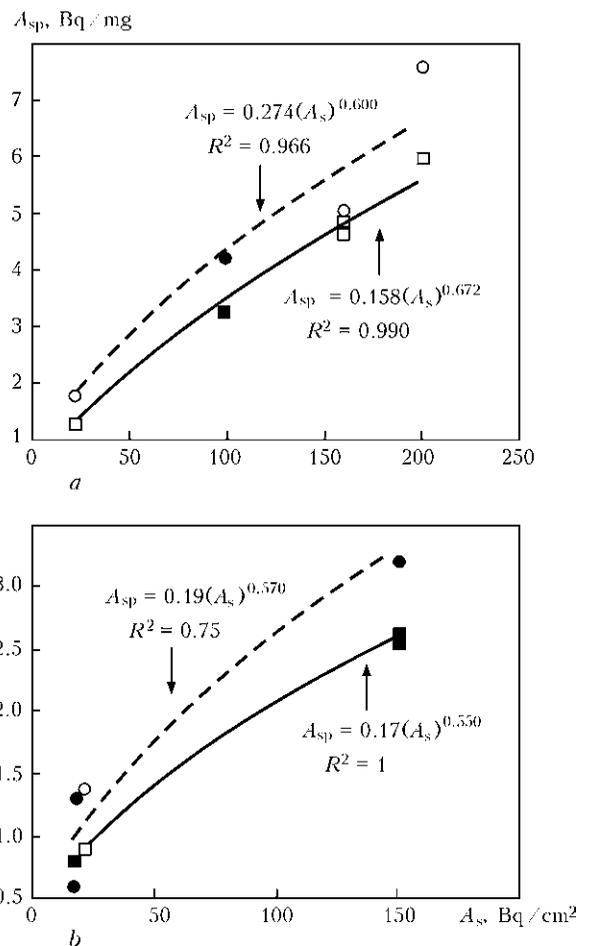


Figure 2. Dependence of ¹³⁷Cs specific activity A_{sp} in SCWA_{2.5} (dashed curve) and SCWA_{tot} (solid curve) on ¹³⁷Cs surface activity A_s of plates at application of electrodes ANO-4 (*a*) and UONI-13/45 (*b*): circles – SCWA_{2.5}; squares – SCWA_{tot}; light signs – at $E_i = 1.3$ kJ/mm; dark signs – at $E_i = 0.8$ kJ/mm



while radioactivity of sampled particles is proportional to their surface area [1].

Indeed, SCWA particles by their dispersion and formation mechanism are subdivided into nano-sized (less than 0.1 μm) forming as a result of condensation of vapours of welding consumables and metals being welded, disintegration and spattering of drops of electrode metal and slag melt of more than 0.5–1.0 μm size, and agglomerates in the form of stringers and clusters of varying density from nano-sized particles of more than 0.1–0.2 μm size [5, 6]. In stick electrode welding particles of the second and third types prevail in the welder's breathing zone at 0.4–0.5 m distance from the arc – 98–99 % of SCWA_{tot} weight [7], in the range of particle sizes of 2.5–20 μm weight fraction of disintegration particles in SCWA_{tot} is not higher than 70 % [8].

A considerable difference in the ratios of activities of ¹³⁷Cs and ⁹⁰Sr in SCWA and in the surfaced plates should be also noted. Under typical experimental conditions (at $E_i = 1.3$ kJ/mm) and sampling time (10–20 s) traces of ⁹⁰Sr ($A_{sp} (^{137}\text{Cs})/A_{sp} (^{90}\text{Sr}) = 135$) were found in SCWA_{2.5} composition only at metal deposition on plate 5, where $A_s (^{137}\text{Cs})/A_s (^{90}\text{Sr}) = 2.86$. At increase of sampling time for SCWA_{2.5} samples up to 50–60 s ($m > 2$ mg) ⁹⁰Sr is found, as was expected, also at metal deposition on plates 1–4, 6 and 7.

Obtained results are due, in our opinion, to insignificant vapour pressure of strontium oxide (with boiling temperature of 3270 K) over the melt in the weld pool, where the average temperature is only by 100–200 K higher than iron melting temperature ($T_m \approx 1812$ K) [9], although in the cathode spot area it may reach 2600 K [10].

Judging from the data given in Figure 2, under comparable conditions specific activity of SCWA_{2.5} when using UONI-13/45 electrodes is on average by 45–65 % lower than in the case of ANO-4 electrodes, although the intensities of their formation differ by just 23 %. This difference is, probably, due to a large amount of carbon dioxide gas, forming at melting of the covering of UONI-13/45 electrodes [2], and the resultant retardation of the reaction of Cs₂CO₃ thermolysis [4].

It is obvious that the values of empirical coefficients N and n in equation (1) depend on the composition of electrode covering and the assumed changes of welding heat input by approximately 1.6 times have an only minor effect here. Indeed, proceeding from the general theoretical notions, N is functionally dependent on the ratio of increment rate of the zone of evaporation of ¹³⁷Cs and two of its oxides ($\Delta S/\Delta t = Lv$ (here L is the width of the evaporation zone) to the intensity of SCWA formation G :

$$N = f\left(\frac{\Delta S/\Delta t}{G}\right).$$

On the other hand, in stick electrode welding a proportional dependence is found of the intensity of SCWA formation on arc power $G \approx IU = E_i v$ [2] and, as follows from [11], heating zone increment proceeded similarly, where $T \geq 880$ K depends on electric arc power at displacement of the linear heat source during metal deposition on a thin plate:

$$\Delta S/\Delta t \sim E_i v.$$

Thus, the width of the heating zone L_{880} on a plate limited by isotherm $T = 880$ K, under the experimental conditions ($E_i = 1.3$ kJ/mm, $v = 0.5$ cm/s, $I = 200$ A, $U = 33$ V) is equal to [11]

$$L_{880} = \frac{\sqrt{2/(\pi e)\eta E_i}}{c_p d \Delta T} \approx 2.2 \text{ cm},$$

where $\eta \approx 0.8$ is the efficiency of direct welding current source in stick electrode welding [10]; $d = 0.8$ cm is the plate thickness; $\Delta T = 880 - 300$ K is the temperature increment; $c_p \approx 5$ J/(cm³·K) is the volumetric heat capacity of low-carbon steel.

In view of the above-said, it could be anticipated that at metal deposition on plate 5 ($A_s = 200$ Bq/cm²) products of thermolysis of ¹³⁷Cs carbonate will come to the gas phase from its surface every second, their activity being equal to

$$A_{\text{calc}} = A_s L_{880} v \approx 220 \text{ Bq/s}.$$

Actually, SCWA activity experimentally established at application of ANO-4 electrodes ($G_{\text{tot}} = 13.1$ mg/s; $G_{2.5} = 10.2$ mg/s; A_{sp} (SCWA_{2.5}) = 7.6 Bq/mg; A_{sp} (SCWA_{tot}) = 6 Bq/mg) is equal to

$$A_{\text{exp}} = G_{\text{tot}} A_{sp} (\text{SCWA}_{\text{tot}}) \approx G_{2.5} A_{sp} (\text{SCWA}_{2.5}) \approx 78 \text{ Bq/s},$$

i.e. A_{exp} is 2.8 times lower than A_{calc} , and is approximately 1.4 times less than could have come from the deposited weld zone ($L_w = 1.1$ cm, where $T > T_m^{\text{Fe}}$):

$$A_w = A_s L_w v \approx 110 \text{ Bq/s}.$$

Judging by the values of A_{calc} , A_{exp} and A_w it is obvious that Cs₂CO₃ thermolysis is accompanied by ¹³⁷Cs transition not only into the gaseous, but also other phases.

During decontamination of the deposited plates it was possible to establish that ¹³⁷Cs is contained in the slag, as well as surface layer of weld metal. Radioactive slag was removed mechanically, and decontamination of deposited metal surface layer was performed only as a result of acid etching of the weld surface.

Indirect confirmation of ¹³⁷Cs transition into the surface layer at metal deposition was obtained as follows. Cs₂CO₃ solution was applied on the surface of two rusted plates of 30 × 30 × 1.5 mm size from low-carbon steel St3 by dripping. The solution had been prepared using sample radioactive solution of ¹³⁷Cs

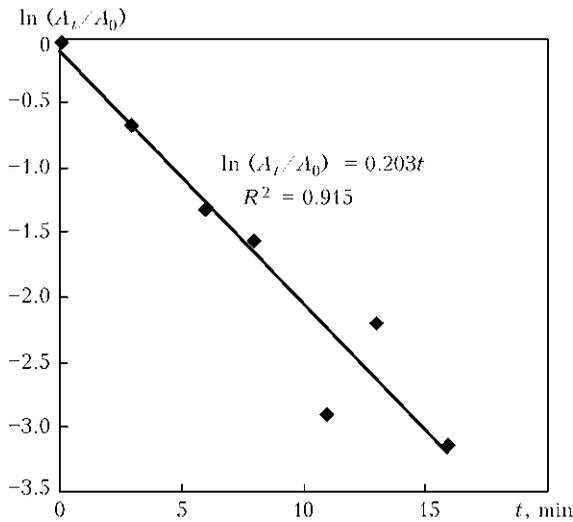


Figure 3. Dependence of $\ln(A_t/A_0)$ on duration of plate heating at $T = 1300$ K

(without carrier) in the chloride form. Dried plates (samples 8 and 9) with initial activity A_0 equal to 5700 and 870 Bq, respectively, were placed into a muffle furnace pre-heated up to 1300 K, and were baked at this temperature for a certain time. Then samples were taken out, cooled and activity A_t was measured. The above sequence of operations (cycles) was repeated thrice. Results of investigation of the dynamics of decontamination of plates 8 and 9 are given in Table 2 and in Figure 3.

It follows from the obtained data that the process of plate surface decontamination is quite well ($R^2 = 0.915$) described by the kinetic equation

$$\frac{A_t}{A_0} = \exp(-kt), \quad (2)$$

where A_0 is the initial ^{137}Cs activity on a plate; $k = 0.203 \text{ min}^{-1}$ is the constant of the rate of evaporation of thermolysis products (plate decontamination) at $T = 1300$ K; t is the current baking time. Under the experimental conditions radioactivity of plate 8 decreased by 89 %, and that of plate 9 – by 95.6 %; for complete decontamination of the plates (after three cycles of their baking) it is enough to mechanically remove the easily removable layer from the contaminated surface.

Thus, investigation results obtained in Chernobyl are the first attempt to establish the regularities and mechanisms of phase transitions of ^{137}Cs and ^{90}Sr radionuclides from the surface of contaminated metal structures into SCWA at metal deposition by stick electrode surfacing.

Our results give grounds for an assertion that competing phase transitions take place in welding, surfacing and cutting of metal structures radioactively contaminated by ^{137}Cs and ^{90}Sr : $G \rightarrow T$ accompanied

Table 2. Dynamics of plate decontamination at baking at $T = 1300$ K

Cycle number	Plate 8 ($A_0 = 5700$ Bq)		Plate 9 ($A_0 = 870$ Bq)	
	Heating duration, min	A_t , Bq	Heating duration, min	A_t , Bq
1	3	2900	6	230
2	5	1200	5	48
3	5	630	5	38

by formation of radioactive aerodispersed SCWA particles as a result of adsorption of vapours of products of Cs_2CO_3 thermolysis; $G \rightarrow T$ and $T \rightarrow T$ leading to radioactive contamination of slag by ^{90}Sr and ^{137}Cs and of surface layer of deposited metal by ^{137}Cs . In the latter case at the temperature of 950–1000 K, most probably, interaction of iron oxide ($T_m \approx 1830$ K) with cesium carbonate/oxide proceeds, and cesium monoferrite (CsFeO_2) and/or polyferrites ($\text{Cs}_2\text{O} \cdot 6\text{Fe}_2\text{O}_3$ and $\text{CsFe}_{11}\text{O}_{17}$) form [12, 13].

The established empirical dependencies can be used in forecasting the radioactive contamination of air in the working zone and rating the need for personal means of respiratory organ protection.

- Ogorodnikov, B.I., Pazukhin, E.M., Klyuchnikov, A.A. (2008) *Radioactive aerosols of the object «Ukrytie»: 1986–2006*. Chernobyl: IPB AES NANU.
- Pokhodnya, I.K., Gorpenyuk, V.N., Milichenko, S.S. et al. (1990) *Metallurgy of arc welding. Processes in arc and fusion of electrodes*. Kiev: Naukova Dumka.
- Ennan, A.A. (2002) Physico-chemical principles of recovery, neutralizing and recycling of welding aerosols. In: *Proc. of 1st Int. Sci.-Pract. Conf. on Protection of Environment, Health, Safety in Welding Production* (Odessa, 11–13 Sept. 2002). Odessa: Astroprint, 10–37.
- Plyushchev, V.E., Stepin, B.D. (1970) *Chemistry and technology of lithium, rubidium and cesium joints*. Moscow: Khimiya.
- Zimmer, A.T., Biswas, P. (2001) Characterization of the aerosols resulting from arc welding processes. *J. Aerosol Sci.*, 32(8), 993–1008.
- Jenkins, N.T., Pierce, W.M.G., Eagar, T.W. (2005) Particle size distribution of gas metal and flux-cored arc welding fumes. *Welding J.*, 84(10), 156–163.
- Sowards, J.W., Lippold, J.C., Dickinson, D.W. et al. (2008) Characterization of welding fume from SMAW electrodes. *Welding Res.*, 81(4), 106–112.
- Ennan, A.A., Oprya, M.V., Kiro, S.A. et al. (2010) About composition of inhalation particles of welding aerosol. In: *Proc. of 24th Sci. Conf. of CIS Countries on Dispersion Systems*. Odessa: Astroprint, 327–330.
- Pokhodnya, I.K. (1972) *Gases in welds*. Moscow: Mashinostroenie.
- Erokhin, A.A. (1973) *Principles of fusion welding. Physico-chemical laws*. Moscow: Mashinostroenie.
- Frolov, V.V., Volchenko, V.N., Yampolsky, M.V. et al. (1988) *Theory of welding processes*. Moscow: Vysshaya Shkola.
- Kachalov, D.V., Stepanov, E.G., Kotelnikov, G.R. (2008) Investigation of processes of formation of catalytically active ferrites of alkaline metals. *Izvestiya Vuzov. Khimiya i Khimich. Tekhnologiya*, 51(7), 45–47.
- Randhawa, B.S. (1995) Mossbauer study on thermal decomposition of cesium tris(oxalato)ferrate(III) dehydrate. *J. Radioanalytical and Nuclear Chemistry, Letters*, 201(1), 57–63.