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Effect of Radioactive Contamination of the Medium on the Durability of Steel 20

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Abstract—The effect that the ionizing radiation caused by radioactive contamination of soil exerts on the surface of carbon steel 20 samples, on their corrosion resistance, and on operation reliability according to low-cycle fatigue tests (taking into account that fatigue is one of the main causes of failures resulting from corrosion and mechanical damage of thin-wall metal structures, in particular, of pipelines) was studied. It was shown that even low activity levels (below maximum permissible levels) caused corrosion loss of the metal and a decrease in the operation reliability. Synergistic protective compounds suppressing the destructive radiation effects and ensuring reliable operation of metal structures due to chelation of the surface metal atoms were developed using computer simulation.

Keywords: radioactive radiation, metal surfaces, corrosion loss, low-cycle fatigue, protection by metal chelation

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The Chernobyl accident caused radioactive contamination of a part of Chernihiv oblast (water bodies, soils, etc.). The territory of Ukraine is saturated with underground, surface, and underwater metal structures. The total acting CIS metal inventory is 1600 million tons [1, 2]. Of this amount, approximately 750, 400, and 150 million tons correspond to the industry, transport, and agriculture, respectively. The corrosion factor is one of the major factors responsible for the growing rate of accidents on technical objects [1–4]. The corrosion losses are distributed as follows, %: fuel and power engineering complex 35, agriculture 20, chemistry and petrochemistry 15, metalworking 5, and other branches 25. The total weight of metal occurring underground exceeds 200 million tons only in Russia, and the surface area of metal structures subjected to the corrosive effect of soil is 1.5 billion m^2 [1, 2]. Destruction of metal structures leads to accumulation of heavy metals in soils and water. The majority of heavy metals are supertoxicants of the XXI century [5, 6], and some of them accelerate corrosion damage [7, 8]. About 200–300 cases of emergency environment pollutions occur annually [7], causing the damage of 7–8 million hryvnias. A single case of emergency pollution of air causes economic loss (thousand hryvnias) of 2.5 for atmosphere, 29 for water resources, and 71 for land [9].

On the other hand, available data on the destructive effect exerted by ingredient (especially with heavy metals) and energy contamination of natural and working media on metal surfaces and on the operation reliability of metal structures as a whole are scarce [3, 4, 7, 8, 10–12]. Therefore, studying the effect of radioactive radiation on metal surfaces becomes a pressing problem and should be aimed at the development of efficient innovative technologies as factors of ecologization of the economy. That was the problem tackled in this study.

EXPERIMENTAL

In our study, we used physical and physicochemical methods (spectrum analysis, IR, ^{1}H NMR, Auger spectroscopy, EDX analysis), complex systems correlation analysis, mathematical statistical methods, computer simulation, and physicomechanical tests [4, 7, 8, 13].

As investigation object we chose low-carbon steel 20, a typical structural material for oil and gas pipelines. This is due to the fact that this steel is more durable than stainless (chromium–nickel) steels under the conditions of transport of natural gas and oil containing H_2S (active stimulator of corrosion, hydrogen absorption, hydrogen embrittlement, fatigue, and cracking). This feature is confirmed by the negative experience of Orenburggazdobycha in the second half of the XX century.

On the other hand, the pressure in pipelines fluctuates with 10% amplitude about the nominal value, which can significantly affect the pipeline performance. Even slight (up to 5%) deviations of pressure in the pipeline from the nominal level decrease by 30% the threshold of stresses at which the corrosion cracking and hydrogen and corrosion fatigue occur [1–4]. Taking this fact into account, we performed experiments with steel specimens in the form of plates (57 × 12 × 2.5 mm) in which the stress was produced by three-point bending using appropriate devices, after which the specimens were placed under laboratory conditions in radioactively contaminated soil. We studies six specimens simultaneously. The soil extract (for studying low-cycle steel fatigue as the major cause of technogenic accidents) was prepared in accordance with DSTU (State Standard of Ukraine) 4287:2004 (Soil Quality. Sampling) by digestion (24 h), stirring, decantation, and filtration (red ribbon filter paper). The low-cycle endurance was determined by pulsing pure bending from the zero point at a loading frequency of 50 cycles per minute with an IP-2 machine. The soil treatment with the protective formulation was performed with automatic keeping of "optimum" conditions of steel corrosion in soil (18% moisture content, 303 K).

The protective compounds were developed using new synergistic polyfunctional additives (SAs), potential polydentate chelating compounds with several reaction sites (endo and exo atoms of nitrogen, sulfur, and oxygen), capable to react with surface metal atoms to form metal chelates [14, 15]. Six groups of heterocyclic compounds (imidazole and thiazole derivatives) were studied. The purity of the products was confirmed by IR and ^{1}H NMR spectra, TLC, and elemental analysis. The optimum SA was determined by computer simulation (MNDO-PM3 semiempirical method) based on atomic charges (q_N, q_S, q_O) and thermodynamic characteristics (ΔH_f, μ, E, I), using the correlations of these characteristics with the protective effect on steel 20 (under the action of radioactively contaminated soil and soil extract). The synergistic protective formulations (SPFs) were developed using a secondary raw material, regional large-tonnage bottom waste from caprolactam distillation in the ε-caprolactam regeneration shop of AO Khimvolokno (Chernihiv). The performance of the developed formulations was evaluated by the corrosion resistance (K_s, mm year^{-1}), low-cycle fatigue (IP-2 machine) [4, 7, 8, 13] [$\beta^N = (N_a/N_m)$, ratio of the number of cycles to failure in air (a) and in the given medium (m)], degree of protection from low-cycle fatigue [$K = (N'_m - N_m)/N_m$, % (the prime refers to the test with protection)], and technological protection efficiency factor γ_t.

RESULTS AND DISCUSSION

The experimental data were processed by methods of mathematical statistics using the standard error S (at $n = 6$, $t = 2.75$, and confidence probability of 0.95, it ranged from ±5 to ±10%). We also determined the correlation coefficient r by regression analysis (least-squares method). The improbable data were discarded using Q-test [16].

We studied the influence exerted on the corrosion resistance of steel 20 (K_s, mm year^{-1}) by the density of the radioactive contamination (RC) of soil (specific activity A, Ci km^{-2}) from the Ripky raion of Chernihiv oblast, which suffered particularly strongly from the Chernobyl accident. The tests were performed for 90 days. The mean values (from three soil samples) of A on the maximally contaminated area of farming lands are given below. For ^{137}Cs, A was below 1 Ci km^{-2} on 97% of the farming land area, and only on 3% A was up to 5 Ci km^{-2}. For ^{90}Sr, A was below 0.15 Ci km^{-2} on 92% of the area, and on 3% A was up to 3 Ci km^{-2}. The γ-ray background was 8–14 μR h^{-1} [17, 18].

Characteristics of RC of soil, A, Ci km^{-2}

Soil sample	^{137}Cs	^{90}Sr	A_Σ
1	0.80	0.12	0.92
2	0.41	0.09	0.50
3	0.22	0.05	0.27

The action of the ionizing radiation on the surface of steel 20 reduced the corrosion resistance of the steel specimens (see below).

Effect of RC on K_s (mm year^{-1}) of steel 20

Sample 1	Sample 2	Sample 3	Soil without RC
0.56	0.30	0.15	0.03–0.05

In the soil extract, compared to the tests in air, the low-cycle fatigue of steel also decreases under the action of RC (see below).

Coefficients of the effect of the medium on the low-cycle fatigue of steel 20 (β^N) under the action of RC in the soil extract (pH 5)

Protection	Sample 1	Sample 2	Sample 3
No	2.6	2.0	1.6
Yes	1.3	1.2	1.1

The coefficient of the effect of the medium in the soil extract without RC was appreciably lower: $\beta^N = 1.3$.

The optimum SA was determined by complex systems analysis of the correlation between the SA structure and synergistic protective properties of the formulations with computer simulation of the effect of substituents in the phenol (Ph), imidazole (Im), and thiazole (Tz) rings, enhancing the metal chelation [14].

The SAs were characterized by the electronic structure [charges q on reaction sites: pyrrole (N_1) and pyridine (N_3) endo nitrogen atoms, endo oxygen atom (Mf), and oxo oxygen atom (CO), and also on the phenyl ring (Ph)] and by the thermodynamic characteristics [enthalpy of formation ΔH_f, ionization potential I, electronic energy E_{el}, dipole moment μ].

The metal chelating activity was evaluated using the complex system with differentiated evaluation of the protective effect by a number of parameters: γ_t, γ_c, γ_a, γ, including partial protective effects (γ_1–γ_4: γ_1 and γ_2 are kinetic and activation parameters; γ_3, blocking parameter; and γ_4, energy parameter). The metal chelating activity of the optimum synergistic additive (SA) is presented in Table 1. The values are given for aggressive media (γ_t, for HCl, pH 0; K and K_H, for 3% NaCl; K_{NACE} and β_H, for NACE).

Treatment of the soil with the synergistic protective formulation (3–5 g kg^{-1}) considerably decreases the radioactive contamination and enhances the corrosion resistance and low-cycle endurance of specimens of steel 20 (Figs. 1, 2).

The technological protection efficiency factors γ_t with respect to A and K_s are given below.

Parameter	Sample 1	Sample 2	Sample 3
A	11.5	10.0	9.4
K_s	14.0	12.5	10.7

Table 1. Characteristics of SA and its protective properties with respect to steel 20 in aggressive media[a]

Thermodynamic characteristics				
M, g mol^{-1}	ΔH_f, kJ mol^{-1}	I, eV	E_{el}, eV	μ, D
437.54	119.20	8.74	49 876.54	1.97
Charges on atoms and groups				
N_3	N_1	O (Mf)	O (CO)	Ph
–0.11495	0.32454.	–0.25562	–0.28384	–0.55347
Protective properties				
γ	γ_1	γ_2	γ_3	γ_4
41.8	2.8	4.2	33.3	1.5
Z, %	K, %	K_H, %	K_{NACE}, %	β_H, %
97.8	85.8	80.1	82.5	79

[a] (Z) Degree of corrosion protection, (K, K_H, K_{NACE}) degree of protection from low-cycle fatigue, and (β_H) degree of protection from hydrogen absorption. Mf denotes the morpholine substituent in Im.

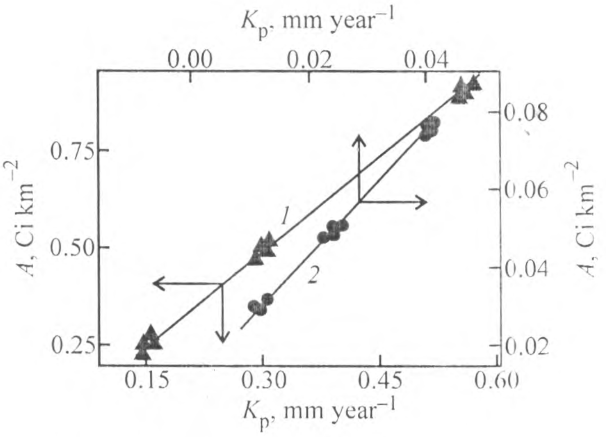

Fig. 1. $K_s = f(A)$ correlation: (1) no protection, $K_s = 0.6A$; (2) with SPF, $K_s = 0.17A + 0.13$.

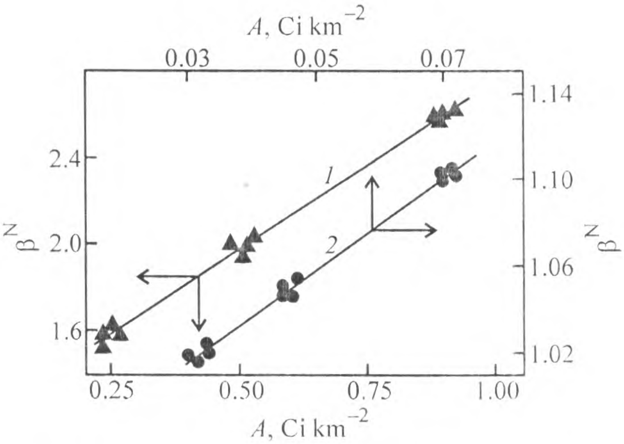

Fig. 2. $\beta^N = f(A)$ correlation: (1) no protection, $\beta^N = 1.54A + 1.22$; (2) with SPF, $\beta^N = 1.79A + 0.74$.

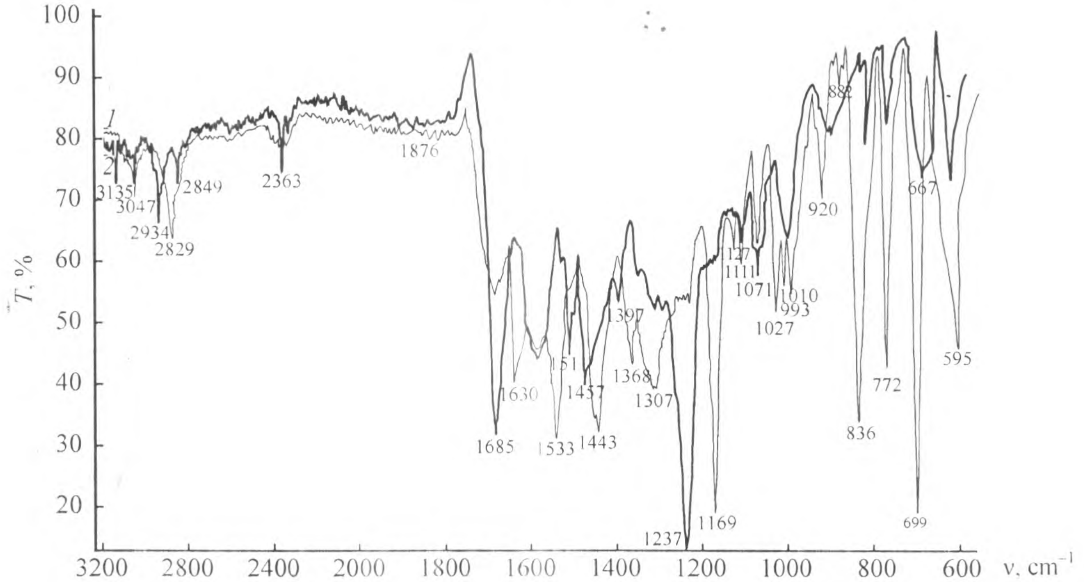

Fig. 3. IR spectra of the (*1*) nanoscale metal chelate and (*2*) synergistic additive.

As can be seen, *A* decreases by 89.4–91.3%, and K_S, by 90.7–92.9%. The low-cycle fatigue increases by 80.1–85.8% (relative to the soil extract without protection) with decreasing specific activity *A*.

The mechanism of the action of radioactive contamination on metal surfaces and of the structure failure acceleration involves three effects: radiolysis, degradation, and photoradiation. The radiolysis leads to generation of active redox radicals which, on the one hand, accelerate cathodic corrosion reactions and, on the other hand, intensify hydrogen absorption. The degradation effect is associated with breakdown of oxide and other films on the surface of metals (in particular, of steel 20), accelerating the anodic reactions of metal corrosion. The photoradiation effect causes changes in the semiconductor properties of surface protecting films with acceleration of cathodic reactions (its contribution to the surface degradation is minimal). The mechanism of the SPF action is primarily associated with the fact that SAs can inhibit cathodic and anodic processes, acting in the forms of molecules, cations (at protonation), and anions (at deprotonation). The ligand denticity L is also an important factor. Enhancement of the efficiency of the protection from radioactive contamination is due to intramolecular synergism associated with promotion of the formation of π-donor–acceptor bonds (L→Me), correlating with the maximal electron density on the O and N_3 atoms and minimal ionization potential *I*. High positive charge on the N_1 and S atoms favors π-dative bonding, which also promotes metal chelation on the steel surface. The intramolecular synergism is associated with the presence of active constituents, polyamide bonds (–NH–CO–), where the N, C, and O atoms have sp^2 hybridization and exhibit negative induction and mesomeric effect. This favors formation of insoluble chelates with heavy metals (Fe, Ni, Cu, Cr, etc.), including radionuclides of Chernobyl origin (^{95}Nb, ^{141}Ce, ^{103}Ru, ^{95}Zr, ^{60}Co, etc.) and their daughter products (^{90}Y, ^{97}Nb, ^{134}La, etc.) on the metal surface. In addition, Cs and Sr are prone to *sd* hybridization, making the contribution of *d* states to σ- and π-bonding more probable. The same follows from the IR and Auger spectra (Figs. 3, 4). The formation of metal chelates is confirmed by the low-frequency shift (Δν) of the identified bands of N–H, C=O, C=C, Ph, C–N, C=N, and Im stretching vibrations (Table 2). The SPFs are protected by Ukrainian patents [19, 20].

Significant contribution of the reaction sites on the N and O atoms in the Ph and Im groups to the metal chelation follows from high values of Δν = 86–97 cm^{-1}. The formation of strong metal chelates via O atoms follows from Δν = 105 cm^{-1} and from appearance of the Fe–O and Fe–N stretching vibration bands in the IR spectra. Possible protonation of the ligands also favors the corrosion protection. In addition, the chelation activity is enhanced in accordance with the theory of hard and soft acids and bases [21], as a relatively "soft" acceptor (surface Fe atom) interacts with a "soft" donor (Im ring).

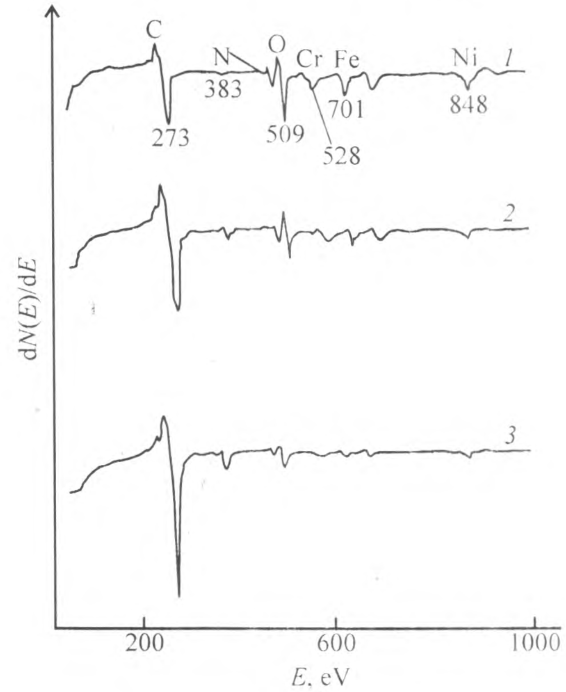

Fig. 4. Auger spectra of the metal chelate on steel 20 (electron escape depth 2 nm). Surface treatment: (*1*) 0.1 M HCl, (*2*) 0.1 M HCl + SA, and (*3*) 0.1 M HCl + SPF.

The Auger spectra (Fig. 4) demonstrate 1.5–2-fold enrichment of the metal surface in carbon and nitrogen. From the electron penetration rate (0.4–0.6 nm min^{-1}), we determined the thickness of the protective metal chelate film on the metal surface (40–50 nm). The data obtained directly prove the formation of a metal chelate protective film with high carbon content, preventing the egress of Fe atoms or ions to the steel surface, i.e., enhancing the corrosion resistance of steel. The stability constant of the metal chelate is high, $K_{\mathrm{st}} = 10^{10}–10^{15}$. The metal chelate formation is also confirmed by thermodynamic calculations of the equilibrium constants:

$$\mathrm{Fe}^{2+} + \mathrm{H_2L} = \mathrm{FeL} + 2\mathrm{H}^+: K_\mathrm{a} = 10^{-5},\ K_\mathrm{s} = 2 \times 10^{-14},$$
$$K = 10^{-5}/2 \times 10^{-14} = 5 \times 10^{8}.$$

High equilibrium constant *K* of the chelate formation demonstrates high thermodynamic probability of the chelation on the metal surface. The protected steel also exhibits high chemical endurance in media that are more aggressive than soil (see above).

Thus, radioactive contamination of the soil (as a consequence of Chernobyl accident) strongly affects the metal surfaces, in particular, the surface of steel 20, leading to a decrease in the corrosion resistance of steel 20 by a factor of 3.7–14 depending on the level of the radioactive contamination of the soil. In the extract from radioactively contaminated soil, the low-cycle fatigue of steel (as one of the main causes of technogenic accidents) increases by a factor of 1.5–2 relative to the tests in air. Modification of the metal surface via chelation by treatment of the soil with the developed synergistic protective formulations not only ensures enhancement of the corrosion resistance of steel by 90.7–92.9% and of the low-cycle fatigue endurance by 80.1–85.8%, but also reduces the radioactive contamination of the soil (*A*, Ci km^{-2}) by 89.4–91.3%.

Table 2. Frequencies of characteristic stretching vibrations of groups, ν, cm^{-1}

Group	Ligand	Chelate	Δν, cm^{-1}
N–H	3135	3047	88
C=O	1685	1599	86
C=C	1511	1443	68
Ph	1457	1368	89
C–N	1237	1169	68
C=N	1630	1533	97
Im	1397	1307	90
C–H	2934	2829	105
Fe–O, Fe–N	–	772, 699, 595	–

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