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## CALCULATION OF ELECTRIC POTENTIALS ON THE SURFACES OF INTERACTION OF DEFORMABLE METAL BODIES WITH HYDROGEN-CONTAINING ENVIRONMENT

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**Summary.** In most cases the metal structures service under operating conditions results in the fact that these structures or their certain elements are constantly affected not only by mechanical factors (load, residual stresses, etc.), but also by the environment. Elements of pipelines, load-bearing sections of thermal and hydroelectric power stations, metal structures of bridges are all influenced by the environment that fills or surrounds them. Such environment depending on the content of acids and alkalis, a number of hydrogen-containing media can be corrosive. It should be also noted that the influence of such corrosive environment and mechanical factors influence are simultaneous and interrelated resulting very often in brittle or quasi-brittle metal fracture. Therefore, the problem of estimating the basic metal structures engineering parameters (strength, reliability, etc.) that are corroded by the simultaneous action of mechanical force factors, is currently an important problem of industrial operation. The paper presents problems based on the theory of elasticity, electrostatics, theoretical electrochemistry and equations of mathematical physics. According to the established analytical ratios for the calculations of effective electric potentials and the corresponding numerical experiments, the estimation of electric potentials on the surfaces of interaction of deformable metal bodies with hydrogen-containing medium is carried out.

**Key words:** deformable metal bodies, electric potential, dielectric constant, electrical double layer, electrostrictive ratio, volume dilatation, specific capacitance of metal, charge density, hydrogen-containing medium.

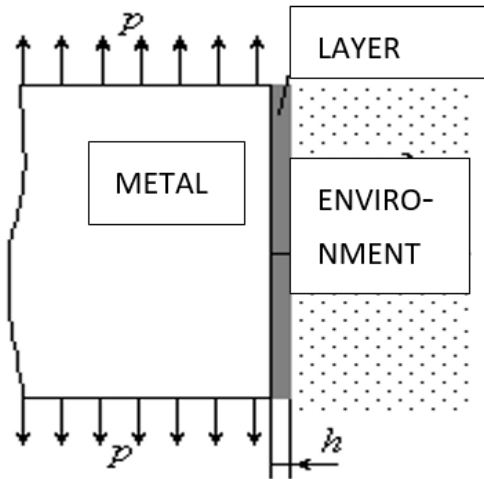
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**Introduction.** Experimental studies of the behavior of deformed metal bodies, in particular with a functional – gradient structure [1], in interaction with hydrogen-containing media, require the development of new theoretical foundations for studying a number of aspects of the corresponding interaction. In [2–4] the approach to analytical definition of electrode potential, which arises on surfaces of interaction of a metal body with the aggressive hydrogen-containing environment is developed. Here we obtain the ratio for the quantitative estimation of the electrode potential in the plane of separation of the body and the medium and in the vicinity of the circular hole, depending on the applied force load.

1. Initial ratios. The problem of interaction of a metal body with the medium at a rectilinear contact boundary. Loaded non-ferromagnetic metal body in an electrically conductive medium is considered. At the moment of contact between the metal and medium, ion exchange takes place, which causes the appearance of a double electric layer, and,

consequently, the potential difference, i.e. the electrode potential [5]. To establish the nature of the electrode change potential  $\Delta\varphi = \varphi_m - \varphi_c$ , which is required in calculations of a number of technological processes, the priority is the assessment of values  $\varphi_m$ ,  $\varphi_c$  – metal electric potential and hydrogen-containing solution in the area of static loads. This is schematically shown in Fig. 1.



**Figure 1.** Calculation scheme of electric potential at interaction of a rectilinear surface with the hydrogen-containing media

Electric potential in metal. We use the model of impurity-free electrically conductive solid body, which takes into account the deformation and electric charge redistribution (electrical conductivity), and for the macroscopic description of these processes – the hypothesis of equilibrium within a physically small element of the body.

The equation of distribution of electric potential in a loaded metal body is written in the form [6]:

$$\nabla^2\varphi_m = \chi_m^2\varphi_m + \beta K\varepsilon_\sigma/\varepsilon_0 \quad (\chi_m^2 = \rho_m C_m/\varepsilon_0), \quad (1)$$

where  $\varepsilon_0$  – dielectric constant,  $\beta$  – electrostriction coefficient,  $K$  – bulk modulus.

$\varepsilon_\sigma = \frac{2}{3} \frac{(1+\nu)}{K(1+4\nu)} P$  – volume dilatation,  $C_m$  – specific electric intensity of metal,  $\rho_m$  – charge density.

*Electric potential in medium.* To evaluate the interaction between charged particles (ions) in a liquid medium, the Debye–Hückel electrolyte model is used [7, 8]. Provided the forces of interaction between ions are electrostatic, and Boltzmann's principle is applied to ion distribution, – the equation for establishing the potential distribution  $\varphi_c$  can be written in the form of:

$$\nabla^2\varphi_c = \chi_c^2\varphi_c \quad (\chi_c^2 = e^2 \sum z_i^2 n_i^2 / (kT\varepsilon\varepsilon_0)), \quad (2)$$

where  $\varepsilon$  – relative dielectric constant of the medium.

$ez_i$  – charge of i-th group ions,  $n$  – number of charges,  $k$  – The Boltzmann constant,  $T$  – absolute temperature.

*Electrode potential and double electric layer.* Potential distribution  $\varphi_{mc}$  in a double electric layer is defined by the Poisson-Boltzmann equation [9–12]:

$$\nabla^2 \varphi_{mc} = \chi_{mc}^2 \varphi_{mc} \quad (\chi_{mc}^2 = 2F^2 I / (\epsilon_{mc} RT)), \quad (3)$$

where  $F$  – the Faraday constant,  $I$  – ionic strength of the solution, calculated by the Debye-Hückel theory of solutions,  $\epsilon_{mc}$  – relative dielectric constant of double electric layer

$$R = kN_A$$

$N_A$  – Avogadro's number,  $k$  – velocity constant of elementary reaction

*Boundary conditions.* From the equations of electrodynamics it follows that on the line of contact of electrically conductive phases continuous normal components of currents and continuous electric potentials in these phases [9–12]. That is, the conditions must be met at the metal – double electric layer boundary.

$$\sigma_m \partial \varphi_m / \partial n = \sigma_{mc} \partial \varphi_{mc} / \partial n, \quad \varphi_m = \varphi_{mc}, \quad (4)$$

and the following conditions should be met at double electric layer-medium boundary

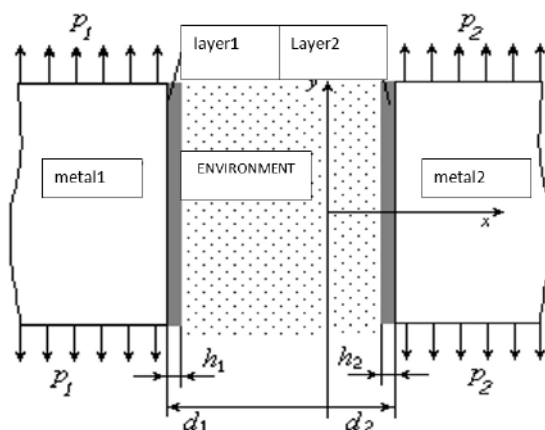
$$\sigma_{mc} \partial \varphi_c / \partial n = \sigma_c \partial \varphi_c / \partial n, \quad \varphi_{mc} = \varphi_c, \quad (5)$$

where  $\partial/\partial n$  – normal derivative to the boundary,  $\sigma_m, \sigma_{mc}, \sigma_c$  – electric conductivity, of a double electric layer and medium correspondingly.

Ratio (1)–(3) with conditions (4), (5) is a complete set of equations of the boundary value problem to determine electric potentials in metal, double electric layer and medium.

It should be noted that electric potentials in metals and medium should meet regularity and boundedness conditions, and therefore tend to standard values, i.e. to the values of the electric potential in medium and metal regardless their interaction.

The equations are similar for a larger number of elastic bodies surrounded by medium.



**Figure 2.** Interaction of two metal bodies, the space between which is filled with medium. is filled with hydrogen-containing medium

**The problem of interaction of two metal bodies, the space between which, is filled with hydrogen-containing medium.** Keeping the conditions and notations of the previous problem unchanged, let us consider two metal bodies (fig. 2), placed at distance  $d_1 + d_2$  one from another, the space between which, is filled with hydrogen-containing medium. Thus we suggest introducing independent parameters  $d_1, d_2$  which allows to obtain boundary cases.

This way, for instance, taking  $d_1 = \infty$ , or  $d_2 = \infty$  we can obtain results of the previous problem.

Values related to the metal and the layer to the left of the y-axis will be denoted by index 1, respectively, those on the right, – by index 2. By analogy with equations (1)–(3), we will write initial equations for both metals, layers and medium liked

$$\begin{aligned} \frac{d^2 \varphi_{m1}}{dx^2} &= \chi_{m1}^2 \varphi_{m1} + \frac{\beta_1 K_1 \varepsilon_{\sigma 1}}{\varepsilon_o}, \quad \frac{d^2 \varphi_{m2}}{dx^2} = \chi_{m2}^2 \varphi_{m2} + \frac{\beta_2 K_2 \varepsilon_{\sigma 2}}{\varepsilon_o}, \\ \frac{d^2 \varphi_{ms1}}{dx^2} &= \chi_{mc1}^2 \varphi_{mc1}, \quad \frac{d^2 \varphi_{ms2}}{dx^2} = \chi_{mc2}^2 \varphi_{mc2}, \\ \frac{d^2 \varphi_s}{dx^2} &= \chi_c^2 \varphi_c, \end{aligned} \quad (6)$$

where  $\varepsilon_{\sigma 1} = \frac{2(1+\nu_1)}{3K_1(1+4\nu_1)} p_1$ ,  $\varepsilon_{\sigma 2} = \frac{2(1+\nu_2)}{3K_2(1+4\nu_2)} p_2$  dilatation of the first and second metal respectively caused by stresses  $p_1$ ,  $p_2$ .

The boundary conditions for this for this problem will be expressed like:

$$\sigma_{m1} \frac{d\varphi_{m1}}{dx} \Big|_{x=-d_1} = \sigma_{ms1} \frac{d\varphi_{mc1}}{dx} \Big|_{x=-d_1}, \quad \varphi_{m1} \Big|_{x=-d_1} = \varphi_{mc1} \Big|_{x=-d_1}, \quad (7)$$

$$\sigma_{mc1} \frac{d\varphi_{mc1}}{dx} \Big|_{x=-d_1+h_1} = \sigma_c \frac{d\varphi_c}{dx} \Big|_{x=-d_1+h_1}, \quad \varphi_{mc1} \Big|_{x=-d_1+h_1} = \varphi_c \Big|_{x=-d_1+h_1}, \quad (8)$$

$$\sigma_c \frac{d\varphi_c}{dx} \Big|_{x=d_2-h_2} = \sigma_{mc2} \frac{d\varphi_{mc2}}{dx} \Big|_{x=d_2-h_2}, \quad \varphi_c \Big|_{x=d_2-h_2} = \varphi_{mc2} \Big|_{x=d_2-h_2}, \quad (9)$$

$$\sigma_{ms2} \frac{d\varphi_{mc2}}{dx} \Big|_{x=d_2} = \sigma_{m2} \frac{d\varphi_{m2}}{dx} \Big|_{x=d_2}, \quad \varphi_{m2} \Big|_{x=d_2} = \varphi_{mc2} \Big|_{x=d_2}. \quad (10)$$

**1. The structure of analytical solutions of mentioned problems.** The problem of interaction of a metal body with a hydrogen-containing medium at a rectilinear contact boundary. Using the fundamentals of the theory of mathematical physics [9], let us write the structure of equation solutions (1)–(3).

$$\varphi_m = A_m e^{\chi_{m1} x} + B_m e^{-\chi_{m1} x} - \frac{\beta K \varepsilon_{\sigma}}{\chi_{m1}^2 \varepsilon_o}, \quad (11)$$

$$\varphi_{ms} = A_{mc} e^{\chi_{mc1} x} + B_{mc} e^{-\chi_{mc1} x}, \quad (12)$$

$$\varphi_s = A_c e^{\chi_c x} + B_c e^{-\chi_c x}. \quad (13)$$

Meeting the conditions of regularity, we have  $B_m = A_c = 0$ .

Meeting equations (11)–(13) with boundary conditions (4)–(5), we obtain a system of four equations for determining unknown constants. Having solved the corresponding system, we find that  $A_m$ ,  $A_{mc}$ ,  $B_{mc}$ ,  $B_c$ .

$$A_m = \frac{\beta K \varepsilon_{\sigma}}{\chi_{m1}^2 \varepsilon_o} \cdot \frac{\sigma_{mc} \chi_{mc}}{\omega} \left[ (\sigma_{mc} \chi_{mc} + \sigma_c \chi_c) e^{2\chi_{mc} h} + \sigma_c \chi_c - \sigma_{mc} \chi_{mc} \right],$$

$$A_{mc} = \frac{\beta K \varepsilon \sigma}{\chi_m \varepsilon_0} \frac{\sigma_m}{\omega} [\sigma_c \chi_c - \sigma_{mc} \chi_{mc}],$$

$$B_{mc} = -\frac{\beta K \varepsilon \sigma}{\chi_m \varepsilon_0} \cdot \frac{\sigma_m}{\omega} [\sigma_c \chi_c - \sigma_{mc} \chi_{mc}] e^{2\chi_{mc} h},$$

$$B_c = -2 \frac{\beta K \varepsilon \sigma}{\chi_m \varepsilon_0} \frac{\sigma_{mc} \chi_{mc}}{\omega} [e^{h(\chi_{mc} + \chi_c)}].$$

Substituting the values of the constants in formulas (11)–(13), we obtain the final form of the electric potential.

$$\varphi_m = \frac{2}{3} \frac{\sigma_{mc} \chi_{mc}}{\chi_m^2 \varepsilon_0} \cdot \frac{\beta(1+\nu)}{(1+4\nu)} p \left[ \frac{e^{2\chi_{mc} h} (\sigma_c \chi_c + \sigma_{mc} \chi_{mc}) + \sigma_c \chi_c - \sigma_{mc} \chi_{mc}}{\omega} e^{\chi_m x} - 1 \right], \quad (14)$$

$$\varphi_{mc} = \frac{2}{3} \frac{\sigma_m}{\chi_m \varepsilon_0} \cdot \frac{\beta(1+\nu)}{(1+4\nu)} p \left[ \frac{\sigma_c \chi_c - \sigma_{mc} \chi_{mc}}{\omega} \cdot e^{\chi_{mc} x} - \frac{(\sigma_c \chi_c + \sigma_{mc} \chi_{mc}) e^{2h\chi_{mc}}}{\omega} \cdot e^{-\chi_{mc} x} \right], \quad (15)$$

$$\varphi_c = -\frac{4}{3} \frac{\sigma_m}{\chi_m \varepsilon_0} \cdot \frac{\beta(1+\nu)}{(1+4\nu)} p \left[ \frac{\sigma_{mc} \chi_{mc} e^{h(\chi_{mc} + \chi_c)}}{\omega} e^{-\chi_c x} \right], \quad (16)$$

where

$$\omega = \sigma_{mc}^2 \chi_{mc}^2 (e^{2\chi_{mc} h} - 1) + e^{2\chi_{mc} h} (\sigma_{mc} \chi_{mc} \sigma_c \chi_c + \sigma_m \chi_m \sigma_c \chi_c + \sigma_m \chi_m \sigma_{mc} \chi_{mc}) + \sigma_{mc} \chi_{mc} \sigma_c \chi_c - \sigma_m \chi_m \sigma_c \chi_c + \sigma_m \chi_m \sigma_{mc} \chi_{mc}.$$

The problem of interaction of two metal bodies, the space between which is filled with hydrogen-containing medium. We write the structure of solutions for equations (6).

$$\varphi_{m1} = A_{m1} e^{\chi_{m1} x} + B_{m1} e^{-\chi_{m1} x} - \frac{\beta_1 K_1 \varepsilon_{\sigma 1}}{\chi_{m1}^2 \varepsilon_0}, \quad \varphi_{m2} = A_{m2} e^{\chi_{m2} x} + B_{m2} e^{-\chi_{m2} x} - \frac{\beta_2 K_2 \varepsilon_{\sigma 2}}{\chi_{m2}^2 \varepsilon_0}, \quad (17)$$

$$\varphi_{ms1} = A_{mc1} e^{\chi_{mc1} x} + B_{mc1} e^{-\chi_{mc1} x}, \quad \varphi_{ms2} = A_{mc2} e^{\chi_{mc2} x} + B_{mc2} e^{-\chi_{mc2} x}, \quad (18)$$

$$\varphi_s = A_c e^{\chi_c x} + B_c e^{-\chi_c x}. \quad (19)$$

Meeting the conditions of regularity at infinity for electric potentials in metals we have  $B_{m1} = A_{m2} = 0$ . Substituting (17)–(19) into boundary conditions (7)–(10), we obtain the appropriate system of equations and by solving it, we can determine unknown constants  $A_{m1}, B_{m2}, A_{mc1}, B_{mc1}, A_{mc2}, B_{mc2}, A_c, B_c$ .

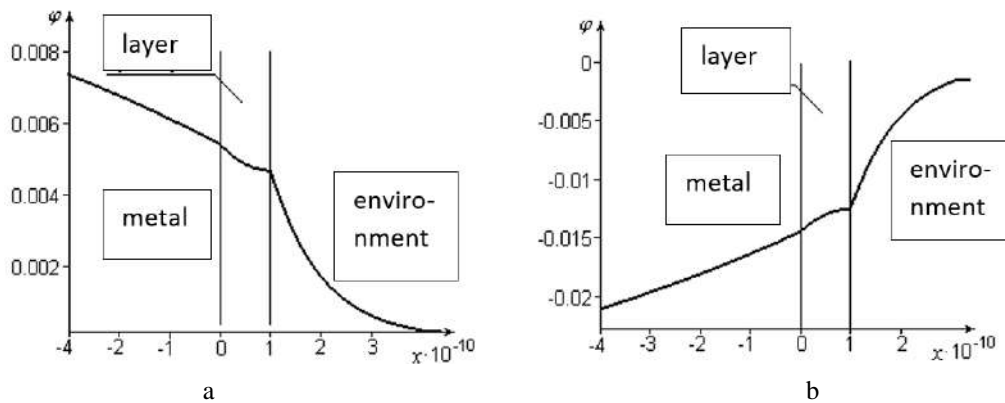
Solving this system is a time-consuming process, and analytical recording of solutions takes up a lot of space. All these inconveniences can be avoided by using one of the math PC programs that work with analytical expressions. In this case, using the MAPLE program this system was solved and analytical formulas for electric potentials were established.

**3. Analysis of the results obtained.** To establish qualitative and quantitative patterns of changes in electrical potentials, calculations were performed for copper and steel with the following initial parameters. Copper:  $\beta = -1.31 \cdot 10^{-4} \frac{1}{V}$ ,  $\nu = 0,35$ ,  $C = 10^3 \frac{C}{kg \cdot V}$ ,

$$\varepsilon_o = 9 \cdot 10^{-12} \frac{F}{m}, \quad \rho = 8,94 \cdot 10^3 \frac{kg}{m^3}. \quad \text{Steel: } \beta = 10^{-4} \frac{1}{V}, \nu = 0,28, \rho = 7,7 \cdot 10^3 \frac{kg}{m^3},$$

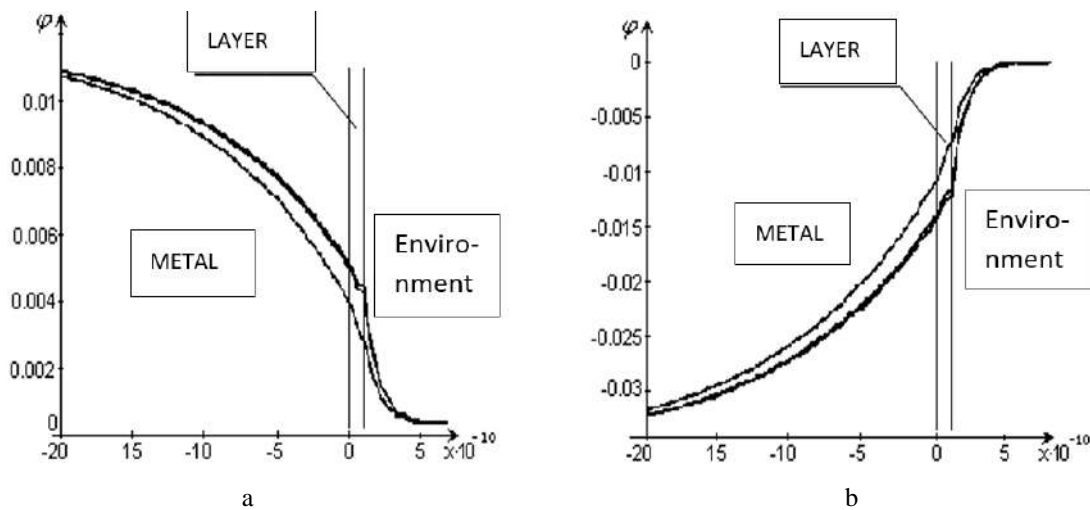
$$C = 10^3 \frac{C}{kg \cdot V}. \quad \text{Medium: } \chi_c = 10^{10} \frac{1}{m}.$$

The ratio of electrical conductivity of metal and medium is equal  $\sigma_m/\sigma_c = 1000$ . Parameters for layer are determined by formulas  $\chi_{mc} = a\chi_m + (1-a)\chi_c$ ,  $\sigma_{mc} = a\sigma_m + (1-a)\sigma_c$ , where  $a = 1/2$ . This choice of parameters is due to the lack of appropriate experimental values and is justified by the application of the known rule of mixtures, which, in most cases, leads to plausible results. The thickness of the layer is the inverted value to  $\chi_c$  and equal to  $h = 10^{-10}m$ . The following figures show the distribution of electric potentials in the metal, layer and medium, calculated by formulas (14)–(16) for copper (Fig. 3 a) and steel (Fig. 3 b) body with a rectilinear contact limit, loaded by effort correspondingly  $p = 2,35 \cdot 10^8 \frac{kg}{m^2}$  – copper, and  $p = -6,86 \cdot 10^8 \frac{kg}{m^2}$  – steel.



**Figure 3.** Distribution of potentials in metals and medium during their interaction

Analyzing formulas (14)–(16) and the last curves, we see that electric conductivity ratios  $\sigma_m/\sigma_c$  and stresses have a significant impact on the distribution of electric potentials. Let us construct the distribution of electric potentials for copper and steel, first (Figs. 4 a, 4 b) with the same load conditions, but the ratio  $\sigma_m/\sigma_c$  will be taken alternately equal to 10, 100, 1000.



**Figure 4.** The influence of the ratio of electrical conductivity on the distribution of electric potentials

The tendency to change the electrical conductivity for copper and steel is maintained almost in a mirror equidistant form. As we can see (Fig. 4) the change in the ratio of electrical conductivity is quite noticeable regardless of the sign «+» or «-» applied load, and with increasing ratio, the difference becomes less noticeable. We can also note that the effect of such a change in electric potentials in the metal is limited to a region of thickness  $20h$ , and  $5h$  in the medium respectively. Let us consider (fig. 5 a, 5 b) with constant correlation  $\sigma_m/\sigma_c = 1000$ , and with different loads.

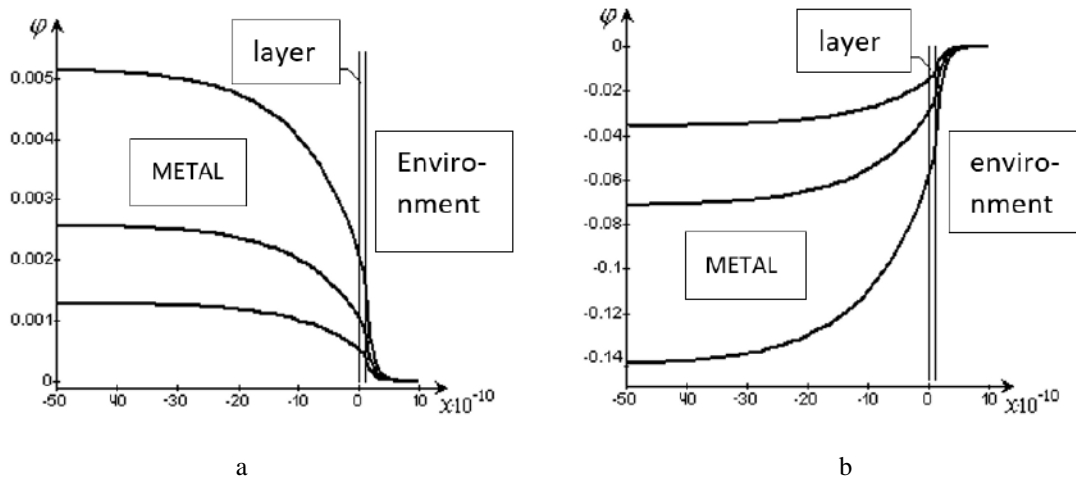


Figure 5. The Influence of voltage on the distribution of electric potentials

First curves in Fig. 5 are constructed for this load, and after its value was increased in two and then four times. Influence of stresses on electric potentials change is more vivid (fig. 5). If in the medium it can be limited by thickness  $h$ , it is not possible to do the same in the metal as potential grows when the load increases, and this doubts the application of results obtained with help of simulation in limitless regions to evaluate the behavior of small bodies at considerable loads.

Let us now consider the case of the interaction of two metals with the medium. Assume that metal 1 is copper,  $p = 2,35 \cdot 10^8 \frac{kg}{m^2}$ , metal 2 – steel,  $p = -6,86 \cdot 10^8 \frac{kg}{m^2}$ . We will accept  $h_1 = h_2 = 0, d_1 = d_2 = 10h$  and using problem solving (12)–(16), build the distribution of electric potentials (fig. 6).

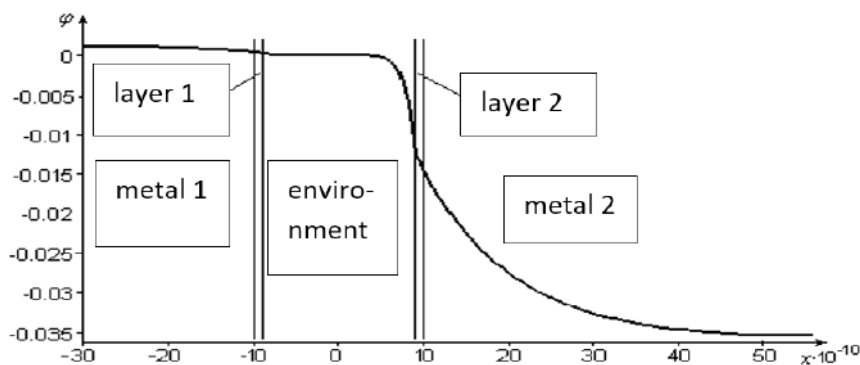
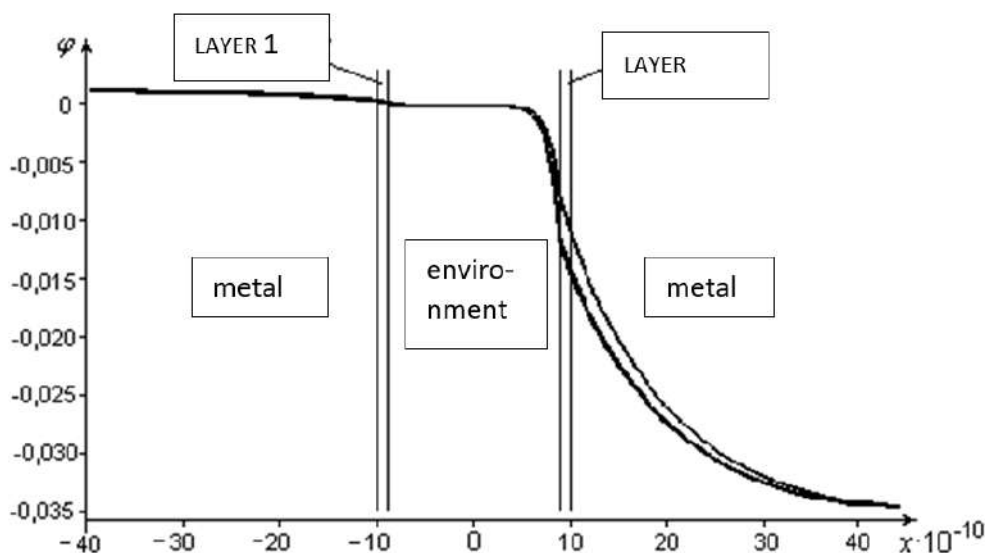
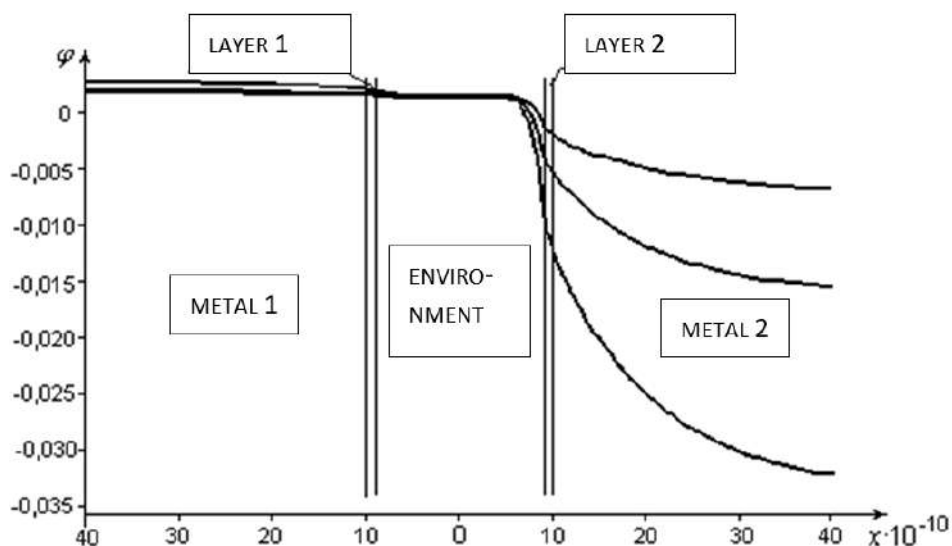


Figure 6. Distribution of electric potentials during the interaction of the medium with two metal bodies

Following the described scheme regarding the choice of constants, let us build graphs that show the influence of stress changes (Fig. 7) and changes in the ratio of metal and medium conductivities (Fig. 8) on the distribution of electric potentials in the interaction of two metal bodies filled with hydrogen.



**Figure 7.** Influence of the electrical conductivity on the distribution of electric potentials in case of interaction of the two metal bodies



**Figure 8.** Influence of voltage on the distribution of electric potentials in the case of interaction of two metal bodies

As can be seen, figures 7 and 8 confirm the influence of stress and conductivity ratio on the distribution of electric potentials in the metal and the medium during their interaction.



Based on the estimates made above, for the problem of interaction of a metal body with a corrosive medium along the rectilinear contact boundary, and for the problem of interaction of two metal bodies, the distance between which is filled with medium, we can say that the ratio of metal conductivity and stress the distribution of electric potentials in the metal and the environment during their interaction, and the influence of stresses is decisive. In the future, the above estimates can be used to solve other, more complex problems, such as problems when the body contains stress concentrators [13]. This is also significant for porous materials [14] given the internal stresses in the metal initiated by hydrogen saturation [15–16]. To some extent, the experimental results concerning the above material are in [17–18]. The peculiarities of hydrogen degradation of nickel heat-resistant alloy and the influence of hydrogen gas on its strength and ductility are highlighted in this work.

**Conclusions.** It has been shown that the electric potential on the surface of one of the charged metal bodies does not depend on the charge on the second body and on the ratio of the electrical conductivity of the medium to the electrical conductivity of the second body.

It has been established that the change of electric potential caused by charges grows (in absolute value) together with the increase in the ratio of electrical conductivity of the medium to the electrical conductivity of the body.

The obtained results can be used for expert assessment of durability, condition and reliability of building and industrial metal structures, loaded elements of machines and devices operating in aggressive hydrogen-containing environment, for non-destructive testing, as well as in designing primary converters of measuring information systems and automated control systems of technological processes to assess their metrological reliability.

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## РОЗРАХУНОК ЕЛЕКТРИЧНИХ ПОТЕНЦІАЛІВ НА ПОВЕРХНЯХ ВЗАЄМОДІЇ ДЕФОРМОВНИХ МЕТАЛЕВИХ ТІЛ З ВОДНЕВОВМІСНИМ СЕРЕДОВИЩЕМ

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**Резюме.** У переважній більшості експлуатація металевих конструкцій в робочих умовах призводить до того, що на ці конструкції або на певні їх елементи постійно діють не лише механічні фактори (навантаження, залишкові напруження і т. п.), але й навколишнє середовище. Елементи трубопроводів, несучі ділянки тепло- та гідроелектростанцій, металеві конструкції мостів протягом усього терміну експлуатації перебувають під впливом середовища, яке їх заповнює або оточує. Таке оточення, залежно від вмісту в ньому кислот та лугів, а також водневовмісних середовищ може виступати як корозійне. Слід також зауважити, що вплив водневовмісного середовища та дія механічних факторів є одночасні й взаємопов'язані між собою, що дуже часто призводить до крихкого чи квазікрихкого руйнування металу. Тому проблема оцінювання основних інженерних параметрів (міцності, надійності й т. п.) металевих конструкцій, які зазнають корозійного впливу при одночасній дії механічних силових факторів, на даний момент є актуальною проблемою промислової експлуатації. В роботі виконано постановку задач на основі торії пружності, електродинаміки, теоретичної електрохімії та рівнянь математичної фізики. За встановленими аналітичними співвідношеннями для розрахунків ефективних електропотенціалів й відповідними числовими експериментами проведено оцінювання електричних потенціалів на поверхнях взаємодії деформованих металевих тіл із водневовмісним середовищем.

**Ключові слова:** деформоване металеве тіло, електричний потенціал, діелектрична стала, подвійний електричний шар, електрострикційний коефіцієнт, відносне об'ємне розширення, питома електроємність металу, густина розподілу заряду, водневовмісне середовище.

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