

## INFLUENCE OF NON-ISOTHERMITY ON THE GENERAL AND LOCAL CORROSION OF COPPER AND IRON

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### Abstract

The effect of normal and tangential temperature gradients on copper's and iron's behavior under conditions of active dissolution, passive state and local depassivation was investigated. It was established that the heat flux directed from metal to solution can: a) to increase corrosion rate (Cu/NaCl); b) to reduce it (Fe/H<sub>2</sub>SO<sub>4</sub>); c) to change the destruction's nature (transition from passive state to pit corrosion - Cu/NaHCO<sub>3</sub> + NaCl, or transition from pit to spot corrosion - Cu/NaHCO<sub>3</sub> + Na<sub>2</sub>SO<sub>4</sub>). The appearance of tangential temperature gradient on metal flat plate contacting with flowing electrolyte is accompanying by the redistribution of destruction in most heated (Fe/H<sub>2</sub>SO<sub>4</sub>; Cu/NaCl) or most cold (Fe/NaOH) zones of the metal. Moreover nature of non-isothermal corroding surface destruction and general metal losses depends not only from temperature difference in system but also from change of temperature distribution law along metal. The discussion of the analyzed phenomenons reason was carried out.

**Key words:** Copper, iron, non-isothermal systems, sulphate, chloride, hydrocarbonate solutions, general and local corrosion.

### Introduction

The heat-exchangers exploitation is accompanying by appearance the tangential (along metal surface ) and normal ( on interface metal/solution) temperature gradients [1-4]. In these conditions the

general corrosion process is including two types of damage: thermogalvanic (TG) corrosion [1,2], connected with thermoelectric effects, and corrosion initiated by thermal flux from metal to aggressive liquid [3,4]. Both type of corrosion differ by specific features and influence on a general metal losses and development of local destruction. The detail analysis of these phenomenons in corrosion active, passive metals and metals undergoing local depassivation was carried out in the present work

## EXPERIMENTAL

Two types of complex plants, which permit to solve this problem, are used: 1- a plant with non-isothermal plate and 2 – a plant with heat-transferring rotation disk electrode[2,4,5].

The researches in conditions of tangential temperature gradient were carried out on the plant type 1[2,5].The design of the plant permits to measure simultaneously temperature distribution, potentials and corrosion currents along metal surface. The basic component of the plant is an electrolytic cell. The electrodes under investigation (6 of them in the experiment) are cylinder-shaped with working surface  $1 \times 10^{-4} \text{ m}^2$  are pressed into the bottom of the cell with electrode spacing  $1 \times 10^{-3} \text{ m}$ . The temperature of each electrode is set by the out contact heating (soldering iron type) and controlled by means of the special temperature meter device with indicator transistor. The technique of electrode heating makes it possible to obtain any temperature within the range of 30-90°C.

To provide laminar flux of electrolyte by the electrodes surface the latter are located in the center of the cell bottom at the distance twice as large as their common horizontal size. The above described location of electrodes allows to consider the system of different temperature gradient streamlined by the laminar flux of the solution.

The thermal and TG effects were estimated with help of special electric and commutation transistor schemes permitting to determine the distribution of temperature, potentials and corrosion currents along non-isothermal surface with absence and presence of the electric contact between it's areas. The experiments were carried out in the study of the TG corrosion of metals, contacting with flowing electrolyte ( $v=27 \times 10^{-4} \text{ m/s}$ ) in the temperature interval 20-70°C using of the different physic-chemical methods.

The influence of normal temperature gradient on electrochemical and corrosion behavior of metals is studied on the original plant type 2. The plant is made up of four blocks: 1 – electrode system; 2 – electrolytic cell; 3 – electronic control; 4 – motor speed control [2,4,6].

Table 1.

The investigated non-isothermal systems	
Metal	Electrolyte
Systems with normal temperature gradient	
Iron	0,05 M H <sub>2</sub> SO <sub>4</sub>
Copper	0,5 M NaCl
Copper	0,1 M NaHCO <sub>3</sub> + 0,01 M NaCl
Copper	0,1 M NaHCO <sub>3</sub> + 0,01 M
Systems with tangential temperature gradient	
Iron	0,005 M H <sub>2</sub> SO <sub>4</sub> + 0,045 M
Iron	0,1 M NaOH
Copper	0,5 M NaCl

The major element of the plant is a cylinder-shaped electrode ( $D=5 \times 10^{-3}$  m). From the inner side a hole is drilled for thermoresistor which is placed at the distance of  $1 \times 10^{-3}$  m from boundary dividing the phases and used for control the temperature on the disk surface. A regulated soldering iron-type heater heats electrode. Control block compresses devices for: 1 – electrode temperature control; 2 – electrode heater control; 3 – polarization; 4 – cell temperature regulation. The latter is a thermostatic glass with capacity  $1 \times 10^{-3}$  m<sup>3</sup>. Hydrodynamic conditions in the system are set by motor speed control block. The number of revolutions is controlled by a specially calibrated voltmeter and may deviate within the range of 120-2500 rpm.

The comparative data were received on the thermal equilibrium metal with electrolyte (TEE) and on heat-transferring (HTE) electrodes. Experiments were carried out at temperature ranging from 20 to 80°C and positive thermal fluxes (PTF) (directed from metal to solution) 14,0-56,8 kWt/m<sup>2</sup> with using the complex physico-chemical methods. The working electrode was an iron or copper. The auxiliary electrode was a platinum spiral or grid. All the

electrode potentials were measured using saturated silver/silver-chloride reference electrode held at 25°C, but all potentials were reported versus the normal hydrogen scale (NHE).

## **RESULTS AND DISCUSSION**

### **SYSTEMS WITH NORMAL TEMPERATURE GRADIENT**

The detail researches were carried out in the systems where 1) the active dissolving metal corrodes with kinetic ( $\text{Fe}/\text{H}_2\text{SO}_4$ ) or diffusion ( $\text{Cu}/\text{NaCl}$ ) control and 2) the passive metal undergoes of local corrosion (LC) ( $\text{Cu}/\text{NaHCO}_3+\text{NaCl}$ ;  $\text{Cu}/\text{NaHCO}_3+\text{Na}_2\text{SO}_4$ ). The experimental results have shown that at all investigated systems heat transfer essentially influences as the general metal corrosion stability as it's ability to local destruction without dependence from the nature of limiting process's stage. Hence the observed effects are differing under the system's nature influence.

Thus, PTF can be considered as the method of corrosion protection for system  $\text{Fe}/\text{H}_2\text{SO}_4$  (Fig.1) where the free corrosion rate HTE decreases in 1,5-1,7 times comparatively with TEE having the corresponding temperature. The interpretation of this effect was obtained at the series additional researches of iron's corrosion-electrochemical behavior under varying pH, sulphate-ions concentration, hydrodynamic and thermic conditions. According to the experimental results in the analyzed system  $\text{Fe}/\text{H}_2\text{SO}_4$  corrosion process taking place with mixed oxygen-hydrogen depolarization with the participation  $\text{OH}^-$  and  $\text{SO}_4^{2-}$ -ions in anodic reaction [7]. PHF 1) reduces general rate of process under parallel retarding of anodic and cathodic reactions at the expense of decreasing temperature of the reaction's zone and change of the adsorption's kinetic on the interface; 2) influences the kinetic order of anodic process in connection with change of adsorption properties of a surface; 3) changers the ratio of oxygen and hydrogen components in cathodic process for the benefit of the first because of intensive convective solution's stirring in near-electrode's zone and oxygen thermodiffusion from the solution's volume to the metal surface.

The opposite effect of heat flux was established in system  $\text{Cu}/\text{NaCl}$  where free corrosion rate for HTE exceeds corrosion rate for TEE (with corresponding surface temperature) in 1,5-2,0 times (Fig. 1).

This effect have been stipulated by the parallel accelerating anodic and cathodic reactions. According to the temperature-kinetic analysis data copper corrosion passes with oxygen depolarization under participation  $\text{Cl}^-$ -ions in anodic reaction [8]. Moreover in the both electrochemical reactions are taking place the diffusion limits. It is necessary to take into account the following facts – change of the

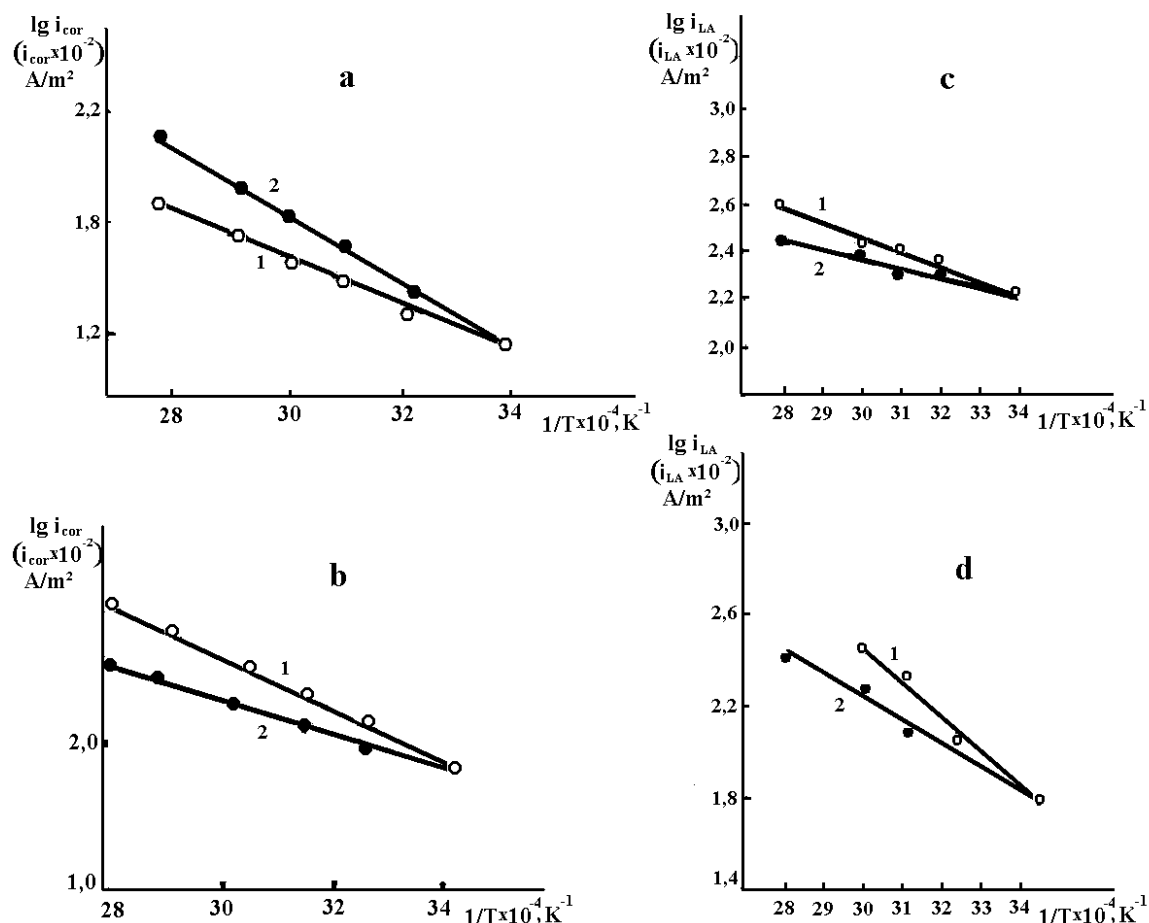


Fig.1. The temperature dependence of the rates of the free corrosion (a,b) and the local corrosion (c,d) of copper (a,c,d) in 0,5MNaCl (a), 0,1MNaHCO<sub>3</sub> +0,01M Na<sub>2</sub>SO<sub>4</sub> (c), 0,1MNaHCO<sub>3</sub> + 0,01MNaCl(d) and of iron in 0,05MH<sub>2</sub>SO<sub>4</sub> (b). 1-TEE; 2-HTE.

anodic product's nature from  $\text{CuCl}$  to  $[\text{CuCl}_2]^-$  under temperature rising TEE from 20 to 80°C and the stimulating PTF action not only on diffusion stages but on kinetic stages. This effect can be connected with change of composition and properties of the oxide-salt layer presenting on surface of heat electrode contacting with cold solution [9]. The presence of this films on copper surface

is confirmed by the established regularities of the cathodic process oxygen reduce in which 1) role of kinetic limits is significant; 2) Tafel coefficient value ( $b_k = 0,20 \text{ B}$ ) is excessive; 3) voltamperograms measuring in direct and opposite directions have the hysteresis. PTF, intensifying the oxygen transport from solution to metal, increases the oxides ratio in oxide-salt film with parallel raising it's defectivity. Most essential acceleration of cathodic process under PTF action was established in regime of limit diffusion current which was increased in 2,1-2,8 times.

Because in most practical cases (75%) corrosion heat-transferring surfaces have local character it was very interesting to estimate the PTF role at these conditions. Two systems differing by the mechanism of local corrosion (LC) were selected for investigation –  $\text{Cu}/\text{NaHCO}_3 + \text{NaCl}$  and  $\text{Cu}/\text{NaHCO}_3 + \text{Na}_2\text{SO}_4$  where copper is undergoing LC at zone potentials 0,500-0,800 V (NHE) more positive than steady state potential. The microscopic and chronoamperometric data have shown that at 20°C the copper surface destruction can be determined as spot corrosion (electrolytes with  $\text{Cl}^-$  -ions) or pit corrosion (solutions with  $\text{SO}_4^{2-}$  -ions) in dependence from ions activators nature. In addition the character of temperature influence in this systems is essentially differing. If the temperature of TEE is increased up to 80°C the process copper LC completely ceases in the solution with the  $\text{Cl}^-$  -ions additives (Fig.1). However under PTF conditions this effect didn't observe and spot corrosion metal surface transfers to pit corrosion (Fig.1). On the contrary, in the bicarbonate-sulphate solutions the temperature raising TEE and HTE is accompanying by the change copper surface destruction from pit corrosion to spot corrosion. But under corresponding surface temperature the PTF regime also reduces the LC rate at that case (Fig. 1).

The received inadequate effect of thermal conditions on the susceptibility of copper to LC in the investigated electrolytes stipulated by the different mechanism of pit initiation process [4,7] and the different nature the particle-activators – in bicarbonate-chloride solutions it is  $\text{CuCl}$ , in bicarbonate-sulphate it is  $\text{SO}_4^{2-}$  – ions. In connection with this the process of copper LC in the first case starts with the primary formation of the nuclear of crystallization  $\text{CuCl}$  on passive oxide-hydroxide film, which growing to the metal surface, causes its local destruction. In the second case, the ions-activators penetrate through the defects of oxide-hydroxide film to the metal/oxide interface and interacts with metal or with adsorption compound on its surface there. The increase of

the TEE temperature up to 80°C suppresses the development of the LC in bicarbonate-chloride mediums as a result of the intensification of the dissolving action of the heated electrolyte. The contact of oxidized copper with a cold solution under PTF condition promotes the formation of the nuclear of crystallization CuCl critical sizes on passive film surface, that stimulates the development of the LC. In solutions with  $\text{SO}_4^{2-}$  – ions additives the concentration of the ions-activators does not change with the increase of the temperature, but its activity grows. This together with the increase of the passive layers defects results in the strong etching of the metal surface. On the HTE the main role is playing the last factor and the LC intensity decreases in comparison with TEE at the appropriate surface temperature.

Thus the established inadequate action of temperature and non-isothermity in investigated systems is permitting to estimate the thermic factor as additional criteria for identification of general and local corrosion mechanism.

### **SYSTEMS WITH TANGENTIAL TEMPERATURE GRADIENT (THERMOGALVANIC CORROSION)**

The model with non-isothermal plate is permitting to program the different temperature distribution along metal surface. At this case temperature gradient's variation can be by two methods: 1) by the changing of plate's ends temperature under linear distribution of temperature along metal surface and 2) under the fixed the temperature difference in system by the varying the law of temperature distribution along metal surface. The second method was selected for present work under the estimation of TG effects role in general corrosion damage of iron in acid sulphate and alkaline solutions and of copper in neutral chloride electrolytes. The comparative data were received under linear (LTD), parabolic (PTD) and exponential (ETD) temperature distribution. (Fig. 2 )

Earlier it was shown that at the all investigated systems tangential temperature gradient due to potential gradient ( $dE/dl$ ) providing of TG corrosion development. Under this the temperature increase induces the linear change of steady state potential but the value and sign  $dE/dT$  essentially depends from the metal nature and the solution's composition.  $dE/dT = -1,6 \times 10^{-3}$  (Fe/ $\text{H}_2\text{SO}_4$ ),  $-0,8 \times 10^{-3}$  (Cu/ $\text{NaCl}$ ) and  $+2,0 \times 10^{-3}$  V/deg (Fe/ $\text{NaOH}$ ). Thus at zone of variable temperature at the first two cases (active metals) had to

act TG elements with the heat anodes but on the passive iron case had to act TG elements with the cold anodes. The results of the present research have shown (Fig.2) that the distribution of steady state potentials along plate from iron and copper in analyzed electrolytes is reproducing of the corresponding temperature distribution. According it under all thermic regimes the steady state potentials of iron in acid sulphate solution and copper in neutral chloride solution is displaced to the negative side in direction from cold to heat end of the plate and consequently the heat areas have to fulfill the anodic function under thermoelectric contacts conditions. The passive iron in alkaline solution demonstrates another behavior – it's steady state potential is displaced to positive direction at temperature increase and in the thermoelectric contact zone had to work TG elements with the cold anodes.

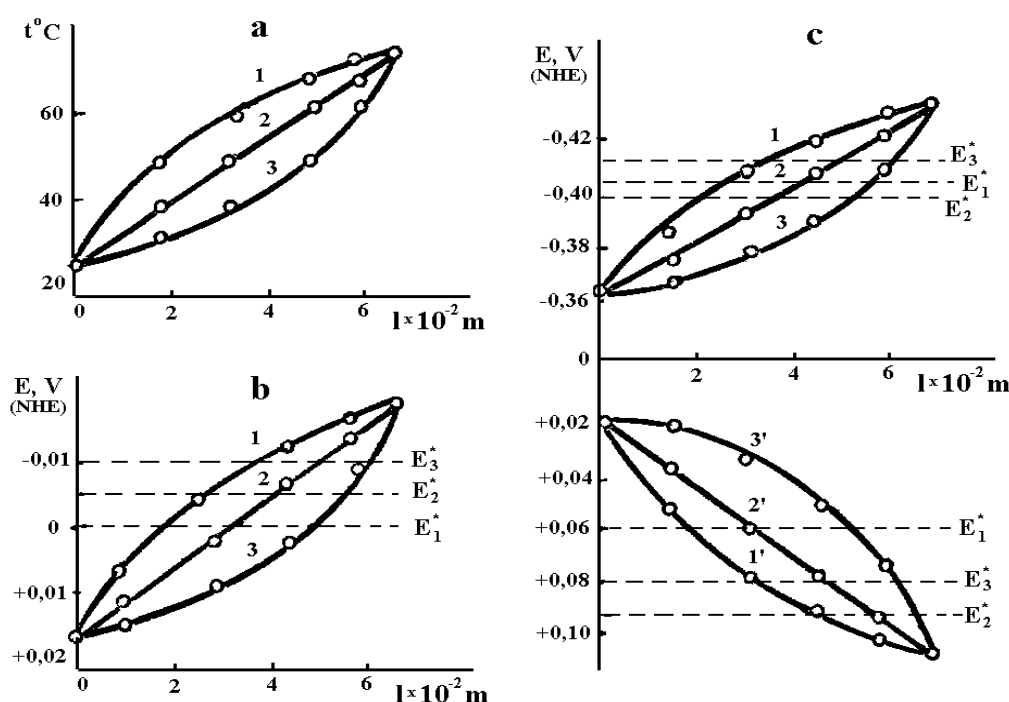


Fig.2. Distribution of the temperature (a) and steady state potential (b,c) along the copper (b) and iron (c) under parabolic (1,1'), linear (2,2'), and exponential (3,3') laws. Solutions- 0,5MNaCl (b); 0,005MH<sub>2</sub>SO<sub>4</sub> +0,45MNa<sub>2</sub>SO<sub>4</sub> (c-1,2,3); 0,1MNaOH (c-1', 2', 3')

In addition the changing of law temperature distribution produces the gradient temperature changing. Thus under LTD temperature gradient remains constant for all non-isothermal plate and under PTD it decreases from cold end to heat end of plate (at 10,0 time for copper, at 3,2 time for active iron and at 5,0 time for passive iron) but under ETD it increases at that direction (at 6,7; 1,7 and 3,5 times consequently for enumerated above systems. It's



naturally to assume that this effect has to be reflected at the character of non-isothermal metal surface destruction. For confirming this supposition the additional experiments and calculations were carried out [2, 5]. The obtained results have shown that a location of a point of a polarity inversion ( $I_0$ ) (in which electrode potential coincides with a mixed potential of short-circuited system with tangential temperature gradient ( $E^*$ ) and which divides non-isothermal metal plate on anodic and cathodic zones [5] at all investigated systems is displacing to the heat end of plate direction under transfer from PTD to LTD and ETD. Thus only under PTD TG corrosion of active metals (Fe/H<sub>2</sub>SO<sub>4</sub>; Cu/NaCl) passes in conditions of commensurable squares of anodic ( $S_a$ ) and cathodic ( $S_c$ ) zones (Fig. 3). For LTD and ETD the most part of non-isothermal plate is situating under cathode protection and the summary square of cathodic zones exceeds the anode's square at 1,9 (LTD); 4,5 (ETD) – Cu/NaCl and at 2,1(LTD); 5,0 (ETD) – Fe/H<sub>2</sub>SO<sub>4</sub>.

The passive iron's TG behavior in alkaline solutions, where the steady state potential of metal linearly shifts to the region of positive values,

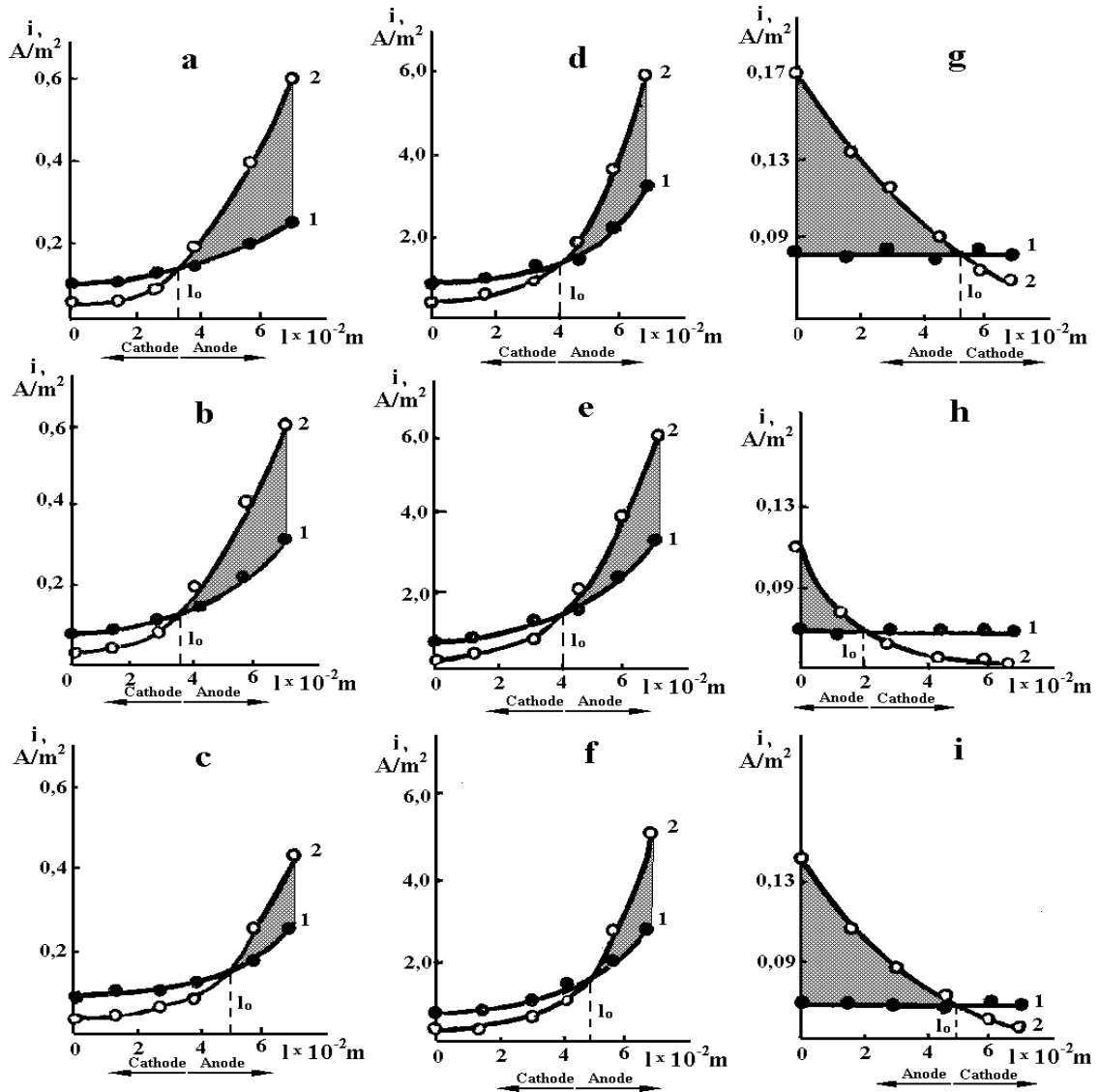


Fig.3. Corrosion destruction profile of the non-isothermal plate from copper in 0,5M NaCl (a,b,c) and iron in 0,005M  $H_2SO_4$  + 0,045M  $Na_2SO_4$  (d,e,f) and in 0,1M NaOH (g, h,i) under the free corrosion (1) and TG corrosion (2) conditions. (a, d, g – LTD, b, e, h – PTD, c, f, i –ETD).

differs from iron's TG behavior in acid electrolyte. It results the appearance TG elements with cold anodes in the thermoelectric contact zone [2,5] and thus thermal and TG effects have the opposite direction (Fig. 3). The TG effects predominant role due to the redistribution of destruction along non-isothermal surface with it's localization on cold sites under final accounting. In addition at line PTD→LTD→ETD the square of heat cathodic zone is decreasing. For example, relation  $S_c/S_a=2,0$  (PTD); 7,3 (LTD) and 12,2 (ETD).

Obviously, that described change of the corrosion damage profile of the investigated metal's non-isothermal plate is reflected on the general mass losses under thermoelectric contact conditions. In addition the important role plays as the nature of system so the temperature distribution law. Thus the development of TG corrosion on copper almost does not change the general losses under PTD, increases it at 3,0 times under LTD and decreases at 3,0 times under ETD. The behavior of active and passive iron is similar under LTD – TG corrosion causes the common increasing of mass losses in 3,2 and 12,6 times respectively. However under the two another laws of temperature distribution for active and passive metal was observed the opposite effects. Thus under ETD TG corrosion does not influence on general mass losses of active iron but sharply at 15,0 times increases it on passive metal. At PTD TG corrosion causes the decrease of general mass losses in 1,9 times for iron in alkaline solution under parallel strengthening of dangerous character of destruction, localized on small cold anode region. Under analogic conditions TG corrosion of active iron is accompanied the increase the general losses of metal in 7,0 times.

## Conclusion

- Influences of normal and tangential temperature gradient on the general and local corrosion copper and iron in the electrolytes with different pH and anion composition were investigated.
- The positive heat fluxes on the interface metal/solution can to stimulate (Cu/NaCl) or to inhibit (Fe/H<sub>2</sub>SO<sub>4</sub>) corrosion process for active dissolving metals but don't influence on it's mechanism.
- The heat-transfer action on copper LC intensity in hydrocarbonate solutions depends from nature of aggressive anions additives. In the presence chloride-ions LC intensity increases under heat fluxes, but in the presence sulphate-ions was observed the opposite effect.
- At the non-isothermal systems with tangential temperature gradients thermal and thermogalvanic (TG) effects can to enhance the action one another (Fe/H<sub>2</sub>SO<sub>4</sub>; Cu/NaCl) or on the contrary to relax it (Fe/NaOH). In the first case the zones of primary damage are being the heat areas, in the second – the cold areas.

- The commensurability of losses from thermal both TG effects and essentially dependence of non-isothermal metal surface destruction's nature from the law of temperature distribution are demonstrated.

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