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ROLE OF IRON OXIDE DEPOSITS IN CORROSION DAMAGE TO THE SURFACES OF STEAM-GENERATING TUBES OF BOILERS OF THERMAL POWER PLANTS

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As follows from thermodynamic calculations and an analysis of in-service data for heat-exchange surfaces of power plants, these surfaces are always characterized by the appearance of a temperature gradient. Even if the difference in temperature of some parts of the surface is small, it results in selective deposition of some ions and compounds dissolved in water, which means that each substance is deposited only at a certain characteristic temperature [1, 2].

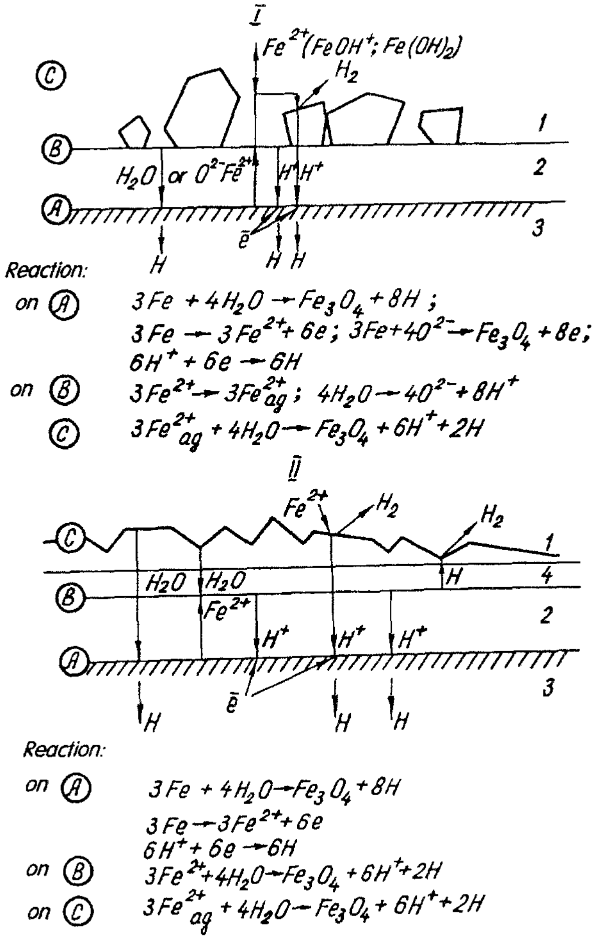

Fig. 1. Schematic representation of a magnetite film deposited on the surface of a steam-generating tube in the first (I) and last (II) stages of its formation: (1) external layer, (2) internal layer, (3) metal, (4) intermediate layer.

On the internal surface of steam-generating tubes, this process leads to the appearance of local thick surface deposits of magnetite. Deposition of magnetite layers is also promoted by the action of other factors such as a mag-

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netic field, vibrations induced by pulsation of water, and the presence of other magnetite layers (formed earlier as a result of corrosion processes). On the basis of an analysis of published experimental and theoretical data (one should especially mention a survey by Tomlinson [2]), the structure of the surface layers and a simplified scheme of diffusion processes at temperatures below 540°C can be represented in the form displayed in Fig. 1 [2–4].

The role of passivating layer is played by the defect-free oxide layer 2. Layer 2 is separated from the medium by the oxide layer 1, mainly formed of crystalline magnetite. The passivating layer of Fe_3O_4 inhibits diffusion of hydrogen atoms into the heat carrier. At the same time, at temperatures of about 340°C, it exhibits low permeability for hydrogen dissolved in water. In this layer, we observe diffusion of ionized oxygen to the metal surface and counterdiffusion of iron ions. Fe^{2+} ions form hydroxides [$FeOH^+$ and $Fe(OH)_2$] and ferrosoferic oxide (Fe_3O_4) (depending on the pH value of the heat carrier) and release protons, which partly undergo discharge and penetrate the heat carrier after formation of molecules and partly diffuse through the oxide layers to the metal surface. This process may promote reactive hydrogen-assisted intercrystalline cracking of low-carbon or low-alloy steels [5, 6]. It is likely that protons discharge on the metal surface and are absorbed by the steel. The portion of absorbed hydrogen may be as high as 90% if the metal surface is not covered with a protective film. In this case, the mass and charge balance is preserved. In [2] it is shown that a three-layer film is formed in the course of extended operation of low-carbon steel (more than 5000 h). At the same time, many researchers believe that this film consists of two layers.

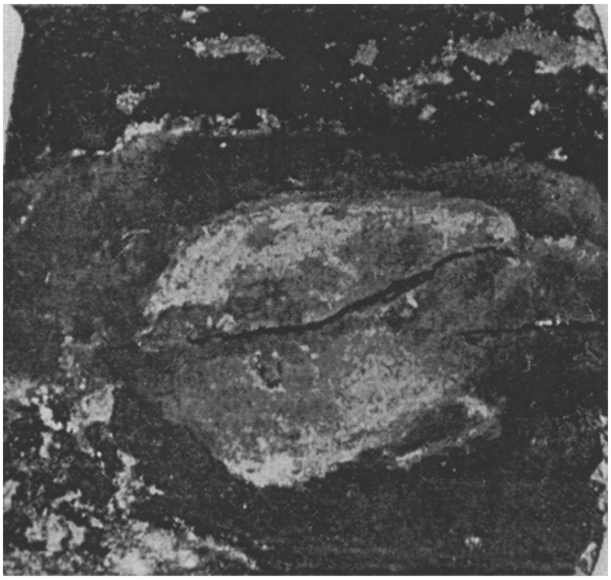

Fig. 2. Typical damage to a steam-generating tube by plastic rupture in the zone of thick multilayer deposits of magnetite.

Coupled reactions on surfaces B ($4H_2O \rightarrow 4O^{2-} + 8H^+$) and A ($3Fe + 4O^{2-} \rightarrow Fe_3O_4 + 8e$ and $H^+ + e \rightarrow H$) are other sources of hydrogen. It is assumed that molecules of water diffuse through the internal oxide layer 2 for $10^3 - 10^4$ h. Then they oxidize iron on surface A according to the reaction $3\,Fe + 4\,H_2O \rightarrow Fe_3O_4 + 8\,H$.

If the mass and charge balance is not preserved, the amount of hydrogen that diffuses in the steel may vary within the range 25–40%. Then, depending on the degree of saturation of the water with ions or iron oxide impurities, oxides leave some surfaces and precipitate on other surfaces.

Thus, the oxidized surface of steam-generating tubes is covered with an external crystalline layer of magnetite. As a result of extended operation, one observes the formation of an additional dense middle layer of oxides coherently connected with the internal layer. An increase in the thickness of this multilayer film, in particular, by the external deposition of magnetite, promotes growth of thermal stresses in local segments of the tube and prolonged or brief overheating of the metal. This leads to local plastic fracture of the metal. This type of fracture is typical of steam-generating tubes of boilers of thermal power plants (Fig. 2).

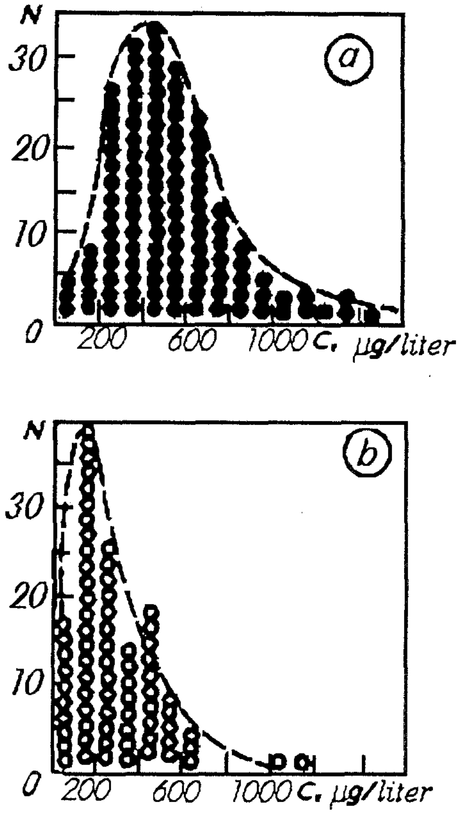

Fig. 3. Diagrams of the concentration of iron impurities in the industrial condensate of the TETs-1 plant (L'viv) before (a) and after (b) cleaning for a length of the nozzle of 0.85 m, an intensity of the magnetic field of 30–40 kA/m, and a filtration rate of 100–150 m/h.

A decrease in the concentration of iron ions and ferromagnetic iron oxide impurities in boiler and feed water and, in particular, in the condensate that returns to central heating and power plants from industrial enterprises should lead to a significant increase in the reliability and durability of heated surfaces of steam boilers. Electromagnetic cleaning proves to be a very efficient procedure for decreasing the concentration of the indicated impurities in water [7, 8].

Compared to well-known methods for magnetic cleaning of water of power plants, the use of electromagnetic filters appears to be more efficient and promising. Electromagnetic filters of improved design developed with the participation of one of the authors make it possible to attain significant improvement of the conditions of magnetization of the entire volume of the nozzle, which decreases considerably the energy consumption and results in better cleaning of return condensates [9, 10]. This is corroborated by the data on industrial use of improved electromagnetic filters in some thermal power plants, in particular, the TETs-1 (L'viv) and the Dobrotvir DRES (Fig. 3). Thus, the maximum content of iron impurities in the condensate prior to cleaning was approximately equal to 350–450 μg/liter. After processing, it was much lower (180–230 μg/liter). Moreover, after magnetic cleaning by improved electromagnetic filters, the maximum concentration of iron impurities in the industrial condensate of the TETs-1 (L'viv) was at most 630 μg/liter, whereas prior to cleaning, it was sometimes as high as 1400 μg/liter (Fig. 3).

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