AN APPARATUS FOR INVESTIGATING ANODIC PROTECTION OF STAINLESS STEELS

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This article describes an experimental apparatus used in developing a method for anodic protection of stainless steels in hydroxylamine sulfate at 40°. Diagrams of the polarization circuits and examples of passivation of tanks are given. The results obtained with the experimental apparatus confirmed our laboratory data on the effectiveness of anodic protection of stainless steels in hydroxylamine sulfate.

The apparatus described below was intended for use in developing a method for anodic protection of stainless steels against corrosion in aggressive media at temperatures between 10 and 120° and in checking the polarization and control circuits, which ensure passivation and automatic regulation of the protective potential.

In the case under consideration, the medium was hydroxylamine sulfate (HAS) produced by the Caprolactam Plant of the Severodonets Chemical Combine. The HAS content was 120-135 g/liter, the bulk weight of the solution was 1240 kg/m^3, and the solution acidity was 80-100 g/liter H_2SO_4.

The feasibility of anodic protection of chrome–nickel steels was preliminarily investigated with laboratory specimens and in a laboratory model with a protected-surface area of 0.1 m^2 [1]. The recommended protection regime was determined and the current densities for passivation and dissolution in the passive state were evaluated in these experiments.

The low aggressiveness of the vapor phase and the prolonged maintenance of the passive state after the current is discontinued (at 40°) makes a system consisting of stainless steel and an HAS solution very convenient for semicommercial tests. An increased corrosion rate in the waterline zone (which is usually encountered at high electrolyte temperatures) did not occur in this case.

Our results enabled us to move on to investigations of anodic protection in a large-scale apparatus (Figs. 1 and 2), which consisted of two tanks (650 liters each) fabricated from 0Kh21N5T (No. 1) and 0Kh21N6M2T (No. 2) steels; the tanks were cylindrical and had spheroidal bottoms. Each tank 1 was equipped with a steam jacket, a float device 2 for measuring the medium level, a funnel 3 for filling it with the aggressive medium, and collars for insertion of the cathode 4 and comparison electrode 5. There was also a hatch 6 for suspending the specimens, a housing for a resistance thermometer 8, and a device 7 for agitating the medium by bubbling nitrogen through it. *

The lower portions of tanks 1 and 2 were connected by piping with cocks 9. The housings for the flat device and resistance thermometer, the bubbler, and the piping in both tanks were made of 1Kh18N12M2T stainless steel.

Since 0Kh21N6M2T steel is self-passivating in an HAS medium [1], tank 2 initially served as a reservoir for the solution. Tank 1 was filled by forcing the medium out of tank 2 with nitrogen (4-5 atm).

The electrical portion of the apparatus consisted of two independent systems: tank passivation and automatic control. The passivation system included storage batteries 12, a knife switch 11, a rheostat 16,

* Nitrogen was selected for technological reasons. During the initial passivation period, the tanks were open to permit access of air and agitation with nitrogen began simultaneously with heating, after the steel had reached complete passivity.

State Institute of the Nitrogen Industry, Severodonets Branch. Translated from Zashchita Metallov, Vol. 4, No. 4, pp. 362-366, July-August, 1968. Original article submitted February 23, 1967.

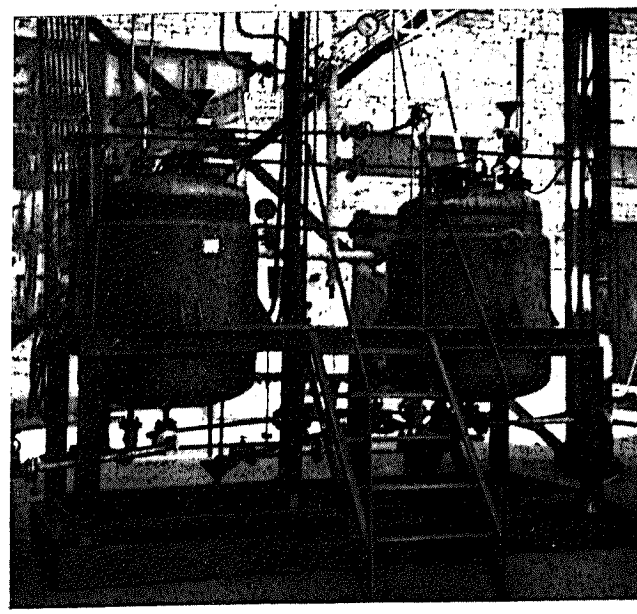

Fig. 1. Experimental apparatus.

a VSA-5 rectifier for charging the batteries 13, and a PSR-01 potentiograph for recording the current 15. This same potentiograph recorded the current during manual and automatic adjustment of the potential.

The automatic control system consisted of a high-resistance ÉPPV–5080 commercial potentiometer 27, a control unit 28, an autotransformer 21 with a reversible RD-09 motor 26, and a VSA-6 rectifier 20. Power was supplied to the system from a voltage stabilizer 23. The potential was measured with a cathode voltmeter.

Zero potential was set with the EPPV-5080 potentiometer. If the tank-wall potential differed from the predetermined value, the imbalance signal was fed through the amplifier of the EPPV-5080 to the reversible motor, which accordingly altered the voltage supplied to the rectifier through the autotransformer and hence the current polarizing the tank.

A platinum cathode is usually employed in anodic-protection equipment using sulfate media [2-4]. Molybdenum [5] and copper [6] can also be used for cathodes. We determined the cathodic polarization curves at M2 copper and molybdenum (TU V. M. No. 2-550-57) in HAS at 40 and 100° and also found the corrosion rates of the copper and molybdenum. Copper exhibited a higher corrosion resistance in HAS at 100°. The protective current density was several times greater for molybdenum than for copper.

The cathode (a copper tube) was placed along the axis of the tank and mounted in a collar, which was insulated from the tank wall by a polyvinyl chloride gasket. The cathode working surface was 776 cm^2 with the tank completely full. The comparison electrode was an immersed sulfate-mercury electrode with a fluoroplast housing. The potentials of this electrode in HAS were 0.37 and 0.38 V at 40 and 100°. *

The passivation of tank 1 was determined by two methods:

1) Tank 1 was filled half-full at 13-15° by forcing the HAS solution over from tank 2, so that the surface to be protected was 2.32 m^2. We measured the steady-state potential (-0.45 V) and an anodic current of 150-200 A was supplied to the tank from the storage batteries for several seconds. After the potential had shifted sharply in the positive direction, the batteries were disconnected and the tank was polarized with a current of 10-20 A from the rectifier. The protective potential was held constant at 0.35 V† by manual adjustment. When the current had decreased to 1-2 A, the automatic potential regulator was switched on. A current density of less than 10^{-5} A/cm^2 was reached over a period of 5-10 min (Fig. 4,

* Here and henceforth, the potentials are with respect to a saturated calomel electrode.

† Although the current density is lower at potentials of –0.1-0.2 V than at 0.2-0.7 V, the former region is close to that observed in the nondeaerated cathode-circuit solution and the true dissolution rate may not correspond to the anodic density [1].

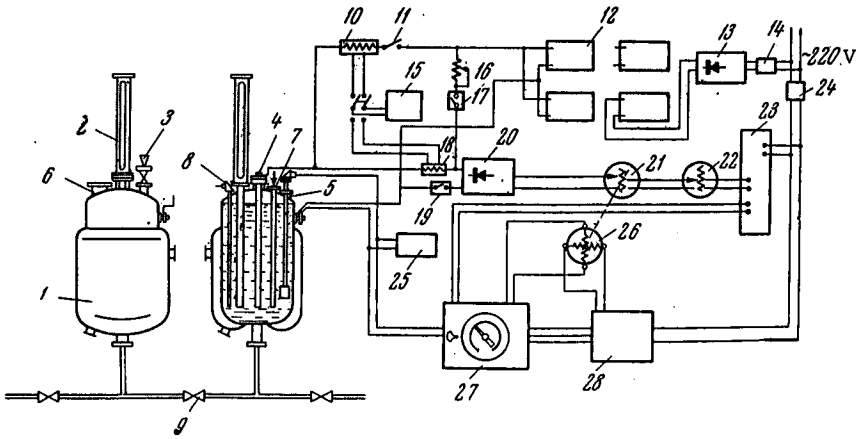

Fig. 2. Technological and electrical diagram of apparatus. 1) Tank; 2) level indicator; 3) funnel for filling; 4) cathode (copper rod); 5) comparison electrode; 6) specimen hatch; 7) nitrogen bubbler; 8) resistance thermometer; 9) draincock; 10) shunt, ×1000 A; 11) knife switch; 12) storage batteries; 13) VSA-5 rectifier; 14, 24) automatic line interlocks; 15) current recorder; 16) rheostat; 17) switch; 18) shunt, ×30 A; 19) switch; 20) VSA-6 rectifier; 21) autotransformer driven by RD-09; 22) autotransformer; 23) voltage stabilizer; 25) cathode voltmeter; 26) RD-09 motor; 27) ÉPPV–5080 pH-meter; 28) switching unit.

curve 1). The heater and bubbler were then switched on (the temperature was adjusted with the aid of a current-ratio indicator). A jump in current was observed during the first 2 h of passivation with the heater and bubble on (peaks B in Fig. 3); no rise in current was observed when the bubbler was subsequently switched on for brief periods. A stable protective current of $1.3 \cdot 10^{-6}$ A/cm^2, which correspond to a corrosion rate of 0.01 mm/year (i.e., less than the corrosion rate without protection by a factor of more than 200 [1]), was established after 3 h.

2) The tank was filled to capacity at 40°, so that the surface to be protected was 4 m^2. Passivation of the tank required a brief current pulse at 300 A. A stable passive state was achieved more slowly than in the first case. One day after the current was applied, the dissolution rate at $\varphi = 0.32$ V was $9 \cdot 10^{-6}$ A/cm^2 and only after several hundred hours was a stable protective current established (Fig. 3, curve 2). While the tank was in a stable passive state at 40°, raising the temperature to 60° almost doubled the protective current (Fig. 3, curve 3).

Under commercial conditions, it is important to know the self-activation time of the protected surface in case the polarization equipment breaks down, the power falls, etc. We discontinued the anodic protection for this purpose. The potential immediately dropped from 0.32 to 0.27 V but remained constant for the next three days. The self-activation time was not established, since the tank was not left unprotected for more than three days. As a result, activation of the tank surface was carried out by cathodic polarization (with a Pt anode) in our subsequent experiments. The activation time decreased as the current density rose (Fig. 4).

We found that both the walls of the tank and the components mounted on them (the level-indicator and resistance-thermometer housings and the funnel) were anodically protected. Five control specimens of 0Kh21N5T steel (three intact and two welded) were suspended in the tank, in contact with the walls. The corrosion rate was the same in all cases, 0.01 g/m^2·h, which corresponded to the current densities set up Only the stopcocks 9 (see Fig. 2) were not anodically protected; they had to be replaced with porcelain cocks.

During the protection period, we took samples to be analyzed for iron (through the hatch, after bubbling nitrogen through the medium for 10 min). The iron was determined by the rhodanide method. The corrosion rate calculated from the amount of iron in the solution was 0.017 mm/year (at 40°).

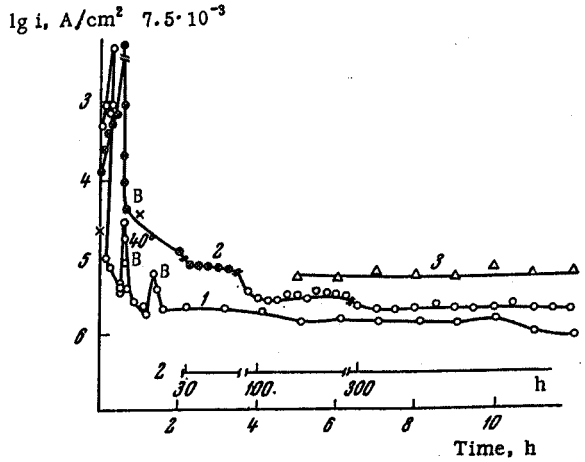

Fig. 3. Dependence of log i on time at $\varphi = 0.32$ V. 1) Passivation by method 1 at 40°; 2) passivation by method 2 at 40°; 3) after raising temperature of passive tank from 40 to 60°.

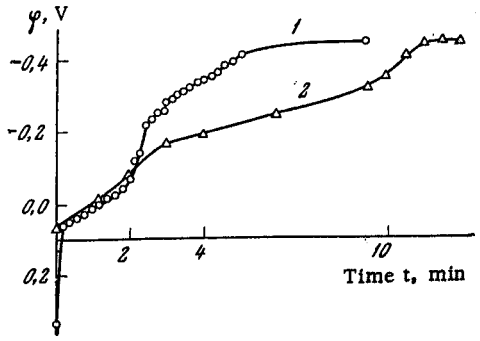

Fig. 4. Curves representing potential activation versus time. 1) $i = 6.5 \cdot 10^{-6}$ A/cm²; 2) $i = 2.2 \cdot 10^{-6}$ A/cm².

Our investigations showed the expediency and reliability of anodic protection of equipment intended for use with hydroxylamine sulfate at temperatures of up to 60° (see [1]) and enabled us to obtain data for practical design of equipment utilizing anodic protection.

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