

SELECTING CORROSION-RESISTING MATERIALS FOR MANUFACTURING INDUSTRIAL EQUIPMENT

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The reliability of chemical plants in service in corrosive media depends mainly on the selection of structural materials with an allowance made for their corrosion resistance under the given conditions determined in most cases in every specific case on the basis of the results of experimental corrosion investigations. The reliability of the results depends on the experimental method [1].

The Scientific Research Institute of Chemical Engineering have developed a method of corrosion tests of metallic specimens in systems operating under specific hydrodynamic conditions, such as autoclaves with mixing devices, filters, separators, dryers, and centrifuges. The following theoretical assumptions were taken into account in developing the method. Corrosion of metals in electrolytes takes place mainly with kinetic or diffusion control. In diffusion control, the corrosion process depends to a large extent on stirring of the solution, whereas in kinetic control stirring has no marked effect on the corrosion process [2]. The presence of solid particles in the solution may exert a certain effect on the corrosion rate of metal, irrespective of the type of inspection.

In all these systems, the medium is usually subjected to turbulent stirring. To evaluate the effect on corrosion resistance of steels of stirring in diffusion and kinetic control, of the concentration of solid particles in the solution and of the position of specimens in equipment, a system was developed for testing a relatively large number of specimens to obtain the results with the required fiducial probability (90-95%).

Equipment consists of a metallic cylindrical container 250 mm high and 280 mm in diameter with a propeller stirrer with blades 60 mm in diameter. The frequency of revolution of the stirrer (1370 rpm) ensures turbulent movement of aqueous solution. The test specimens, 20 × 80 × 3 mm in size, were prepared for tests in accordance with the requirements of the experimental procedure [3]. Under every test condition 12 specimens, insulated with rubber interlayers, were secured to the internal surface of the wall of the container using screws, and 8 specimens were placed in a special device 40 mm from the wall of the container. The specimens were distributed along the height in such a manner that they were completely immersed in the solution with the stirrer both operating and switched off. This was determined in advance on modeling equipment in a container made of plexiglass. The same equipment was used to determine the maximum amount of abrasive – silica sand (8%) which was completely transferred during stirring to the suspended state in the volume of the container. Specimens of St3 (GOST 380–88) and 12Kh18N10T (GOST 5632–72) steels were examined.

The following rules were taken into account in selecting test media: the corrosion rate of St3 steel in these solutions without mixing at 20-23°C should be in the range 0.05-1 g/(m²·h) which resulted in sufficiently short-term tests, and control of the corrosion process should be of the diffusion type in certain media and kinetic or mixed in others.

Corrosion tests without stirring were carried out in flasks.

To evaluate the controlling factor of the process of corrosion of St3 steel, we determined the corrosion potential and recorded the cathodic polarization curve using a platinum electrode pickled in advance in a solution: 3 volumes of HCl (density 1.19 g/cm³) + 1 volume of HNO₃ (density 1.4 g/cm³) for 3-5 sec at the boiling point. The electrode was then thoroughly rinsed in distilled water. Reproducible results were only obtained after this electrode preparation. Cathodic potentiodynamic curves were recorded at a rate of 7.2 V/h in a three-electrode cell in a P-5827 potentiostat. The resultant polarization curve can be regarded as the true cathodic curve of St3 but with a lower value of the depolarizing overvoltage. All potential values were determined in relation to a saturated silver chloride electrode.

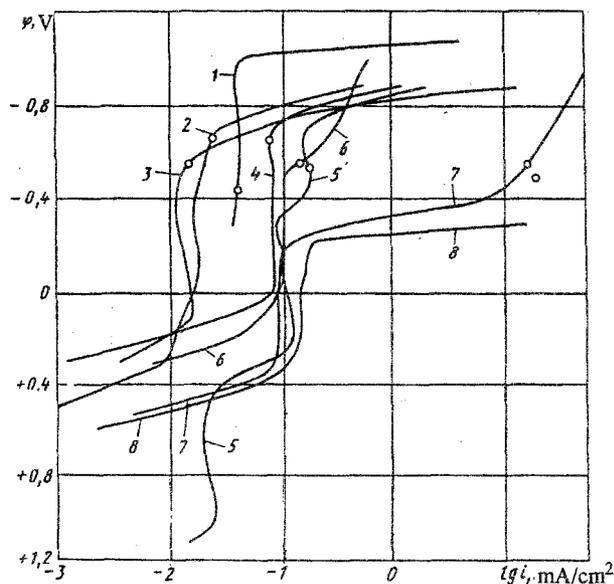


Fig. 1. Cathodic potentiodynamic polarization curves recorded at a rate of 7.2 V/h on a platinum electrode in different solutions (the values in the columns are the corrosion potentials φ_c , V, in relation to a silver chloride electrode): 1) 10% NaOH (-0.44); 2) 9% Na₂SO₄ (-0.68); 3) saturated Na₂SO₄ (-0.68); 4) 65% HNO₃ (+0.72); 5) 3% NaCl (-0.64); 6) 4% H₃BO₄ (-0.56); 7) 0.5% H₃PO₄ (-0.52); 8) 0.5% H₂SO₄ (-0.47); - corrosion potential of St3 steel.

Preliminary corrosion tests of St3 steel were carried out in the solution: 9% Na₂SO₄; saturated Na₂SO₄; 3% NaCl; saturated NaCl; 10% K₂SO₄; saturated K₂SO₄; 0.5, 1 and 3% H₂SO₄; 0.5, 1, 2 and 3% H₃PO₄; 4 and 5% H₃BO₃; 65% HNO₃; 10% NaOH. In neutral and alkaline solutions (see Fig.1) corrosion of St3 steel takes place with oxygen depolarization with nominant cathodic control as a result of oxygen diffusion. The corrosion potential of St3 steel is in the region of the threshold diffusion current of oxygen. Self-dissolution current were low and in all media they were all in the same order. Consequently, the corrosion rates should be similar, as confirmed by the results of corrosion tests (Table 1).

In acid media (H₃BO₃, H₃PO₄, H₂SO₄) the corrosion potential of St3 steel is situated in the region of generation of hydrogen and the corrosion process takes place preferentially as a result of hydrogen depolarization. However, in boric acid as a result of a low degree of dissociation of ions the self-solution current of steel is lower than in two other acids, and depolarization as a result of oxygen takes place with the intensity comparable with the depolarization caused by hydrogen. In sulfuric and phosphoric acids, corrosion of St3 steel takes place preferentially with hydrogen depolarization under kinetic inspection as a result of occurrence of the reaction of the solution of metal. The detected displacement to the positive side of the overvoltage of hydrogen generation on the cathodic curve in the boric phosphoric acid is caused by a reduction of the pH value of the solution during recording the curve (since the overvoltage of hydrogen generation depends on pH of the solution).

Tests were carried out in experimental equipment to determine the corrosion resistance of these steels in solutions during stirring at a temperature of 20-23°C. The test time both with and without stirring was 200 to 340 h, with the exception of tests in sulfuric acid (96 h). The results are presented in Table 1. The resultant values of the corrosion rate were statistically processed so that it was possible to determine the experiment error, carry out comparative analysis of the results and determine the minimum required number of parallel specimens of corrosion tests [4]. It was shown in [4] that the maximum and minimum rates of corrosion of the specimens under the same testing regimes may differ 3-6 or more times. The mean values, determine on three or four specimens differ by 20-35%. This difference is not the experimental error and is caused by the special features of the process of corrosion failure of metals which depends greatly on the physico-chemical heterogeneity of the metal of industrial melts [5].

The combined results of testing of the specimens in unstirred and stirred media are presented in Table 1.

TABLE 1

| No. of the group of media | No. of medium | Composition of medium | Mean corrosion rate of specimens of steels, g/(m ² ·h) | | |
|---------------------------|---------------|--|---|-------------------------------|-------------------------|
| | | | St3 | | 12Kh18N10T |
| | | | on the wall | in the volume of the solution | on the wall |
| 1 | 1 | 9% Na ₂ SO ₄ solution | $\frac{0,799}{0,039}$ | 0,627 | $\frac{0,0008}{0,0006}$ |
| | 2 | 9% Na ₂ SO ₄ solution + 2% sand | $\frac{0,658}{-}$ | 0,555 | - |
| | 3 | 9% Na ₂ SO ₄ solution + 8% sand | $\frac{0,35}{-}$ | 0,307 | 0,0053 |
| | 4 | Saturated (19%) Na ₂ SO ₄ solution without the deposit | $\frac{0,345}{0,029}$ | 0,372 | 0,08 |
| | 5 | Saturated Na ₂ SO ₄ solution + 4% deposit | $\frac{0,223}{0,003^*}$ | 0,295 | - |
| 2 | 6 | 3% NaCl solution | $\frac{0,519}{0,055}$ | 0,397 | $\frac{-}{0,0006}$ |
| | 7 | 3% NaCl solution + 8% sand | $\frac{0,296}{-}$ | 0,314 | 0,003 |
| | 8 | Saturated (36%) NaCl solution + 4% deposit | $\frac{0,139}{0,007^{**}}$ | 0,118 | - |
| 3 | 9 | 4% H ₃ BO ₃ solution | $\frac{0,296}{0,373}$ | 0,572 | 0,0006 |
| | 10 | 4% H ₃ BO ₃ solution + 8% sand | $\frac{0,265}{-}$ | 0,381 | - |
| 4 | 11 | 0.5% H ₂ SO ₄ solution | $\frac{1,745}{1,888}$ | 1,434 | 0,0315 |
| | 12 | 0.5% H ₂ SO ₄ solution + 8% sand | $\frac{1,466}{-}$ | 1,252 | 0,026 |
| 5 | 13 | 0.5% H ₃ PO ₄ solution | $\frac{0,481}{-}$ | 0,518 | - |

*The specimens and their layer of deposit.

**Saturated NaCl solution without the deposit.

Note. The numerator gives the values obtained in stirring the medium, the denominator without stirring.

Since at a large scatter of the data the evaluation of the mean corrosion rate gives a large error, the significance of the differences in the test results under different conditions was verified using Student's statistical criterion [4]. The calculated results are presented in Table 2. It may be seen that the significance of the differences in the corrosion rate of the specimens in the vessel wall and in the volume of the stirred solution is insignificant (within the limits of the statistical scatter). An exception is represented by the results of tests in boric and phosphoric acids. This is explained by the fact that the concentration of both acids are low and the cylindrical container was made of St3 steel whose walls, like the specimens, react with the acid. Therefore, the rate of reduction of the concentration of hydrogen ions at the wall is higher than in the volume of the solution and this also results in the difference in the corrosion rate. A rapid reduction of the concentration of hydrogen ions in corrosion of St3 steel in these acids is indicated by the results of electrochemical investigations (see Fig. 1).

Sulfuric acid the concentration of hydrogen ions is relatively high and no large difference forms during the test period in the concentration of the acid in the vessel wall and in the volume. Therefore, the significance in the difference of the corrosion rate of the specimens is not high. In neutral media (groups Nos. 1 and 2, see Tables 1 and 2) the process of corrosion of St3 steel is controlled by oxygen diffusion and mixing increases the corrosion rate 10 or more times. This corresponds to verification carried out using the statistical criterion (the significance of the difference is high).

In boric acid, the fraction of depolarization with oxygen during corrosion reaches approximately 50%. Consequently, stirring also increases the corrosion rate approximately five times (the significance of the difference is high).

In the phosphoric and sulfuric acids hydrogen acts as a depolarizer (the fraction of hydrogen is not higher than 0.1%) and, consequently, in stirring the significance of the difference of the corrosion rate is not high.

TABLE 2

| No. of the group of media | No. of the medium (see Table 1) | Significance of different corrosion rates of specimens tests under different conditions | | | |
|---------------------------|---------------------------------|---|---|----------------------------|---|
| | | without and with stirring | on the wall and in the volume of the solution | in media of the same group | |
| 1 | 1 | + | - | 1-2 | - |
| | 2 | + | - | 1-3 | + |
| | 3 | + | - | 1-4 | + |
| | 4 | + | - | 1-5 | + |
| | 5 | + | - | 2-3 | + |
| | | | | 2-4 | + |
| | | | | 2-5 | + |
| | | | | 3-4 | - |
| 2 | 6 | + | - | 3-5 | + |
| | 7 | + | - | 4-5 | + |
| | 8 | + | - | 6-7 | + |
| | | | | 6-8 | + |
| 3 | 9 | + | + | 7-8 | + |
| | 10 | + | + | 9-10 | + |
| 4 | 11 | - | - | | |
| | 12 | - | - | 11-12 | - |
| 5 | 13 | - | + | | |

Note. The plus indicates a high significance of the differences, the minus sign a low significance.

In all stirred neutral solutions the significance of the difference of the corrosion rates of St3 steel is high (see Table 2), with the exception of solutions Nos. 1-2 and 5-4. An addition of 2% sand into the 9% solution of a Na_2SO_4 has no effect on the significance of the difference of the corrosion rates of St3 steel. An increase of the salt concentration to the saturated solution reduces the corrosion rate of St3 steel. This is explained by a reduction of the solubility of oxygen [6]. The same effect is exerted by an increase of the concentration of sand to 8% in 9% solution of Na_2SO_4 . The presence in the saturated solution of Na_2SO_4 of 4% salt crystals reduces to an even greater extent (comparison with the solution without the crystals) the corrosion rate of St3 steel. Similar dependences were detected in the NaCl solution.

Thus, the presence of solid particles in stirred neutral solutions does not cause erosion, as initially expect, but, on the contrary, reduces the corrosion rate of St3 steel. It is probable that the presence of solid particles in the solution prevents the access of oxygen to the surface of the specimen.

In slightly acidic stirred solutions – boric acid (group No. 3) – the addition of 8% sand makes the difference in the corrosion rate of St3 steel significant. The reason is the same as in the neutral solutions, because in the boric acid depolarization of the corrosion process to 50% takes place as a result of oxygen. In 0.5% sulfuric acid (group No. 4) where the amount of the depolarizer (hydrogen ion) is relatively large, the addition of 8% sand does not cause any large change of the significance of the differences in the corrosion rate of the St3 steel (see Table 2).

These data as well as the reduction of the corrosion rate of St3 steel in the neutral solutions under the salt deposit (see Table 1) confirm the accuracy of the assumption on the screening effect on the solid particles on the access of oxygen to the surface of the specimen in the neutral solutions.

12Kh18N10T corrosion-resisting steel is in the passive state in the examined solutions and its corrosion rate in the neutral media does not exceed $0.003 \text{ g}/(\text{m}^2 \cdot \text{h})$ and in the acid media $0.03 \text{ g}/(\text{m}^2 \cdot \text{h})$. Stirring of the medium at the presence of up to 8% abrasive unit have no marked effect on the corrosion rate of the steel – the significance of the difference of the corrosion rates is not high.

The following conclusions may be drawn on the basis of the results of laboratory investigations. The tests that were carried out a larger number of specimens than that usually used in corrosion tests have made it possible to determine reliably the relationships governing the effect on the corrosion rate of stirring of the medium and the presence of solid particles in it. Statistical processing of the results showed whether the difference in the corrosion rates of St3 steel was caused by a difference in the process conditions or by random deviations.

In the media with mainly cathodic control with the process decelerated mainly by oxygen diffusion (neutral and slightly alkaline media) stirring of the solution increases the corrosion rate of the steel 10-30 times.

An increase of the salt content of the solution or the presence of solid particles (to 8%) slightly reduces the corrosion rate of the steel.

As a result of mainly cathodic control of the corrosion process with prevailing hydrogen depolarization (in acids) and in media with prevailing anodic inspection (in passivation of the metal) turbulent mixing and the presence of an abrasive in the solution has no marked effect on the corrosion rate of the steel.

The results may be used in selecting materials for systems such as filters, centrifuges, separators, and autoclaves with stirring devices. In these systems stirring of the medium (with the exception of certain types of filters in which the flow is laminar) and it is often not possible to place the specimens for testing in the working equipment. In this case, operation should start with determining the controlling factor of the corrosion process in the working media by recording, in this medium, the potentiodynamic polarization curve on a platinum electrode and measuring the corrosion potential of the examined steels.

In kinetic control, tests of the specimens may be carried out in the working medium without stirring, for example, in normal flasks. In diffusion or mixed control, the medium should be stirred and this can be carried out using the equipment described previously, because in turbulent movement of the flow its interaction with the wall of the container of equipment will be similar to that taking place in the apparatus. In laminar motion of the flow (in filters) the effect of the solution on the metal of the filter is vertical with the effect of the solution on the specimens tested in the flasks under a deposit without stirring. Likewise, if working equipment is available, corrosion tests of the specimens should be conducted in the receiving and supplying containers of the centrifuges, filters, separators, in areas where the solution is mixed with relatively high intensity. If it is possible to place specimens in working autoclaves with a stirrer or in a dryer, the laboratory tests are not required. The specimens must be placed in the system developed by the Scientific Research Institute of Chemical Engineering [1], on the internal wall of the autoclave or in the volume of the solution, and secure them firmly at a distance of no more than 40 mm from the wall. In the dryer, the specimens should also be secured to the wall, and in the drum drier also on the blades.

Calculations of the number of specimens required for the tests and evaluation of the results should be carried out taking into account the natural scatter of the test results, using statistical methods in accordance with recommendations in [4].

REFERENCES

1. I. G. Volikova, T. V. Strelkova, E. L. Rodicheva, and B. V. Lebedev, "Problem of the method of corrosion testing specimens of metals in working industrial equipment with external heating and a circulated medium," in: *New Materials of Corrosion Protection* [in Russian], Scientific Research Institute of Chemical Engineering, Moscow (1982) pp. 127-136.
2. N. D. Tomashov and G. P. Chernova, *Corrosion Theory and Corrosion-Resisting Structural Alloys* [in Russian], Metallurgiya, Moscow (1986).
3. RD 24.200.16—90. *Methods of Corrosion Testing Metallic Materials. Main Requirements. Evaluation of Results.*
4. R. G. Mannapov and I. G. Volikova, "Evaluation of the error of the results of corrosion tests of specimens," *Khim. Neft. Mashinostr.*, No. 1, 27-30 (1994).
5. R. G. Mannapov, *Methods of Evaluating the Reliability of Equipment Subjected to Corrosion: Review Information, Ser. KhM-9* [in Russian], Central Scientific Research Institute of Petrochemical Engineering, Moscow (1990).
6. *A Chemist's Handbook, Vol. 3* [in Russian], Khimiya, Moscow (1968).