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EVALUATION OF THE ERROR IN SPECIMEN CORROSION TEST RESULTS

R. G. Mannapov and I. G. Volikova

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The share of failures of petrochemical production equipment as the result of corrosion is ~60%. One of the primary reasons for this is incorrect selection of constructional materials based on the criterion of their corrosion resistance.

Normally constructional materials for specific chemical equipment are selected on the basis of data of experimental investigations. The reliability of the results obtained depends both upon the method of conducting the investigations and upon the correctness of evaluation of the test results. In this work a statistical analysis and an evaluation are made of the error in corrosion test results of normal size specimens [1] made on a special machine imitating industrial conditions and making it possible to simultaneously test 20 specimens fastened on the wall of a vessel with the investigated solution and at some distance from the wall.

The corrosion test results of specimens under the same conditions frequently have a significant spread. Table 1 shows data of tests in one of the media (9% Na_2SO_4 solution) of 26 specimens and their average values by area of location in the vessel of the machine. It may be seen that the maximum and minimum corrosion rates of specimens under the same test conditions differ by 3-6 times and the average corrosion rates determined for 3-4 specimens differ by 20-35% (in one case by 100%). This is not an experimental defect but is caused by features of the corrosion failure process of metals, which to a large degree is dependent on the physicochemical inhomogeneity of production melted metal and of unavoidable variations in the intensity of mass exchange of different portions of the corroding surfaces with the solution [2].

Statistical evaluations of the test results of specimens in other media are given in Table 2.

Since with a large spread in data evaluation of corrosion rate based on several specimens has a significant error, the relationship of the differences in test results under different conditions must be checked using statistical criteria such as the Student criterion:

$$t = \frac{|\bar{K}_1 - \bar{K}_2|}{S\sqrt{(1/n_1) + (1/n_2)}} < t_T ,$$

where $\bar{K}_1$ and $\bar{K}_2$ are the average corrosion rates under the first and second conditions, respectively, n_1 and n_2 are the numbers of tested specimens under each condition, S is the combined determination of the mean-square deviation calculated using the equation

$$S = \sqrt{\frac{S_1^2(n_1 - 1) + S_2^2(n_2 - 1)}{n_1 + n_2 - 2}} ;$$

S_1 and S_2 are the determinations of the mean-square deviations of the test results for the first and second conditions,

$$S_{1(2)} = \sqrt{\frac{\sum_1^{n_{1(2)}} (K_i - \bar{K}_{1(2)})^2}{n_{1(2)} - 1}} ;$$

and K_i is the corrosion rate of the i-th specimen.

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TABLE 1

Specimen material	Place of fastening the specimens	Number of specimens	Corrosion rate $K \cdot 10^2$, $g/(m^2 \cdot h)$			Test time, h
			single specimen	average for		
				group (3-4) of specimens	all specimens	
St3	on the vessel wall	12	40—112	72—97	80	200
St3	on hangers (in the volume of the solution)	8	32—83	56—69	63	200
12Kh18N10T	on the vessel wall	6	0,03—0,19	0,05—0,1	0,08	314

TABLE 2

Sample No.	Medium composition, %	Test time, h	Average corrosion rates K, $g/(m^2 \cdot h)$ and their variation coefficients V for steels			
			St3		12Kh18N10T	
			K	V	K	V
1	$9Na_2SO_4$	200	0,8 / 0,63	0,25 / 0,35	0,0008 / —	0,8 / —
2	$9Na_2SO_4$ + 2 sand	203	0,66 / 0,56	0,31 / 0,32	—	—
3	$9Na_2SO_4$ + 8 sand	194	0,35 / 0,31	0,17 / 0,17	0,0053 / —	0,84 / —
4	saturated Na_2SO_4 solution without sediment	204	0,34 / 0,37	0,08 / 0,15	0,008 / —	0,26 / —
5	saturated Na_2SO_4 solution + 4 sediment	197	0,22 / 0,3	0,48 / 0,35	—	—
6	3NaCl	203	0,52 / 0,4	0,33 / 0,29	—	—
7	3HCl + 8 sand	204	0,3 / 0,31	0,13 / 0,17	0,003 / —	0,67 / —
8	saturated NaCl solution + 4 sediment	209	0,14 / 0,12	0,28 / 0,51	—	—
9	$4H_3BO_3$	195	0,3 / 0,57	0,15 / 0,1	—	—
10	$4H_3BO_3$ + 8 sand	199	0,26 / 0,36	0,15 / 0,008	—	—
11	$0,5H_2SO_4$	96	0,74 / 1,43	0,26 / 0,35	0,0032 / —	2,05 / —
12	$0,5H_2SO_4$ + 8 sand	89	1,47 / 1,25	0,2 / 0,26	0,0026 / —	0,66 / —
13	$0,5H_3PO_4$	206	0,46 / 0.52	0,06 / 0.07	—	—

Note. The upper figures are the data of tests of specimens fastened on the wall and the lower on suspensions.

The table values of the Student criterion t_T are determined in relation to the level of fiducial probability and the number of degrees of freedom.

Such a checking procedure was done for the primary test conditions and the results are partially shown in Table 3, from which it may be seen that for the majority of test conditions the difference in corrosion rate for specimens fastened to the wall

TABLE 3

Sample No. (from Table 2)	Number of specimens in the samples	Ratio of the average corrosion rates in the samples	Calculated value of t	Table value of t_T (with γ = 0.95)	Significance of the difference* in corrosion rates
1	12–8	1,28	1,84	2,10	–
2	12–8	1,18	1,17	2,10	–
3	6–8	1,14	1,43	2,18	–
4	6–8	0,93	1,09	2,18	–
5	12–8	0,76	1,48	2,10	–
6	12–8	1,31	1,77	2,10	–
7	6–8	0,95	0,66	2,18	–
8	12–8	1,18	0,95	2,10	–
9	6–8	0,53	8,83	2,18	+
10	6–8	0,73	5,28	2,18	+
11	6–7	1,21	1,15	2,20	–
12	4–8	1,17	1,09	2,23	–
13	6–8	0.89	3.32	2.18	+

*+) Significant significance; –) insignificant.

and suspended in the volume of the agitated solution is not significant but within the limits of statistical spread. An exception is the test results in boric and phosphoric acids, the difference of which is significant and is caused by physicochemical reasons.

An analysis of the data of Table 3 shows that even a significant, at first glance, difference in average corrosion rate of more than 20% may be random and not be revealed reliably (with a fiducial probability of $\gamma = 0.95$) even in tests of 8-12 specimens. An even larger value of random deviations caused by the natural statistical spread may be observed with a small number of test specimens. This indicates that in comparative tests of specimens of different materials researchers may be in error. Therefore, before drawing conclusions from the results of such tests it is necessary to verify the statistical significance of differences in data obtained.

A comparison of test results in different media (Table 2) showed that the statistical significance of differences in average corrosion rates is not significant for samples 1-2, 2-13, 3-4, 3-7, 3-10, 4-7, 4-9, 4-10, 5-7, 6-9, 6-13, 7-10, 9-13, and 11-12. For the remaining combinations the difference is significant and is revealed with a fiducial probability of 0.99.

Verification of the hypothesis of uniformity of the variation coefficients of corrosion rate determined in different media showed agreement of it with the statistical data obtained. This indicates that the spread in data does not depend upon the composition of the medium but is determined primarily by the physicochemical homogeneity of the steel. Consequently, in planning of the necessary number of tests the average variation coefficient determined for all of the test data equal to 0.22 for carbon steels may be used.

The limiting error Δ of the test result is determined using the equation of the normal rule of distribution [2] characteristic of uniform corrosion

$$\Delta = t_\gamma \nu/\sqrt{N}\ , \tag{1}$$

where t_γ is the quantile of Student distribution corresponding to the fiducial probability γ. The average value of ν in tests of St3 steel specimens was 0.22 and in tests of specimens of 12Kh18N10T steel 0.84. Apparently in this case the higher value of ν is the result of lower corrosion losses comparable to the error related to removal of corrosion products and the impossibility of providing identical specimen preparation and absolutely similar test conditions, which influences the time of establishment of the steady state, which with a low corrosion rate is longer.

For example, in tests of 20 specimens of St3 steel the limiting error with a bilateral fiducial probability of 0.8 (t_γ = 1.73) using Eq. (1) does not exceed $\Delta = 0.085$ and with $\gamma = 0.9$ ($t_\gamma = 2.1$) $\Delta = 0.103$, that is, ~10%.

In tests of three specimens (minimum number according to GOST 9.909–82 [3]) the limiting error with $\gamma = 0.8$ is Δ = 0.371, that is, ~40%, and with $\gamma = 0.9$ $\Delta = 0.547$, that is, more than 50%. the most probable error (with $\gamma = 0.5$) is Δ = 0.229, that is, up to 25%.

In tests of 12Kh18N10T steel with small corrosion losses the coefficient of variation (0.84) is significantly higher and therefore in this case the error in determination of corrosion rate is significantly higher than in tests of St3 steel specimens.

With an increased area of specimen surface S in comparison with S_0 determined in RD 24.200.16−90 [1] the error decreases in the same way as with an increase in the number of specimens, that is, proportionally to the S/S_0 ratio. Consequently, in this case the limiting error may be determined from the equation

$$\Delta = t_\gamma v / \sqrt{N(S/S_0)} \ . \tag{2}$$

The necessary number of specimens for reliable tests

$$N = (t_\gamma v / \Delta) \ . \tag{3}$$

On the basis of the analysis conducted the following conclusions may be drawn.

With normally used number of specimens (2-4) of carbon steel the most probable error in the determined average rate of continuous corrosion is 25% and in 10% of the cases it exceeds 50%. In tests of corrosion-resistant steel specimens, the corrosion losses of which are much less, the error in evaluation is significantly higher, which must be taken into consideration in selection of materials. The number of specimens for tests must be calculated based on the allowable error taking into consideration the surface area of the specimens using Eqs. (1)-(3).

In comparative tests of different materials and also in investigation of the influence of the factors acting conclusions on the difference in the corrosion rates determined must be drawn only after checking the significance of the differences in the data obtained using statistical criteria such as the Student criterion.

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