Technical Note: Error Propagation in Coupon Immersion Tests*

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INTRODUCTION

Coupon immersion testing remains one of the most common methods of estimating corrosion rates or of making a final evaluation of alloy resistance to an environment. In this test, a metal specimen (coupon) of known dimensions is immersed in a fluid for a specified length of time. The corrosion or penetration rate is estimated from the mass lost during the exposure. The rate is estimated by

$$R = \frac{K\,(m_1 - m_2)}{A\,(t_1 - t_2)\,\rho} \qquad (1)$$

where R is the penetration (corrosion) rate (mm/y), A is the exposed area (cm), m_1 and m_2 are the initial and final masses (gm), t_1 and t_2 are the starting and ending times (h), ρ is the density (gm/cm^3), and K is a constant for unit conversion.

One question that arises when examining reproducibility of immersion test results is the amount of uncertainty that measurement of each of the observables, time, mass loss, and area, contributes to the total uncertainty in Equation (1). This error defines the minimum uncertainty in the penetration rate that is possible during a given experiment. Such minimum uncertainty would be possible when (a) there is no localized corrosion, (b) the penetration is uniform across the coupon surface, (c) the projected and actual surface areas are the same, (d) weights are unaffected by corrosion product removal, (e) areas have not changed during the exposure, and (f) the penetration rate is independent of time. The goal of this note is to provide the corrosion practitioner with an understanding of how exposure time, mass change, and area can impact the error propagation and uncertainty in Equation (1). This information should provide the practitioner with an idea of the best accuracy that can be achieved with this test as a function of these observables.

PROCEDURE

The variance of the corrosion rate may be estimated by using a two-step process. First, Equation (1) is linearized about the measured values of m_1, m_2, A, t_1, and t_2.[1] Second, the variance of the corrosion rate is estimated by using the linearized function and the theory of error propagation. This variance is found by using a weighted sum of the variances of each of the measured values of m_1, m_2, A, t_1, and t_2. The weights are the squares of the coefficients of each of the terms resulting from the linearization process. The variance in the corrosion rate (V[R]) may be expressed in terms of the variance of the measured variables as

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$$V(R) = \left[\frac{\partial R}{\partial m_1}\right]^2 \sigma_m^2 + \left[\frac{\partial R}{\partial m_2}\right]^2 \sigma_m^2 + \left[\frac{\partial R}{\partial t_1}\right]^2 \sigma_t^2 + \left[\frac{\partial R}{\partial t_2}\right]^2 \sigma_t^2 + \left[\frac{\partial R}{\partial A}\right]^2 \sigma_A^2 \qquad (2)$$

where σ_m, σ_t, and σ_A are the standard deviations of the measured values of mass, time, and area.[2] Equation (2) defines the relationship of the uncertainty in measurement of weight, time, and area with the resulting uncertainty in the corrosion rate. The partial derivatives of Equation (2) are determined by taking the partial derivatives with respect to each of the variables in Equation (1).

The standard deviations of the measurement of weight (σ_w) and the measurement of area (σ_A) can be determined by multiple weight determinations of the same sample coupon and by multiple measurements of the area of the same coupon. Often the measurement of the duration of the corrosion test is expressed as t ± e. The error, e, represents the uncertainty in the time measurement caused by the manner in which the beginning and ending times of the experiment are recorded. For example, if the initial time of the experiment is reported to the nearest hour, then e is 0.5 h (30 min). By assuming that the actual duration of the experiment is likely to fall anywhere in the range of t – e to t + e, the standard deviation of the time measure is[3]

$$\sigma_t = \frac{2e}{\sqrt{12}} \qquad (3)$$

The uncertainty being contributed by variation in exposure time, coupon dimensions, and mass was explored for five cases. These are the ASTM Standard G-31[4] recommendations on accuracy, the somewhat "typical" practices in the laboratory and plant, the recommended time vs corrosion rate criterion outlined in ASTM Standard G-31 (time in h = 2000/corrosion rate in mpy), and results for experiments using a weighing accuracy of 0.0005 g instead of 0.0001 g. The calculation was made using a 5.08 cm by 2.54 cm by 0.3175 cm (2 in. by 1 in. by 1/8 in.) coupon with a 0.9525 cm (3/8 in.) diameter hole. The density was assumed to be that of iron (7.86 gm/cc). Corrosion rates of 2.54, 25.4, and 254 µm/y (0.1, 1, and 10 mpy) were used in all cases. Exposure times were assumed to be 1, 7, and 30 days for the first three cases and fifth case. The results are shown in Tables 1 through 5.

Table 1 shows that the uncertainty in the weight measurement is the dominant source of experimental error for short test durations and low corrosion rates when using the ASTM recommendations for accuracy. As test duration increases or the corrosion rate increases, the dominant uncertainty shifts from the weight measurement to the area measurement. When the corrosion rate is low (2.54 µm/y) and the duration is short (1 to 7 days), the resulting uncertainty in the corrosion rate is large.

Reporting experimental duration to the nearest 0.01 h (36 s) would be the exception, not the rule. Table 2 shows that when using a "more typical" 0.5 h reporting accuracy, the error in time dominates the variation for short duration experiments and larger corrosion rates. In general, the standard deviation and standard error are similar to those in Table 1 implying that the stringent ASTM G-31 recommendation for time reporting does not gain anything in accuracy for estimating corrosion rates.

Table 3 shows an estimate of the uncertainty that can result from a typical in-plant coupon immersion test. The exact dimensions are often not measured, but they are estimated by assuming the dimensions to be the nominal coupon dimensions. The test time is

TABLE 1

Uncertainty in Corrosion Test Results When Using ASTM G31 Recommendations on Accuracy

Corrosion Rate µm/y	Corrosion Rate mpy	Test Duration days	Standard Deviation of Corrosion Rate, µm/y	Standard Error	Percent of Total Variation Due to		
					Weight	Area	Time
2.54	0.1	1	2.080	81.9%	100.00	0.00	0.00
25.4	1	1	2.080	8.2%	99.85	0.15	0.00
254	10	1	2.080	0.8%	86.86	12.99	0.15
2.54	0.1	7	0.297	11.7%	99.83	0.07	0.00
25.4	1	7	0.307	1.2%	93.17	6.82	0.00
254	10	7	0.856	1%	12.01	87.97	0.02
2.54	0.1	30	0.069	2.7%	98.67	1.33	0.00
25.4	1	30	0.107	0.4%	42.64	57.36	0.00
254	10	30	0.081	0.3%	0.74	99.26	1.33

(A) Standard deviation of weight measurement of 0.0001 g.
(B) Standard deviation of area measurement of 0.1 cm^2.
(C) Time measurement error of ±0.01 h.
(D) Standard error of measurement is standard deviation/predicted or measured value.

often rounded to the nearest half of a shift (approximately 4 h). The corrosion rates determined by this procedure make the area measurement the major source of uncertainty. However, since the tests are usually long (e.g., 90 days), the standard error of the corrosion rate is less than 5 percent.

Table 4 shows the results using the ASTM Standard G-31 recommendations for test duration assuming a reporting accuracy of 30 min. In all cases, the standard errors of the experiments are less than 1 percent. Errors in the area calculation dominate the uncertainty.

Finally, Table 5 shows the results when either the balance is poorly calibrated or when a small amount of dirt or deposit remains on the coupon after cleaning. The weights are assumed to be accurate to 0.0005 g, all other parameters with respect to the variables time and area are the same as in Table 1. The weight measurement is the dominating contributor to the standard error in all but the last case. More

TABLE 2

Uncertainty in Corrosion Test Results When Using Typical Laboratory Practices on Accuracy

Corrosion Rate µm/y	Corrosion Rate mpy	Test Duration days	Standard Deviation of Corrosion Rate, µm/y	Standard Error	Percent of Total Variation Due to		
					Weight	Area	Time
2.54	0.1	1	2.080	81.9%	99.96	0.00	0.04
25.4	1	1	2.126	8.4%	95.72	0.14	4.13
254	10	1	4.851	1.9%	18.29	2.73	78.98
2.54	0.1	7	0.297	11.7%	99.88	0.07	0.04
25.4	1	7	0.315	1.2%	89.57	6.56	3.87
254	10	7	1.057	0.4%	7.91	57.94	34.15
2.54	0.1	30	0.070	2.7%	98.63	1.33	0.04
25.4	1	30	0.107	0.4%	41.87	56.33	1.81
254	10	30	0.820	0.3%	0.72	96.20	0.72

(A) Standard deviation of weight measurement of 0.0001 g.
(B) Standard deviation of area measurement of 0.1 cm^2.
(C) Time measurement error of ±0.5 h.
(D) Standard error of measurement is standard deviation/predicted or measured value.

TABLE 3

Uncertainty in Corrosion Test Results When Using Corrosion Coupons Installed in an Operating Plant

Corrosion Rate µm/y	Corrosion Rate mpy	Test Duration days	Standard Deviation of Corrosion Rate, µm/y	Standard Error	Percent of Total Variation Due to		
					Weight	Area	Time
2.54	0.1	90	0.075	2.9%	9.49	90.24	0.26
25.4	1	90	0.714	2.8%	0.10	99.61	0.29
254	10	90	7.137	2.8%	0.00	99.71	0.29

(A) Standard deviation of weight measurement of 0.0001 g.
(B) Standard deviation of area measurement of 0.886 cm^2. This corresponds to a possible measurement error of 0.254 cm (0.01 in.) in length on each face of the coupon.
(C) Time measurement error of ±4 h.
(D) Standard error of measurement is standard deviation/predicted or measured value.

TABLE 4

Uncertainty in Corrosion Test Results When Using ASTM G31 Recommendations on Experiment Duration

Corrosion Rate µm/y	Corrosion Rate mpy	Test Duration h	Standard Deviation of Corrosion Rate, µm/y	Standard Error	Percent of Total Variation Due to		
					Weight	Area	Time
2.54	0.1	20,000.00	0.008	0.3%	8.79	91.21	0.00
25.4	1	2000.00	0.008	0.3%	8.75	90.87	0.38
254	10	200.00	0.988	0.4%	6.37	66.13	27.50

(A) Standard deviation of weight measurement of 0.0001 g.
(B) Standard deviation of area measurement of 0.1 cm^2.
(C) Time measurement error of ±0.5 h.
(D) Standard error of measurement is standard deviation/predicted or measured value.
(E) Duration of experiment in h = 2000/corrosion rate in mpy.

TABLE 5
Uncertainty in Corrosion Test Results When Using a Poorly Calibrated Scale

Corrosion Rate µm/y	Corrosion Rate mpy	Test Duration days	Standard Deviation of Corrosion Rate, µm/y	Standard Error	Percent of Total Variation Due to		
					Weight	Area	Time
2.54	0.1	1	10.389	409.%	100.00	0.00	0.00
25.4	1	1	10.414	41.%	99.82	0.01	0.17
254	10	1	11.278	4.4%	84.84	0.51	14.65
2.54	0.1	7	1.486	58.5%	100.00	0.00	0.00
25.4	1	7	1.488	5.9%	99.54	0.29	0.17
254	10	7	1.798	0.7%	68.23	19.99	11.78
2.54	0.1	30	0.345	13.6%	99.94	0.05	0.00
25.4	1	30	0.356	1.4%	94.74	5.10	0.16
254	10	30	0.886	0.4%	15.26	82.11	2.64

(A) Standard deviation of weight measurement of 0.0005 g.
(B) Standard deviation of area measurement of 0.1 cm^2.
(C) Time measurement error of ±0.5 h.
(D) Standard error of measurement is standard deviation/predicted or measured value.

importantly, low corrosion rates cannot be measured accurately in less than a week. Even after a month of exposure, there may be a significant error. An accurate balance is essential.

CONCLUSIONS

Several conclusions can be made from these results.

❖ The longer the immersion test, the smaller the error, assuming that the environment remains unchanged. Adhering to the ASTM Standard G-31 recommendation for the test time (h) divided by the expected corrosion rate (mpy) is a good rule-of-thumb, if the error is to be minimized. The ability to control the environment may limit the test duration so that the long test times needed for accurate measurement of low corrosion rates may not be achievable.

❖ Accurate weight determination is essential to minimize the uncertainty. The balance should have an accuracy of at least 0.0001 g. Weighing each coupon at least three times and taking the average would decrease the uncertainty somewhat.

❖ Normal laboratory practice of reporting the experimental time to the nearest 30 min is adequate for tests lasting 7 or 30 days.

❖ Normal field practice of using the nominal coupon size to determine the surface area is adequate if the test duration is at least 90 days.

❖ Accurate determination of low corrosion rates (contamination rates) by coupon immersion tests may not be achievable. Use of additional techniques such as solution analysis by inductively coupled plasma (ICP) or use of electrochemical impedance spectroscopy (EIS)[5] should be considered to supplement and corroborate such mass loss results.

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