

LETTERS TO THE EDITORS

The Editors do not hold themselves responsible for opinions expressed by their correspondents. No notice is taken of anonymous communications.

Distribution of Attack on Iron or Zinc Partly Immersed in Chloride Solutions

IRON or zinc partially immersed in sodium or potassium chloride at first remains unattacked at the water-line. Corrosion occurs at a zone somewhat below the water-line, and researches at Cambridge¹ have indicated it to be connected with the electric current flowing between this zone as anode and a cathodic zone at the water-line, where oxygen, the cathodic stimulator, can most easily be renewed. The corrosion rate has been found to be approximately equivalent, in the sense of Faraday's Law, to this current, which, for solutions of high conductivity, may approach the limiting value given by the intersection of the anodic and cathodic polarization curves; for less conducting liquids, it is that value i , which will make an intercept iR , where R is the resistance. Thus the short-period phenomena have been fairly well cleared up. However, the long-period corrosion researches of Bengough and Wormwell² at Teddington have shown that finally both metals became more attacked at the water-line than anywhere else. The violent attack at the zone previously immune tended to suggest that the mechanism of corrosion in the later stages was different from that in the early stages; but by introducing the essential distinction between probability and conditional velocity³, a common explanation appears for the seemingly divergent facts.

If the probability that corrosion will commence at a given point within a time element dt be defined as $p dt$, the chance that the point will escape corrosion for time t and then commence to corrode in dt will be $e^{-pt} p dt$. The 'expected' corrosion over an experiment lasting time T will be

$$\int_0^T e^{-pt} pu (T-t) dt, \quad \text{or} \quad uT - \frac{u}{p} (1 - e^{-pT}),$$

where u is the conditional velocity (mass per unit time and area). This approaches the limiting values of $\frac{1}{2}upT^2$ and uT , as T approaches zero and infinity respectively.

Now p will be minimal at the water-line, since the cathodic product (sodium or potassium hydroxide) is a powerful inhibitor; on the other hand, u will be maximal at the water-line, although it will vary little with level, unless the 'intercept-correction', referred to above, is considerable. Numerous measurements of potential at different distances from the water-line have indicated⁴ that the intercept-correction is small, except in very dilute solution; we may expect, therefore, that u will be maximal at the water-line, but that its variation with level will be much less than that of p . Consequently, in the early stages where u and p enter symmetrically into the expression $\frac{1}{2}upT^2$, the expected corrosion will in effect be least where p is lowest, thus explaining the immunity at the water-line. In the later stages, where p does not enter into the expression (uT), the expected corrosion will be greatest at the water-line, where u is highest. Thus we arrive at an explanation of the apparently discordant facts that *the water-line is unattacked in the early stages and severely attacked in the later stages.*

Other possible causes for the severe water-line attack in the advanced stages may deserve consideration, but for the moment the mechanism suggested seems capable of explaining the known facts. The argument just sketched has, however, neglected the possibility that the value of p or u may be shifted by previous occurrences at the same point, or by simultaneous occurrences at neighbouring points. The accumulation of alkali at the water-line (if not dissipated by stirring or by conversion to carbonate) may cause p to fall with the time, thus postponing, perhaps indefinitely, the breakdown at the water-line. Experiments by Dr. T. P. Hoar and by Dr. R. S. Thornhill at Cambridge, largely unpublished, have shown that, if such disturbances be avoided, the water-line will remain immune for long periods (60–90 days). Zinc is more liable to attack at the water-line than iron, while wetting of the specimen above the water-line is found to increase the chance of breakdown, as would, of course, be expected.

Metallurgical Laboratories, Ulick R. EVANS.
University, Cambridge.
July 16.

¹ Evans, U. R., *J. Inst. Met.*, **30**, 257 (1923); Evans, U. R., and Hoar, T. P., *Proc. Roy. Soc.*, A, **137**, 343 (1932); Agar, J. N., unpublished work summarized by Evans, U. R., *J. Iron Steel Inst.*, **141**, 221P (1940).

² Bengough, G. D., and Wormwell, F., *Proc. Roy. Soc.*, A, **140**, 402 (1933); *Chem. Ind.*, 262 (1936).

³ Evans, U. R., Mears, R. B., and Queneau, P., *Engineering*, **136**, 689 (1933); Evans, U. R., and Mears, R. B., *Proc. Roy. Soc.*, A, **146**, 164 (1934); *Trans. Faraday Soc.*, **31**, 530 (1935).

⁴ Evans, U. R., Bannister, L. C., and Britton, S. C., *Proc. Roy. Soc.*, A, **131**, 366 (1931); Evans, U. R., and Hoar, T. P., *Proc. Roy. Soc.*, A, **137**, 358 (1932).

Determination of Absolute from Relative X-Ray Intensity Data

In the 'absolute measurements' of X-ray intensities of reflexions from a crystal, a measurement must be made of the monochromatic radiation incident upon the crystal in one second¹, which, though it can be done fairly conveniently by the ionization chamber method², requires a complicated design of apparatus in the use of the rotation photographic method. I have considered the problem in the light of a new synthesis of X-ray data³ and found that the absolute values of $|F(h)|^2$ may be deduced to a close approximation from the relative intensity data without any further experimental work. The derivation of the equations needed in this deduction in the case of a linear crystal is shown below.

We first assume the relative intensities are known, deduced, in the case of the photographic methods, from the total blackening of the reflexion lines or spots registered on a photographic film. We then assume that corrections are made to these observed data for the various geometrical factors such as the polarization factor, the Lorentz factor, planar factor, and so on. We further assume that we have corrected for the temperature factor. (This assumption is in general not exactly true of course.) The final result is a set of numerical values $H(h)$ which are linearly related to $|F(h)|^2$ by $H(h) = c |F(h)|^2$, where c is the constant multiplying factor we intend to determine. For the moment we assume c is known. Then according to Y. L. equation (5) [the notation stands for

equation (5) in Yü's letter³] we have, $E(h) = \frac{H(h)}{2c\psi(j)^2}$.

If we denote $\frac{H(h)}{\psi(j)^2}$ by K_h for $h \neq 0$ then $E_h = \frac{K_h}{c}$.