

# THE MEASUREMENT OF CORROSION USING ELECTROCHEMICAL $1/f$ NOISE\*

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Abstract - Amplitude spectra of low frequency electrochemical noise are presented which show a correlation between the rate and mode of corrosion attack and fluctuations of the corrosion potential. The results indicate the possibility of a non-perturbative electrochemical corrosion monitoring technique capable of detection of pitting and crevice attack.

## INTRODUCTION

SPONTANEOUS fluctuations of the potential of a freely corroding electrode are a well known and easily observable phenomenon. The fluctuations constitute an important source of error in electrochemical corrosion rate monitoring<sup>1</sup> and are a cause of the large scatter usually observed in low frequency electrochemical impedance measurements<sup>2</sup>. The nature of the fluctuations is such that the accuracy of measurement cannot be improved by an increase in the measurement time as is possible with purely random, "white", sources of noise where the accuracy increases as the square root of the measurement time<sup>3</sup>. A survey of available literature reveals that very little is known of the origin of these fluctuations and that there is no single theory explaining their behaviour<sup>4-6</sup> although general mechanical models which could be applicable to electrochemical situations do exist<sup>7</sup>.

Observations of low frequency fluctuations are not confined to electrochemistry. Fluctuations of this nature have been observed in almost all areas of science, ranging from biochemistry to astronomy,<sup>8,9</sup> and have received thorough investigation in the field of semiconductor science<sup>10,11</sup>. In electronics low frequency (flicker or  $1/f$ ) noise has been the chief obstacle in the design of low noise low frequency amplifiers<sup>12</sup>.

Attempts have been made to quantify electrochemical noise. Blanc and co-workers measured electrochemical noise with a system of carefully screened battery-powered galvanostats and amplifiers<sup>13</sup>. Using essentially analogue techniques Blanc *et al.* were able to determine the noise output of several electrochemical systems<sup>14</sup>. Their early publications presented the data in the unusual form of correlation function but more recent results were presented in the conventional terms of power spectral density<sup>15</sup>.

Bertocci investigated electrochemical noise using a specially constructed low noise potentiostat<sup>16</sup> together with a Fourier spectrum analyser and measured the current noise of polarized aluminium electrodes undergoing pitting<sup>17,18</sup>. Bertocci noted a  $1/f$  type of relationship between the measured noise power and its frequency for the electrodes tested.

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Analogue measurements are inherently inaccurate and are very susceptible to external interference. At high frequencies, the observed amplitudes of electrochemical noise are very low, necessitating the use of very high gain electronic amplifiers. At the low frequencies most electronic amplifiers are appreciably noisy; their noise contribution is of the same  $1/f$  type as the incoming electrochemical noise signal and is difficult to remove by the usual techniques of filtering or averaging. A possible solution is to use amplifiers of the "CAZ" type which are free of low frequency  $1/f$  noise.

Our first experiments used such a system of high gain analogue amplifiers and our measurements were aimed at the detection of pit and crevice corrosion<sup>19</sup>. For the continuation of this work we used computer controlled apparatus, digital in nature. The results presented here show that the free corrosion potential behaviour contains valuable information pertaining to the rate and type of corrosion attack and that such measurements could form the basis of a non-perturbative electrochemical technique of corrosion measurement.

## EXPERIMENTAL METHOD

### *Description of apparatus*

The apparatus used for the measurements employed a Hewlett-Packard HP-85A desk-top computer acting as a controller for the IEEE-488 interface bus connecting all the other instruments. Potentials were measured with a Solartron 7055 digital microprocessor voltmeter and amplitude spectra were computed using a Hewlett-Packard 3582A spectrum analyser. Hard copy plots of the results were then produced on a Hewlett-Packard 7225A graphics plotter.

Electrode noise was measured as the potential difference between two "identical" electrodes. We found this technique preferable to the more conventional reference electrode arrangement although both these techniques gave essentially identical results. The voltmeter used employed digital techniques for mains interference rejection and drift correction making it possible to measure electrode potentials to an accuracy of  $\pm 0.1$  mV even in the presence of strong mains frequency fields without the need for any special screening arrangements.

The potential difference between the two electrodes was sampled by the voltmeter under programme control at a rate derived from the computer's internal clock. The readings were transferred to the computer and the resulting "time record" was digitally filtered using suitable mathematical manipulations of the data in order to remove the d.c. component and components at frequencies outside the range of interest<sup>20</sup>. The time record, comprising 1024 data points, was then transferred to the memory of the spectrum analyzer. Using programmes internal to the analyzer, the Fourier transform of the data was computed and plotted on the analyzer display screen. Eight consecutive amplitude spectra were r.m.s. averaged by the analyzer and the result was transferred back to the computer. Spectral amplitude smoothing was then applied, again using suitable computational algorithms,<sup>20</sup> and the resulting corrected amplitude spectrum was plotted on the graphics plotter and stored on magnetic tape cartridge.

The overall accuracy of measurement was limited by the resolution of the voltmeter. Dynamic range limitations resulted from the 16 bit arithmetic used to compute the transform, restricting that range to *ca* 90 dB. In this respect we were balancing accuracy against speed; the analyzer took about 0.3 s to carry out the transform, a transform run solely by the computer took up to 5 min to compute. The results presented below were obtained using an effective sampling rate of 1.024 Hz after filtering. Theoretically we were able to measure over a frequency range of 1 mHz-0.512 Hz; practical limitations reduced this to 1-255 mHz with 1 mHz resolution. The results were corrected for the bandwidth of measurement and plotted as logarithm of frequency vs logarithm of amplitude (dB V/Hz<sup>1/2</sup>).

### *Materials*

The metals tested were 99.99% copper, an aluminium alloy containing 2.1 %Mg and mild steel. Electrodes were made from these three metals, masked off with epoxy putty compounds and ground to a "1200" grit size finish. The exposed areas were 5 cm<sup>2</sup> for copper, 12.5 cm<sup>2</sup> for aluminium and 5.5 cm<sup>2</sup> for mild steel. Sea water was prepared from BDH Chemicals sea water mixture and the solution was aerated both before and during the test runs.

The electrodes were set up in a cell vessel containing 500 ml of the test solution and were connected to the voltmeter with suitable lengths of insulated copper wire. No attempts were made to screen out external electromagnetic fields apart from shielding of the cell from direct sunlight (photopotential effects can cause significant errors in this type of measurement).

## EXPERIMENTAL RESULTS AND DISCUSSION

### *Copper*

Copper in aerated sea water forms a film of  $\text{Cu}_2\text{O}$ ; the corrosion rate is initially high but decreases rapidly with immersion time<sup>21</sup>. After approx. 30 min of immersion the oxide film became visible on parts of the electrodes and eventually covered both of the electrodes by the end of the test.

Figure 1 shows noise amplitude spectra obtained after 2, 38 and 113 h of immersion. After 2 h of immersion the oxide film was still growing, the overall noise level was relatively high. The amplitude spectrum shows a clear "roll-off" at frequencies above 20 mHz, the rate of this roll-off approaches -40 dB/decade. After 38 h the noise output showed an overall drop in amplitude. Output at 1 mHz was some 20 dB lower (a factor of 10), the higher frequency output was 6 dB less than previously (a factor of 2). The slope of the roll-off remained constant, approaching -40 dB/decade. The spectrum obtained after 113 h shows similar features but the roll-off begins nearly a decade of frequency lower, indicating a possible increase of the time constant of the electrode process impedance. The noise levels are 40 dB lower at 1 mHz (a factor of 100) compared to those observed initially. At frequencies above 20 mHz the electrode noise begins to be masked by the noise background of the measurement apparatus.

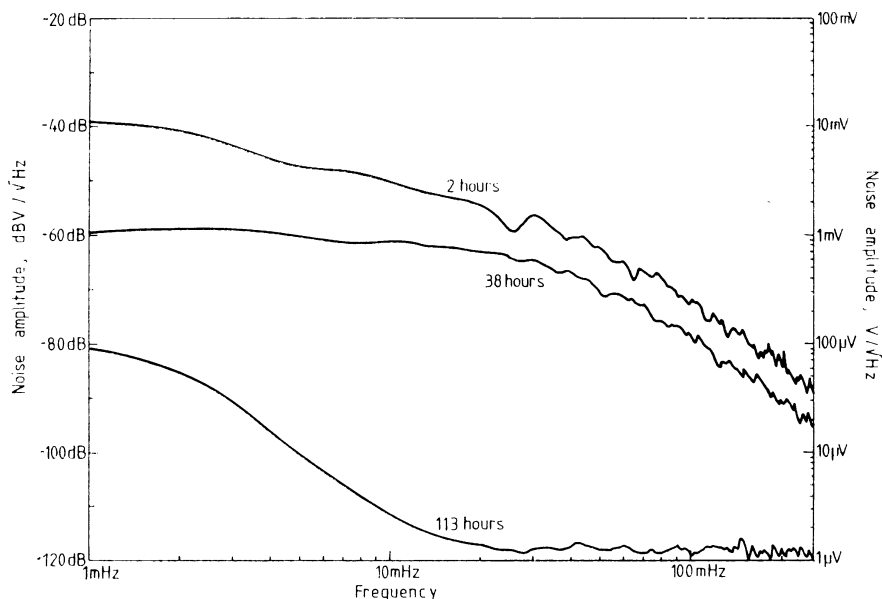


FIG. 1. Copper in aerated sea water. Electrochemical noise amplitude spectra obtained after 2, 38 and 113 hours of immersion

At present it is difficult to quantify these results but some qualitative observations can be made. This ( $1/f$ ) type of noise, where the noise power varies inversely with frequency, should result in a slope of up to  $-10$  dB/decade on the amplitude spectrum plot.<sup>7</sup> Any additional slope can only be caused by secondary effects such as contributions of resistance-capacitance (R-C) combinations. The effect of double layer capacitance and charge transfer resistance would cause an additional increase of the slope by  $-20$  dB/decade. Similarly Warburg diffusion effects would cause a  $-10$  dB/decade increase.<sup>21-23</sup> Existing impedance measurements indicate that the film formation process on copper in aerated sea water is controlled both by activation (charge transfer) and by concentration (diffusion) effects<sup>21</sup>. It therefore seems possible to conjecture that the  $-40$  dB/decade slope observed is made up from the  $1/f$  noise contribution ( $-10$  dB/decade), a charge transfer-double layer effect ( $-20$  dB/decade) and a diffusion contribution  $-10$  dB/decade).

Throughout this and the other tests careful investigations were made of the convection effects of aeration on the electrode noise output. We found that by a judicious positioning of the sintered glass aerator it was possible to eliminate such effects in nearly all situations with the possible exception of the copper electrodes after prolonged periods of immersion. In that instance the electrochemical noise output was so low that effects of solution movement, building vibration, light intensity variations, etc. became significant.

#### Aluminium

The alloy tested had a reasonable corrosion resistance to sea water and the

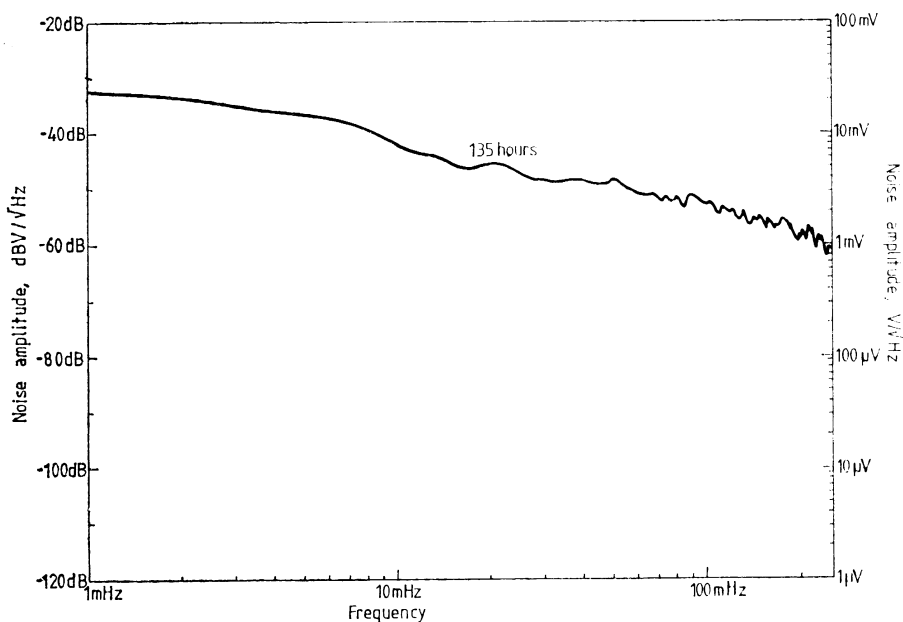


FIG.2. Aluminium alloy in aerated sea water. Electrochemical noise amplitude spectrum obtained after 135 h of immersion showing effects of pitting corrosion.

corrosion attack had the form of a localized "etch" of the electrode surface, detailed examination revealed this to consist of a large number of small pits close together. The noise output was found to be invariant with time and only one amplitude spectrum is shown in Fig. 2. This was recorded after 15 h of immersion. The noise output covers a wide frequency range and the sharp high frequency roll-off observed with copper electrodes is absent. The only roll-off present approaches -10 dB/decade.

Our previous work<sup>19</sup> indicated that the potential fluctuations associated with pit initiation are characterized by a series of sharp decreases of the electrode potential followed by exponential recoveries. Halford<sup>7</sup> has shown that in general such behaviour will result in a typical  $1/f$  noise spectrum, giving a -10 dB/decade slope of the amplitude plot. We have carried out tests on other systems undergoing pitting corrosion and can conclude that this type of noise output with its shallow slope is a characteristic indication of pitting attack.

### Mild Steel

After immersion the mild steel electrodes rapidly formed a film of "green rust" - presumably  $\text{Fe}^{2+}$  compounds which later changed in parts to "red rust" -  $\text{Fe}^{3+}$  compounds.

Figure 3 shows noise amplitude spectra obtained after 2 and 72 h of immersion. The noise amplitude at 1 mHz was initially similar to those observed on copper and aluminium shortly after immersion but the high frequency roll-off was much sharper; approaching -50 dB/decade. With time the low frequency output decreased but

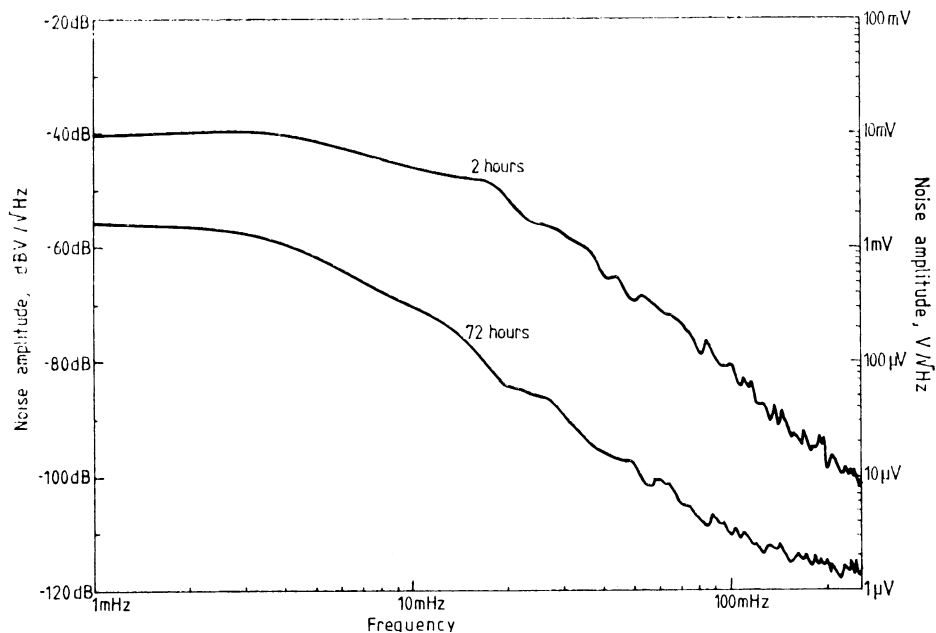


FIG.3. Mild steel in aerated sea water. Electrochemical noise amplitude spectra obtained after 2 and 72 h of immersion.

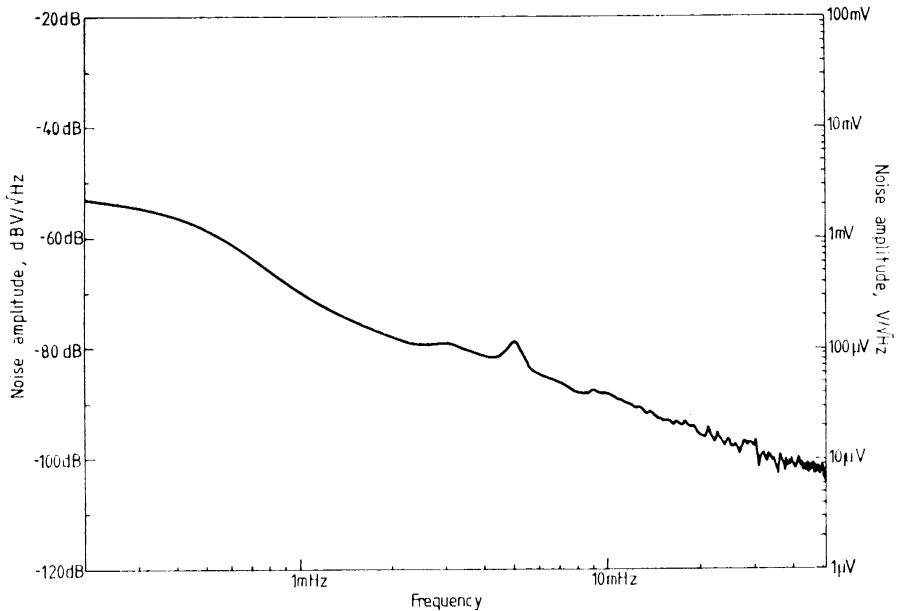


FIG. 4. "Memory" alloy (Ti-Ni) in 0.3M HCl. Electrochemical noise amplitude spectrum showing effects of crevice attack.

the slope remained unchanged. The high frequency output seen on the 72 h spectrum is again masked by the noise floor of the measurement apparatus.

The high slope could be a consequence of attenuation of the  $1/f$  noise by two R-C combinations, such an explanation fits the observed behaviour of the electrode impedance in this system<sup>2</sup>. It is interesting to consider the effect of this type of behaviour of the electrode noise on any impedance measurements. The sharp increase of electrode noise with decreasing frequency should lead to a sudden increase in the scatter of the impedance data as the frequency of measurement is swept downwards, this has indeed been observed experimentally<sup>2</sup>.

#### *Crevice Corrosion*

None of the electrodes tested exhibited any signs of crevice attack. However we have tested a number of other systems and found that crevice corrosion gives rise to a single sharp peak on the noise amplitude spectrum. This correlates well with our earlier findings<sup>19</sup> which showed that crevice corrosion results in well defined cyclic fluctuations of the electrode potential. Figure 4 shows the noise output typical of the early stages of crevice attack. The particular combination tested was a "memory" alloy (Ti-Ni) in 0.3M HCl solution and the frequency range covered was slightly different from that of the previous examples. The single peak at 5 mHz is just visible above the  $1/f$  noise background present.

### SUMMARY AND CONCLUSION

There is a correlation between the nature of the corrosion attack and the low

frequency fluctuations of the electrode potential. The electrochemical noise output is of a constant amplitude over a range of very low frequencies and decreases in amplitude at frequencies above this range. The slope of the high frequency roll-off bears a relation to the nature of the corrosion attack. A roll-off slope of -10 dB/decade or less is indicative of pitting corrosion. A sharp peak at a single frequency indicates crevice attack.

Subjectively there appears to be a qualitative correlation between the rate of attack and the r.m.s. amplitude of the noise (or more precisely the standard deviation of the noise)<sup>3</sup>. We are at present carrying out detailed measurements to ascertain the validity of this observation. Data obtained so far indicate that the r.m.s. noise amplitude is independent of the geometry and the area of the corroding electrode, in other words the r.m.s. noise amplitude seems to qualitatively relate to the actual penetration rate, independent of the magnitude of the area under attack.

At this stage in our researches we have not attempted to quantify our findings. We feel that although some of the features observed can be explained using our knowledge of the behaviour of the electrochemical impedance of the systems tested such explanations are inadequate and misleading. Our results show that real corroding electrodes maintain a state of dynamic equilibrium, the corrosion potential fluctuations reflect changes in this equilibrium and the electrode noise spectra reflect the range of rates at which that equilibrium can change.

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