4.2.3 HARMONIC COMPONENTS OF FARADAIC CURRENT

It is possible to derive mathematical expressions for the effect of an alternating voltage superimposed on a direct polarising voltage. Following the excellent treatment given by Devay & Meszaros[78] it is assumed that the polarisation curve of the electrode is expressed by equation (21);

$$j = j_k\left(\exp\frac{\Delta E}{b_a} - \exp-\frac{\Delta E}{b_c}\right) \qquad (21)$$

where Devay & Meszaros use j for Δi in equation (21) and j_k for i_{corr}.

If the electrode is now polarised by a sinusoidal voltage having an angular frequency w and amplitude U_o superimposed on the direct voltage $\overline{\Delta E}$, ie.

$$\Delta E = \overline{\Delta E} + U_o \sin wt \qquad (22)$$

the current density is then found from the substitution of (22) in (21). ie.

$$j = j_k\left(\exp\frac{\overline{\Delta E} + Uo \sin wt}{b_a} - \exp-\frac{\overline{\Delta E} + Uo \sin wt}{b_c}\right) + C\frac{d(\Delta E)}{dt} \quad . (23)$$

The parameter C, in equation (23), is the double layer capacitance - it is assumed that this is independent of frequency and potential. This is a very sweeping assumption and will be examined in due course. The solution resistance is taken to be negligible in order to simplify the derivation. Thus, the faradaic current density is;

$$j_f = j_k\left(\exp \frac{\overline{\Delta E} + Uo \sin wt}{b_a} - \exp - \frac{\overline{\Delta E} + Uo \sin wt}{b_c}\right) \quad (24)$$

Rearranging equation (24) gives;

$$j_f = j_k \left(\left(\exp \frac{\overline{\Delta E}}{b_a} \exp \frac{Uo \sin wt}{b_a}\right) - \left(\exp - \frac{\overline{\Delta E}}{b_c} \exp - \frac{Uo \sin wt}{b_c}\right)\right) \quad (25)$$

The exponential terms involving Uo sin wt can be expanded in a Fourier series, as shown by Devay and Meszaros [79], to separate the harmonics.

It may be of use at this stage to recap what we have done. We have assumed a non-linear voltage response. Next a pure voltage sine wave is added to that system (either at the corrosion potential, in which case $\overline{\Delta E}$ in equation (25) is zero, or at some DC polarisation $\overline{\Delta E}$). The corresponding output current is not a pure sine wave but is distorted by this non-linear response, this is illustrated in figure 3.

Now, in 1807 the French mathematician J.B.Fourier made an assertion that it is possible to take any periodic function and analyse it into an infinite series of sine functions [80]. This has been done to equation (25) giving;

$$j_f = j_k \Bigg\{ \Bigg[Io\left(\frac{Uo}{b_a}\right) + 2\sum_{k=o}^{\infty}(-1)^k \, I_{2k+1}\left(\frac{Uo}{b_a}\right) \sin(2k+1)wt \; +$$

$$+ \; 2\sum_{k=1}^{\infty}(-1)^k \, I_{2k}\left(\frac{Uo}{b_a}\right) \cos\, 2kwt \Bigg] \exp \frac{\overline{\Delta E}}{b_a} \; -$$

$$- \; \Bigg[Io\left(\frac{Uo}{b_a}\right) - 2\sum_{k=o}^{\infty}(-1)^k \, I_{2k}\left(\frac{Uo}{b_c}\right) \sin(2k+1)wt \; +$$

$$+ \; 2\sum_{k=1}^{\infty}(-1)^k \, I_{2k}\left(\frac{Uo}{b_c}\right) \cos\, 2kwt \Bigg] \exp \frac{\overline{\Delta E}}{b_c} \Bigg\} . \tag{26}$$

Equation (26) involves functions known as Bessel functions of the first type [81,82]. It is a gradually decaying function, for example see figure 4;

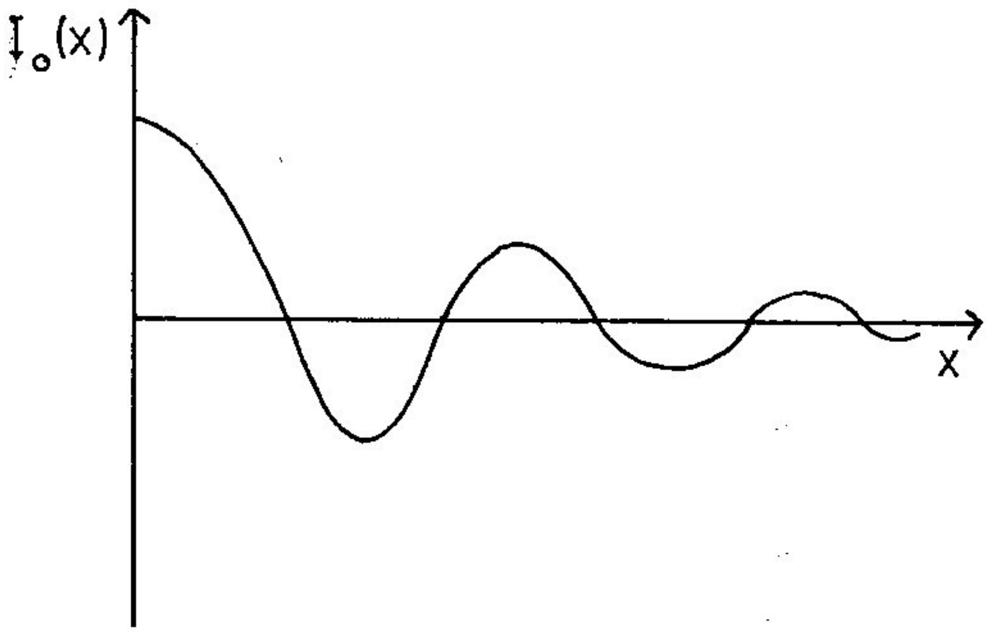

FIGURE 4 An example of a Bessel function Io(x), showing the form and trend of this type of function.

This daunting equation has summations going upto infinity, this is totally impractical for experimental use as any of the waves components over the third harmonic are, in practice, very difficult to measure amongst the background noise. If only the first three harmonics are considerdd equation (26) yields;

$$j_f = j_k \left\{ Io\left(\frac{Uo}{b_a}\right) \exp \frac{\overline{\Delta E}}{b_a} - Io\left(\frac{Uo}{b_c}\right) \exp - \frac{\overline{\Delta E}}{b_c} \right\} +$$

$$+ \quad 2j_k \left\{ I_1\left(\frac{Uo}{b_a}\right) \exp \frac{\overline{\Delta E}}{b_a} + I_1\left(\frac{Uo}{b_c}\right) \exp - \frac{\overline{\Delta E}}{b_c} \right\} \sin wt \quad -$$

$$- \quad 2j_k \left\{ I_2\left(\frac{Uo}{b_a}\right) \exp \frac{\overline{\Delta E}}{b_a} - I_2\left(\frac{Uo}{b_c}\right) \exp - \frac{\overline{\Delta E}}{b_c} \right\} \cos wt \quad -$$

$$- \quad 2j_k \left\{ I_3\left(\frac{Uo}{b_a}\right) \exp \frac{\overline{\Delta E}}{b_a} + I_3\left(\frac{Uo}{b_c}\right) \exp - \frac{\overline{\Delta E}}{b_c} \right\} \sin 3wt. \tag{28}$$

The first term is the D.C. component ($\bar{j}$), while the others are the first, second and third harmonics. Therefore,

$$\bar{j} = j_k \left\{ Io\left(\frac{Uo}{b_a}\right) \exp \frac{\overline{\Delta E}}{b_a} - Io\left(\frac{Uo}{b_c}\right) \exp - \frac{\overline{\Delta E}}{b_c} \right\} \tag{29}$$

The faradaic rectification is given by subtracting equation (21) from equation 29, ie.

$$\overline{\Delta j} = j_k \left\{ Io\left(\frac{Uo}{b_a}\right) \exp \frac{\overline{\Delta E}}{b_a} - Io\left(\frac{Uo}{b_c}\right) \exp - \frac{\overline{\Delta E}}{b_c} - j_k \left\{ \exp \frac{\overline{\Delta E}}{b_a} - \exp - \frac{\overline{\Delta E}}{b_c} \right\} \right.$$

$$= j_k \left\{ \left(Io\left(\frac{Uo}{b_a}\right) - 1\right) \exp \frac{\overline{\Delta E}}{b_a} - \left(Io\left(\frac{Uo}{b_c}\right) - 1\right) \exp - \frac{\overline{\Delta E}}{b_c} \right\} \tag{30}$$

The amplitudes of the harmonics are given by;

$$1^{st}, \quad \hat{j}_1 = 2j_k \left\{ I_1\left(\frac{Uo}{b_a}\right) \exp \frac{\overline{\Delta E}}{b_a} + I_1\left(\frac{Uo}{b_c}\right) \exp - \frac{\overline{\Delta E}}{b_c} \right\} \tag{31}$$

$$2^{nd}, \quad \hat{j}_2 = 2j_k\left\{ I_2\left(\frac{Uo}{b_a}\right) \exp\frac{\overline{\Delta E}}{b_a} - I_2\left(\frac{Uo}{b_c}\right) \exp -\frac{\overline{\Delta E}}{b_c}\right\} \tag{32}$$

$$3^{rd}, \quad \hat{j}_3 = 2j_k\left\{ I_3\left(\frac{Uo}{b_a}\right) \exp\frac{\overline{\Delta E}}{b_a} - I_3\left(\frac{Uo}{b_c}\right) \exp -\frac{\overline{\Delta E}}{b_c}\right\} \tag{33}$$

Equations 30 to 33 can be simplified by reducing Uo to about 10 mV, which allows the substitution of the Bessel function by the first terms of their Taylor polynomials. The Bessel functions give;

$$I_{n(x)} = \frac{(-1)^r}{r!(n+r)!}\left(\frac{x}{2}\right)^{n+2r}, \tag{34}$$

$$I_{o(x)} = 1 + \left(\frac{x}{2}\right)^2 \tag{35}$$

$$I_{1(x)} = \frac{x}{2} \tag{36}$$

$$I_{2(x)} = \frac{1}{2}\left(\frac{x}{2}\right)^2 \tag{37}$$

$$I_{3(x)} = \frac{1}{6}\left(\frac{x}{2}\right)^3 \tag{38}$$

Thus, $\overline{\Delta j}$, $\hat{j}_1$, $\hat{j}_2$, and $\hat{j}_3$, become;

$$\overline{\Delta j} = j_k\left(\frac{1}{b_a^{\,2}} \exp\frac{\overline{\Delta E}}{b_a} - \frac{1}{b_c^{\,2}} \exp\frac{\overline{\Delta E}}{b_c}\right)\frac{Uo^2}{4}, \tag{39}$$

$$\hat{j}_1 = j_k\left(\frac{1}{b_a} \exp\frac{\overline{\Delta E}}{b_a} + \frac{1}{b_c} \exp -\frac{\overline{\Delta E}}{b_c}\right) Uo \tag{40}$$

$$\hat{j}_2 = j_k\left(\frac{1}{b_a^{\,2}} \exp\frac{\overline{\Delta E}}{b_a} - \frac{1}{b_c^{\,2}} \exp\frac{\overline{\Delta E}}{b_c}\right)\frac{Uo^2}{4} \tag{41}$$

$$\hat{j}_3 = j_k \left(\frac{1}{b_a^3} \exp \frac{\overline{\Delta E}}{b_a} + \frac{1}{b_c^3} \exp - \frac{\overline{\Delta E}}{b_c} \right) \frac{Uo^3}{24} \tag{42}$$

4.2.4 DETERMINATION OF CORROSION CURRENT AND TAFEL SLOPES

Using equations 39 to 42 the corrosion current and Tafel slopes can be evaluated from measurements made on an electrode; either D.C. polarised, or held at the rest potential. If the electrode is polarised anodically to a value of $\overline{\Delta E}_a$ such that $\overline{\Delta E}_a / b_a > 1$ in the range of validity of Tafel's equation, equations 31, 32, & 33 reduce to;

$$\hat{j}_{1a} = 2 j k I_1 \left(\frac{Uo}{b_a} \right) \exp \frac{\overline{\Delta E}_a}{b_a} \tag{43}$$

$$\hat{j}_{2a} = 2 j_k I_2 \left(\frac{Uo}{b_a} \right) \exp \frac{\overline{\Delta E}_a}{b_a} \tag{44}$$

$$\hat{j}_{3a} = 2 j_k I_3 \left(\frac{Uo}{b_a} \right) \exp \frac{\overline{\Delta E}_a}{b_a} \tag{45}$$

Now, b_a can be caluated by employing recursion formulas [83] valid for Bessel functions of the first kind. This yields;

$$b_a = \frac{Uo}{4} \cdot \frac{\hat{j}_{1a} - \hat{j}_{3a}}{\hat{j}_{2a}} \tag{46}$$

When $j_{3a} \ll j_{1a}$, equation 46 reduces to;

$$b_a \approx \frac{Uo}{4} \cdot \frac{\hat{j}_{1a}}{\hat{j}_{2a}} \tag{47}$$

Thus, b_a can be determined by measuring the amplitude of the first, second and third harmonics at $\overline{\Delta E}_a$.

If the electrode is polarised cathodically such that $-\overline{\Delta E}_c/b_c > 1$, then;

$$b_c = \frac{Uo}{4} \cdot \frac{\hat{j}_{1c} - \hat{j}_{3c}}{\hat{j}_{2c}} \quad , \tag{48}$$

and when $j_{3c} \ll j_{1c}$ equation 48 yields;

$$b_c \approx \frac{Uo}{4} \cdot \frac{\hat{j}_{1c}}{\hat{j}_{2c}} \tag{49}$$

Knowing b_a or b_c and the polarisation employed during the measurement of $\hat{j}_{1a}$, $\hat{j}_{2a}$, and $\hat{j}_{3a}$ (or $\hat{j}_{1c}$, $\hat{j}_{2c}$, and $\hat{j}_{3c}$) and using equations 43, 44, & 45 (or their cathodic equivalents) it is possible to calculate corrosion current density. ie.

$$\begin{aligned} j_k &= \frac{\hat{j}_{1a}}{2I_1\left(\frac{Uo}{b_a}\right)} \cdot \exp - \frac{\overline{\Delta E}_a}{b_a} = \frac{\hat{j}_{2a}}{2I_2\left(\frac{Uo}{b_a}\right)} \cdot \exp - \frac{\overline{\Delta E}_a}{b_a} = \\ &= \frac{\hat{j}_{3a}}{2I_3\left(\frac{Uo}{b_a}\right)} \cdot \exp - \frac{\overline{\Delta E}_a}{b_a} = \frac{\hat{j}_{1c}}{2I_1\left(\frac{Uo}{b_c}\right)} \cdot \exp - \frac{\overline{\Delta E}_c}{b_c} = \\ &= \frac{\hat{j}_{2c}}{2I_2\left(\frac{Uo}{b_c}\right)} \cdot \exp - \frac{\overline{\Delta E}_a}{b_c} = \frac{\hat{j}_{3c}}{2I_3\left(\frac{Uo}{b_c}\right)} \cdot \exp - \frac{\overline{\Delta E}_c}{b_c} \end{aligned} \tag{50}$$

Now, using the approximate form of the Bessel function shown in equations 35 to 38 for $Uo \leqslant 10$ mV gives, on substitution into equation 50;

$$j_k = \hat{j}_{1a} \frac{b_a}{Uo} \exp - \frac{\overline{\Delta E}_a}{b_a} = \hat{j}_{2a} \frac{4b_a^2}{Uo^2} \exp - \frac{\overline{\Delta E}_a}{b_a} =$$

$$= \hat{j}_{3a} \frac{24b_a^3}{Uo^3} \cdot \exp - \frac{\overline{\Delta E}_a}{b_a} = \hat{j}_{1c} \frac{b_c}{Uo} \cdot \exp \frac{\overline{\Delta E}_c}{b_c} =$$

$$= \hat{j}_{2c} \frac{4b_c^2}{Uo^2} \cdot \exp \frac{\overline{\Delta E}_c}{b_c} = \hat{j}_{3c} \frac{24b_c^3}{Uo^3} \exp \frac{\overline{\Delta E}_c}{b_c} \tag{51}$$

Thus, the corrosion current can be determined at a single polarisation potential, either anodic or cathodic, within the Tafel range by measuring the amplitudes of the harmonic components and using equations 46, 48, and 51 to evaluate j_k. The need to plot a complete polarisation curve is thus eliminated. Unfortunately massive polarisation often so alters the system that measurements taken and rates inferred from these can show little resemblance to the rates at the corrosion potential.

4.2.5 MEASUREMENTS AT THE CORROSION POTENTIAL

The merit of this method of corrosion rate measurement lies in the fact that only a very small polarising potential is needed. The same is true of linear polarisation, but with that technique the values of the Tafel slopes need to be known. This is often not the case and therefore a Tafel plot needs to be done. In many systems the massive polarisation involved in a Tafel plot destroys the previous electrochemical paths and leads to totally erroneous results. If $\overline{\Delta E} = 0$ is substituted into equations 31 to 33 the first three harmonics become;

$$\hat{j}_{1o} = 2j_k\left\{I_1\left(\frac{Uo}{b_a}\right) + I_1\left(\frac{Uo}{b_c}\right)\right\} ,$$

$$\hat{j}_{2o} = 2j_k\left\{I_2\left(\frac{Uo}{b_a}\right) - I_2\left(\frac{Uo}{b_c}\right)\right\} ,$$

$$\hat{j}_{3o} = 2j_k\left\{I_3\left(\frac{Uo}{b_a}\right) + I_3\left(\frac{Uo}{b_c}\right)\right\} . \qquad (52)$$

Hence, corrosion current density can be evaluated if b_a and b_c are known. Substituting $\overline{\Delta E} = 0$ into equation 30 the faradaic rectification is given by;

$$\overline{\Delta j}_o = j_k\left\{I_o\left(\frac{Uo}{b_c}\right) - I_o\left(\frac{Uo}{b_c}\right)\right\} . \qquad (53)$$

Corrosion current and Tafel slopes can be evaluated by measuring any three data among $\hat{j}_{1o}$, $\hat{j}_{2o}$, $\hat{j}_{3o}$, and $\overline{\Delta j}_o$,and using equations 52 and 53 to form a set linear equations (which can be solved by computer).

If Uo is limited to $\leqslant$ 10mV equations 39 to 42 yield,on substitution of $\overline{\Delta E} = 0$;

$$\overline{\Delta j}_o = j_k\left(\frac{1}{b_a^2} - \frac{1}{b_c^2}\right)\frac{Uo^2}{4} \qquad (54)$$

$$\hat{j}_{1o} = j_k\left(\frac{1}{b_a} + \frac{1}{b_c}\right) Uo \qquad (55)$$

$$\hat{j}_{2o} = j_k\left(\frac{1}{b_a^2} - \frac{1}{b_c^2}\right)\frac{Uo^2}{4} \qquad (56)$$

$$\hat{j}_{3o} = j_k\left(\frac{1}{b_a^3} + \frac{1}{b_c^3}\right)\frac{Uo^3}{24} \qquad (57)$$

Solving equations 55 to 57 gives, for the corrosion current;

$$\boxed{j_k = \frac{\hat{j}_{1o}^{\,2}}{\sqrt{48}\,.\sqrt{2\hat{j}_{1o}\hat{j}_{3o} - \hat{j}_{2o}^{\,2}}}} \qquad (58)$$

Equation 58 is important, showing how the corrosion current can be determined by measuring the current amplitudes of the first, second and third harmonics resulting from a low frequency, low amplitude potential sine wave at the rest potential.

The Tafel slopes can be evaluated from 55 to 57, ie:
If $b_a < b_c$;

$$\frac{1}{b_a} = \frac{1}{2Uo}\left(\frac{\hat{j}_{1o}}{j_k} + 4\,\frac{\hat{j}_{2o}}{\hat{j}_{1o}}\right), \qquad (59)$$

$$\frac{1}{b_c} = \frac{1}{2Uo}\ \frac{j_{1o}}{j_k} - 4\,\frac{j_{2o}}{j_{1o}} \ . \qquad (60)$$

or, if $b_a > b_c$;

$$\frac{1}{b_a} = \frac{1}{2Uo}\left(\frac{\hat{j}_{1o}}{j_k} - 4\,\frac{\hat{j}_{2o}}{\hat{j}_{1o}}\right), \qquad (61)$$

$$\frac{1}{b_c} = \frac{1}{2Uo}\left(\frac{\hat{j}_{1o}}{j_k} + 4\,\frac{\hat{j}_{2o}}{\hat{j}_{1o}}\right). \qquad (62)$$

The proof, or otherwise, of this hypothesis is shown in a later chapter.