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# Reliability and Usefulness of Causality Factors of Electrochemical Frequency Modulation

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In this paper the importance of causality factor 2 and causality factor 3 of electrochemical frequency modulation (EFM) for corrosion monitoring has been discussed in comparison to two newly found causality factors. The derivation of these new causality factors namely causality factor 4 and causality factor 6 has been summarized. Moreover, the reliability and usefulness of EFM along with its causality factors to monitor pitting, stress corrosion cracking (SCC) and uniform corrosion for different corroding systems has been discussed. In many cases, EFM claims to be a suitable corrosion monitoring technique because of good comparisons with other corrosion measurement methods.

**Keywords:** EFM, causality factors, pitting, stress corrosion cracking

## 1. INTRODUCTION

The working principle [1] of electrochemical frequency modulation (EFM) technique is based on applying a potential perturbation signal generated by combining two sine waves to get current response at different harmonic and intermodulation frequencies. The current response at different frequencies obtained by applying potential perturbation signal at a corroding system facilitates the measurement of corrosion rate. With the help of EFM, the corrosion rate can be measured rapidly by using a small polarizing signal without prior knowledge of the so-called Tafel parameters. The distinguished characteristics of the EFM measurements include the capability to validate the results of corrosion parameters with the help of causality factors. A potential perturbation signal composed of two frequencies namely, $\omega_1$ and $\omega_2$ is applied to obtain current response at different frequencies. The set of frequencies consists of harmonic ($\omega_1$, $2\omega_1$, $3\omega_1$, …, $\omega_2$, $2\omega_2$, $3\omega_2$, …) and intermodulation ($\omega_1 \pm \omega_2$, $2\omega_1 \pm \omega_2$, $2\omega_2 \pm \omega_1$, …) frequencies.

In this paper the derivation of two new causality factors, namely causality factor 4 and causality factor 6 have been summarized. Usually causality factor 2 and causality factor 3 are used to validate the corrosion parameters determined through EFM. Recently EFM has been used to detect localized corrosion [2] by recording the behavior of causality factors. The results of corrosion parameters obtained by using EFM [1] were in good comparison with weight loss measurement and linear polarization resistance (LPR) technique.

## 2. THE ROLE OF CAUSALITY FACTORS

An experimental and theoretical ratio between the current components at harmonic and intermodulation frequencies defines the causality factor [1, 3]. The current response is analyzed to measure various current components; for instance, the current component $i_{2\omega_1}$ is measured at frequencies $2\omega_1$ and the intermodulation current component $i_{\omega_2\pm\omega_1}$ at frequency $\omega_2\pm\omega_1$ respectively.

Causality factors are defined with the help of following equations;

$$\text{Causality factor 2} = \frac{i_{\omega_2 \pm \omega_1}}{i_{2\omega_1}} \tag{1}$$

$$\text{Causality factor 3} = \frac{i_{2\omega_2 \pm \omega_1}}{i_{3\omega_1}} \tag{2}$$

Distortion in elementary transistor circuits was studied by Sansen [4] who found the relationship between harmonic and intermodulation components. Consisting of frequencies $\omega_1$ and $\omega_2$ with amplitude U, the sum of two cosine waveforms [4] is applied to obtain output signal containing harmonic and intermodulation components at all combinations of $\omega_1$ and $\omega_2$. The second and third order distortions were defined mathematically both at harmonic and intermodulation frequencies. One-to-one relationship between harmonic and intermodulation distortion was found under low distortion conditions. The intermodulation components can be superior to the harmonic components because of two reasons. Firstly, they appear very close to the two fundaments depending upon the preselected pair of applied frequencies. Secondly, likewise in the case of both causality factors, the intermodulation component is two or three times larger in magnitude than the corresponding harmonic component.

These two arguments guide to choose the input frequencies to obtain the intermodulation components in the vicinity of the fundamentals and larger in magnitude. The outputs might be reduced at high frequencies due to amplitude-frequency characteristics. In an analogous fashion, causality factors are used to judge the quality and validity of the results obtained through EFM while measuring the uniform corrosion rate. The results obtained by EFM are considered erroneous if causality factors deviate from their respective normal values of 2 and 3. Theoretically and experimentally both causality factors stay close to 2 and 3 to validate the good quality of the corrosion parameters obtained by using

EFM. A new research [2] has explored the untapped ability of both causality factors to detect pitting corrosion. These findings have enhanced the significance of causality factors as they provide further insights of corrosion phenomena.

The current response obtained through EFM contains many harmonic and intermodulation components at harmonic ($n\omega_{2,1}$) and intermodulation ($n\omega_2 \pm m\omega_1$) frequencies, where n and m vary between 1 and infinity. Besides the newly observed interesting behavior [2] of causality factor 2 and causality factor 3 during pitting corrosion, two new causality factors have been derived by expanding Taylor series to higher order term. For this purpose the initial step is to find the derivatives of the applied signal with the help of Taylor approach.

$$\begin{aligned} i &= i(U_0) + \frac{di(U_0)}{dU}(U_{tot}(t) - U_0) + \frac{1}{2}\frac{d^2i(U_0)}{dU^2}(U_{tot}(t) - U_0)^2 + \cdots \\ &\frac{1}{6}\frac{d^3i(U_0)}{dU^3}(U_{tot}(t) - U_0)^3 + \frac{1}{24}\frac{d^4i(U_0)}{dU^4}(U_{tot}(t) - U_0)^4 \end{aligned} \tag{3}$$

The derivatives in the above equation can be replaced simply by a, b, c, d and e to obtain,

$$\begin{aligned} i &= a + b(U_{tot}(t) - U_0) + \frac{1}{2}c(U_{tot}(t) - U_0)^2 + \cdots \\ &\frac{1}{6}d(U_{tot}(t) - U_0)^3 + \frac{1}{24}e(U_{tot}(t) - U_0)^4 \end{aligned} \tag{4}$$

After applying the external potential perturbation signal, the total potential of the metallic sample becomes,

$$U_{tot}(t) = U_0 + \Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t \tag{5}$$

Substituting the value of applied signal in equation (4) with the help of equation (5) yields the following response,

$$\begin{aligned} i &= a + b(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t) + \frac{1}{2}c(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)^2 + \cdots \\ &\frac{1}{6}d(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)^3 + \frac{1}{24}e(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)^4 \end{aligned} \tag{6}$$

The power containing terms in the above equation can be expanded by the following expressions,

$$(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)^2 = \Delta U^2(\sin^2\omega_1 t + \sin^2\omega_2 t + 2\sin\omega_1 t \sin\omega_2 t) \tag{7}$$

Further expansion yields,

$$= \Delta U^2 \left[ \frac{1-\cos 2\omega_1 t}{2} + \frac{1-2\cos \omega_2 t}{2} + 2\left( \frac{\cos(\omega_1 t - \omega_2 t) - \cos(\omega_1 t + \omega_2 t)}{2} \right) \right] \quad (8)$$

$$= \Delta U^2 \left( \frac{1}{2} - \frac{\cos 2\omega_1 t}{2} + \frac{1}{2} - \frac{\cos 2\omega_2 t}{2} + \cos(\omega_1 t - \omega_2 t) - \cos(\omega_1 t + \omega_2 t) \right) \quad (9)$$

$$= \Delta U^2 \left( 1 - \frac{\cos 2\omega_1 t}{2} - \frac{\cos 2\omega_2 t}{2} + \cos(\omega_1 t - \omega_2 t) - \cos(\omega_1 t + \omega_2 t) \right) \quad (10)$$

Similarly,

$$\begin{aligned} &(\Delta U \sin \omega_1 t + \Delta U \sin \omega_2 t)^3 = \Delta U^3 (\sin^3 \omega_1 t + \sin^3 \omega_2 t + \cdots \\ &3\sin \omega_1 t \sin \omega_2 t (\sin \omega_1 t + \sin \omega_2 t) \end{aligned} \quad (11)$$

Further expansion gives,

$$= \Delta U^3 \left( \begin{aligned} &\frac{3\sin \omega_1 t - \sin 3\omega_1 t}{4} + \frac{3\sin \omega_2 t - \sin 3\omega_2 t}{4} + \cdots \\ &3\sin \omega_2 t \frac{1-\cos 2\omega_1 t}{2} + 3\sin \omega_1 t \frac{1-\cos 2\omega_2 t}{2} \end{aligned} \right) \quad (12)$$

$$= \Delta U^3 \left( \begin{aligned} &\frac{3\sin \omega_1 t}{4} - \frac{\sin 3\omega_1 t}{4} + \frac{3\sin \omega_2 t}{4} - \frac{\sin 3\omega_2 t}{4} + \cdots \\ &\frac{3\sin \omega_2 t}{2} - \frac{3\sin \omega_2 t \cos 2\omega_1 t}{2} + \frac{3\sin \omega_1 t}{2} - \frac{3\sin \omega_1 t \cos 2\omega_2 t}{2} \end{aligned} \right) \quad (13)$$

$$= \Delta U^3 \left( \begin{aligned} &\frac{9\sin \omega_1 t}{4} + \frac{9\sin \omega_2 t}{4} - \frac{1}{4}(\sin 3\omega_1 t + \sin 3\omega_2 t) \cdots \\ &-\frac{3}{2}(\sin \omega_2 t \cos 2\omega_1 t + \sin \omega_1 t \cos 2\omega_2 t) \end{aligned} \right) \quad (14)$$

$$= \Delta U^3 \left( \begin{aligned} &\frac{9}{4}(\sin \omega_1 t + \sin \omega_2 t) - \frac{1}{4}(\sin 3\omega_1 t + \sin 3\omega_2 t) \cdots \\ &-\frac{3}{2}\left( \frac{\sin(\omega_2 t + 2\omega_1 t) + \sin(\omega_2 t - 2\omega_1 t}{2} + \frac{\sin(\omega_1 t + 2\omega_2 t) + \sin(\omega_1 t - 2\omega_2 t}{2} \right) \end{aligned} \right) \quad (15)$$

Similarly,

$$(\Delta U \sin \omega_1 t + \Delta U \sin \omega_2 t)^4 = (\Delta U \sin \omega_1 t + \Delta U \sin \omega_2 t)(\Delta U \sin \omega_1 t + \Delta U \sin \omega_2 t)^3 \quad (16)$$

Put value of $(\Delta U \sin \omega_1 t + \Delta U \sin \omega_2 t)^3$ from above derived equation (15) to get,

$$= \Delta U^4 (\sin \omega_1 t + \sin \omega_2 t) \begin{pmatrix} \frac{9}{4}(\sin \omega_1 t + \sin \omega_2 t) - \frac{1}{4}(\sin 3\omega_1 t + \sin 3\omega_2 t) \cdots \\ -\frac{3}{4}\begin{pmatrix} \sin(\omega_2 t + 2\omega_1 t) + \sin(\omega_2 t - 2\omega_1 t \cdots \\ + \sin(\omega_1 t + 2\omega_2 t) + \sin(\omega_1 t - 2\omega_2 t \end{pmatrix} \end{pmatrix} \quad (17)$$

Expansion of above equation (17) yields,

$$= \Delta U^4 \begin{pmatrix} \frac{9}{4}\sin^2 \omega_1 t + \frac{9}{4}\sin \omega_1 t \sin \omega_2 t - \frac{1}{4}\sin \omega_1 t \sin 3\omega_1 t - \frac{1}{4}\sin \omega_1 t \sin 3\omega_2 t \cdots \\ -\frac{3}{4}\sin \omega_1 t \sin(\omega_2 t + 2\omega_1 t) - \frac{3}{4}\sin \omega_1 t \sin(\omega_2 t - 2\omega_1 t) \cdots \\ -\frac{3}{4}\sin \omega_1 t \sin(\omega_1 t + 2\omega_2 t) - \frac{3}{4}\sin \omega_1 t \sin(\omega_1 t - 2\omega_2 t) \cdots \\ +\frac{9}{4}\sin \omega_1 t \sin \omega_2 t + \frac{9}{4}\sin^2 \omega_2 t - \frac{1}{4}\sin \omega_2 t \sin 3\omega_1 t - \cdots \\ \frac{1}{4}\sin \omega_2 t \sin 3\omega_2 t - \frac{3}{4}\sin \omega_2 t \sin(\omega_2 t + 2\omega_1 t) \cdots \\ -\frac{3}{4}\sin \omega_2 t \sin(\omega_2 t - 2\omega_1 t) - \frac{3}{4}\sin \omega_2 t \sin(\omega_1 t + 2\omega_2 t) \cdots \\ -\frac{3}{4}\sin \omega_2 t \sin(\omega_1 t - 2\omega_2 t) \end{pmatrix} \quad (18)$$

The following equation is obtained by putting values for square terms and changing the products to sums,

$$= \Delta U^4 \begin{pmatrix} \frac{9}{4}\left(\frac{1 - \cos 2\omega_1 t}{2}\right) + \frac{9}{2}\left(\frac{\cos(\omega_1 t - \omega_2 t) - (\cos \omega_1 t + \omega_2 t)}{2}\right) \cdots \\ -\frac{1}{4}\left(\frac{\cos(3\omega_1 t - \omega_1 t) - \cos(3\omega_1 t + \omega_1 t)}{2}\right) - \frac{1}{4}\left(\frac{\cos(3\omega_2 t - \omega_1 t) - \cos(3\omega_2 t + \omega_1 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_2 t + 2\omega_1 t - \omega_1 t) - \cos(\omega_2 t + 2\omega_1 t + \omega_1 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_2 t - 2\omega_1 t - \omega_1 t) - \cos(\omega_2 t - 2\omega_1 t + \omega_1 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_1 t - \omega_1 t - 2\omega_2 t) - \cos(\omega_1 t + \omega_1 t + 2\omega_2 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_1 t - \omega_1 t + 2\omega_2 t) - \cos(\omega_1 t + \omega_1 t - 2\omega_2 t)}{2}\right) \cdots \\ +\frac{9}{4}\left(\frac{1 - \cos 2\omega_2 t}{2}\right) - \frac{1}{4}\left(\frac{\cos(3\omega_1 t - \omega_2 t) - \cos(3\omega_1 t + \omega_2 t)}{2}\right) \cdots \\ -\frac{1}{4}\left(\frac{\cos(3\omega_2 t - \omega_2 t) - \cos(3\omega_2 t + \omega_2 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_2 t + 2\omega_1 t - \omega_2 t) - \cos(\omega_2 t + 2\omega_1 t + \omega_2 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_2 t - 2\omega_1 t - \omega_2 t) - \cos(\omega_2 t - 2\omega_1 t + \omega_2 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_2 t - \omega_1 t - 2\omega_2 t) - \cos(\omega_2 t + \omega_1 t + 2\omega_2 t)}{2}\right) \cdots \\ -\frac{3}{4}\left(\frac{\cos(\omega_2 t - \omega_1 t + 2\omega_2 t) - \cos(\omega_2 t + \omega_1 t - 2\omega_2 t)}{2}\right) \end{pmatrix} \quad (19)$$

Further expansion gives,

$$= \Delta U^4 \left( \begin{array}{l} \frac{9}{8} - \frac{9}{8}\cos 2\omega_1 t + \frac{9}{4}\cos(\omega_1 t - \omega_2 t) - \frac{9}{4}\cos(\omega_1 t + \omega_2 t) - \frac{1}{8}\cos 2\omega_1 t + \frac{1}{8}\cos 4\omega_1 t \cdots \\ - \frac{1}{8}\cos(3\omega_2 t - \omega_1 t) + \frac{1}{8}\cos(3\omega_2 t + \omega_1 t) - \frac{3}{8}\cos(\omega_2 t + \omega_1 t) + \frac{3}{8}\cos(\omega_2 t + 3\omega_1 t) \cdots \\ - \frac{3}{8}\cos(\omega_2 t - 3\omega_1 t) + \frac{3}{8}\cos(\omega_2 t - \omega_1 t) - \frac{3}{8}\cos 2\omega_2 t + \frac{3}{8}\cos(2\omega_1 t + 2\omega_2 t) \cdots \\ - \frac{3}{8}\cos 2\omega_2 t + \frac{3}{8}\cos(2\omega_1 t + 2\omega_2 t) \cdots \\ + \frac{9}{8} - \frac{9}{8}\cos 2\omega_2 t - \frac{1}{8}\cos(3\omega_1 t - \omega_2 t) + \frac{1}{8}\cos(3\omega_1 t + \omega_2 t) \cdots \\ - \frac{1}{8}\cos 2\omega_2 t + \frac{1}{8}\cos 4\omega_2 t - \frac{3}{8}\cos 2\omega_1 t + \frac{3}{8}\cos(2\omega_2 t + 2\omega_1 t) \cdots \\ - \frac{3}{8}\cos 2\omega_1 t + \frac{3}{8}\cos(2\omega_2 t - 2\omega_1 t) - \frac{3}{8}\cos(\omega_2 t + \omega_1 t) + \frac{3}{8}\cos(\omega_1 t + 3\omega_2 t) \cdots \\ - \frac{3}{8}\cos(3\omega_2 t - \omega_1 t) + \frac{3}{8}\cos(\omega_1 t - \omega_2 t) \end{array} \right) \quad (20)$$

Rearrangement yields,

$$= \Delta U^4 \left( \begin{array}{l} \frac{9}{8} + \frac{9}{8} - \frac{9}{8}\cos 2\omega_1 t - \frac{1}{8}\cos 2\omega_1 t - \frac{3}{8}\cos 2\omega_1 t - \frac{3}{8}\cos 2\omega_1 t \\ - \frac{3}{8}\cos 2\omega_2 t - \frac{3}{8}\cos 2\omega_2 t - \frac{9}{8}\cos 2\omega_2 t - \frac{1}{8}\cos 2\omega_2 t \\ + \frac{1}{8}\left(\cos 4\omega_2 t + \cos 4\omega_1 t\right) \cdots \\ + \frac{9}{4}\cos(\omega_2 t - \omega_1 t) + \frac{3}{8}\cos(\omega_2 t - \omega_1 t) + \frac{3}{8}\cos(\omega_2 t - \omega_1 t) \cdots \\ - \frac{9}{4}\cos(\omega_2 t + \omega_1 t) - \frac{3}{8}\cos(\omega_2 t + \omega_1 t) - \frac{3}{8}\cos(\omega_2 t + \omega_1 t) \cdots \\ - \frac{1}{8}\cos(3\omega_2 t - \omega_1 t) - \frac{3}{8}\cos(3\omega_2 t - \omega_1 t) + \frac{1}{8}\cos(3\omega_2 t + \omega_1 t) + \frac{3}{8}\cos(3\omega_2 t + \omega_1 t) \cdots \\ - \frac{1}{8}\cos(\omega_2 t - 3\omega_1 t) - \frac{3}{8}\cos(\omega_2 t - 3\omega_1 t) + \frac{1}{8}\cos(\omega_2 t + 3\omega_1 t) + \frac{3}{8}\cos(\omega_2 t + 3\omega_1 t) \cdots \\ + \frac{3}{8}\cos(2\omega_2 t - 2\omega_1 t) + \frac{3}{8}\cos(2\omega_2 t - 2\omega_1 t) + \frac{3}{8}\cos(2\omega_2 t + 2\omega_1 t) + \frac{3}{8}\cos(2\omega_2 t + 2\omega_1 t) \end{array} \right) \quad (21)$$

The above equation can be simplified to get,

$$= \Delta U^4 \left( \begin{array}{l} \frac{9}{4} - 2(\cos 2\omega_2 t + \cos 2\omega_1 t) + \frac{1}{8}\left(\cos 4\omega_2 t + \cos 4\omega_1 t\right) \cdots \\ + 3\cos(\omega_2 t - \omega_1 t) - 3\cos(\omega_2 t + \omega_1 t) \\ - \frac{1}{2}\cos(3\omega_2 t - \omega_1 t) + \frac{1}{2}\cos(3\omega_2 t + \omega_1 t) \\ - \frac{1}{2}\cos(\omega_2 t - 3\omega_1 t) + \frac{1}{2}\cos(\omega_2 t + 3\omega_1 t) \cdots \\ + \frac{3}{4}\cos(2\omega_2 t - 2\omega_1 t) + \frac{3}{4}\cos(2\omega_2 t + 2\omega_1 t) \end{array} \right) \quad (22)$$

And,

$$= \Delta U^4 \begin{pmatrix} \frac{9}{4} - 2(\cos 2\omega_2 t + \cos 2\omega_1 t) + \frac{1}{8}(\cos 4\omega_2 t + \cos 4\omega_1 t)\cdots \\ + 3(\cos(\omega_2 t - \omega_1 t) - \cos(\omega_2 t + \omega_1 t))\cdots \\ -\frac{1}{2}(\cos(3\omega_2 t - \omega_1 t) - \cos(3\omega_2 t + \omega_1 t))\cdots \\ -\frac{1}{2}(\cos(\omega_2 t - 3\omega_1 t) - \cos(\omega_2 t + 3\omega_1 t))\cdots \\ +\frac{3}{4}(\cos(2\omega_2 t - 2\omega_1 t) + \cos(2\omega_2 t + 2\omega_1 t)) \end{pmatrix} \quad (23)$$

And then finally,

$$= \Delta U^4 \begin{pmatrix} \frac{9}{4} + 2(\cos 2\omega_2 t + \cos 2\omega_1 t) + \frac{1}{8}(\cos 4\omega_2 t + \cos 4\omega_1 t)\cdots \\ + 3(\cos(\omega_2 t - \omega_1 t) - \cos(\omega_2 t + \omega_1 t))\cdots \\ +\frac{1}{2}(-\cos(3\omega_2 t - \omega_1 t) + \cos(3\omega_2 t + \omega_1 t) - \cos(\omega_2 t - 3\omega_1 t) + \cos(\omega_2 t + 3\omega_1 t))\cdots \\ +\frac{3}{4}(\cos(2\omega_2 t - 2\omega_1 t) + \cos(2\omega_2 t + 2\omega_1 t)) \end{pmatrix} \quad (24)$$

Now put all the above derived values in the following equation (25) to get equation (26)

$$i = a + b(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t) + \frac{1}{2}c(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)^2 + \cdots$$
$$\frac{1}{6}d(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)^3 + \frac{1}{24}e(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)^4 \quad (25)$$

$$\begin{aligned} i &= a + b(\Delta U \sin\omega_1 t + \Delta U \sin\omega_2 t)\cdots \\ &+ \frac{1}{2}c\Delta U^2\left(1 - \frac{\cos 2\omega_1 t}{2} - \frac{\cos 2\omega_2 t}{2} + \cos(\omega_1 t - \omega_2 t) - \cos(\omega_1 t + \omega_2 t)\right)\cdots \\ &+ \frac{1}{6}d\Delta U^3 \begin{pmatrix} \frac{9}{4}(\sin\omega_1 t + \sin\omega_2 t) - \frac{1}{4}(\sin 3\omega_1 t + \sin 3\omega_2 t)\cdots \\ -\frac{3}{2}\begin{pmatrix} \frac{\sin(\omega_2 t + 2\omega_1 t) + \sin(\omega_2 t - 2\omega_1 t)}{2} + \\ \frac{\sin(\omega_1 t + 2\omega_2 t) + \sin(\omega_1 t - 2\omega_2 t}{2} \end{pmatrix} \end{pmatrix}\cdots \\ &+ \frac{1}{24}e\Delta U^4 \begin{pmatrix} \frac{9}{4} + 2(\cos 2\omega_2 t + \cos 2\omega_1 t) + \frac{1}{8}(\cos 4\omega_2 t + \cos 4\omega_1 t)\cdots \\ + 3(\cos(\omega_2 t - \omega_1 t) - \cos(\omega_2 t + \omega_1 t))\cdots \\ +\frac{1}{2}\begin{pmatrix} -\cos(3\omega_2 t - \omega_1 t) + \cos(3\omega_2 t + \omega_1 t) - \cos(\omega_2 t - 3\omega_1 t) \\ +\cos(\omega_2 t + 3\omega_1 t) \end{pmatrix}\cdots \\ +\frac{3}{4}(\cos(2\omega_2 t - 2\omega_1 t) + \cos(2\omega_2 t + 2\omega_1 t)) \end{pmatrix} \end{aligned} \quad (26)$$

The terms with same frequency can be rearranged to get,

$$
\begin{aligned}
i &= a + \frac{c}{2}\Delta U^2 + \frac{3e}{32}\Delta U^4 + \left(b\Delta U + \frac{3d}{8}\Delta U^3\right)(\sin\omega_2 t + \sin\omega_1 t)\cdots \\
&- \left(\frac{c}{4}\Delta U^2 + \frac{e}{12}\Delta U^4\right)(\cos 2\omega_2 t + \cos 2\omega_1 t)\cdots \\
&- \left(\frac{c}{2}\Delta U^2 + \frac{e}{8}\Delta U^4\right)(\cos(\omega_1 t + \omega_2 t) - \cos(\omega_1 t - \omega_2 t))\cdots \\
&- \left(\frac{d}{8}\Delta U^3\right)\begin{pmatrix}\sin(\omega_1 t + 2\omega_2 t) + \sin(\omega_1 t - 2\omega_2 t) + \sin(\omega_2 t + 2\omega_1 t) + \\ \sin(\omega_2 t - 2\omega_1 t)\end{pmatrix}\cdots \\
&- \left(\frac{d}{24}\Delta U^3\right)(\sin 3\omega_1 t + \sin 3\omega_2 t)\cdots \\
&+ \left(\frac{e}{192}\Delta U^4\right)(\cos 4\omega_1 t + \cos 4\omega_2 t)\cdots \\
&+ \left(\frac{e}{48}\Delta U^4\right)\begin{pmatrix}\cos(3\omega_1 t + \omega_2 t) - \cos(3\omega_1 t - \omega_2 t) + \cos(\omega_1 t + 3\omega_2 t) - \\ \cos(\omega_1 t - 3\omega_2 t)\end{pmatrix}\cdots \\
&+ \left(\frac{e}{32}\Delta U^4\right)(\cos(2\omega_1 t + 2\omega_2 t) + \cos(2\omega_1 t - 2\omega_2 t))
\end{aligned} \tag{27}
$$

Now different causality factors can be derived from above equation (27),

$$\text{Causality factor 2} = \frac{i_{\omega_2\pm\omega_1}}{i_{2\omega_{2,1}}} = \frac{\frac{c}{2}\Delta U^2}{\frac{c}{4}\Delta U^2} = 2 \tag{28}$$

$$\text{Causality factor 3} = \frac{i_{2\omega_2\pm\omega_1,\,\omega_2\pm2\omega_1}}{i_{3\omega_{2,1}}} = \frac{\frac{d}{8}\Delta U^3}{\frac{d}{24}\Delta U^3} = 3 \tag{29}$$

Two new causality factors called as causality factor 4 and causality factor 6 have been derived in following way,

$$\text{Causality factor 4} = \frac{i_{3\omega_2\pm\omega_1,\,\omega_2\pm3\omega_1}}{i_{4\omega_{2,1}}} = \frac{\frac{e}{48}\Delta U^4}{\frac{e}{192}\Delta U^4} = 4 \tag{30}$$

$$\text{Causality factor 6} = \frac{i_{2\omega_2\pm2\omega_1}}{i_{4\omega_{2,1}}} = \frac{\frac{e}{32}\Delta U^4}{\frac{e}{192}\Delta U^4} = 6 \tag{31}$$

Interestingly all four causality factors can be seen in the form of apex-internal triangle inside the Pascal’s triangle as shown below,

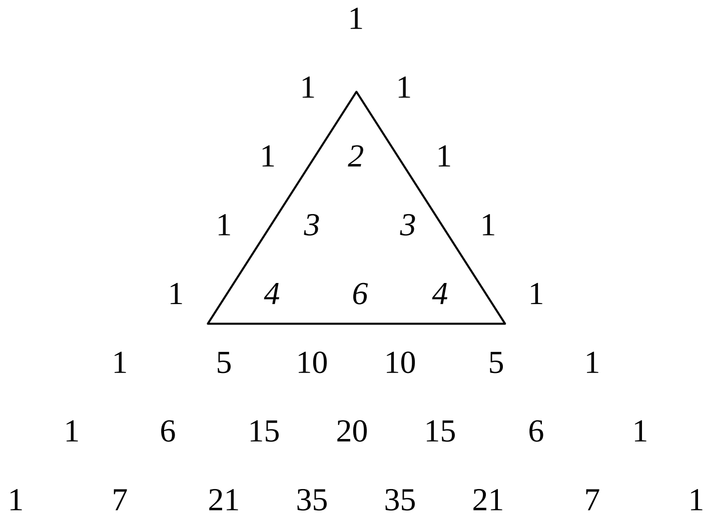


**Figure 1.** Pascal's triangle containing all causality factors of EFM inside a smaller triangle

## 3. INTERMODULATION FREQUENCIES AND PASCAL'S TRIANGLE

The numbers (2, 3, 4, and 6) shown in a triangle with the help of Figure 1 inside the Pascal's triangle are the same as the causality factors both previous and new ones of the EFM method.

The third diagonal of Pascal's triangle represents a series of triangular numbers which are 1, 3, 6, 10..., shown in Figure 2a. These triangular numbers indeed correspond to any triangle with respect to its size as shown in Figure 2b. Hexagonal numbers (1, 6, 15, 28, 45, 66 ...) shown in Figure 2c are also present inside the triangular numbers (third diagonal of Pascal's triangle). These numbers (both triangular and hexagonal) also exist dramatically as a special arrangement shown in Table 1 for the intermodulation frequencies of EFM.

**Table 1.** Selected values of intermodulation frequencies in a special pattern compose the triangular numbers, which are similar to the third diagonal of a Pascal's triangle. Similarly, selected sequence of hexagonal numbers is shown.

| $\omega_2$-2$\omega_1$ | $\omega_2$-$\omega_1$ | **$\omega_2$ (Hz)** | $\omega_2$+$\omega_1$ | $\omega_2$+2$\omega_1$ | $\omega_2$+3$\omega_1$ | 3$\omega_2$-$\omega_1$ | **$\omega_1$ (Hz)** |
|---|---|---|---|---|---|---|---|
| **1** | **3** | 5 | 7 | 9 | 11 | 13 | 2 |
| 2 | **6** | **10** | 14 | 18 | 22 | 26 | 4 |
| 3 | 9 | **15** | **21** | 27 | 33 | 39 | 6 |
| 4 | 12 | 20 | **28** | **36** | 44 | 52 | 8 |
| 5 | 15 | 25 | 35 | **45** | **55** | 65 | 10 |
| 6 | 18 | 30 | 42 | 54 | **66** | **78** | 12 |
| 7 | 21 | 35 | 49 | 63 | 77 | 91 | 14 |

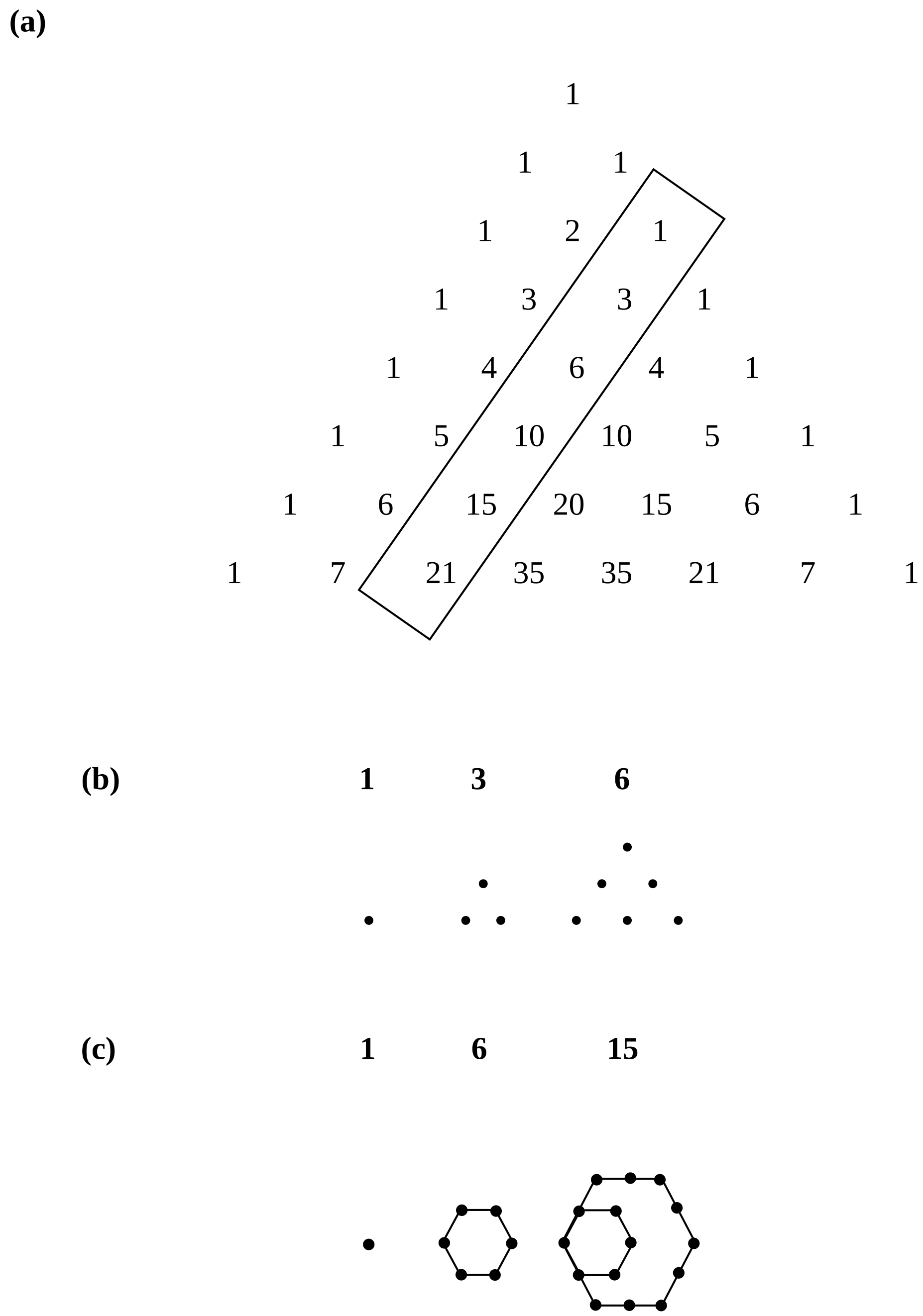


**Figure 2.** Third diagonal (a) of a Pascal's triangle represents the triangular numbers (1, 3, 6, 10, 15, 21, 28, 36, 45 ...) as shown in (b) and hexagonal numbers (1, 6, 15, 28, 45, 66 ...) as shown in (c). These numbers also have been found as a sequence in the Table 1 of intermodulation frequencies.

## 4. DISCUSSION

To detect pitting corrosion with the help of EFM method, the fluctuating behavior of causality factors [2] was investigated. Usually the causality factors are used to validate the data obtained during uniform corrosion. These causality factors show different behavior during pitting corrosion. The nonlinear behavior changes during pitting corrosion and is most reflected by causality factors that are only valid in the so-called low distortion region. Kendig [5] applied lower amplitude single sinusoidal perturbation signal to detect onset of pitting corrosion with the help of higher harmonic content in the current response. In contrast, EFM uses two sine waves instead of one. The detection of pitting propagation with the help of single sine wave is not possible for the case of passive system because the linear ohmic resistance increases relative to the nonlinear faradaic transfer function. EFM owing to use of two sine waves has advantage over single wave method because of larger currents at intermodulation frequencies as compared to current response at harmonic frequencies.

A mathematical model [6] simulated the behavior of causality factors during the propagation of stress corrosion cracking (SCC). According to this model the active area increases with time as a result of the increasing number of cracks during SCC. The higher values of causality factor 3 obtained theoretically at the start of SCC are consistent with the small contribution of active area experimentally. This model also predicts the normal values of 2 and 3 for both causality factors when the total area of the metal is supposed to become active, which is equally true for the case of uniform corrosion. The current potential relationship used in this model was tested to predict satisfactorily the Tafel behavior when the total area is active and similarly pure passive behavior for the active area equal to zero. The response of EFM was tested experimentally during SCC of sensitized stainless steel 304 in different concentrations of sodium thiosulfate ($Na_2S_2O_3$) at ambient temperature. The experimental values of both causality factors were normal in the absence of SCC but rose and fluctuated during SCC. The values of causality factors for SCC in all experiments were noisy and their amplitude was much higher than during the pitting.

With the help of linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and EFM methods, Lenard [7] measured and compared the corrosion rates in the flowing seawater for 90/10 and 70/30 copper-nickel specimens by using a multiplexer and potentiostat. A potential perturbation signal composed of two sine waves having frequencies of 20 mHz and 50 mHz was used in case of EFM measurements based on an active corrosion model with 10 mV as the amplitude of the applied voltage. EFM was found as a reliable online corrosion monitoring technique by Lenard for long-term measurements to highlight the changes in corrosion mechanism and corrosion environment. His results were significantly affected by the variable choice of the amplitude of applied signal. An increase in corrosion rate was observed by LPR and EFM methods when shortly exposed to sulfides before the protective films were fully formed. Cathodic Tafel constants measured for copper alloys (90/10 and 70/30) with the help of EFM were very sensitive to the exposure conditions and the growth of protective films. EIS measurements supported the findings of EFM that corrosion rate was under diffusion control for the unprotected alloy surface immersed in clean sea water. The best results were obtained with the help of EFM by using smaller amplitude of the applied signal and were validated through causality factors and well compared with EIS and LPR methods. EFM can be considered a reliable technique for long term online corrosion monitoring because of using smaller amplitude and thus causes less perturbation of the surface under investigation.

For the corrosion of low alloy steel in aerated 0.5 M HCl solutions, Glycine [8] was tested as a reliable inhibitor by using impedance and potentiodynamic polarization techniques. EFM provided accurate corrosion rates without the prior knowledge of Tafel parameters as it was difficult to get the linear Tafel region for the anodic part of the polarization curves for this work. Chemical analysis and

EFM technique were found appropriate to evaluate corrosion inhibition of low alloy steel in 0.5 M HCl with various concentrations of glycine at different temperatures. In this case, EFM provided validated corrosion parameters. Similarly for pure iron in 1 M HCl, a good comparison was found among EFM [9], EIS, Tafel and weight loss measurements for corrosion inhibition studies in case of four indole derivatives. These indole derivatives were found as cathodic type of inhibitors with the help of Tafel polarization studies. EFM technique was used to study the effect of 2-carboxymethylthio-4-(p-methoxyphenyl)-6-oxo-1,6-dihydropyrimidine-5-carbonitrile [10] as corrosion inhibitor for copper in aerated stagnant 3.5% NaCl solution at 25 °C. It was found that the corrosion rate decreased with the increased concentration of the inhibitor. The adsorption of the inhibitor molecules on the copper surface in chloride containing solution was found to obey Langmuir's adsorption isotherm. The corrosion rates measured by EFM showed good agreement with traditional electrochemical techniques. Han [11] investigated corrosion of mild steel in seawater with the help of polarization curve analysis, EFM and weight loss methods. The early corrosion rate was determined with EFM technique by considering activation-controlled equation and analysis of the polarization curve in the vicinity of the corrosion potential. The results were consistent with other electrochemical techniques and weight loss method. The corrosion rates measured by EFM were higher particularly during longer exposed times when diffusion-controlled effect was obvious. The reliable measurements through EFM should be performed by using sufficiently low value of perturbation frequency to avoid the capacitive behavior of the electrochemical double layer according to the system under investigation and proper formula according to the actual reaction mechanism. The results [12] obtained by EFM technique demonstrate good agreement with traditional dc and ac techniques. EFM technique takes very short time to measure different corrosion parameters in a single measurement and claims to be ideal for the online corrosion monitoring. New synthesized thiourea derivative named 1,3-diarylidenethiourea was examined as a corrosion inhibitor for iron in 1 M HCl solution. The corrosion rate decreases with increase of the inhibitor concentration due to adsorption of the inhibitor on the iron surface. The values of both causality factors with and without various concentrations of the inhibitor were $>1$ and $\leq 3$ (in comparison to theoretical values of 2 and 3) verifying the validity of data obtained during uniform corrosion.

The corrosion rates measured by EFM for the systems Cu/NaCl, Al5083/NaCl and stainless steel/NaCl were higher as compared to other two techniques but good results were obtained in case of high corrosion rate for mild steel in sulfuric acid ($H_2SO_4$). Kuş [13] has mentioned that it is not practicable to measure the corrosion parameters for Cu/NaCl and Al/NaCl systems because the assumptions will remain unfulfilled on which the EFM analysis is based and the impedance will be affected due to the contributions from diffusion and localized corrosion. Polarization technique also confronts such problems because a meaningful anodic polarization data is difficult to scan due to high polarization resistance for Cu/NaCl system and pitting occurs for Al/NaCl system at the corrosion potential. Kuş suggested that EFM should be used cautiously in case of systems with low corrosion rates but promising results can be obtained for the systems demonstrating high corrosion rates.

## 5. CONCLUSIONS

1. Theoretically two new causality factors have been derived for the EFM method along with the identical equations for existing causality factors ( 2 and 3)
2. The response of new causality factors can be tested during corrosion monitoring as well as compared with existing causality factors.
3. The new causality factors are called as causality factor 4 and causality factor 6.
4. The previous and new causality factors together make a group of small triangle inside a Pascal's triangle.
5. The derivation of new causality factors is just a scientific novelty because the interference with harmonics of the perturbation frequency is possible. The higher harmonics are too small to measure and can be buried in the background noise.

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