Quantitative simulation of Mathematical modeling of Iron Corrosion Problem and its Numerical Solutions

S R Rajkumar [a], M Alagar [b]

a.   Assistant Professor, Department of Physics, Rajapalayam Rajus' College, Madurai Kamaraj University, Rajapalayam-626117, TamilNadu, India.
b.   Head & Associate Professor, DST – FIST Sponsored Center for Research and Post Graduate Department of Physics, Ayya Nadar Janaki Ammal College (Autonomous), Madurai Kamaraj University, Sivakasi -626124, TamilNadu, India.

Abstract:

Corrosion process is a natural phenomenon that occurs with the various metals, where the corrosion process in electrochemical environment can be elucidated by using a galvanic cell. The iron corrosion process is based on the pH of a condensation, condensation temperature of electrolyte and iron concentration. These are applied at electrochemical cell. The corrosion process is competent to root electrical potential and electric current during the process. Based on iron concentration, condensation temperature, iteration time, electrical potential and electric current, a mathematical model of iron corrosion is constructed. Further the mathematical model is solved using the finite element method (FEM).   In the potential electric model, is based on the electric potential and the iteration time applied. Whereas the electric current density model, the current is generated between the cathode and anode poles and the iteration time applied. The numerical results show that the part of iron sample, attacked by corrosion, is a function of time, depth difference, iron concentration, condensation temperature and the sum of reduced mass during corrosion process.

Keywords: Deposition kinetics; Numerical modeling, finite element Method, iron corrosion Galvanic corrosion;

1. Introduction

Corrosion of iron occurred physically. corrosiveness can be described as a material ravage by action which embroidery area, where resistance of a material on the corrosiveness depends on the copious variables such as environmental characteristics and

material properties[1].The central characteristic in a material corrosiveness is mass transport quality, that occur due to diffusion , migration and evacuation of temperature. The distribution character effects are generated in an object depends on force system characteristics only.

Genuine corrosiveness is a galvanic process with metal that works as an anode, a cathode and as one conductor for the electrons. The quantitative simulation of iron corrosion relates to prospect that weakening of firm stones are in the iron item, consequently at same time critical to build a rustiness model as achievable as in physically and can be interfaced to a model of chemical reaction using a mathematical modeling of corrosion process and the model then solved using finite element method (FEM), in which it is shown geometrically as an electrochemical cell process by using a partial differential model.

2. Existing Equation for transport migration in a material

The central characteristic in a material corrosiveness is mass transport worth that occurs due to diffusion, migration and evacuation of temperature. These are suitable with condensation mass $\mathbb{J}_k$ of species k, as cited in Planck- Nernst's law, i.e.:

$$\mathbb{J}_k = -\mathbb{D}_k \nabla \mathbb{C}_k - \mathbb{C}_k \nabla \phi \qquad [1]$$

Where: $\mathbb{D}_k$ $-$diffusion constant $\mathbb{C}_k$ $-$concentration in Molar (moles/liter) $\phi -$ the electric potential in the electrolyte.

This condensation mass further is transported by electrical field on molecular diffusion process[2]. For both types, the equation of transportation of accumulator acid, i.e.:

$$\frac{\partial \mathbb{C}_k}{\partial \mathbb{t}} + \nabla . \left[\left(-\frac{\mathbb{z}_k . \mathbb{F} . \mathbb{D}_k}{\mathbb{R} . \mathbb{T}} . \nabla \phi \right) . \mathbb{C}_k \right] - \mathbb{D}_k . \nabla^2 . \mathbb{C}_k = \mathbb{S}_k \qquad [2]$$

Where $\mathbb{z}_k$ $-$charge number $\mathbb{F} -$ Faraday's constant $\mathbb{R} -$ gas constant $\mathbb{T} -$ absolute temperature $\mathbb{S}_k -$ is ion production or undoing of type k. In this corrosion process, it is taken place in the interface between electrodes and condensation of electrolyte.

Newman (1996) explains that the power of the electrical current i ,in condensation of the electrolyte, is flown in the condensation mass constant change from iron. Electrical tension can be obtained by considering the total electrical current and it disregards the neutrality electric condensation of electrolyte. It can be originated using the Faraday's law:

$$i = \mathbb{F} \sum_k \mathbb{z}_k . \mathbb{J}_k \qquad [3]$$

By electro-neutrality conceptual that the electric current density is non -divergent, that is:

$$\nabla . i = 0 \qquad [4]$$

Substituting the Expression (3) in Eqn. (4), we get

$$\nabla . \left(\sum_k \mathbb{z}_k . \mathbb{J}_k \right) = 0 \qquad [5]$$

By using the Planck–Nernst's law Eqn. (1), then we end up with the electric potential equation, i.e.:

$$\nabla . \left[\left(\sum_k \frac{\mathbb{z}_k . \mathbb{F} . \mathbb{D}_k}{\mathbb{R} . \mathbb{T}} . \mathbb{C}_k \right) \nabla \phi \right] = -\sum \mathbb{D}_k . \nabla^2 . \mathbb{C}_k \qquad [6]$$

Note that when the concentration gradients may be neglected, Eqn. (6) then reduces to the Laplace's equation, i.e.:

$$\nabla^2 . \phi = 0 \qquad [7]$$

3. Boundary Conditions for Locating the anode and cathode in a one- dimensional galvanic cell corrosion process

Through observing the electrochemical cell, iron corrosiveness process is occurrence of iron metal oxidation by the oxygen that comes from the air. Fig.1. shows that H_2O condensation electrolyses with (Fe) iron electrode. In this condensation there are some species, such as H^+ and OH^- ions obtained from the result of H_2O ionization as solvent and Fe^{2+} ion that come from electrode ionization. Fe^{2+} ions roving towards negative pole and OH^- ions roving towards positive pole[3].
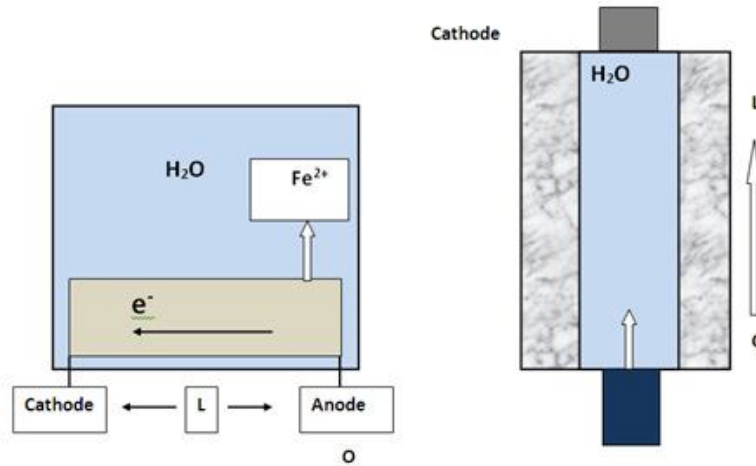

Fig. 1: (a) Location of the anode and cathode in a   (b) one- dimensional galvanic cell. corrosion process

During the corrosion process occurred , it will entrap the reaction of reduction - oxidation (redox) in electrolytic cell by using a partial differential model. Newman (1996) explains that the only reaction takes place in anode is disconnection of metal. In this case, reaction of (Fe) iron can be printed as

$$(A)\ \mathcal{F}e \longrightarrow \mathcal{F}e^{2+} + 2e^- \quad E_A^0 = -0.44\ V \qquad \text{(Oxisation)} \qquad [8]$$
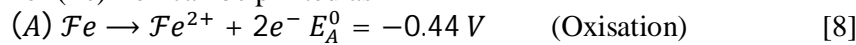
Where $E_A^0 -$ is the standard potential of (A) reaction. The current density is formed by (A) reaction and it can be written by the Butler-Volmer's equation as[5]:

$$i_A = i_{OA} \cdot \left\{ exp\left[(1-\alpha_A)\frac{\mathbb{F}.\mathbb{z}.A}{\mathbb{R}.\mathbb{T}} \cdot \eta_A\right] - exp\left[-\alpha_A \frac{\mathbb{F}.\mathbb{z}.A}{\mathbb{R}.\mathbb{T}} \cdot \eta_A\right]\right\} \qquad [9]$$

Where $i_{OA} -$ exchange current density of (A) reaction, that is the current density calculated, in which the net current at the electrode is worthless (this value is attained experimentally)[6],

$\alpha_A -$ transfer coefficient for (A) reaction (this value is attained experimentally, although a good approximate is 1/2),

$\mathbb{z}.A -$ number of electrons contributes in (A) reaction,

$\eta_A -$ overvoltage $\ddot{a}\ddot{o} - E_A$ where $\ddot{a}\ddot{o} -$ is the variation in potential between the electrode and the electrolyte (double layer)[7] and $E_A -$ Eelectrode potential at zero current.

A the same time as only Fe^{2+} are involved in the anode reaction, that its mass flux will be non-zero only. Therefore, the density current is estimated from Eqn. (2), with help of Faraday's law to calculate the mass flux:

$$\mathbb{J}_{\mathcal{F}e^{2+}} = \frac{i_A}{\mathbb{F}.\mathbb{z}.\mathcal{F}e^{2+}}$$

$$\mathbb{J}_{H^+} = 0 \; ; \quad on \; x = 0 \qquad\qquad [10]$$

The fluxes are used as boundary condition at the anode for the transport equation. Additionally, the cathode pole, between the matters experiences reduction is H_2O molecule that occurred reduction to H_2O

$$(B) \; 4H^+ + O^2 + 2H_2O \qquad E_A^0 = 1.23 \, V \quad \text{(Reduction)} \qquad [11]$$
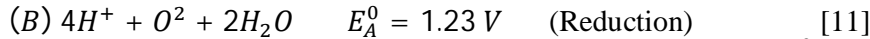
The cathodes current density can once again be calculated[8] according to the Butler Volmer's equation, by considering the (B) reaction only:

$$i_B = -i_{OB} \cdot \left\{ exp\left[(1 - \alpha_B) \frac{\mathbb{F}.\mathbb{z}.B}{\mathbb{R}.\mathbb{T}} \cdot \eta_B \right] - exp\left[-\alpha_B \frac{\mathbb{F}.\mathbb{z}.B}{\mathbb{R}.\mathbb{T}} \cdot \eta_B \right] \right\} \qquad [12]$$

Where i_{OB} − exchange current density of (B) reaction, α_B − transfer coefficient for (B) reaction, $\mathbb{z}.B$ − number of electrons participating in (B) reaction, η_B −over voltage,

With the negative sign it means that the flow of current proceeds from the electrode to the electrolyte, on the reverse of direction with respect to the axis.

The boundary conditions[8] for the Transport Eqn.(2) are obtained as before, by considering that only the H^+ ions are involved in the cathode reaction, and therefore only its mass flux will be non-zero

$$\mathbb{J}_{\mathcal{F}e^{2+}} = 0$$

$$\mathbb{J}_{H^+} = \frac{i_B}{\mathbb{F}.\mathbb{z}.H^+} \; ; \quad on \quad x = L \qquad\qquad [13]$$

4. Initial characters of condensation Conditions

Svante Arhenius comments that acid are a compound, which if it is dissolved in water then it will yield (H^+) Hydronium ion. While alkaline is a compound dissolved in water will yield[8] (OH^-) Hydroxide ion[4]. Every condensation has acidity of hydrogen ion exponent at different control to the corrosion process of a metal. The same as identified a small fraction from (H_2O) water molecules are dissociated in H^+ and OH^- ions in the amount are established by the constant equilibrium from dissociation reaction , that is

$$H_2O \qquad H^+ + OH \leftrightarrows \qquad\qquad [14]$$

In particular condensation in water ,concentration of (H^+) Hydronium ion and (OH^-) Hydroxide ion in a liquid condensation commonly very low but hardly determines characters of condensation. Sorensen (1868 -1939) [10] further proposes pH and pOH concept to avoid usage of a real small number[4]. According to Sorensen pH and pOH are the function of negative logarithm from the concentration of H^+ and OH^- ions in a condensation, and formulated as follows

$$pH = -log[\mathbb{C}_{H^+}] \; and \; pOH = -log[\mathbb{C}_{OH^-}] \qquad [15]$$

with $\mathbb{C}_{H^+}$ − is concentration from ion H^+ and $\mathbb{C}_{OH^-}$ − is concentration of OH^- ion where at equilibrium of pure water, applies

$$pH + pOH = 14 \qquad\qquad [16]$$

The concentration of the ions expressed in a set of Molar (M), where the molarity expresses that the various solute moles in every one condensation liter (mol/liter). Pure water has pH = 7, so that concentration from both of good ions of H^+ and OH^- - ions equal to 10^{-7}

Molar. Smaller pH value of condensation consequently level of the solution acidity and do on the converse.

5. Results and Discussion

5.1 Approach of Finite element method (FEM)

Every part of element that is named by finite element bases on the problems approach numeric method is known as Finite element method(FEM). Every problem that exists with the quadratic approach, where element method has form of matrix equation

$$[\mathbb{K}]\{\mathbb{r}\} + [\mathbb{K}_t]\{\dot{\mathbb{r}}\} = \{\mathbb{R}\} \qquad [17]$$

Where$[\mathbb{K}]$, $[\mathbb{K}_t] -$ assemble matrix, $\{\mathbb{r}\} -$vector from node magnitude whichunknown, $\{\mathbb{R}\} -$assemble style parameter vector

Global matrix equation will be finalized, where in this solution it will be used approach of finite difference with the Crack-Nicholson's pattern[11]. Equation of global matrix compiler can be written down in the form of finite difference as

$$[\mathbb{K}]\left(\theta\{\mathbb{r}\}_{t+\Delta t} + (1-\theta)\{\mathbb{r}\}_t\right) + [\mathbb{K}_t]\left\{\theta\left\{\frac{\partial\{\mathbb{r}\}}{\partial t}\right\}_{t+\Delta t} + (1-\theta)\left\{\frac{\partial\{\mathbb{r}\}}{\partial t}\right\}_t\right\} = \{\mathbb{R}\}_{t+\Delta t}$$

$$[18]$$

If it is taken è = 1/2 hence will be obtained Crack pattern approach rnodel of equation as :

$$\frac{1}{2}\left\{\left\{\frac{\partial\{\mathbb{r}\}}{\partial t}\right\}_{t+\Delta t} + \left\{\frac{\partial\{\mathbb{r}\}}{\partial t}\right\}_t\right\} = \{\mathbb{R}\}_{t+\Delta t} \qquad [19]$$

Global matrix equation will have an approach to time as below

$$\left([\mathbb{K}] + \frac{2}{\Delta t}[\mathbb{K}_t]\right)\{\mathbb{r}\}_{t+\Delta t} = 2\{\mathbb{R}\}_{t+\Delta t} - \left(\left([\mathbb{K}] - \frac{2}{\Delta t}[\mathbb{K}_t]\right)\{\mathbb{r}\}_t\right) \qquad [20]$$

5.2 Electrochemical computations by MATLAB and Visual Studio 7.0 program.

Numerical as well as electrochemical computations were executed through indigenously designed computer programs[13] in MATLAB and Visual Studio. The numerical solution of those equations which will be visualized by using MATLAB 7.0 program. MATLAB programming codes are available for individual interpolation models. From the extensive computational numerical analysis, absolute relative error is significantly low for individual interpolation models .The result is shown in Fig. 2:
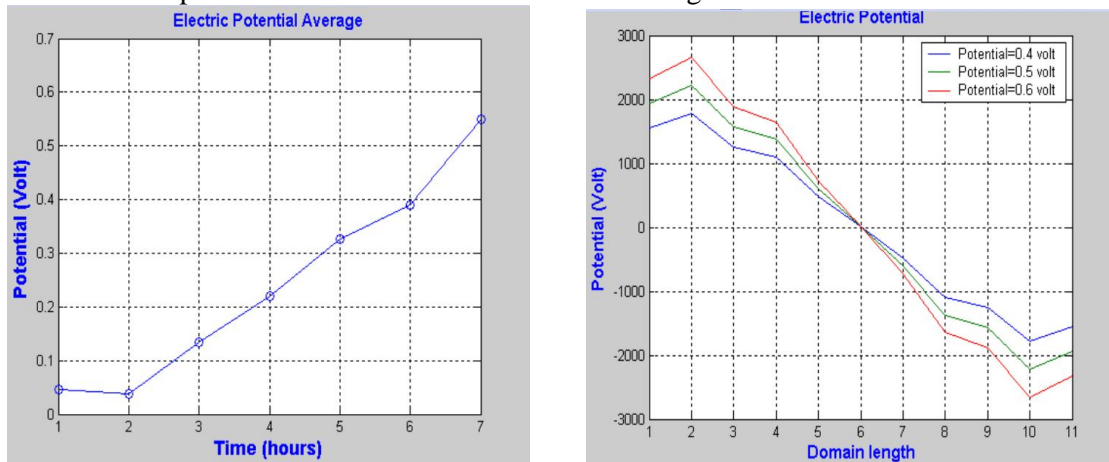
(a)   (b)

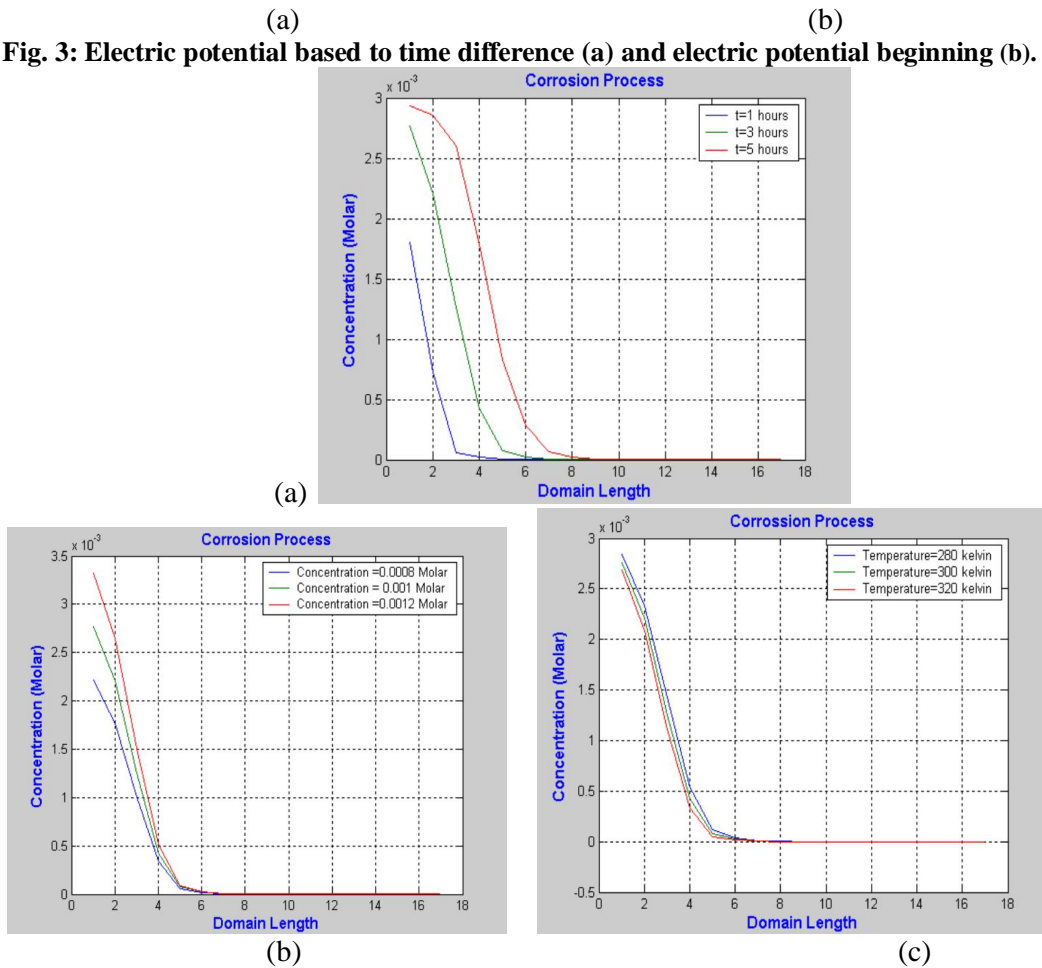**Fig. 3: Electric potential based to time difference (a) and electric potential beginning (b).**

(a)

(b)

(c)

Fig. 2: Iron Corrosion Process based on difference Time (a),Concentration of Iron (b), and Temperature condensation (c).
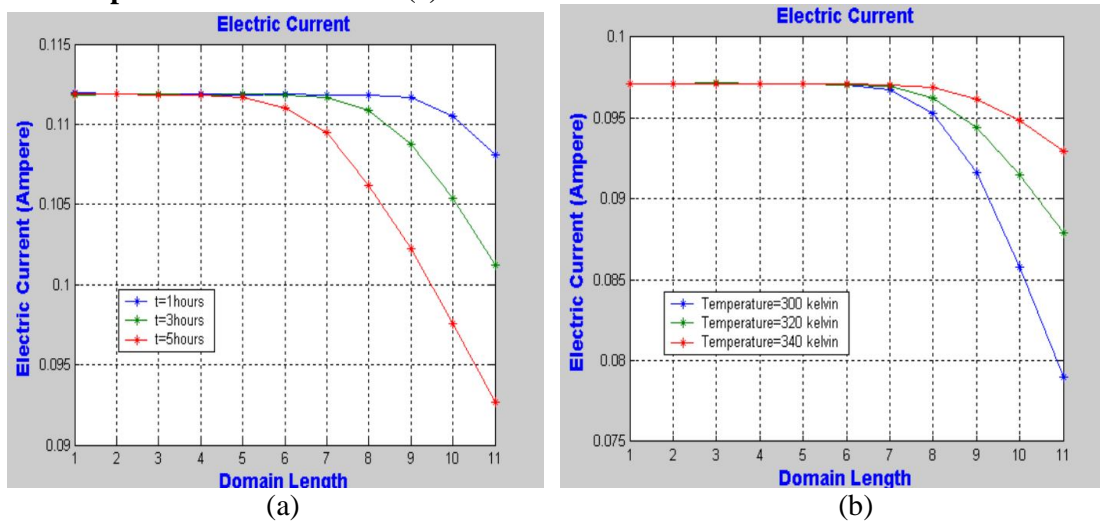

(a)

(b)

Fig. 4: Electric current based to time difference (a) and condensation temperature (b).
5.3 Iron Corrosion Process based on difference Time

Based on the obtained result above, it can be determined that the relation of the longer time required. Thus, the chances that ensure corrosion is substantially increase, and so do on the dissimilar. The concentration control of iron towards the iron corrosion process is greater than the applied iron concentration. The statement rings with Planck-Nernst law about mass transport and First Faraday's law where mass that's yielded or reduced compares straight to time and concentration of metal that's applied but proportional inversely with condensation temperature.

Therefore, the chance that the ensure iron corrosion increasingly increases and equally. Third factor[12] that has produce on is condensation temperature used, ever greater of temperature used so chance that the occurrence of corrosion closely minimizes. Numerical result of the electrical potential equation is also be visualized by using MATLAB 7.0 program and it is plotted in Fig. 3:

5.4 Electric potential based to time difference

From above Fig. 3, which obtained for required time level of electrical tension value of mean emerging at every node would increasingly increases. The beginning electric potential influence that applied hence electric potential average value also increasingly minimizes. This clears the statement of   Planck-Nernst's about mass transport, where potential electric is compared straight to time. The electrical current also arises during the corrosion process at electrochemical cell as shown in Fig. 4:

5.5 Electric current based to time difference

In Fig. 4 shows that the longer time required so electric current that emerges at every node increasingly declines. Temperature factor also influences to electrical current value that emerges during corrosion process to take place that is ever greater of condensation temperature used thus electric current ensued at every node also increasingly increased. Both of these relationships agreed with Faraday's first law and mass transport Planck-Nernst's law.

6. Conclusion

This model addresses the precise determination of inferential part of gristle metal part of functioning metal as anode support, If the time is longer applied hence part of metal experiencing impairment concentration by the end of iteration would increasingly long in meaning of   gristle area corrosion to be longer so that metal mass that reduce by the corrosion more and more. The concentration factor of initial iron also influences to corrosion process, that is value concentration of iron used in mutilation concentration of iron by the end of iteration also increasingly long in meaning of area so that number of masses that's yielded for the concentration of larger one. Temperature factor also influences to iron corrosion that is more high condensation temperature used in condensation of electrolyte the degradation of concentration of increasingly short, in meaning of affected area corrosion to be more minimizes. At the electrical potential increasingly of time and the potential electrical average value also increases, while greater of electric potential that's applied at every node and electric potential average value

also increases. While growing of condensation temperature of electrolyte value which emerges to increasingly.

7. References

1. Shifter D. A, "Corrosion Science", Physical Science, Vol. **47**, **2005**, pp. 2335–2352.
2. Atkins P.W., Physical Chemistry, Oxford University Press, Oxford, **1990**
3. Newman, J. S., Electrochemical Systems, Prentice-Hall, Englewood Cliffs, New Jersey, **1996**.
4. Sudarmo U., Chemistry, Erlangga, Jakarta, **2006**.
5. Chaudouet A., Lange D, The use of boundary integral equation method in mechanical engineering, Second international conference on Applied Numerical Modeling, Madrid, **1978**.
6. Druesne F., Paumelle P., Simulating electro chemical plating for corrosion protection, Corrosion Prevention and Control, Vol.**45** (**1998**), 118-123.
7. Druesne F., Paumelle P.and Villon P., Boundary Element Method applied to electrochemical plating, European revue of finite elements, Volume **8**, n°1, February **1999**.
8. Prentice G.A., and Tobias C.W., A survey of numerical methods and solutions for current distribution problems, Journal of Electrochemical Society, Vol.**129** (**1982**), 72.
9. Gerstenberger A, Wall WA. An embedded Dirichlet formulation for 3D continua. International Journal for Numerical Methods in Engineering; **82**(5): **2010**, 537–563.
10. Georgiadou M. Modeling current density distribution in electrochemical systems. Electrochimica Acta, **48**: **2003**. 4089–4095.
11. Buoni M, Petzold L. An efficient, scalable numerical algorithm for the simulation of electrochemical systems on irregular domains. Journal of Computational Physics , **225**: **2007**;2320–2332
12. Wolters C. H., Anwander A., Berti G. and Hartmann U. Geometry-adapted hexahedral meshes improve accuracy of finite element method based EEG source analysis IEEE Trans.Biomed.Eng, **54**(8), volume54, , **2007**:1446-1453
13. M Kanagasabapathy ,Technical computation by MATLAB,MathForum (Research), Drexel university Philedephia, USA, Online: http://mathforum.org /library /view/ 75575. html
14. MATLAB programming codes are available for individual interpolation models at http://techmatlab.blogspot.in.