CHAPTER II

THEORY

1. Electrochemistry

Electrochemistry has been classically defined as the science of the chemical change produced by the electric current or the production of electricity from the energy of chemical reaction [1]. It deals with reactions proceeding at the expense of external electrical energy or serving as a source of this energy. Such reactions are known as electrochemical reaction, a heterogeneous chemical process involving the transfer of charge to or from an electrode [2].

Electrochemical processes have two factors that effect on the transport of charge across the interface between chemical phases. The factors are electrolytes and electrodes.

Electrolytes are merely a phase through which charge is carried by the movement of ions. They may be liquid solutions of fused salts, or they may be ionically conducting solid, such as sodium β- alumina, which has mobile sodium ions.

Electrodes are phases through which charge is carried by electronic movement. They can be metals or semiconductors, solid or liquid. In an electrochemical cell, electrodes are normally included.

-Reference electrode is the electrode which has a constant potential without changing when a current passed through. This kind of electrode must be stable with respect to time and temperature.

-Working electrode or cathode is a electrode coupled with the reference electrode. At this terminal, the reduction of active species occurs.

-Counter electrode or anode is the pole at which the oxidation takes place.

1.1 Oxidation - reduction processes

In an oxidation - reduction or redox reaction, electrons are transferred from one reactant to another. One of the reacting species is converted to a higher oxidation state and as a consequence is oxidized; the other reactant suffers a decrease in oxidation state is thus reduced. A substance that has a strong affinity for electrons and thus tends to extract them from other species is called an oxidizing agent or an oxidant and posses a strong tendency to cause oxidation of other species. A reducing agent, or reductant, is a reagent that readily donates electrons to another species and tends to cause reductions. In this processes, one or more charged particles are transferred from a donor to an acceptor. The particles being electrons in the former case and products of an oxidation - reduction reaction are a conjugate oxidant and a conjugate reductant. The fundamental step is an exchange of one or more electrons as following reactions [3].

Reduction $$O_1 + ne^- \longleftrightarrow R_1 \qquad \text{(II.1a)}$$

Oxidation $$R_2 \longleftrightarrow O_2 + ne^- \qquad \text{(II.1b)}$$

Redox $$O_1 + R_2 \longleftrightarrow O_2 + R_1 \qquad \text{(II.1c)}$$

Where O and R represent the oxidized and reduced form, respectively. At one electrode, the anode, the reductant transfers one or more electrons to the metal electrode as equation (II.1b), while to maintain overall electrical balance, an equal number of electrons must leave this electrode and pass through the external wiring. Simultaneously, the cathode yields up the same number of electrons to the oxidant as equation (II.1a).

If equilibrium in this process favors the products, O_1 is more effective electron acceptor (and thus a stronger oxidizing agent) than O_2, the species that results from the loss of electrons from R_2. By the same reasoning, R_2 is a more effective electron donor (and hence a stronger reducing agent) than R_1 [4]. The equation that described the oxidation and the reduction separately is called half-reaction. Two previous equations (II.1a & II.1b) can be rewritten in term of half - reaction by

$$O + ne^- \longleftrightarrow R \qquad \text{(II.2)}$$

1.2 Nernst equation

The value of equilibrium potential can be calculated by the Nernst equation. The relationship between electrode potential and concentration of electrode species was first evaluated in the nineteenth century by a German chemist namely Nernst. Consider the generized reversible half - reaction.

$$aA + bB + \ldots\ldots\ldots + ne^- \longleftrightarrow cC + dD + \ldots. \qquad \text{(II.3)}$$

where the capital letters are formulas for species participating in the electron transfer. According to the Nernst Equation, the equilibrium electrode potential for this reaction is given by

$$E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d\ldots..}{[A]^a[B]^b\ldots..} \qquad \text{(II.4a)}$$

or

$$E = E^0 + \frac{nF}{RT} \ln \frac{[A]^a[B]^b\ldots..}{[C]^c[D]^d\ldots..} \qquad \text{(II.4b)}$$

Upon converting the natural logarithm to the normal logarithm (a base ten), the foregoing equation becomes at 25 ^{0}C.

$$E = E^0 - \frac{0.0592}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{(II.5)}$$

If the substance A is a gas, [A] is partial pressure in atmospheres and if A is a solute, [A] is activity of species A.

1.3 Electrode potentials

An electrode potential is defined as the potential of a cell consisting of the electrode and the standard hydrogen electrode. It should be emphasized that an electrode potential is in fact that the potential of an electrochemical cell involving a carefully defined reference electrode. In general, the potential of a cell is the difference between the electrode potential of the cathode and that of anode.

$$E_{cell} = E_c - E_a \qquad \text{(II.6)}$$

It should be stressed that both E_c and E_a are electrode potentials and are therefore the potentials of the half - reactions written as reductions. The positive sign for the cell potential indicates that the reaction occurs spontaneously and that the cell is a galvanic cell. Therefore, the negatives sign indicates the nonspontaneously of the reaction.

1.4 Standard electrode potential (E^0)

The standard electrode potential can be defined as the electrode potential of a half - cell reaction versus the standard hydrogen electrode when all reactants and products exist at unit activity. Several facts regarding this constant should always be kept in mind.

1. The standard electrode potential is a relative quantity in the sense that it is the potential of an electrochemical cell in which the anode is the standard hydrogen electrode.

2. Standard electrode potentials refer exclusively to half - cell processes that are written as reductions, it is a relative reduction potential.

3. Standard electrode potentials bear a sign that is based upon the driving force of the reduction reaction relative to the reduction of hydrogen ion at unit activity. A positive sign indicates that the electrode will behave as the cathode (when the reactants and products are at unit activity) when coupled with the standard hydrogen electrode. A negative sign, on the other hand, indicates that the system will be the anode where oxidation takes place.

4. Standard electrode potentials are temperature dependent.

5. The standard electrode potential is independent of the notation employed to express the half - cell process.

1.5 Equilibrium constants from standard electrode potentials

At equilibrium, the potential of the cell thus becomes zero

$$E_{cell} = E_c - E_a = 0 \qquad \text{(II.7)}$$

or

$$E_c = E_a \qquad \text{(II.8)}$$

This equation expresses an important and general relationship for an oxidation - reduction system. At a chemical equilibrium, the electrode potentials at all half - reactions of the system will be equal. Consider the oxidation - reduction equilibrium

$$aA_R + bB_O \longleftrightarrow aA_O + bB_R \qquad \text{(II.9)}$$

when the components of this system are at chemical equilibrium,

$$E_A = E_B \qquad \text{(II.10)}$$

With this equality expressed in terms of the Nernst Equation at 25 °C, we find that at equilibrium

$$E_A^{0} - \frac{0.0592}{n} \log \frac{[A_R]^a}{[A_O]^a} = E_B^{0} - \frac{0.0592}{n} \log \frac{[B_R]^b}{[B_O]^b} \qquad \text{(II.11)}$$

which yields upon rearrangement and combination of the log terms

$$E_A^{\ 0} - E_B^{\ 0} = -\frac{0.0592}{n} \log \frac{[A_O]^a [B_R]^b}{[A_R]^a [B_O]^b} = -\frac{0.0592}{n} \log k_{eq} \qquad \text{(II.12)}$$

This relationship was derived for equilibrium conditions. The concentration terms are thus equilibrium concentrations; hence, the quotient is the equilibrium constant for the reaction. That is,

$$\log k_{eq} = \frac{n\left(E_B^{\ 0} - E_A^{\ 0}\right)}{0.0592} \qquad \text{(II.13)}$$

1.6 Potentials of real cells

1.6.1 Liquid - junction potential

This potential is observed when two electrolyte solutions of different composition are brought in contact with one another. A potential develops at the interface and arises from differences in rates of migration of anions and cations between the two solutions.

1.6.2 Ohmic potential (*iR* drop)

When electricity flows in an electrochemical cell, the overall potential is altered by amount that corresponds to the driving force necessary to overcome the resistance of ions to movement toward the anode and the cathode. This force is generally referred to as the ohmic potential, or the *iR* drop which follows Ohm's law and equals to the product of the current in amperes and resistance of the cell in ohms.

The net effect of *iR* drop is to increase the potential required to operate an electrolytic cell and to decrease the measured potential of a galvanic cell. Therefore, the *iR* drop is always subtracted from the theoretical cell potential. This is

$$E_{cell} = E_c - E_a - iR \qquad \text{(II.14)}$$

1.6.3 Polarization effects

The current - voltage relationship in an electrolytic cell is convenient to rewrite in the form

$$i = -\frac{1}{R} E_{ap} + \frac{1}{R}\left(E_c - E_a\right) \tag{II.15}$$

For small currents and brief periods of time, E_c and E_a remain relatively constant. Thus, the cell behavior can be approximated by the relationship

$$i = -\frac{1}{R} E_{ap} + k \tag{II.16}$$

where k is a constant.

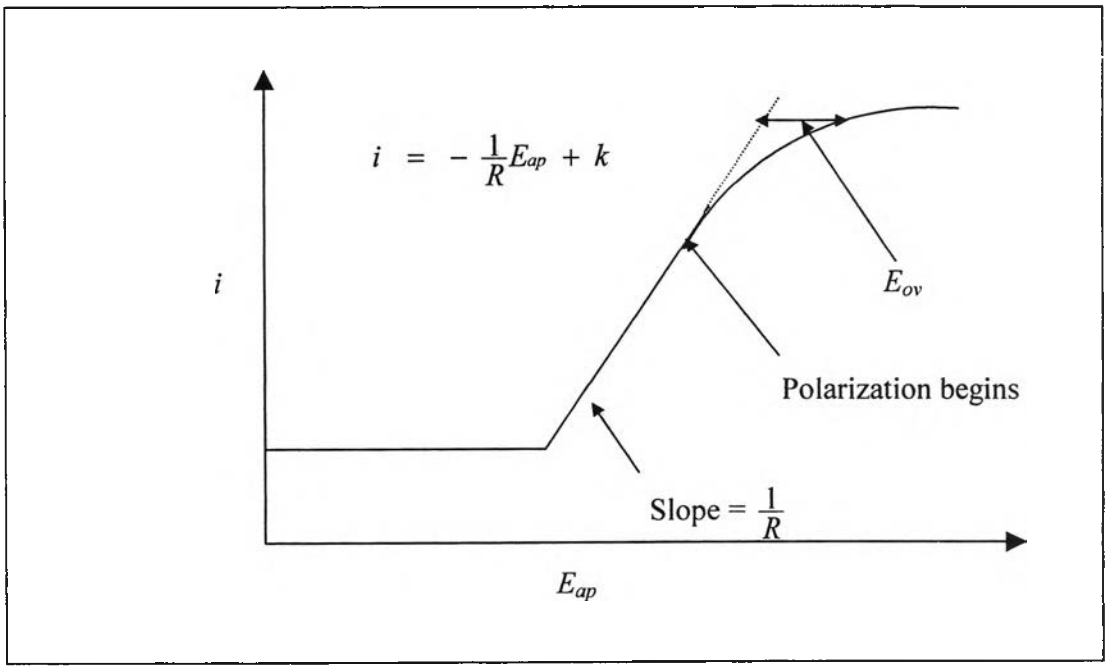


Figure II.1: Current - voltage curve for an electrolytic cell [5].

A plot of the instantaneous current as a function of applied potential would in theory yield a straight line with a slope that equals the reciprocal of the resistance. The linear relationship between current and applied potential suggested by the foregoing equation is frequency observed when *i* is small; as shown by the solid line in Figure II.1, however, marked departures from linearity appear at higher currents. Under these circumstances the cell is said to be polarized. Thus, polarized electrolytic cell requires application of a potential larger than theoretical in order to provide a given current. This added potential is termed an overvoltage or over potential. Thus,

$$E_{cell} = E_c - E_a - iR - \eta \qquad \text{(II.17)}$$

The presences of polarization increase, makes more negative, the potential required to operate an electrolytic cell. Thus, overpotential, like *iR*, is always subtracted from the thermodynamic cell potential.

1.7 Electrochemical thermodynamic

Any redox reaction (II.18a) corresponding to a cell reaction may be divided into two partial reactions representing an oxidation (II.18b) and a reduction (II.18c)

$$A + C \longleftrightarrow B + D \qquad \Delta G \qquad \text{(II.18a)}$$

$$C \longleftrightarrow D + e^- \qquad \Delta G_1 \qquad \text{(II.18b)}$$

$$A + e^- \longleftrightarrow B \qquad \Delta G_2 \qquad \text{(II.18c)}$$

A general redox reaction can be only taken place spontaneously if the Free Energy ΔG is negative. In the case of an electrochemical reaction, two different situations have to be considered; free energy and reversible cell voltage [6]. If ΔG is negative, the reaction occurs spontaneously in the cell, converting the stored chemical energy into usable electrical energy. The total free energy can be calculated by free energy of single electrode reaction as following reaction

$$\Delta G = \Delta G_1 - \Delta G_2 \qquad \text{(II.19)}$$

The free energy of half - reaction can be expressed in terms of reversible electrode potential (E^0) by

$$\Delta G_i = -nFE_i^0 \qquad \text{(II.20)}$$

The reaction is spontaneous when the total free energy have the negative sign. In another way, the electrochemical cell reaction is characterized by its reversible cell voltage (U_0).

$$\Delta G = nFU_0 \qquad \text{(II.21)}$$

$$U_0 = E_{0,1} - E_{0,2} \qquad \text{(II.22)}$$

The sign conventions of the reversible electrode potential indicate the reaction by

$U_0 < 0$ spontaneous reaction

$U_0 > 0$ reaction can be only performed by consumption of electrical energy.

The temperature dependence of E^0 is related to the standard entropy change (ΔS^0) of the reaction by the equation

$$\left(\frac{\partial E^0}{\partial T}\right)_p = -\frac{\Delta S^0}{nF} \qquad \text{(II.23)}$$

If the constant entropy is assumed over a small temperature range, the integration of the previous equation gives

$$E_2 - E_1 = -\frac{\Delta S^0}{nF}(T_2 - T_1) \tag{II.24}$$

The change in the reversible potential with pressure can be expressed by

$$\left(\frac{\partial E_0{}^0}{\partial p}\right)_T = -\frac{\Delta V}{nF} \tag{II.25}$$

1.8 Electrode polarization

Information about an electrode reaction is gained by determining current as a function of potential, *i* - *E* curve, [7]. The departure of the electrode potential (or cell potential) from the reversible value upon passage of faradaic current is termed polarization.

An ideal polarized electrode is an electrode at which no charge transfer across the metal solution interface. It shows a very large change in potential upon the passage to an infinitesimal current.

An ideal nonpolarizable electrode or ideal depolarized electrode is thus an electrode whose potential does not change upon passage of current0, that is, an electrode of fixed potential.

A substance that tends to cause the potential of an electrode to be nearer its equilibrium value by virtue of its being oxidized and reduced state is called depolarizer. Two polarization curves are demonstrated in Figure II.2

The extent of polarization is measured by the overpotential which is the deviation of potential from the equilibrium value.

$$\eta = E - E_{eq} \tag{II.26}$$

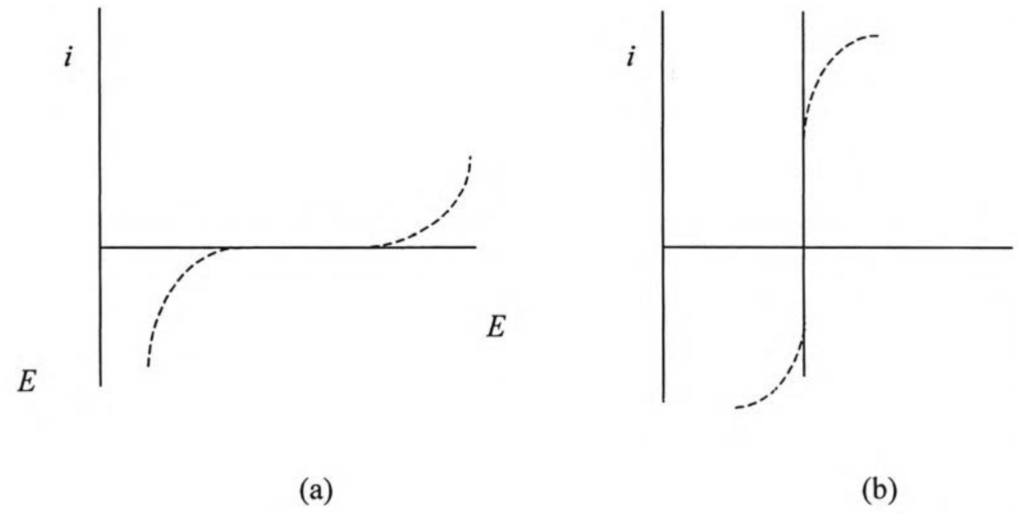


Figure II.2: Current potential curves for ideal polarizable (a) and non polarizable electrodes (b). (Dashed lines show behaviour of actual electrodes)

At given current density, there will be a certain overpotential. This overpotential can be considered as sum of different overpotential terms associated with the different reaction step: η_{mt} is the mass transfer overpotential or concentration overpotential, η_{ct} is the charge transfer overpotential or activation overpotential and η_{rxn} is the overpotential associated with a preceding reaction or reaction polarization.

Concentration overpotential is the overpotential associated with mass transport limitation [8]. It causes by change in the concentrations of species participating in an electrode reaction. When a current passes, a depletion or accumulation of some species occurs in the electrolyte solution adjacent to an electrode. The electrode is thus surrounded by a solution of different composition to that in the bulk which would cause a shift in the electrode potential away from its equilibrium.

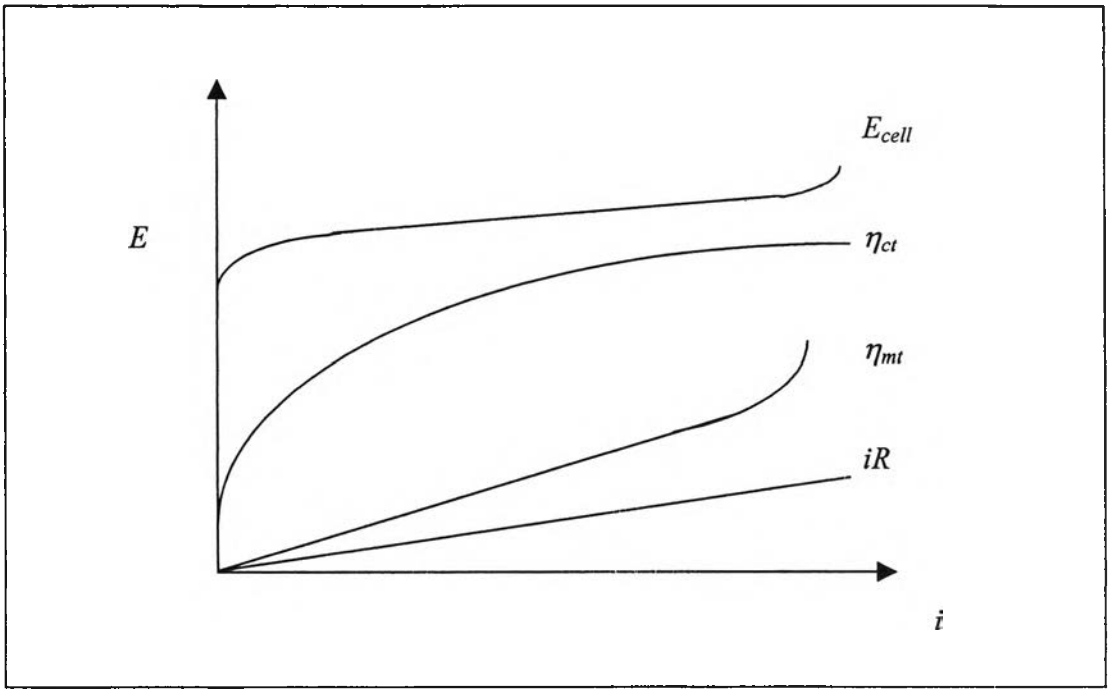


Figure II.3: The cell potential and its various components.

Activation overpotential is the potential resulted by kinetic limitation. The essential feature of any electrode reaction is electron transfer across the electrode/solution interface but this process is only one in a sequence of reaction step. The actual sequence is unique for any reaction included adsorption and adsorption of reactants, products and intermediates together with surface diffusion and surface chemical reaction. The rate of reaction is determined by the lowest step known as *rate determining step* which represents the state of maximum energy required to achieve the reaction. This energy is called activation energy. A portion of the activation energy is lost during the reaction and this irreversibility gives rise to an activation overpotential.

Figure II.3 represents the plot between possible observed potentials as a function of current. The increasing of concentration overpotential increases when current increases and tends to constant at very high current. On the other hand, the *iR* drop increases with direct proportion to current and activation overpotential have the same tendency as *iR* drop at low current but it sharply increases when higher current density is applied. The summation of all potentials have the tendency to increase when current increases as shown by the highest line on the figure.

1.9 Current - overpotential equation

Early studies of electrochemical systems showed that the current is often related exponentially to the overpotential η. That is,

or $$\eta \quad = \quad a + b\log i \qquad \text{(II.27)}$$

This equation is known as Tafel equation. The current - overpotential characteristic can be expressed by

$$i \quad = \quad nFAk^{0}\left[C_{O(0,t)}\exp\left\{-\alpha nf\left(E-E^{0'}\right)\right\} - C_{R(0,t)}\exp\left\{(1-\alpha)nf\left(E-E^{0'}\right)\right\}\right] \qquad \text{(II.28)}$$

At equilibrium, the net current is zero. The faradaic activity can be expressed in terms of exchange current (i_0) which is equal in magnitude to either component current i_c or i_a. That is

$$i_0 \quad = \quad nFAk^{0}C_0^{*}\exp\left\{-\alpha nf\left(E_{eq}-E^{0'}\right)\right\} \qquad \text{(II.29)}$$

but $$\left(\frac{C_0^{*}}{C_R^{*}}\right)^{-\alpha} \quad = \quad \exp\left\{-\alpha nf\left(E_{eq}-E^{0'}\right)\right\} \qquad \text{(II.30)}$$

then $$i_0 \quad = \quad nFAk^{0}\, C_0^{*(1-\alpha)} C_R^{*\alpha} \qquad \text{(II.31)}$$

So that, the current - overpotential equation can be expressed by

$$i = i_0 \left[\frac{C_{O(0,t)}}{C_O^*} \exp\{-\alpha n f \eta\} - \frac{C_{R(0,t)}}{C_R^*} \exp\{(1-\alpha) n f \eta\} \right] \qquad \text{(II.32)}$$

The behavior predicted by this equation is depicted in Figure II.4. The solid curve shows the actual total current, which is the sum of the components i_c and i_a, shown as dashed traces.

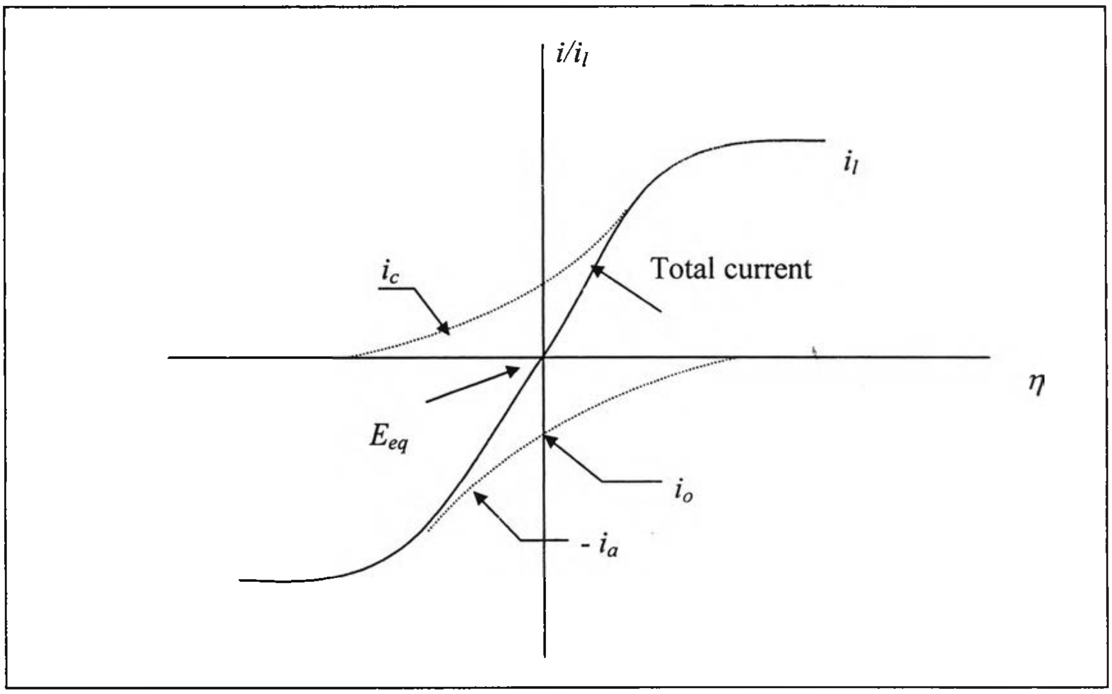


Figure II.4: Current overpotential curves for the system $O + ne^- \longrightarrow R$.

For large negative overpotentials, the anodic component is negligible, hence the total current curve merges with that for i_c. At large positive overpotentials, the cathodic component is negligible, and i_a is essentially the same as the total current. In going either direction from E_{eq}, the magnitude of current rises rapidly because the exponential factors dominate behavior, but at extreme η, the current levels off. In these level regions, the current is limited by mass transfer rather than heterogeneous kinetics. The exponential factor in above equation are then kept under control by the factors $C_O(0,t)/C_O^*$ and

$C_R(0,t)/C_R^*$, which manifest the reactant supply. The approximate forms of the current-overpotential equation can be classified by the following types

1.9.1 No mass transfer effects

If the solution is well stirred or currents are kept so low that surface concentrations do not differ appreciably from the bulk values, then

$$i = i_0 \left[\exp\{-\alpha nf\eta\} - \exp\{(1-\alpha)nf\eta\}\right] \qquad \text{(II.33)}$$

which is known generally as the Butler - Volmer equation. This equation is used to describe the current-overpotential relationship for an electrode at specified temperature, pressure and concentration of reacting species.

1.9.2 Linear characteristic at small η

For small value of x, the exponential, e^x, can be approximated as $1+x$; hence for sufficiently small η, then

$$i = i_0(-nf\eta) \qquad \text{(II.34)}$$

which shows that the net current is linearly related to overpotential in a narrow potential range near E_{eq}. The ratio $-\eta/i$ has dimensions of resistance and is often called the charge transfer resistance (R_{ct}).

$$R_{ct} = \frac{RT}{nFi_0} \qquad \text{(II.35)}$$

1.9.3 Tafel behavior at large η

For large values of η (either negative or positive), then

$$i = i_0 \exp(-\alpha f\eta) \qquad \text{(II.36)}$$

or
$$\eta = \frac{RT}{\alpha F}\ln i_0 - \frac{RT}{\alpha F}\ln i \qquad \text{(II.37)}$$

1.9.4 Tafel plots

A plot of log i vs. η shown as a Tafel plot, is a useful device for evaluating kinetic parameter. In general, there is an anodic branch with slope $(1-\alpha)\ nF/2.3\ RT$ and a cathodic branch with slope $-\alpha\ nF/2.3\ RT$. As shown in Figure II.5, both linear segments extrapolated to an intercept of log i_0. The actual current plots deviate sharply from linear behavior as η approaches zero, because the back reactions can no longer be regarded as negligible. The transfer coefficient α and the exchange current i_0 are obviously readily accessible from this kind of presentation.

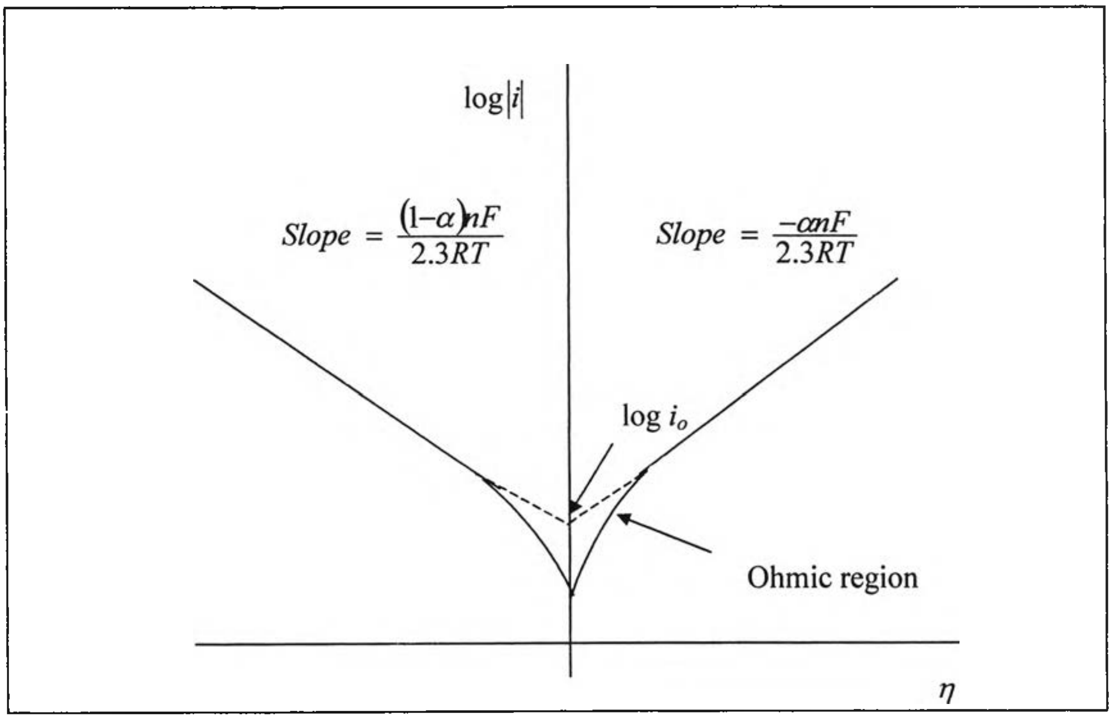


Figure II.5: Tafel plot for anodic and cathodic branches of the i - η curve.

1.10 Double - layer region

Figure II.6 shows the model of electrode-solution, double - layer region and Figure II.7 shows the electrostatic potential (ϕ) profile across double - layer region.

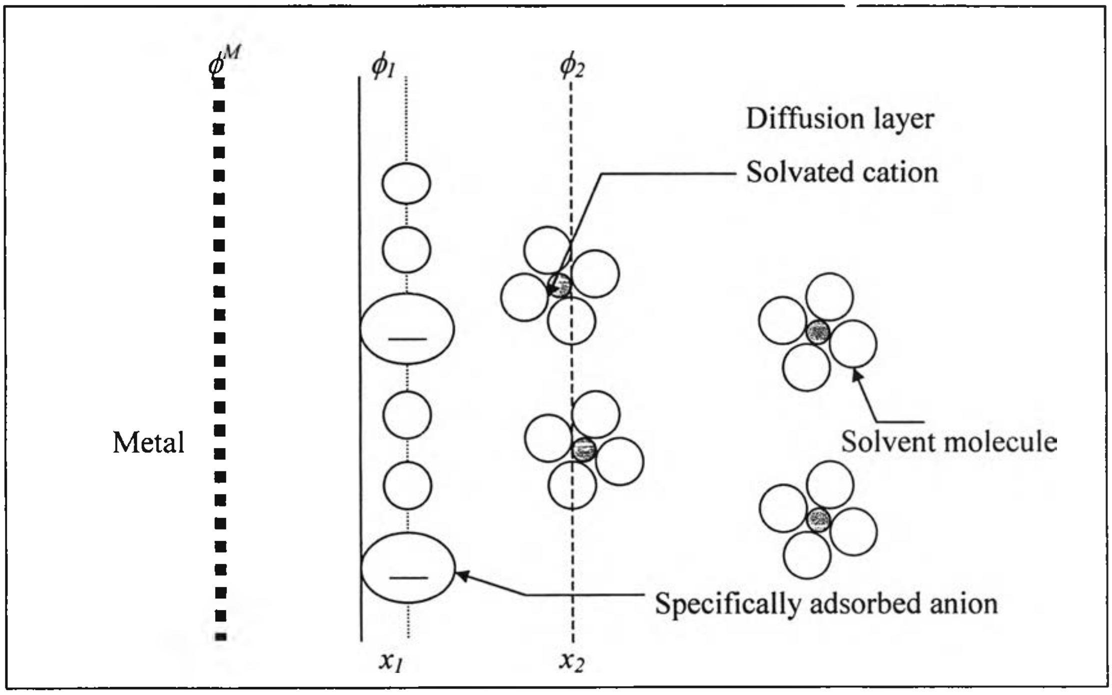


Figure II.6: Proposed model of the electrode - solution, double - layer region [9].

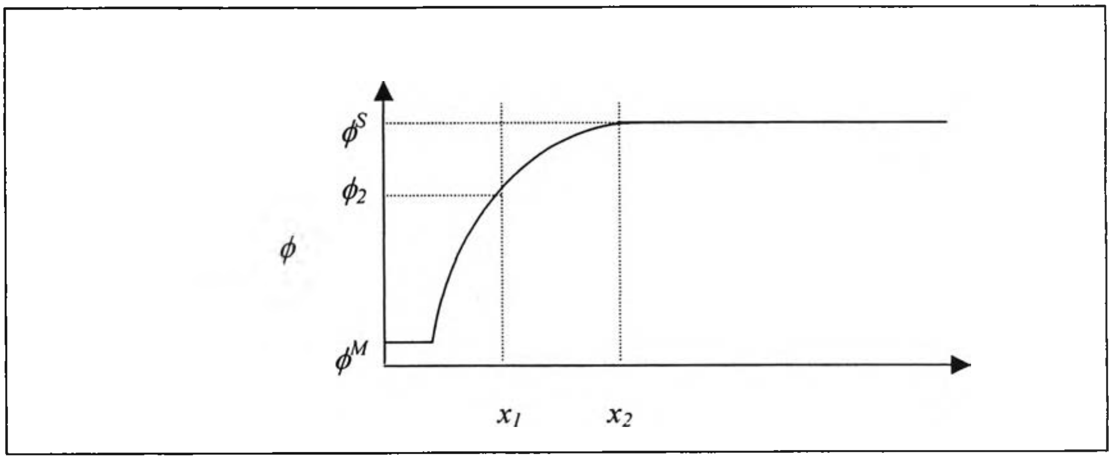


Figure II.7: Potential profile across double - layer region.

When a potential is applied to electrode, the charges, which necessarily accumulate on the electrode surface, attract ions of the opposite charges from the electrolyte. The solution side of the double layer is through to be made up of the several layers. The layer closest to the electrode, the inner layer, contains solvent molecules and sometimes other species that are said to be specifically adsorbed.

1.11 Mass transport in electrochemical system

Since electrochemical reactions belong to heterogeneous chemical processes various transport phenomena have to be taken into account. The phenomenon of charge transport is unique to electrochemical processes, and this must be considered along side mass transport, heat transport and momentum transport. The charge transport determines the current distribution in an electrochemical cell. Mass transport concerns with the transportation of reactants to the electrode and the products transported away and heat transport also plays an important role. The relationships are represented in Figure II.8.

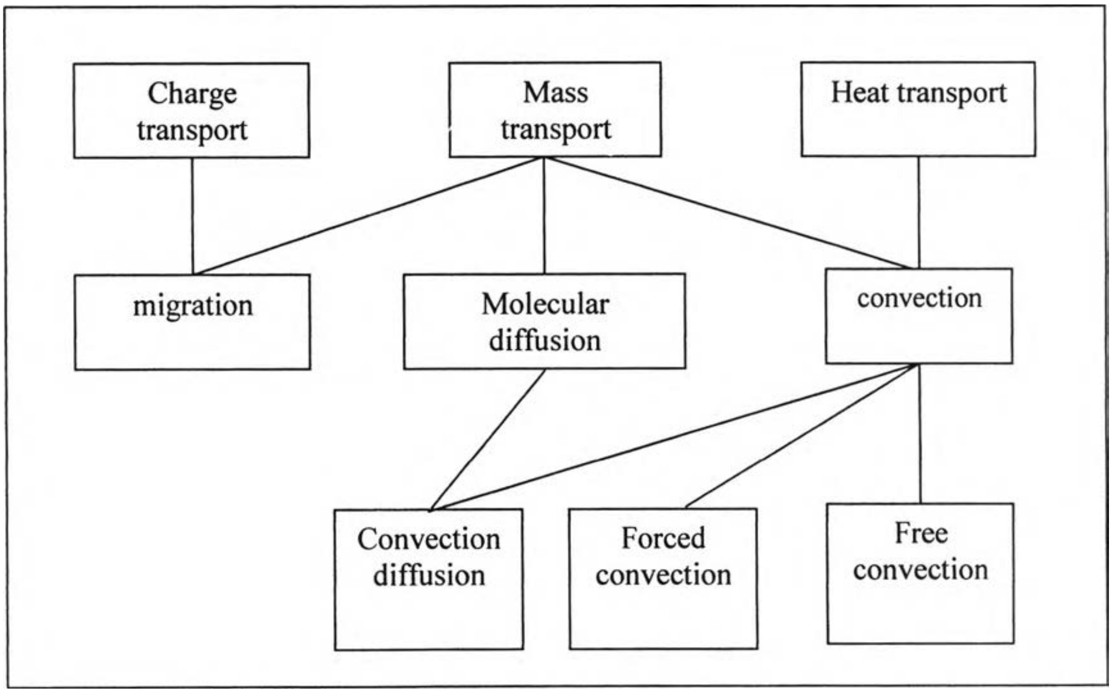


Figure II.8: The relationships between charge, mass and heat transport.

In the electrolytic process, mass transport, the movement of material from one location in solution to another due to the differences in electrical and chemical potential at two locations or due to the movement of a volume element of solution, takes place by migration, diffusion and natural or turbulent convection.

Migration is resulted from the potential gradient existing in a fluid medium in an electric field [10]. A charged particle, charge q, is then submitted to an electric force, being proportional to the charge q and to the potential gradient.

$$\vec{F} = q\,\vec{E} \tag{II.38}$$

The specific flux of migration for the species i,($\vec{N}_{i,m}$) is defined as the product $Ci\vec{U}i$.

$$\vec{N}_{i,m} = -n_i F \mu_i C_i \; grad \; \vec{\phi}_S \tag{II.39}$$

Diffusion is due to the difference between the bulk and surface concentration. Ions in solution are transfer from high concentration region to low concentration region. The rate of diffusion is directly proportional to the concentration gradient [Vassos, 1983]. The flux of matter is written by following equation

$$\vec{N}_{i,diff} = -D_i \frac{dC_{i(x)}}{dx} \tag{II.40}$$

Convection is the movement of species under the influence of a stirring or hydrodynamic transport. The fluid consists of various types of particles. One can define an average velocity as

$$\vec{U} = \frac{1}{C_T} C_i \vec{U}_i \tag{II.41}$$

The convection flux is defined as

$$\bar{N}_{i,conv} = C_i \bar{U}_i \tag{II.42}$$

The total flux of species *i* in dilute solution can be expressed as

$$\bar{N}_{i,m} = C_i \bar{U}_i - D_i \frac{dC_i}{dx} - n_i F \mu_i C_i \; grad \; \bar{\phi}_S \tag{II.43}$$

For the system where concentration gradients cannot be neglect, the simplification is to treat the mass transport boundary layer near an electrode surface as a region where the concentration gradient is linear or assuming that only diffusion takes place near the electrode. The concentration gradient is taken to be the gradient correspond to the flux at the electrode surface. This model is known as Nernst diffusion layer.

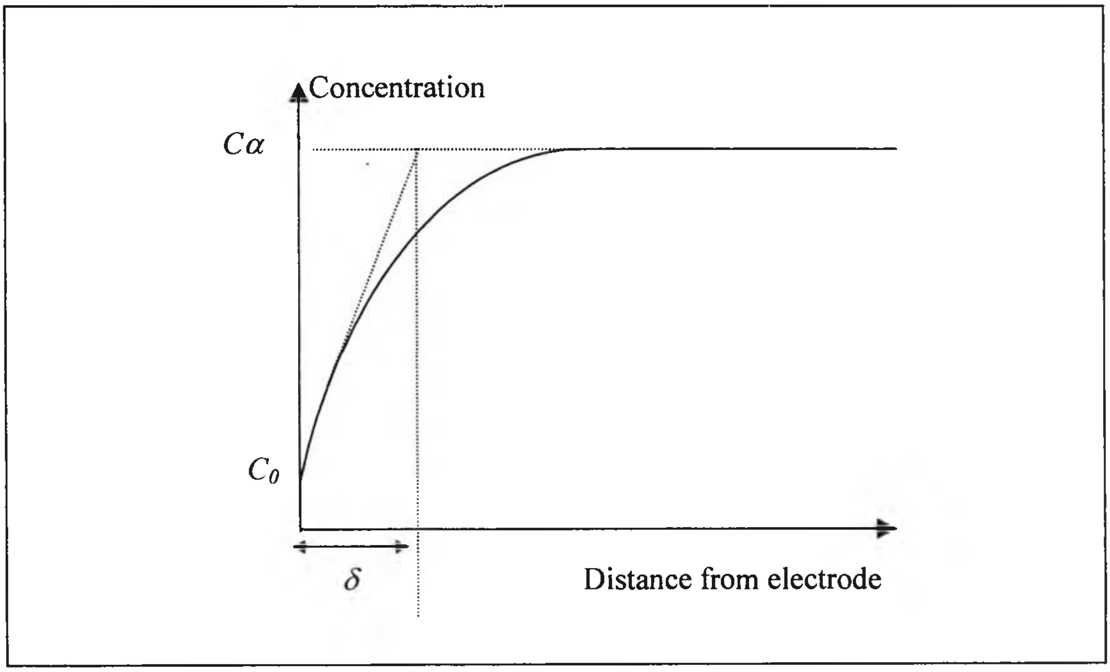


Figure II.9: Nernst diffusion layer model.

Figure II.9 shows the Nernst diffusion layer model. The solid line represents the actual concentration profile, and the dash line from C_0 is the extrapolation of the initial slope. The thickness of this layer is a function of system hydrodynamics, fluid agitation and facilitated mass transport. From Nernst diffusion layer model the current is due to the flux of all ions expressed by

$$i = \frac{-nFD(C_\alpha - C_0)}{\delta} \tag{II.44}$$

where C_α is the bulk concentration, C_0 is the surface concentration and δ is the Nernst diffusion layer thickness. In case of metal deposition when the current density is increased to a point where the concentration at the surface falls to zero, a further increase in current does not result in an increased deposition rate. The current density corresponding to zero surface concentration is called limiting current density (i_l).

$$i_l = \frac{-nFDC_\alpha}{\delta} \tag{II.45}$$

In application the ratio between D and δ is generally defined by mass transfer coefficient (k_L) then the previous equation is rewritten by

$$i_l = -nFk_LC_\alpha \tag{II.46}$$

This mass transfer coefficient principally depends upon the condition of process. At electrode surface, the overall electrode reaction composes of a series of steps that cause the conversion of the dissolved oxidized species to a reduced form. The current or electrode reaction rate is governed by the rate of processes such as; mass transfer, electron transfer at the electrode surface, chemical reactions preceding or following the electron transfer and other surface reactions. The process at electrode surface shows in Figure II.10.

Generally, the electrochemical reaction takes place at electrode surface. The active species are forced to electrode surface from bulk solution by mass transport mechanism. The loss of some electrons is observed for the reduced species and the oxidized species will obtain the equal number of electrons. After they are desorbed from the electrode and move to the bulk solution.

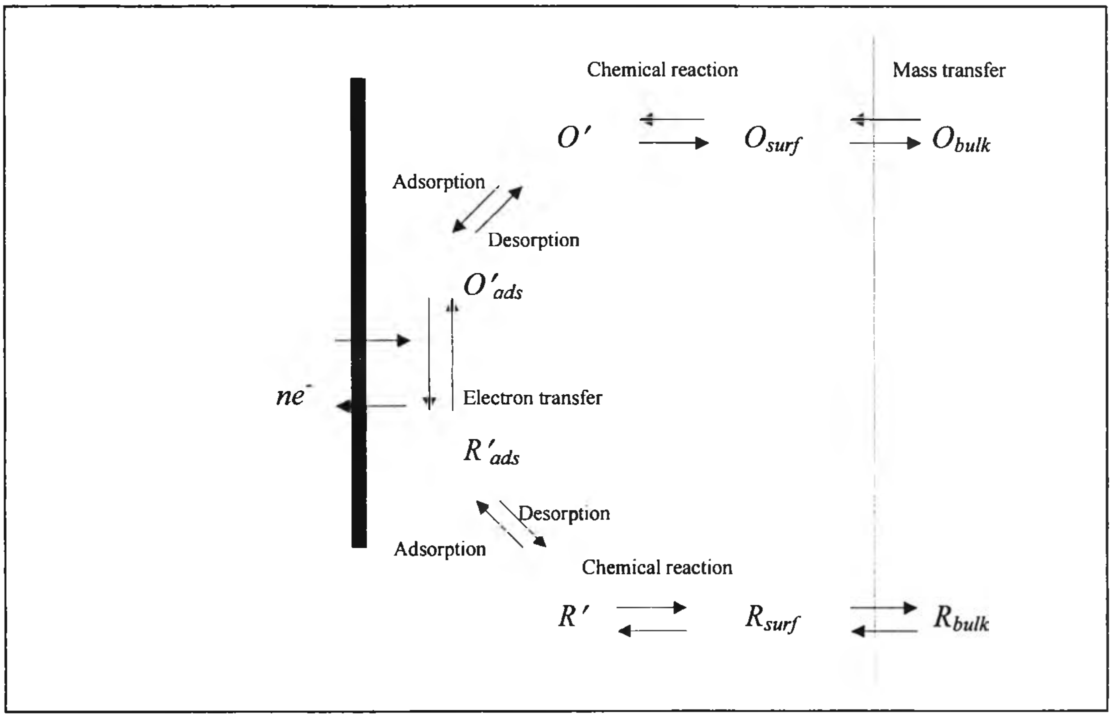


Figure II.10: Pathway of a general electrode reaction.

1.12 Faraday's laws

The relationship between charge passed and amount of a substance oxidized or reduced at an electrode was first quantity by Michael Faraday. His ideas are embodied in two statements pertinent to electrolytic processes [11].

1. The quantities of substance set free at the electrodes are directly proportional to the quantity of electricity which passes through the solution.
2. The same quantities of electricity set free the same number of equivalents of substances at the electrodes.

These two principles can be concisely stated in one equation, as shown in equation (II.47)

$$m = \frac{sM_W it}{nF} \tag{II.47}$$

By Faraday's law, the amount of some produced species can be determined at several applied current intensity.

Consider an electrolytic or energy consuming process, the current efficiency can be expressed by following equation

$$\text{Current efficiency} = \frac{\text{theoretical quantity of electricity required}}{\text{actual quantity of electricity consumed}} \tag{II.48a}$$

$$= \frac{\text{actual amount of product formed}}{\text{theoretical amount}} \tag{II.48b}$$

$$= \frac{\text{actual chemical charge (desired)}}{\text{theoretical chemical charge}} \tag{II.48c}$$

$$\text{Faradaic efficiency} = \frac{\text{theoretical reactant required}}{\text{amount of reactant consumed}} \tag{II.49}$$

$$\text{Energy efficiency} = \frac{\text{theoretical quantity of energy required}}{\text{actual quantity of energy consumption}} \tag{II.50a}$$

$$= \frac{(\text{Decomposition potential})\times(\text{Current efficiency})}{\text{actual voltage required}} \tag{II.50b}$$

2. Depollution processes

The contamination of heavy metal in processed water is a serious problem of many industrial sectors such as textile mills, chemical industries, finishing industries, plating industries or electronic industries. The contaminated heavy metals such as chromium, lead, copper have toxic properties for human beings. These metals discharged into the rivers are very harmful for aquatic life and other living organisms. Hence, removal of them before discharging becomes necessary. Many processes have been developed for metal removal from wastewater.

2.1 Chemical precipitation process

This method is the most common method for heavy metal removal from wastewater. Heavy metals are precipitated by adding some chemical substances until rise a pH level which corresponds to minimum solubility.

2.1.1 Metal hydroxide precipitation

At a given pH, different metals exhibit different solubility. The amount of metal in solution as a function of pH can be calculated theoretically from the solubility product (k_{sp}) of hydroxide [12]. For divalent metals, this takes the form as expressed by equation (II.51).

$$C_{H^+} = \left(\frac{C_{M^{2+}}}{k_{sp}}\right)^{1/2} k_W \qquad \text{(II.51)}$$

This correlation relates the equilibrium metal concentration C_M^{2+} with the hydrogen ion concentration C_{H+}.

2.1.2 Metal sulfide precipitation

The solubility products of metal sulfides are lower than those of corresponding hydroxides. The pH range for the precipitation of metals as sulfides is much broader. The products for metal sulfide are MeS, Me_2S and Me_2S_3. Metal sulfide precipitation occurs if the solubility product is smaller than the cross product of metal concentration and sulfide ion concentration.

Table II.1: Zone of metal precipitation [13].

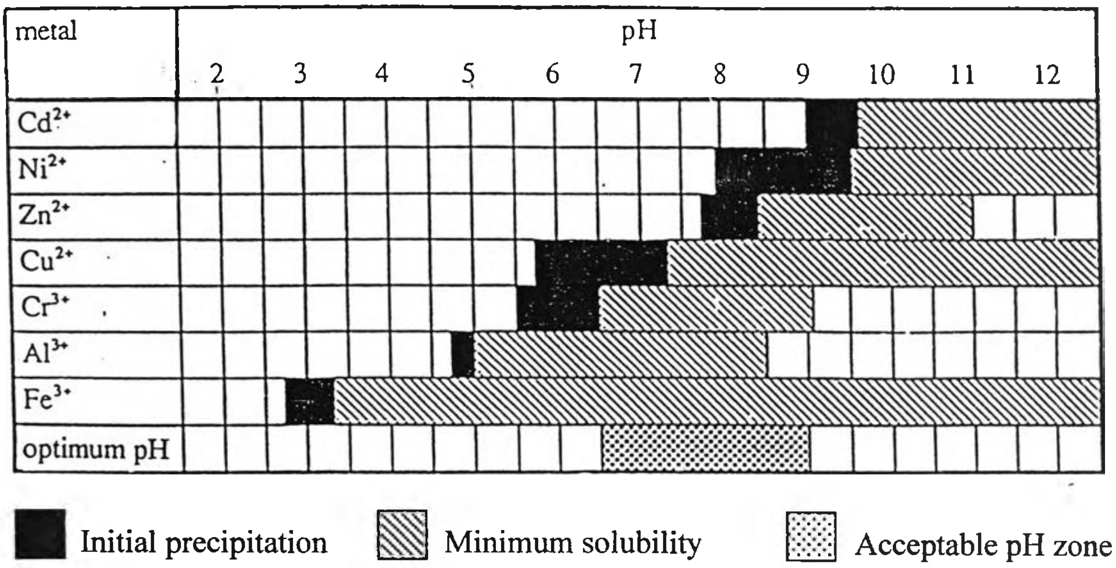


Table II.2: Advantages and disadvantages of chemical precipitations [14].

Chemical precipitation	Advantages	Disadvantages
Hydroxides	-low solubility of metal	-large volume of sludge -equilibrium of solubility changes due to complexing agent
Carbonates	-low solubility of metal -easy to filtrate or separate	-the solubility of carbonates is changeable in another solution. -the solubility of nickel carbonates is fairly high
Sulfers	-weak solubility of metal -possible to precipitate metal in a presence of complexing agent	-toxic -difficult to recover total precipitant.
Ferric oxide	-precipitation with fairly compact	
Polymers	-low metal concentration in residual	-no recovery of polymer

The correlation can be expressed by

$$k_{sp} \leq C_{M^{2+}} \times C_{S^{2-}} \qquad (II.52)$$

Sulfide (S^{2-}) is the dissociation product of H_2S which can be added in soluble form of Na_2S or $NaHS$. The degree of metal precipitation is dependent on pH as shown in Table II.1. Beside metal precipitation with hydroxide and sulfide, Table II.2 shows advantages and disadvantages of metal precipitation with several kinds of chemical substance.

2.2 Sorptive flotation process

Flotation is a separation process capable of removing suspended matters that range from the particle size of pulverized mineral fines down to chemical ions.

It is upon the fact that surface - active material tends to concentrate at the gas/liquid interface. Therefore, when air is bubble through the solution the surface active material absorbs at the surface of the rising bubble, which then separates it from the solution. The substance to be removed can be made surface active through union with or adsorption of a surface active material. Flotation can be classified into three broad categories; dispersed-air flotation, dissolved-air flotation and electrolytic flotation.

This process involves two steps. The first step is the mixing between scavenging toxic metals and sorbent particles which exist at fine or ultrafine particle - size range such as activated carbon or ion exchangers. The last step is a subsequence flotation stage to separate metal-loaded sorbent particles from the treated solution.

This process is more conventionally used as a solid/liquid separation process. The overall steps are demonstrated in Figure II.11. By this process, the reuse of sorbent is possible by recovery from product. However, its drawbacks are long processing time, high pressure loss, has blocking problem and slows settling process for low - density material.

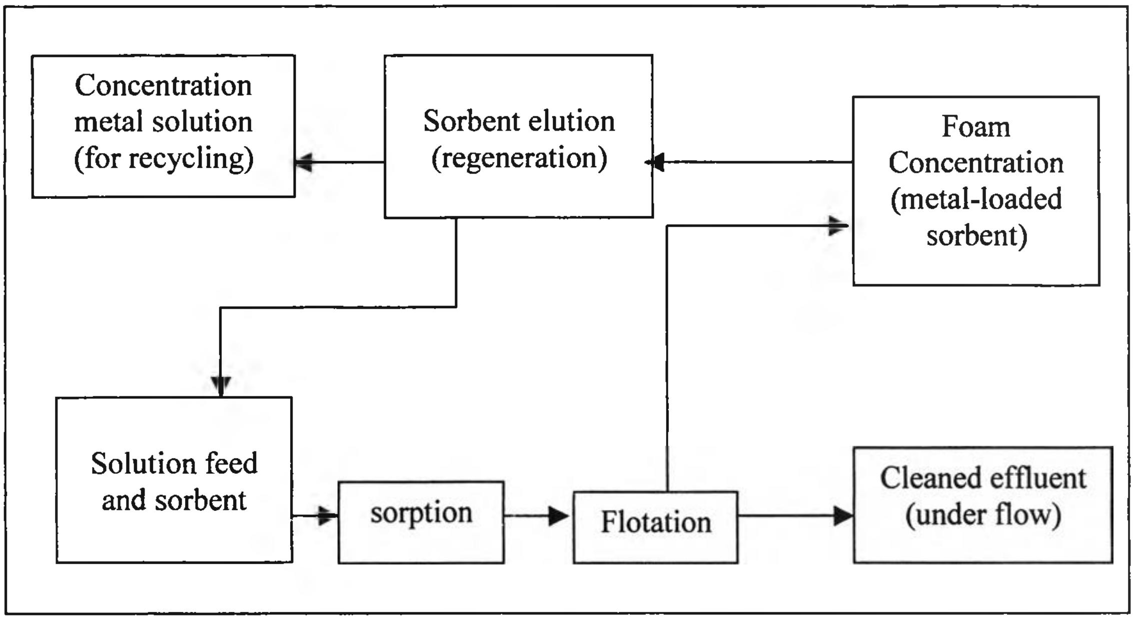


Figure II.11: Overall scheme for sorptive flotation [15].

2.3 Electrodialysis process

Electrodialysis is a membrane-based separation process in which the partial separation of the electrolytic components of an ionic solution is included by an electric current. A schematic diagram for an electrodialysis membrane stack is shown in Figure II.12. The stack consists of a series of alternating cation - exchange and anion - exchange membranes; each separated by a spacer through which the solution flow.

When an electrical potential is applied across the stack, a cation in solution begins to migrate toward a cathode whereas an anion towards to an anode. When a cation encouters a cation - exchange membrane, it will pass freely to the other sides. As cation continues to migrate, it subsequently encounters an anion-exchange membrane. The electrostatic repulsion force between the cation and the fixed cationic charges with in the anion - exchange membrane resist the tendency for the cation to travel further toward the cathode. When the similar phenomenon is considered for the migrating anions, the net effect is that each compartment bounded on the cathode side by an anion - exchange membrane becomes increasingly enriched in electrolyte (concentrate stream). The compartment bounded on the cathode side by a cation - exchange membrane becomes increasingly depleted in electrolyte (dilute stream). The overall current efficiency of this process is the transfer of chemical equivalent from the dilute to the concentrate divided by the net passage of electrical equivalent across the membrane stack over some interval time and they always less than unity due to a number of contributing factors: the permselectivity, current leakage, transport by water dissociation ions and counter ions back diffusion.

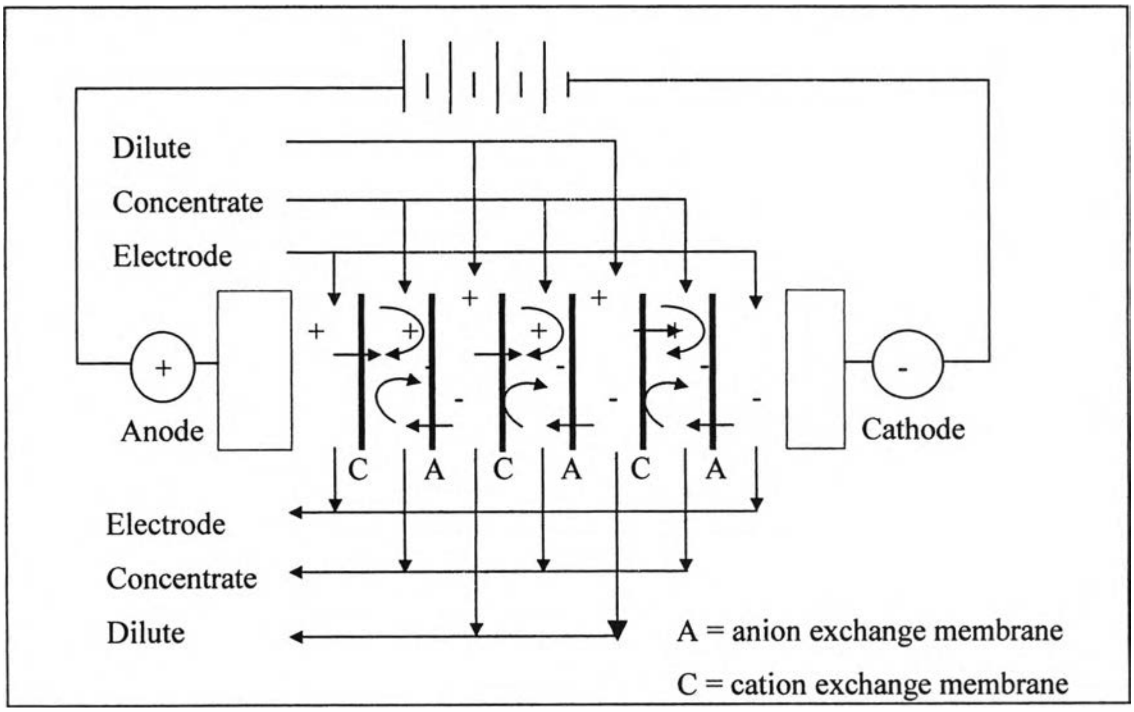


Figure II.12. Schematic diagram of electrodialysis membrane stack [16].

2.4 Biological process

This method is suitable for wastewater containing metal when metal concentration is lower than 0.1 ppm. Micro - organism such as bacteria is included in this process. These organisms, able to biosorp or bioprecipitrate heavy metals, grow up in biofilm on a supporting material. During contacting with heavy metal in the wastewater, the biofilm adsorbs the metal. Afterwards the metal loaded biomass is removed from the supporting material. The resting biomass (basic layer of the biofilm) can be reused by hydrometallurgical treatment in a shaft furnace.

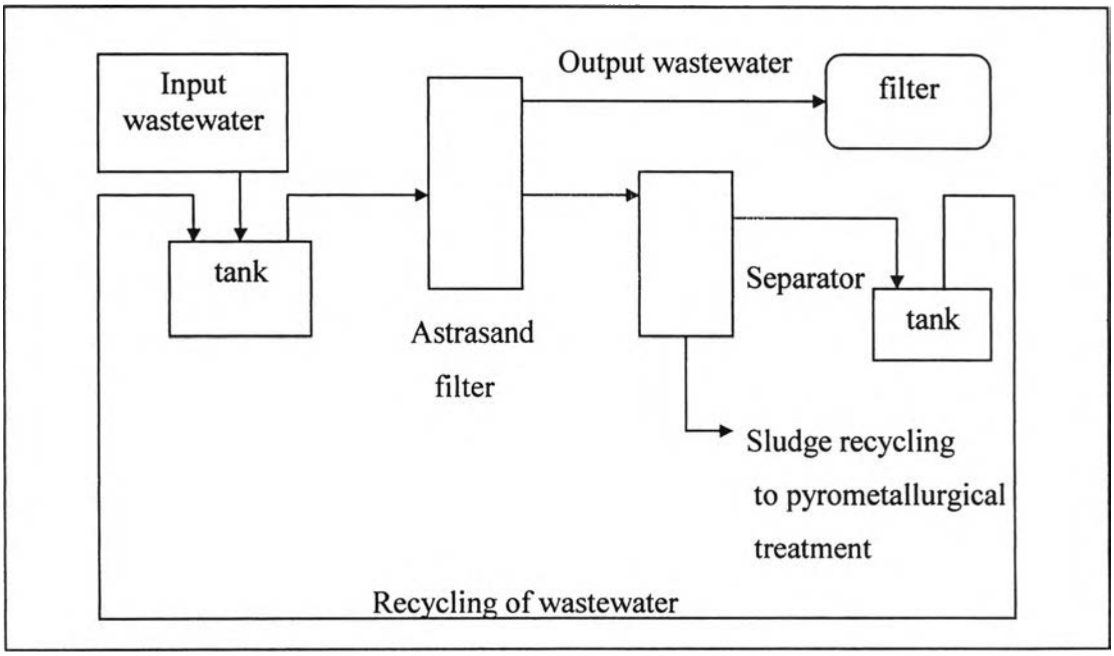


Figure II.13. Flow sheet of the biological method [17].

The complete wastewater treatment system is shown in Figure II.13. Wastewater is pumped through the AstraSand filter and then purified. The wastewater, containing the metal loaded biomass, is drained to a lamella separator or setting tank. The water, coming from the thickener, is reintroduced in sand filter. The sludge coming from the thickener is treated further in a filter press or in a decanting centrifuge. The obtained filter cake, containing the metals, is recycled in a hydrometallurgical treatment facility. The disadvantages of this method are that this process is appropriate to the system containing low metal concentration and furthermore, it needs process to treat sludge. Moreover, the applied micro - organism in this process is specific.

2.5 Reverse osmosis process

Reverse osmosis removes species containing in a solution or a colloidal suspension in two steps. The first one is ultra filtration, in which water moves through pores, or discrete holes in the filtering media, and solute rejection is based primarily on size. The second one is reverse osmosis in which each species is rejected as a result of its chemical characteristics rather than its size.

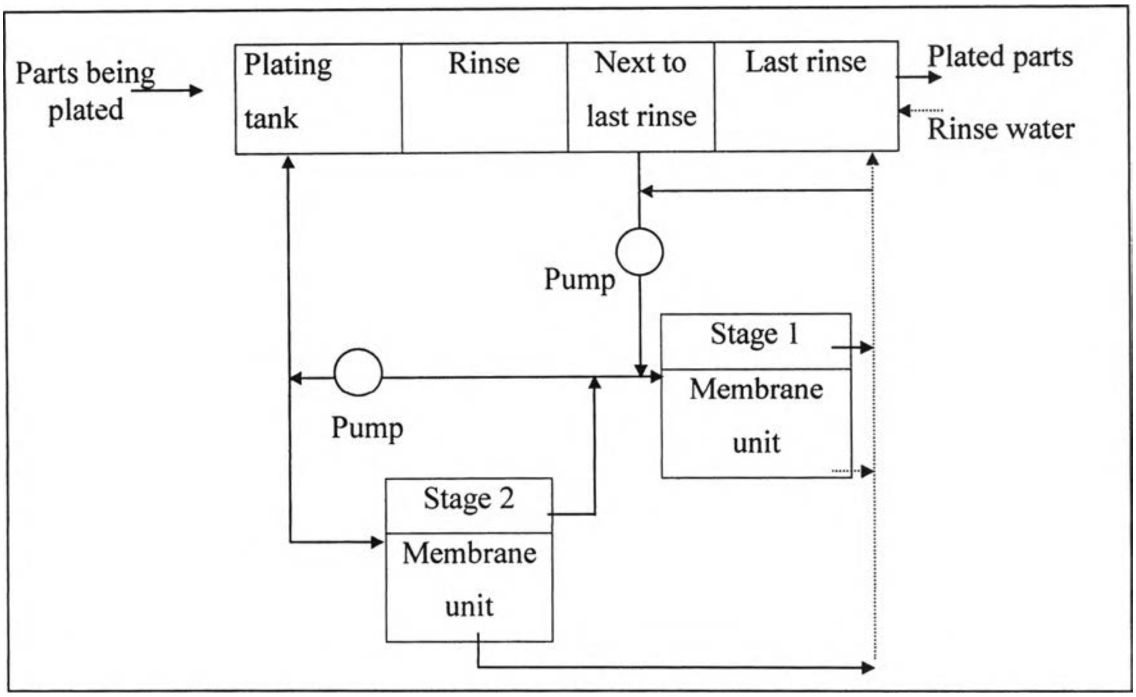


Figure II.14: Possible metal recovery flow sheet of pressure - driven membrane [18].

A pressure difference provides the energy to transport the water molecule. The solute is largely insoluble in the water - swollen membrane or diffuses very slowly. Figure II.14 shows the possible set up of pressure-driven membrane at electroplating unit. By this process, the chemical substances are not included, high operating and high maintenance costs are required. Sludge disposal may be a problem.

2.6 Ion exchange process

Ion exchange materials are high molecular weight polymers with dissociable acid or base groups in the polymer chains. They are anion and cation exchange membranes. Anion exchange membrane contain cationic groups, which are fixed in a high polymer matrix. These fixed cations are in equilibrium with mobile anions in the pore system of the high polymer lattice, in such a way that the electroneutrality is maintained. If this type of membrane is placed in an electrolyte solution, the anions in the solution will migrate into the polymer matrix, displacing the original anions, while the cations will be repelled by the fixed cations in the ion exchanger. The equation during the exchange process can be expressed by

$$Ca^{2+} + Na_2Z \quad \underset{Regeneration}{\overset{Rxn}{\rightleftarrows}} \quad 2Na^{+} + CaZ \qquad \text{(II.53)}$$

where Z is the cation exchanger.

In contrast to anion exchange resin which actually exchanges different ionic species, an ion exchange membrane is strictly only concerned with ion transport, since the mobile ions of the membrane are identical to the type of ion in the electrolyte which is to be transported. Ion exchange membranes separate the ions of an electrolyte according to the polarity and charge number. Reaction of anion exchanger is written by

$$SO_4^{2-} + 2(R_3NHCl) \quad \underset{Regeneration}{\overset{Rxn}{\rightleftarrows}} \quad 2Cl^{-} + (R_3NH)_2SO_4 \qquad \text{(II.54)}$$

where R_3NH is the free anion exchanger.

Treatment of wastewater by ion exchange involves a sequence of operating steps. The wastewater is passed through the resin until the available exchange sites are filled and the contaminant appears in the effluent. This point is defined as the breakthrough. The treatment is stopped at this point and the bed is backwashed to remove dirt and to regrade the resin. The bed is then regenerated. The use of ion exchange processes, however, offers the possibility of metal recovery from very dilute solution and delivering them in the form of solutions several hundred or a thousand fold more concentrated. Table II.3 shows several types of ion exchangers.

Table II.3: Classification of ion exchangers [19].

Functional group	Principal region of application
	Acid Resins
$-SO_3H$ (nuclear)	Very low pH
$-CHCO_3H$	Low pH
$-COOH$	Neutral solutions
$-OH$ (phenolic)	High pH
$-CH_2OH$	Not investigated
$-CH_2SH$	Not investigated
	Basic Resins
$-NH_2$ (aromatic)	Acid solutions
$-NH_2$ (aliphatic)	Acid and neutral solutions
$=NH$ (aromatic and aliphatic)	Not fully investigated
$\equiv N$ (aromatic and aliphatic)	Not fully investigated

2.7 Adsorption process

Adsorption is usually used on the removal of refractory organics and heavy metals presented in many industrial effluents. The concept of this process is a solid surface in contact with a solution which tends to accumulate a surface layer of solute molecules because of the unbalance of surface forces. The most commonly used adsorbent is activated carbon which is made by the roasting of various materials such as bituminous coal and lignite to granular carbon. The regeneration of absorbent is performed by thermal, stream, solvent extraction, acid or base treatment, or chemical oxidation.

3. Recovery of metal by electrochemical technique

The application of electrochemical technique to remove heavy metal contaminated in wastewater stream is generally performed in two ways, electrochemical process without membrane and electrochemical process with membrane. The first technique is performed by trial to reduce metallic ions in solution to metal which will deposit on cathode. The second procedure concerns precipitation of metal with hydroxide ions produced in the system.

3.1 Electrochemical process in classical reactor without membrane

This technique can be applied into two ways, cathodic reduction and electrocoagulation. Cathodic reduction of metals ions provides recovery of pure metals, operation involves an oxidation - reduction reaction in which electrons are supplied by an electrical source reducing the metal ions in the electrolyte to form elemental metals at the cathode surface as shown in Figure II.15.

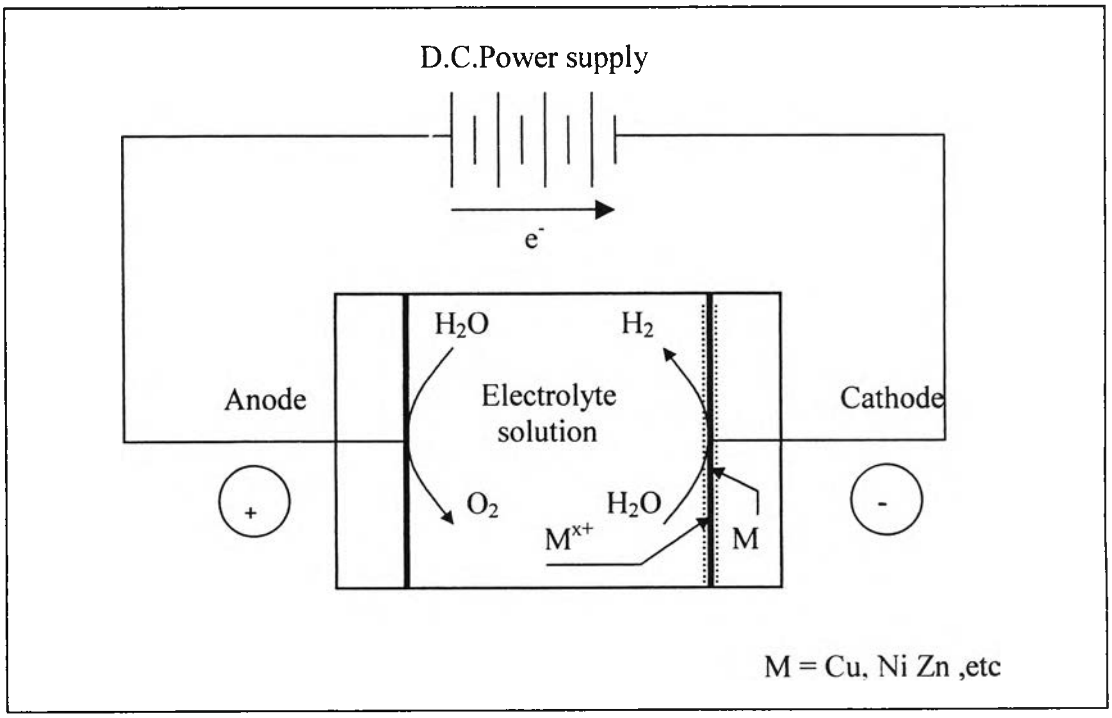


Figure II.15: Electrochemical process with cathodic reduction.

The reaction observed at anode is oxidation of water to oxygen gas and reduction of water to hydrogen gas at cathode beside reduction of metal ions to metal elements. Electrocoagulation using soluble anode, a precipitation process occurs due to ions generation from the consumable electrode such as iron and aluminum or their alloys, as shown in Figure II.16. Oxidation reaction of soluble anode is observed at cathode and these oxidized species will form a complex with metal ions in solution and precipitate in complexing forms.

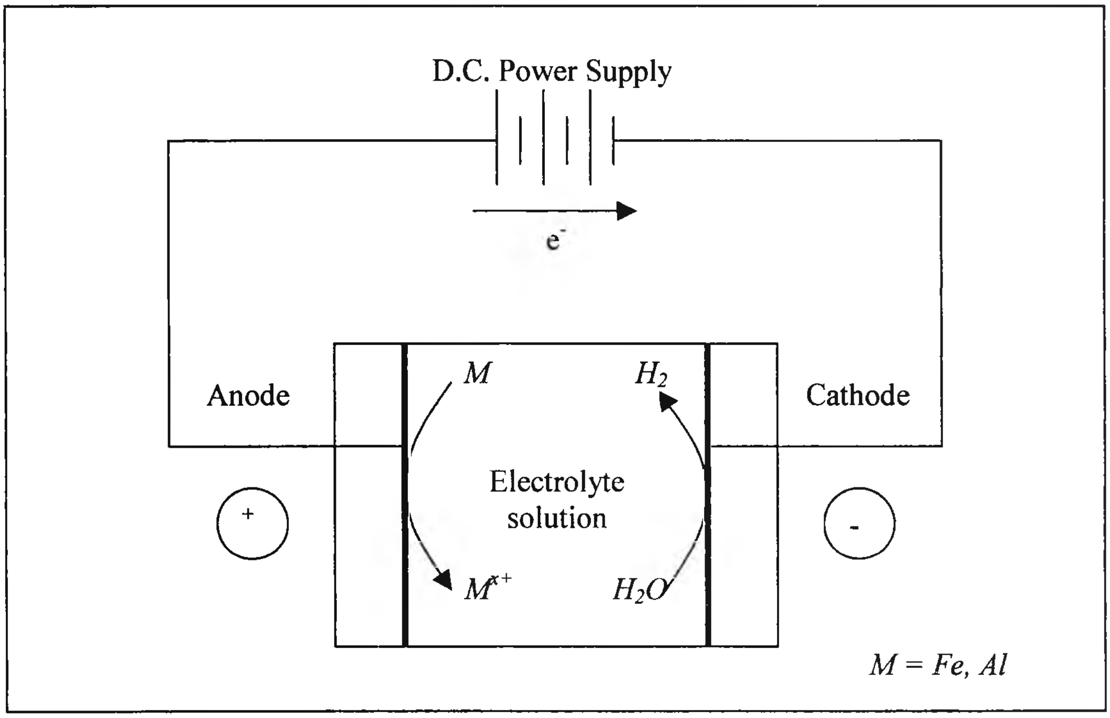


Figure II.16: Electrochemical process with soluble electrode.

3.2 Electrochemical process in classical reactor with membrane

The recovery of some metals such as chromium is not efficient in classical reactor without membrane because it needs a specific condition (H_2SO_4/CrO_3 = 1/100 by weight) [20]. One technique given a good efficiency is called electroprecipitation.

This process corresponds to the use of a membrane reactor. Tuwiner [21] defined the definition of membrane in that membrane is a material or device that act as a physical barrier between two fluids. The membrane reactor always consists of two reactor parts which is separated by membrane, anodic and cathodic compartments. Two types of membrane are widely used in water treatment process; anion - exchange membrane and cation - exchange membrane.

Cation - exchange membranes contain fixed anionic groups that permit intrusion and exchange of cations from an external source, but exclude anions. Anion - exchange membranes contain cationic groups fixed to the resin matrix. The fixed cation are in electroneutrality with mobile anions in the interstices of the resin. When such a membrane is immersed in a solution of an electrolyte, the anions in solution can intrude into the resin matrix and replace the anions initially present, but the cation are prevented from entering the matrix by the repulsion of the cation affixed to the resin. The following are reactions by which this transfer of charge may be accomplished:

Anode	$H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e^-$	acidic solution	(II.55a)
	$2OH^- \longrightarrow 1/2O_2 + 2H_2O + 2e^-$	basic solution	(II.55b)
Cathode	$2H^+ + 2e^- \longrightarrow H_2$	pH < 7	(II.56a)
	$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	pH > 7	(II.56b)
	$M^{+x} + xe^- \longrightarrow M^0$	metal deposition	(II.56c)
	$M^{+x} + xOH^- \longrightarrow M(OH)_x$	precipitation	(II.56d)

The pH in anodic part is decreased by oxidation reaction of water to oxygen gas. On the other hand, in cathodic part, hydrogen is released by reduction reaction of water. The pH in this part is slowly increased until it reaches the precipitation pH of metal contained in the solution. Some parts of metal can be deposited during the pH is lower than precipitation pH. Figures II.17 and II.18 display two types of mechanism in membrane reactor.

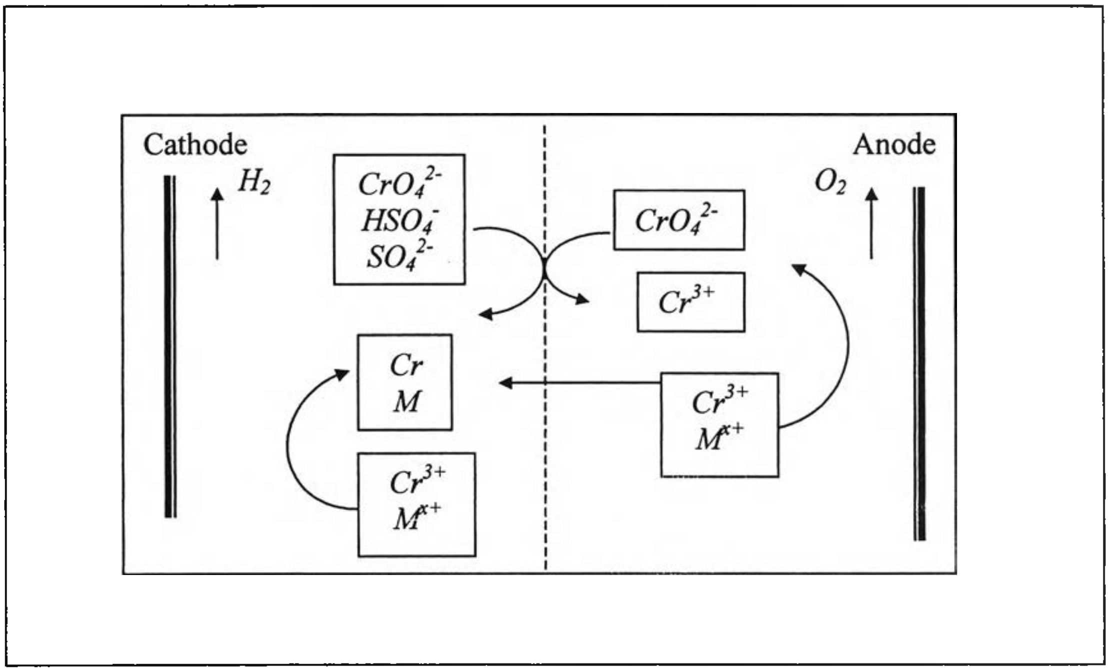


Figure II.17: Evolution of exchange process with cationic membrane.

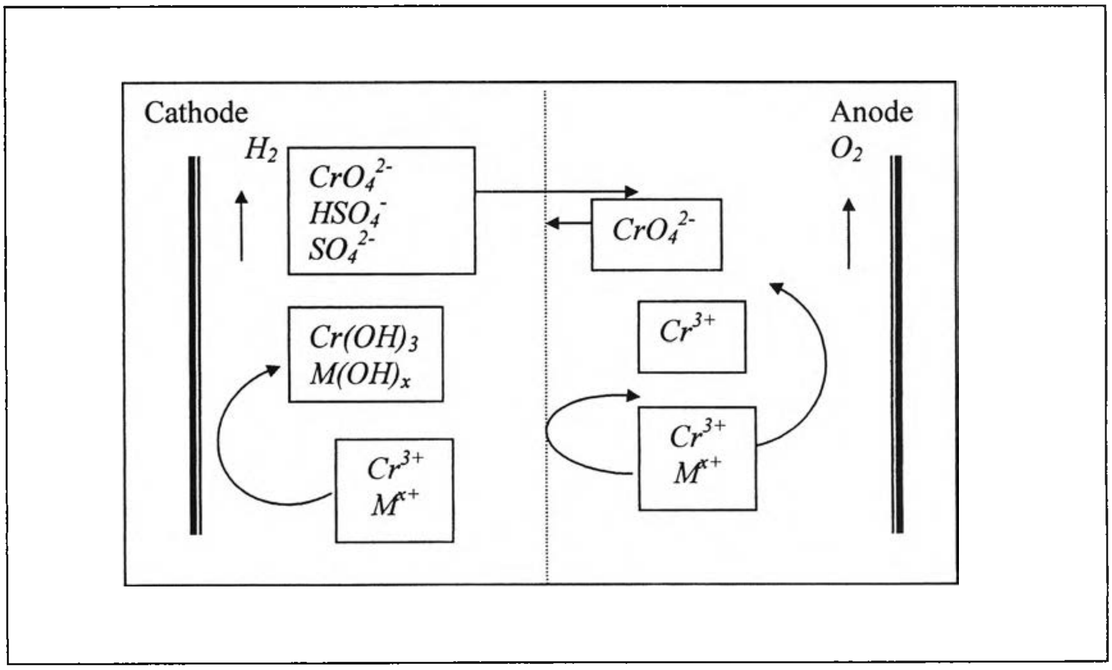


Figure II.18: Evolution of exchange process with anionic membrane.

3.3 Electrochemical process in Pulsed Porous Percolated Electrode (3PE reactor)

The new type of electrochemical reactor called 3PE reactor (Pulsed Porous Percolated Electrode) has been developed in order to achieve more efficiency of metal recovery. This reactor can be considered as a compromise between fixed and fluidized bed reactors. This reactor composes of the following components.

1. *A solid matrix* in contact with a current feeder. It is consisted of granular particles that act as a voluminal cathode with high specific surface area such as graphite.

2. *A counter* electrode or anode having a small geometric surface area. The material used must be resist to oxidizing condition such as platinum or titanium coated with ruthenium oxide.

3. *A circulation pump* is used to circulate the electrolyte in the system through the granular bed. Two advantages of this electrolyte circulation are renewal of the solution around the particles and structural improvement of metal layer deposited.

4. *A pulsating system* creates movement of the granular bed in the reactor forcing the movement of metals- coated particles to the bottom of the bed and avoiding the problem of clogging.

The pulsation of the liquid phase allows a momentary destabilization for the bed with a fluid velocity obtained when the ratio $2\pi af/U_o$ is greater than 1 [22]. The equation of electrolyte velocity can be expressed in the following sinusoidal form [23, 24]

$$U(t) = U_o - 2\Pi af \sin(2\Pi aft) \qquad \text{(II.57)}$$

When a difference in voltage is applied across the electrode terminals, a potential gradient is created within the electrolysis cell. The solution to be treated percolates throughout the cell with a pulsed flow. The ions contained in the solution are reduced to metallic state and deposited on the particles which faces to the anode. The metal concentration in the solution is consequently decreased.

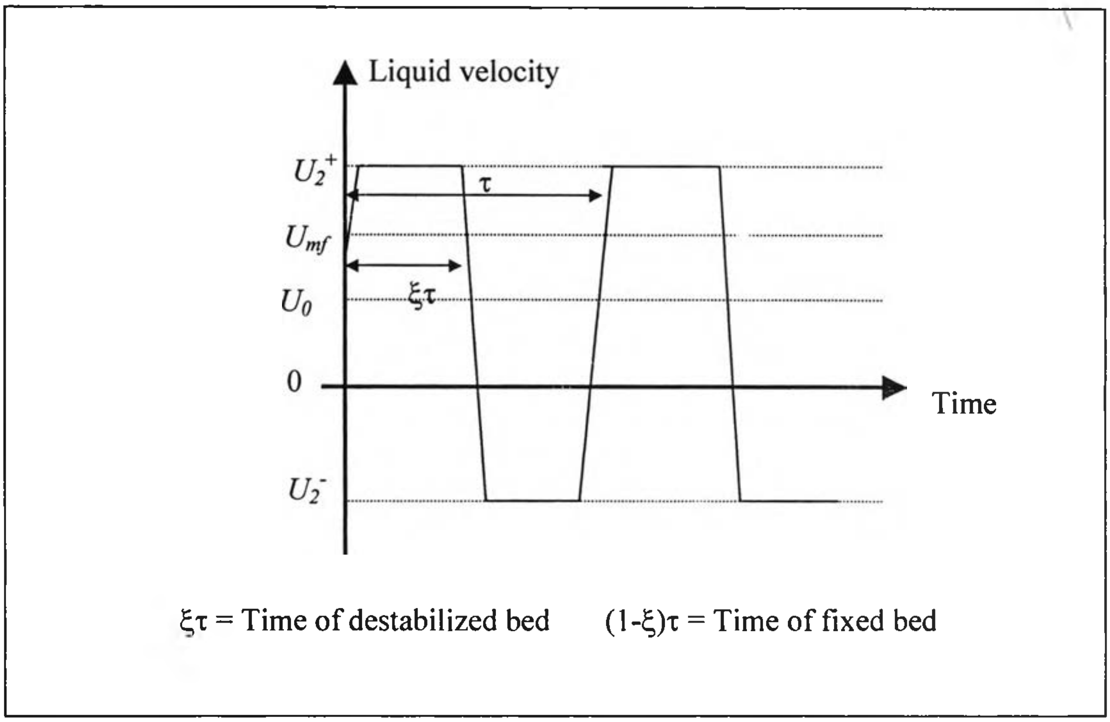


Figure II.19: The periodic destabilization of the granular cathode bed [25].

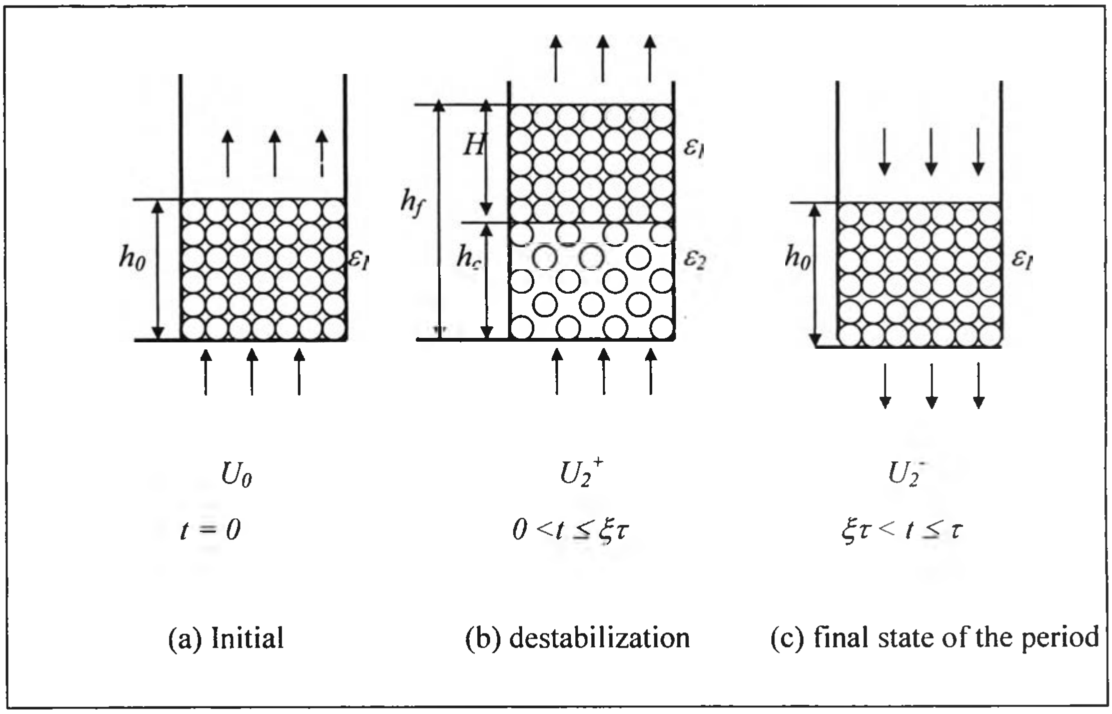


Figure II.20: Behaviour of particles in 3PE reactor [26].

The behaviour of particle in bed can be expressed as Figures II.19 and II.20. At initial, it is no pulse [$(1-\xi)\tau$ period], the behaviour of particles is similar to fixed bed as shown in Figure II.20(a). During this period, the granular bed is contacting with the current feeder so the reduction of metal ions to metallic state is observed and they will be deposited on the cathode surface. During the destabilization phase ($\xi\tau$ period), the behaviour of granular particles resembles to fluidized bed (Figure II.20(b)). The particle surface is covered by metal and consequently becomes heavier so the particles are recycled to the bottom of the reactor and replaced by lighter ones by pulsating system. The addition of pulsating motion to the permanent liquid velocity (U_o) permits the destabilization of the granular electrode.

From the microscopic point, two different regions can be observed during the destabilization of fluid by pulsating system, a fixed bed in the upper zone of height H and a destabilized region in the lower zone of height h_c. The liquid velocity for the upward motion generated by a pneumatic system may be expressed by

$$U_2^+ = U_0 + \frac{2a}{\xi\tau} \tag{II.58}$$

$$U_2^- = U_0 - \frac{2a}{(1-\xi)\tau} \tag{II.59}$$

If the particle motion starts with the beginning of the bed fluidization characterized by U_{mf}, the upward particle velocity can be written by

$$U_p^+ = \frac{2a}{\xi\tau} - (U_{mf} - U_0) \tag{II.60}$$

$$U_p^- = \frac{2a}{(1-\xi)\tau} + (U_{mf} - U_0) \tag{II.61}$$

The voidage after fluidized (ε_2) is estimated by

$$\varepsilon_2 = 1.58 \, \mathrm{Re}^{0.33} Ar^{-0.21} M^{-0.22} \qquad \varepsilon_2 < 0.85 \tag{II.62}$$

$$\varepsilon_2 = 1.20\ \mathrm{Re}^{0.17} Ar^{-0.11} M^{-0.21} \qquad \varepsilon_2 > 0.85 \tag{II.63}$$

$$Ar = \frac{d_p{}^3 \rho^2 g}{\mu^2} \tag{II.64}$$

$$M = \frac{(\rho_p - \rho)}{\rho} \tag{1.65}$$

The knowledge of the height (H) allows to determine the volume of the electrochemical active zone during the destabilization. For the lower region the destabilization allows a segregation of particle by their densities. The critical height bed (h_c) remains to be calculated. For this purpose, the volume of particles (V) per cross section unit of the bed (S) is written as

$$\frac{V}{S} = h_0(1 - \varepsilon_1) = h_C(1 - \varepsilon_2) + (h_f - h_C)(1 - \varepsilon_1) \tag{II.66}$$

$$h_C = (h_f - h_0)\,\frac{1 - \varepsilon_1}{\varepsilon_2 - \varepsilon_1} \tag{II.67}$$

The final height of bed (h_f) may be calculated with the velocity

$$h_f = h_0 + U_p{}^{+} \xi \tau \tag{II.68}$$

and

$$H = h_f - h_C \tag{II.69}$$

The height of the two regions of different voidage can be predicted when the liquid velocity is in an upward direction.

3.3.1 Types of 3PE reactor

Depending on the respective directions of the electric field and of the liquid velocity, two types of 3PE cells have been developed; 3PE in axial field configuration and 3PE in radial field configuration.

3.3.1.1 3PE in axial field configuration

The axial field configuration reactor is shown in Figure II.21(a). The directions of electric field and liquid velocity are in parallel direction. The reaction occurred in this reactor is mainly the electrodeposition reaction.

Anode $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ (II.70)

Cathode $M^{x+} + xe^- \longrightarrow M$ (II.71a)

$2H^+ + 2e^- \longrightarrow H_2$ (II.71b)

$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$ (II.71c)

M corresponds to metal (Cu, Zn...)

3.3.1.2 3PE in radial field configuration

The electrical field is perpendicular to the liquid flow as shown in Figure II.21(b). A porous granular cathode supplied with a current field connection located in the center of the lateral anodes and separated by diaphragm permitting cation transfer.

In this case, the electrocoagulation process is obtained based on the electrolytic water decomposition in a separated compartment reactor. Water reduction involves a cathodic pH increase, which enables the metal precipitation at a suitable pH and the decrease of the metal concentration in the cathodic compartment. The reaction of chromium, for example, observed at both anodic and cathodic part is presented by the following reaction [27].

Anodic compartment

$$Cr^{3+} + 4H_2O \longrightarrow CrO_4^{2-} + 8H^+ + 3e^- \tag{II.72a}$$

$$2H_2O \longrightarrow 4e^- + 4H^+ + O_2 \tag{II.72b}$$

Cathodic compartment

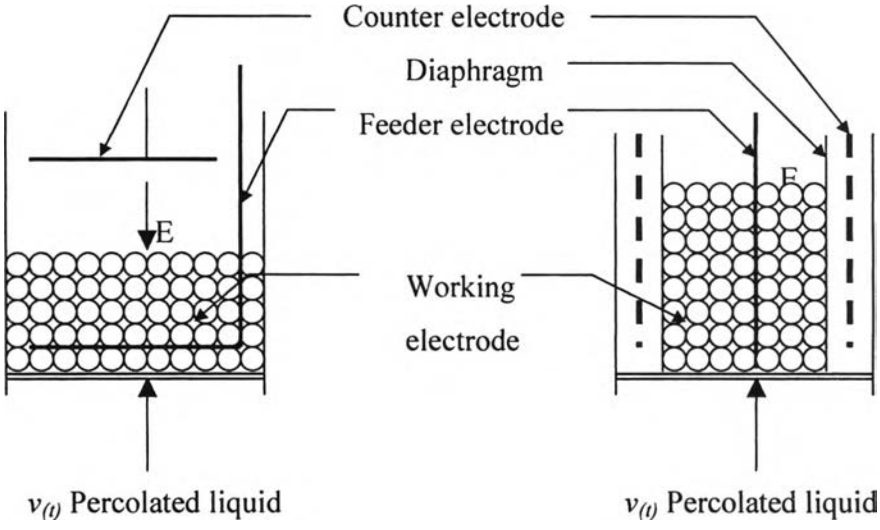
$$CrO_4^{2-} + 4H_2O + 3e^- \longrightarrow Cr^{3+} + 8OH^- \tag{II.73a}$$

$$Cr_2O_7^{2-} + 7H_2O + 6e^- \longrightarrow 2Cr^{3+} + 14OH^- \tag{II.73b}$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \tag{II.73c}$$

followed by hydroxide precipitations

$$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3 \tag{II.74}$$



(a) Axial field configuration.

(b) Radial field configuration.

Figure II.21: Schematic diagram of 3PE reactor.

The main advantages of this type of electrode are [28]

- large metal - solution interface area per unit of electrode volume resulting from its granular form,
- absence of clogging of the dispersed phase (as opposed to fixed granular beds),
- good conductivity of the granular electrode (as opposed to fluidized beds),
- possible high variation of the metal concentration without clogging problems (as opposed to fixed granular beds),
- major increase of the mass transfer between the particles and the solution resulting from the forced pulsed flow of the electrolyte,
- reuse of the deposited metal by anodic dissolution or matrix fusion.

4 .Chemical engineering approach for electrochemical recovery of metals

4.1 Mass balance on electrochemical reactor

Electrochemical reactor is generally assigned to many reactor types as conventional chemical reactor. The classification of electrochemical reactors is relevant not only to methodical considerations, but in particular to the formulation of mathematical models of reactors.

4.1.1 Equations of mass conservation

4.1.1.1 Balance of component *i*

Consider the element of volume without electrode as shown in following equation, the mass conservation of component *i* can be expressed by

$$\boxed{\begin{array}{c}\text{Flux of}\\ \text{component } i\\ \text{input}\end{array}} + \boxed{\begin{array}{c}\text{rate of production}\\ \text{of component } i \text{ in}\\ \text{homogeneous}\\ \text{phase}\end{array}} = \boxed{\begin{array}{c}\text{Flux of}\\ \text{component } i\\ \text{output}\end{array}} + \boxed{\begin{array}{c}\text{Rate of}\\ \text{accumulation of}\\ \text{component } i\end{array}}$$

The surface (A) is limited by volume. The total balance of component i is written by

$$\underbrace{\iiint_V R_i dV}_{\text{Mass product}} = \underbrace{\iint_A \bar{N}_i d\bar{A}}_{\text{Total flux out}} + \underbrace{\iiint_V \frac{\partial C dV}{\partial t}}_{\text{Accumulation of mass}} \qquad \text{(II.75)}$$

but

$$\iint_A \bar{N}_i d\bar{A} = \iiint_V div\ \bar{N}_i dV \qquad \text{(II.76)}$$

substitute into above equation then, the conservation equation is obtained and expressed by

$$R_i = div\ \bar{N}_i + \frac{\partial C_i}{\partial t} \qquad \text{(II.77)}$$

where R_i is the rate of production of component i. The density of local flux is expressed by

$$\bar{N}_i = \bar{U}_i C_i - D_i gradC_i - n_i F \mu_i C_i grad\bar{\phi}_S \qquad \text{(II.78)}$$

Then

$$R_i = div(\bar{U}_i C_i) - div(D_i gradC_i) - n_i F div(\mu_i C_i grad\bar{\phi}_S) + \frac{dC_i}{dt} \qquad \text{(II.79)}$$

If D_i and μ_i are independent from C_i then

$$R_i = \bar{U} gradC_i + C_i div\bar{U} - D_i \Delta C_i - n_i F \mu_i (C_i \Delta\bar{\phi}_S + gradC_i grad\bar{\phi}_S) + \frac{dC_i}{dt} \qquad \text{(II.80)}$$

4.1.1.2 Total balance

The total balance is the summation of all species presented in solution.

$$\sum_i R_i \quad = \quad div\ \bar{N}_T + \frac{\partial C}{\partial t} \tag{II.81}$$

and $\bar{N}_T \quad = \quad \bar{U}C_T$, then

$$\sum_i R_i \quad = \quad div\ (\bar{U}C_T) + \frac{\partial C}{\partial t} \tag{II.82}$$

If the total concentration (C_T) do not depend on time and position then

$$div\bar{U} \quad = \quad \frac{\sum R_i}{C_T} \quad = \quad 0 \tag{II.83}$$

4.1.1.3 Balance of electrical charge

From conservation equation, multiplying both side by n_iF and summation all of species, we obtained

$$\sum_i n_i F R_i \quad = \quad div\left(\sum_i n_i F \bar{N}_i\right) - \frac{\partial\left(\sum_i n_i F C_i\right)}{\partial t} \tag{II.84}$$

and
$$\sum_i n_i F R_i \quad = \quad div\ \bar{i} \tag{II.85}$$

The second right - hand side term is not valid for electroneutrality equation. The balance of electrical charge is expressed by

$$div\ \bar{i} \quad = \quad 0 \tag{II.86}$$

4.1.2 Material balance around ideal electrochemical reactor

Consider the general electrochemical mechanism

$$a_1A_1 + a_2A_2 + \ldots\ldots + a_e e^- \longrightarrow a_1'P1 + a_2'P_2 + \ldots\ldots \qquad \text{(II.87)}$$

Given γ is the rate of heterogeneous reaction then

$$\gamma = -\frac{1}{a_1}R_{A1} = -\frac{1}{a_2}R_{A2} = \ldots\ldots = \frac{1}{a_1'}R_{p1} = \frac{1}{a_2'}R_{p2} \qquad \text{(II.88)}$$

where R_{Ai} is the rate of the production, A_e is active surface area of electrode and v is the stoichiometrice coefficient of component i. If j is the current density then

$$\gamma = \frac{j\phi}{nF} \qquad \text{(II.89)}$$

If the current efficiency equals to 100% then

$$\gamma = \frac{j}{nF} \qquad \text{(II.90)}$$

4.1.3 Material balance around batch reactor

The most straightforward type of batch reactor consists of a reactor having a constant internal volume of electrolyte which is well - mixed as shown in Figure II.22.

Solution movement serves to improve the rate of mass transport as well as ensuring a uniform electrolyte composition. Methods of solution movement consist of air agitation of electrode gas, pumped flow, impellers, rotation of electrode or movement of particles [30]. In this reactor type, the concentration and temperature gradients are not existed in the reaction. It has no both input and output flux, it has only accumulation appearence or disappearence of species by reaction.

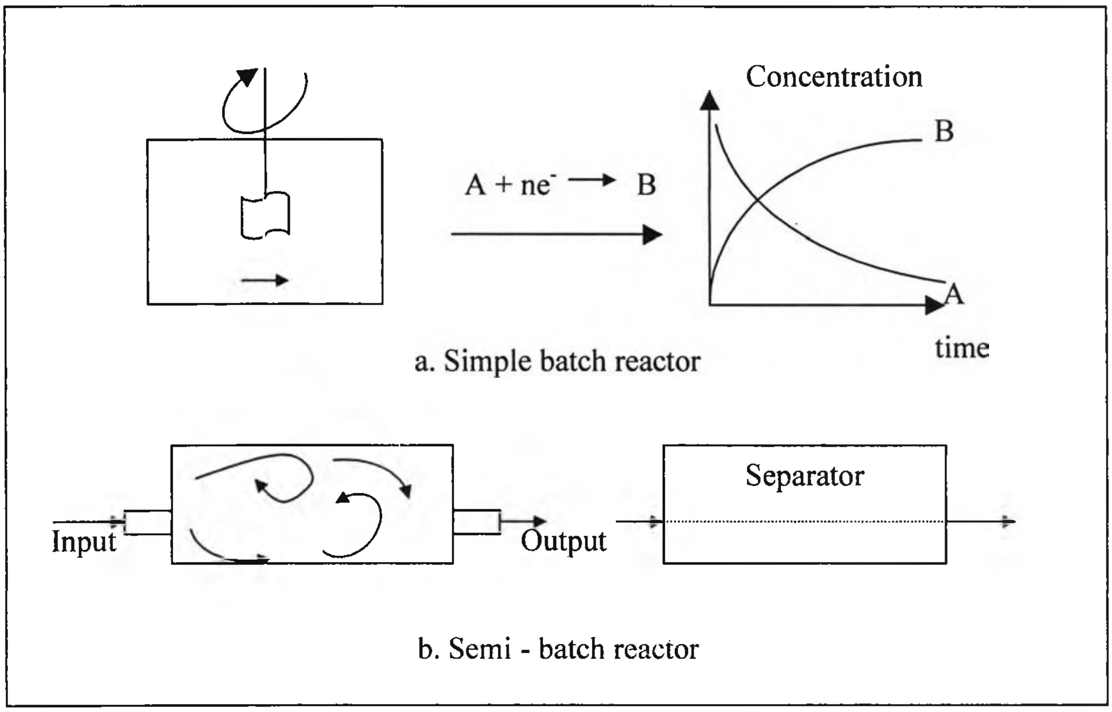


Figure II.22: Representation of batch reactor [29].

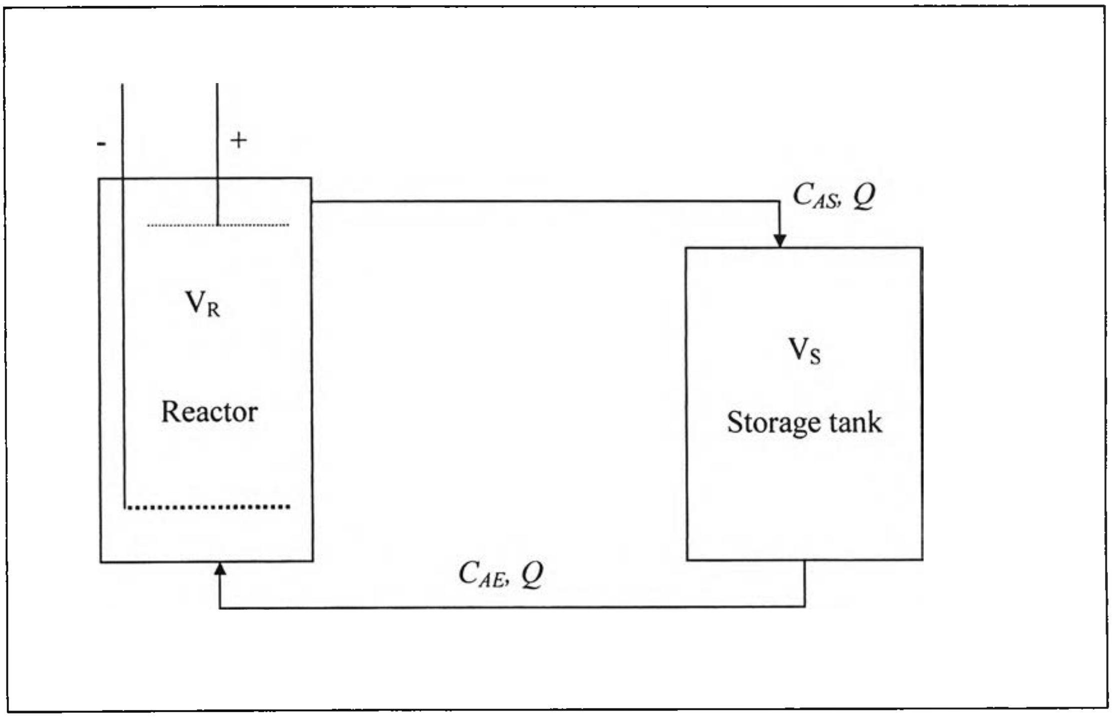


Figure II.23: Global disposal of apparatus.

The installation of batch reactor connected with storage tank is shown in Figure II.23. The inlet solution to the reactor is supported homogenously with concentration C_{AE} and the outlet concentration C_{AS} with constant flow rate Q. The concentration in storage tank equals to C_{AE}. The material balance of species A on reactor and on storage tank is generally expressed by the law of conservation of mass.

The assumption in this material balance is that batch reactor acts as a CSTR, so we have

$$QC_{AE} = QC_{AS} + \gamma A_e \qquad \text{(II.91)}$$

The flow rate is constant due to a continuous supply. So

$$Q(C_{AE} - C_{AS}) = \gamma A_e \qquad \text{(II.92)}$$

In our case,

$$\gamma = \frac{j}{nF}\phi \qquad \text{(II.93)}$$

Then

$$Q(C_{AE} - C_{AS}) = \frac{j}{nF}\phi A_e \qquad \text{(II.94)}$$

If the current efficiency equals to 1 and

$$j = nFk_L C_{AS} \qquad \text{(II.95)}$$

Then

$$Q(C_{AE} - C_{AS}) = \frac{j}{nF}A_e = k_L A_e C_{AS} \qquad \text{(II.96)}$$

k_L is mass transfer coefficient.

For the storage tank, if it is considered as continuous stirrer tank reactor. The volume of solution in storage tank is V_S. The concentration evolution is a function of process time. The material balance in this storage tank can be expressed by

$$Q(C_{AS} - C_{AE}) = V_S \frac{dC_{AS}}{dt} \tag{II.97}$$

or write in general form by

$$- V_S \frac{dC_S}{dt} = Q(C_E - C_S) = k_L A_e C_S \tag{II.98}$$

If we connect this mass balance to those on the reactor, we obtain

$$- V_S \frac{dC_S}{dt} = k_L A_e C_S \tag{II.99}$$

Rearrangement and integration from C_o to C_t and 0 to t, we obtain

$$\ln\frac{C_t}{C_o} = -\left(\frac{k_L A_e}{V_S}\right) t \tag{II.100}$$

The mass transfer coefficient can be determined by the slope of equation (II.100).

4.1.4 Material balance around continuous stirrer tank reactor, CSTR

This reactor type has the perfect mixing, there is absolutely no spatial dependence of composition and concentration of any species is uniformly the same everywhere in the reactor as presented in Figure II.24. If the CSTR has constant electrolyte flow rate Q and effective volume V_R. The active ion concentration in the inlet electrolyte is C_1 and in the exit electrolyte is C_2.

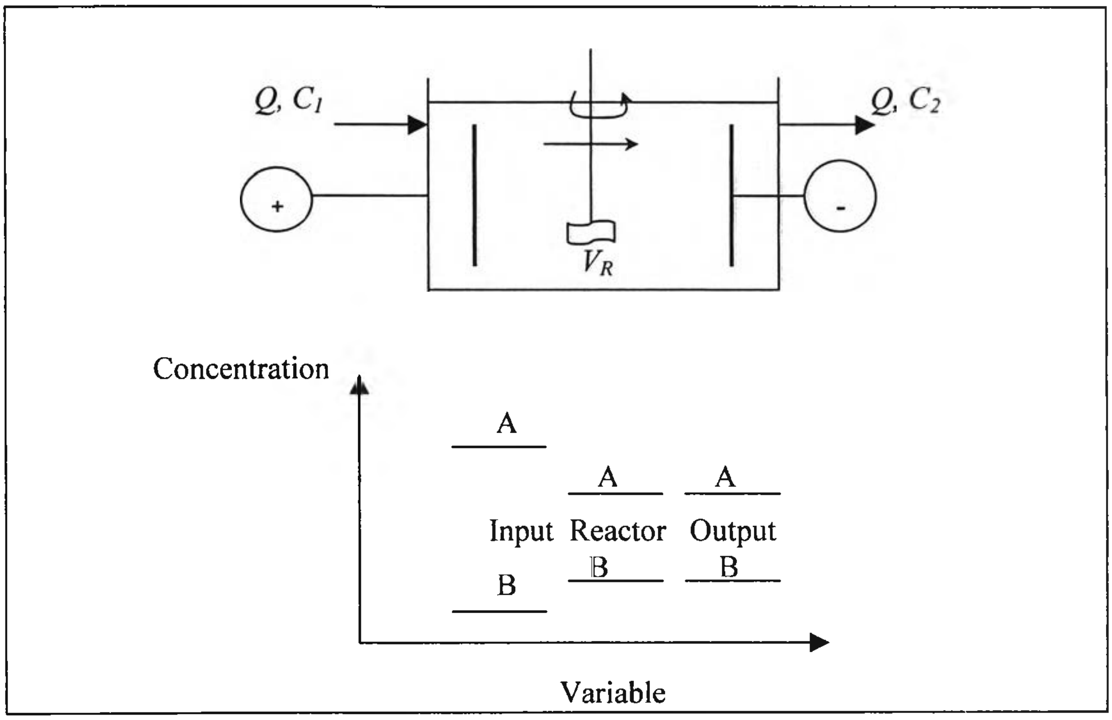


Figure II.24: Continuous stirrer tank reactor [29].

The overall mass balance for CSTR is written by

$$QC_1 = QC_2 + \frac{i}{nF} \tag{II.101}$$

In terms of the exit concentration and concentration at the electrode, the current density (j) can be expressed by

$$j = nFk_L(C_2 - C_1) \tag{II.102}$$

If the reaction takes place at limitting current condition, then

$$j_l = nFk_LC_2 \tag{II.103}$$

The oulet concentration can be written by

$$C_2 = \frac{QC_1}{Q + k_L A_e} = \frac{C_1}{1 + \frac{k_L A_e}{Q}} \qquad \text{(II.104)}$$

or express in terms of the time dependent concentration of metal ions in the system

$$C_t = C_o \exp\left\{ -\frac{tQ}{V_R} \left[1 - \frac{1}{1 + \frac{k_L A_e}{Q}} \right] \right\} \qquad \text{(II.105)}$$

In terms of conversion *x*,

$$x = \frac{C_1 - C_2}{C_1} = \frac{k_L A_e / Q}{1 + \frac{k_L A_e}{Q}} \qquad \text{(II.106)}$$

Both C_2 and x are independent of the current and its density.

4.1.5. Material balance around plug flow reactor, PFR

Consider plug flow reactor included two electrode, anode and cathode, separated by a certain distance as shown in Figure II.25. An instantaneous mass balance over the reactor gives following equations [30].

$$V_T \frac{dC_1}{dt} = Q\left(C_2 - C_1\right) \qquad \text{(II.107)}$$

while, over the PFR,

$$C_2 = C_1 \exp\left(-\frac{k_L A_e}{Q} \right) \qquad \text{(II.108)}$$

Manipulation of equations (II.107) and (II.108) gives an expression for the concentration of metal ions in the system

$$C_t = C_0 \exp\left(-\frac{t}{\tau_T}x\right) = C_0 \exp\left(-\frac{t}{\tau_T}\left[1 - \exp\left(-\frac{k_L A_e}{Q}\right)\right]\right) \qquad \text{(II.109)}$$

The conversion (x) is equal to ($1 - \frac{C_{in}}{C_{out}}$); C_0 is the initial metal concentration and C_t is metal concentration at time t. The residence time (τ_T) in PFR reactor is

$$\tau_T = \frac{V_T}{Q} \qquad \text{(II.110)}$$

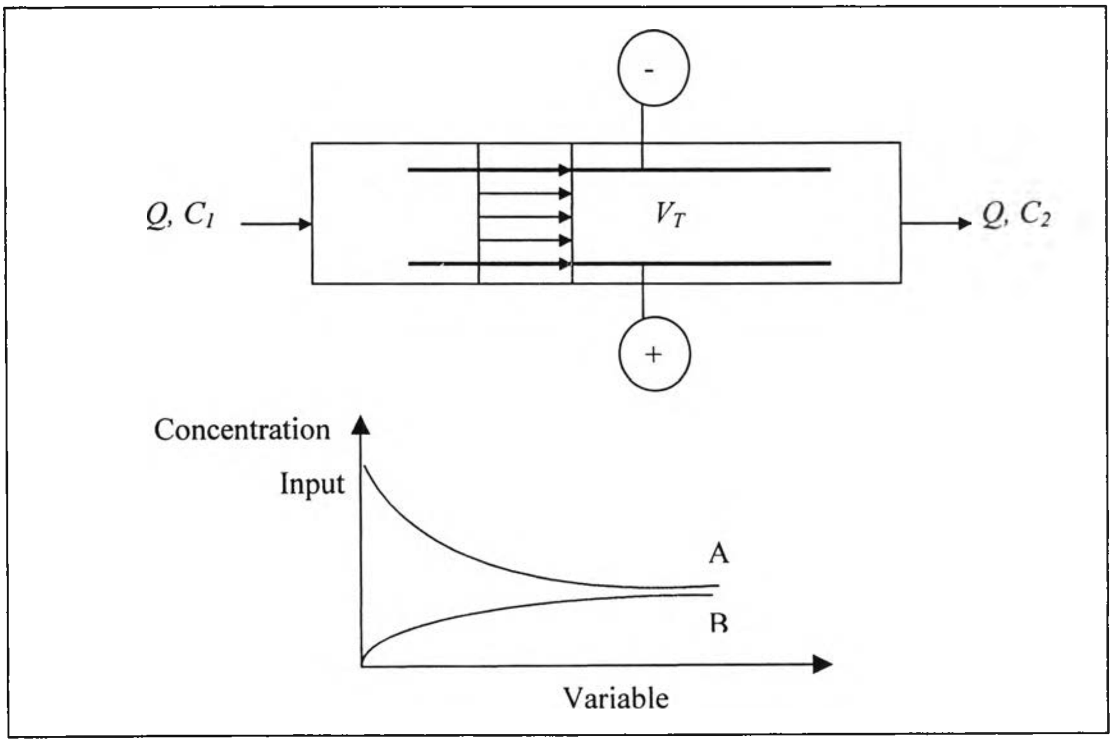


Figure II.25: Plug flow reactor [29].

4.2 Dimensionless numbers

In most systems, the mass transfer coefficient characterizes the rate of transport due to convection and diffusion. Rigorous solutions to the pertinent transport equation are rarely available except in special cases, more than hundreds of correlations are available in literature. They are often given in terms of dimensionless number [31] and it always depends upon the hydrodynamics of the system such as flow rate or liquid property. It can be written in terms of Sherwood number as a function of Reynolds number and Schmidt number.

$$Sh = f\ (\mathrm{Re}, Sc) \qquad \text{(II.111)}$$

or

$$Sh = a\ \mathrm{Re}^{b}\ Sc^{c} \qquad \text{(II.112)}$$

In another form, it can be expressed in terms of length and hydraulic diameter.

$$Sh = a\ \mathrm{Re}^{b}\ Sc^{c} \left(\frac{d_h}{L}\right)^{d} \qquad \text{(II.113)}$$

Several dimensionless groups can be defined by

-Sherwood number (Sh) is the ratio of effective mass transport to mass transport by molecular diffusion.

$$Sh = \frac{k_L d_h}{D_a} \qquad \text{(II.114)}$$

-Reynolds number (Re) is the ratio of inertia force to friction force.

$$\mathrm{Re} = \frac{\rho U_0 d_h}{\mu} \qquad \text{(II.115)}$$

-Schmidt number (*Sc*) is the ratio of momentum transport to mass transport by molecular diffusion.

$$Sc = \frac{\mu}{\rho D_a} \tag{II.116}$$

In reactor with parallel palte electrode, the definition of hydraulic diameter is

$$d_h = \frac{2lh}{(h + l)} \tag{II.117}$$

The notation is explained in Figure II.26.

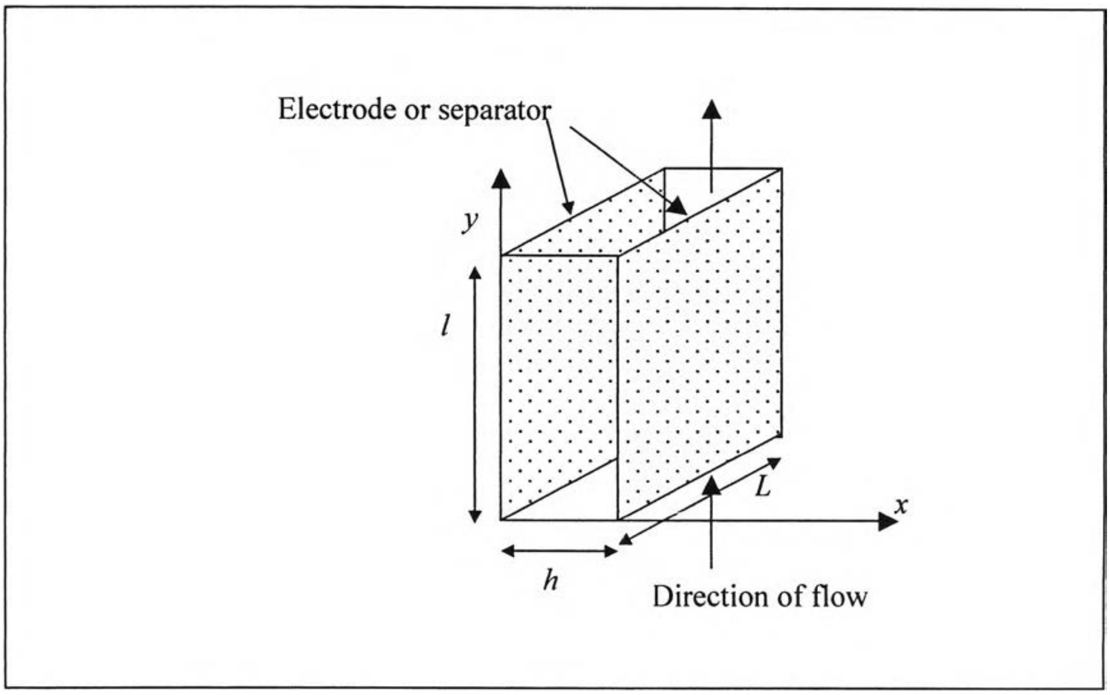


Figure II.26: Definition for calculation of hydraulic diameter in parallel plate electrodes.

Besides the previous dimensionless number, the dimensionless group can be expressed in terms of Chilton - Colburn factor [29].

$$j_d = \frac{k_L}{v} Sc^{2/3} = \frac{Sh}{\mathrm{Re} Sc^{1/3}} \qquad \text{(II.118)}$$

Then the general equation expressed the relation between j_d, *Re and Sc* numbers can be demonstrated by

$$j_d = a\ \mathrm{Re}^{-b}\ Sc^{c} \qquad \text{(II.119)}$$

5. State of pollutant activities in Thailand

Currently, Thailand is a developing country so many of industries are presented such as plating industry, finishing industry, electronic industry, textile industry, and so on. Wastes from processes are generated by those industries especially for the contamination of metal in processed water. The amount of metal contained in water is generally higher than the limit permited by law so treatment of these contaminants is required to keep metal concentrations lower than acceptable values. Table II.4 shows the acceptable value of effluent from electroplating industry.

Table II.4: Acceptable value of electroplating effluent.

Characteristics	Acceptable value
pH	5-9
Cyanide	< 0.2 mg/l
Zinc	< 5 mg/l
Copper	< 1 mg/l
Nickel	< 0.2 mg/l
Chromuim	< 0.5 mg/l

5.1 Electroplating process

The major process contibuting to heavy metals contaminated in water is electroplating process. This process is the way to deposit some needed metals on the surface of another metal. The steps of plating process are surface preparation, polishing, degreasing and so on as shown in Figure II.27. The figure shows that both acid, base and chemical substances are included in every steps except drying process. By this reason, this industry releases large amount of wastewater.

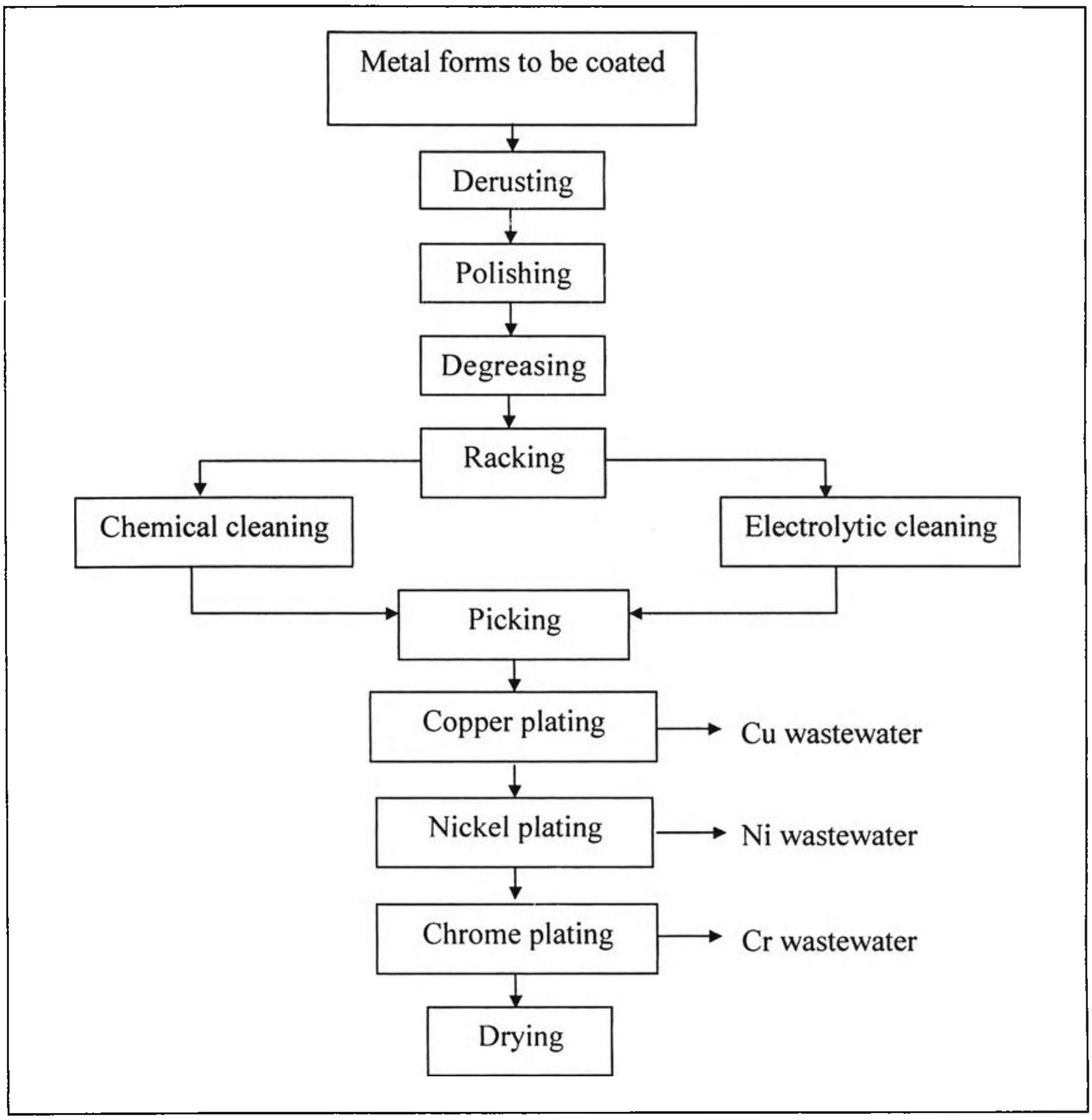


Figure II.27: Typical electroplating processes [32].

The electroplating units generate effluents containing various contaminants such as acid cyanide, heavy metals, alkaline cleaning agents, degreasing solvents, and oils. The characteristics of generated wastewater generally depend upon the characteristics and limitation of raw materials.

Figure II.28 shows a sequence of electroplating steps. The first step is an electrolytic deposition of metal on the items in an active bath. General metal and additive contents in the active bath are kept constant through addition of new products. The next step is the rinsing with water in stand - still bath and the last step is cleaning of electroplated item with fresh water. When the number of process increases, the concentration in stand - still bath will be gradually increased causing the concentration in fresh water bath to increase. In order to keep the concentration in fresh water bath at the acceptable value, the wastewater treatment process is set at stand - still bath. The metal from the treatment process can be reused and the treated water is ready to discharge.

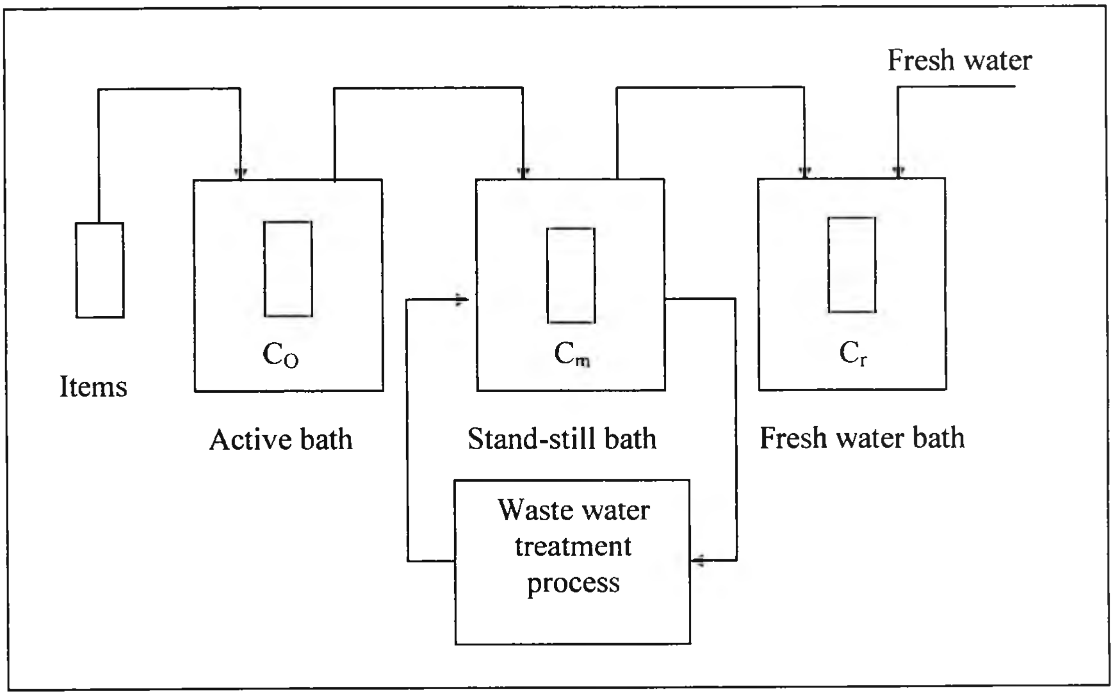


Figure II.28: Operation mode of an electroplating unit [33].

Table II.5 demonstrates the properties of water from electroplating industry in Thailand. The solutions are generally in form of suspended solution with pH between 1 to 12. The conductivity is between 1 to 12 mS/cm. The observed heavy metals contaminated in wastewater mainly consist of copper, chromium, nickel, zinc and a little quantity of lead and cadmium.

Table II.5: Characteristics of electroplating effluents in Thailand.

Sample No.	Characteristics of solution	pH	Conductivity (mS/cm)	Metal concentration (mg/l)					
				Cu	Cr	Ni	Zn	Pb	Cd
1	Suspended solution Green light	1.76	7.9	73	213	400	191	1.58	0.02
2	Suspended solution Yellow	2.81	3.69	25	231	488	5.60	0.11	0.02
3	Suspended solution Yellow	1.38	12.80	168	38	83	22	0.33	0.02
4	Suspended solution Brown	12.8	9.68	71	81	58	3.56	-	0.02
5	Suspended solution Yellow	6.09	3.17	1.71	174	1.36	9.28	-	0.01
6	Suspended solution Brown yellow	9.95	5.11	288	379	0.19	-	0.67	0.02

5.2 Conventional methods for treatment electroplating effluents

The conventional method to eliminate metal contents in electroplating wastewater is performed by following procedure [34, 35].

5.2.1 Chromium elimination

The process for chromium contained in wastewater is reduction of hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}) by sodium bisulphide ($NaHSO_3$). Chromium is mainly presented in wastewater in a form of chromic acid (H_2CrO_4) or sodium dichromate ($Na_2Cr_2O_7$). The reactions are

$$4H_2CrO_4 + 6NaHSO_3 + 3H_2SO_4 \longrightarrow 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 10H_2O \qquad (II.120)$$

followed by precipitation of trivalent chromium

$$Cr_2(SO_4)_3 + 6NaOH \longrightarrow 2Cr(OH)_3(s) + 3Na_2SO_4 \qquad (II.121)$$

5.2.2 Heavy metal elimination

Heavy metals including in plating process are Fe^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Cr^{6+}. These heavy metals are eliminated by precipitation with sodium hydroxide.

$Fe^{2+} + 2NaOH \longrightarrow Fe(OH)_2(s) + 2Na^+$ pH = 7.5 - 10 (pH > 11 reversible) (II.122a)

$Cr^{3+} + 3NaOH \longrightarrow Cr(OH)_3(s) + 3Na^+$ pH = 8 - 10 (pH > 11 reversible) (II.122b)

$Cu^{2+} + 2NaOH \longrightarrow Cu(OH)_2(s) + 2Na^+$ pH = 7 - 12 (Non reversible) (II.122c)

$Zn^{2+} + 2NaOH \longrightarrow Zn(OH)_2(s) + 2Na^+$ pH = 9 - 11 (pH > 11 reversible) (II.122d)

$Ni^{2+} + 2NaOH \longrightarrow Ni(OH)_2(s) + 2Na^+$ pH = 9 - 10 (Non reversible) (1.122e)

5.2.3 Cyanide compound

The widely used method for treating cyanide compound is known as alkaline chlorine method. Cyanide content in industrial waste water is generally in a form of free cyanogens and cyanogens complex.

5.2.3.1 Free cyanogens treatment

This process is performed by adding sodium hypochlorite ($NaOCl$) in basic solution. The reactions are two - step reaction expressed by

1st step $NaCN + NaOCl \longrightarrow NaCNO + NaCl$ $pH \geq 10.5$ (II.123a)

2nd step $2NaCNO + 3NaOCl + H_2O \longrightarrow N_2 + 3NaCl + 2NaHCO_3$ $pH = 7$ (II.123b)

Total $2NaCN + 5NaOCl + H_2O \longrightarrow N_2 + 5NaCl + 2NaHCO_3$ (II.123c)

The cyanide compound is changed to nitrogen gas which is non toxic.

5.2.3.2 Cyanogens complex

The complex of cyanide with heavy metals such as zinc, copper and so on is found in wastewater industry. The treatment process is done by adding sodium hypochlorite ($NaOCl$) in basic condition as shown by the following reactions.

$$Na_2[Zn(CN)_4] + 2NaOH + 4NaOCl \longrightarrow Zn(OH)_2 + 4NaCl + 4NaCNO \quad \text{(II.124a)}$$

$$2Na_2[Cu(CN)_3] + 2NaOH + 7NaOCl + H_2O \longrightarrow 2Cu(OH)_2 + 7NaCl + 6NaCN \quad \text{(II.124b)}$$

Heavy metals will precipitate with hydroxide ion and the cyanogens complex is changed to free cyanogens. These free cyanogens are treated by the 2nd step as mentioned in equation (II.123b).

6. Literature review

The removal of copper from acidic dilute solution and alkaline cyanide solution was performed in rotating tubular bed reactor [36]. They demonstrated that the addition of an oxidizer and complexing agent achieves the copper reduction in alkaline cyanide solutions. A batch reactor consisting of a monopolar plate electrode was conducted to recover copper from industrial effluent [37]. They pointed out that the flow rate of electrolyte principally influenced residential time rather than mass transport. A higher inlet concentration favours metal deposition and decreases current yield.

Panizza et al [38] examined the removal of copper by foam electrodes in a single - pass cell in order to study the behaviour of reactor at different flow rate. The results showed high fractional conversion reaching in a single pass. The filtration unit becomes necessary to reduce the copper salts and phthalocyanine which effect to the process. The complexing of copper ion with organic compound including citric acid, NTA and EDTA was investigated in electrochemical membrane reactor [39]. The increasing of current density leads to a monotonous decrease in current efficiency (ϕ) whereas percentage of copper recovery (R_{Cu}) increased first and then reached a plateau. Under comparable condition, ϕ and R_{Cu}, decreased in order of the complex citric acid > NTA > EDTA and they reached a maximum value at pH = 2.2. 0.0 - 0.2 M Anolyte $NaNO_3$ were practically unaffected to the ϕ and R_{Cu} of the system.

Zinc ion in hydrochloric solutions coming from a hydrometallurgical process was removed in a reactor with diaphragm [40]. The results showed that zinc was removed from hydrochloric solutions even at low pH with good recovery and quality and low concentration of impurity such as iron influenced to the recovery system. The coprecipitation and adsorption processes were conducted in an electrochemical iron addition process [41]. The results showed that conversion of ferrous ions to the ferric state resulted in reduction of hexavalent chromium to trivalent chromium. The presence of arsenic in ground water necessitated a chemically induced oxidation. Hydrogen peroxide was introduced to convert arsenate to arsenic with 99.8 % efficiency.

The possibility of hexavalent chromium removal from synthetic solution was tested in a classical electrochemical reactor [42, 43]. The proposed mechanism is proceeded in two steps: electrochemical reduction of hexavalent chromium to trivalent chromium and and the formation of an insoluble chromium hydroxide generated at high pH. *Upadhyat* [44] studied the removal of hexavalent chromium from chrome plating effluent by using reduction and precipitation techniques. Sodium bisulphite and ferrous sulphate were used as a reducing agent at low pH with a contact time of 10 minutes. The results showed that 99.4% removal of chromium was obtained at pH 2.5 by using 250 mg/l of sodium bisulphite with lime addition and 99.0% removal of chromium was obtained at pH 3.5 with 450 mg/l dose of ferrous sulphate followed by lime addition.

The removal of hexavalent chromium from an electroplating wastewater using the electrochemical precipitation process was studied in laboratory scale [32]. They found that the optimum conditions were electrical potential of 75 V; current intensity of 4.8 A; hydraulic retention time of 50 min; initial pH of above 3.2. *Robert et al* [45] used a flow - through carbon felt electrode to remove hexavalent chromium from electroplating effluent. They have confirmed that the removal of by electroprecipitation was very sensitive to pH. The removal process involved electrochemical reduction of hexavalent chromium to trivalent chromium, and consequently hydroxide precipitation of trivalent chromium. In addition, they suggested that the extent of removal was a function of the current density, and the solution flow rate. The optimum bulk pH and current density were around 3.5 and 400 A/m^2, respectively.

A multi - stages process was used to elimination of copper, nickel and chromium present in wastewater [46]. Metals in wastewater are trapped by activated sludge in a biological treatment then sludge is leached with acid solution to remove metals. In addition, this leaching solution is regenerated and purified from its metals by electrochemical methods. The results showed that a multi-stages process able to treat large quantities of diluted solution of waste has been presented 80 - 90% of metals are trapped by activated sludge and 86 - 91% of metals in sludge are recovered by acid solution. Leaching solution is simultaneously purified and regenerated by electrochemical method with good results. *Doulakas et al* [47] showed the selective electrodeposition of mixed solution of heavy metals including copper, lead, cadmium and zinc under potentiostatic condition. The selective electrodeposition was more than 99 % in purities. For copper, lead and cadmium, the optimum condition of deposit purity, current efficiency and time were achieved at pH = 1.5. The deposited layer of copper, lead and cadmium showed dendritric morphology whereas the compact morphology was observed on zinc deposited layer. *Rodriguez et al* [48] studied the electrolytic treatment of zinc and nickel from the leaching solution of sludge with glycine in a batch reactor with membrane operated in a recycle mode. They reported that more than 90 % zinc contained in solution was recovered at the cathode with approximately 50 % current efficiency. On the other hand, nickel deposition appeared to be inhibited by glycine and the efficiency of the overall process was poor. The abatement extent was in a range of 10 - 20 %.

The new type of electrochemical reactor called the 3PE reactor (Pulsed Porous Percolated Electrodes) was used to recover zinc, copper and nickel from electroplating units [33]. They reported that the best support for metal deposition was carbon granules used for energy production. The recovery rates of zinc, copper and nickel were respectively around 93, 99 and 82 %. The same reactor type was constructed in axial field configuration to recover copper and that in radial field configuration to recover chromium [22]. They reported that the final concentration of copper could be decreased to the level of ppm with high deposition rates and good current efficiency. The concentration of chromium has decreased when the time increased and mixed cations precipitated together at pH > 4 as hydroxide sludge.