# UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session of 2006/2007

October/November 2006

## EBB 522/3 – Corrosions and Protection

Time : 3 hours

Please ensure that this paper consists of NINE printed pages and FIVE pages APPENDIX before you proceed with the examination.

This paper contains SEVEN questions.

Answer any FIVE questions. If a candidate answer more than five questions, only the first five answered will be examined and awarded marks.

Answer to any question must start on a new page.

All questions must be answered in English.

1. Consider potential-pH equilibrium diagrams for the system Fe – $H_2O$ and Al – $H_2O$ at 25°C (298K) in the Appendices.

[a] Briefly differentiate the corrosion behavior of aluminum and steel.

(20 marks)

[b] Describe five protection methods that can be applied to control iron corrosion exposed in a neutral environment.

(20 marks)

[c] Show how to construct the equilibrium lines number a, b, 1', 2, and 5 in the potential-pH diagram for the system Al-$H_2O$ at **25°C**.

Data:

| **Substance** | $\mu^0_{298K}$ **(cal.)** |
|---|---|
| Al | 0 |
| $Al_2O_3.3H_2O$ hydrargillite | - 554 600 |
| $Al^{3+}$ | -155 000 |
| $AlO_2^-$ | - 200 710 |
| $H^+$ | 0 |
| $OH^-$ | - 37 595 |
| $H_2O$ | - 56 690 |
| $H_2$ | 0 |
| $O_2$ | 0 |

(60 marks)

...3/-

2. [a] Derive the anodic and cathodic Tafel equations from the following Butler-Volmer equation:

$$i_T = \overleftarrow{i} - \overrightarrow{i} = i_0\left(\exp\left[\frac{\vec{\alpha}F\eta_{ac}}{RT}\right] - \exp\left[-\frac{\vec{\alpha}F\eta_{ac}}{RT}\right]\right)$$

(30 marks)

[b] Pure zinc is corroding under mixed control in a solution of deaerated hydrochloric acid solution with a pH of 2 and containing $Zn^{2+}$ ions with the activity of 1 at 25°C. The cathodic reaction occurs on the two thirds of the entire surface and the anode reaction on the reminder.

(i) Calculate its corrosion rate in mm/year.

(ii) Calculate its corrosion potential.

Data: Exchange current densities for Zn and for hydrogen on Zn are 0.1 and $10^{-4}$ A/m, respectively.

$$\vec{\alpha}_{an} = \vec{\alpha}_{cat} = 0.5$$

$$E^0_{Zn^{2+}/Zn} = -0.673V$$

The mol. weight and density of zinc are 65.4 g/mol and 7.14 g/cm$^3$ respectively.

(70 marks)

3. According to mixed potential theory the relationship between applied current density ($i_{app}$) and potential ($\overline{E}$) at any potential which is slightly higher or lower than the corrosion potential, $E_{cor}$ might be presented as:

$$i_{app} = i_{0,an}.\exp\left(\frac{\overline{E} - E_{Fe^{2+}/Fe}}{b'_{an}}\right) - i_{0,cat}.\exp\left(-\frac{\overline{E} - E_{2H^{+}/H_2}}{b'_{cat}}\right)$$

[a] Show the derivation for finding the following basic equation for linear polarization resistance:

$$i_{cor} = \frac{B}{R_p}$$

where $B = \dfrac{b_{an} b_{cat}}{2.303(b_{an} + b_{cat})}$

$b_{an} = 2.303 b'_{an}$ and $b_{cat} = 2.303 b'_{cat}$

and $b_{an}$ and $b_{cat}$ are the anodic and cathodic Tafel slopes respectively.

(50 marks)

[b] Engell has proposed a method to determine the corrosion current density, $i_{cor}$ and the anodic Tafel slope from polarization measurements in the vicinity of the corrosion potential for the metal corrosion which is controlled by the rate of mass transfer of dissolved oxygen toward the metal ($b_{cat} \rightarrow \infty$).

Derive the relationship between applied current density ($i_{app}$), corrosion current density ($i_{cor}$) and potential ($\overline{E}$) in the vicinity of the corrosion potential ($E_{cor}$), and then show how to determine $i_{cor}$ and $b_{an}$.

(30 marks)

[c] Corrosion of a metal is controlled by the diffusion rate of dissolved oxygen toward the metal. The corrosion rate of the metal is 0.1A/m$^2$ and the charge transfer coefficient of anodic process ($\vec{\alpha}_{an}$) is equal to 0.5. By assuming the anodic and cathodic reactions occur on the entire surface area of the metal, determine its polarization resistance.

(20 marks)

4. [a] Corrosion in a storage tank was monitored by an electrical resistance probe consisting of a wire with a diameter of 0.2" and made of the same material as the tank. After six months of usage, the measured resistance increased from 20.40 to 22.34 ohms, both measured at the same temperature. After cleaning, microscopic examination of the interior surface of the tank reveals sparse pitting with some pits as deep as 0.010" (0.010 inch).

(i) What is the uniform corrosion rate in mpy?

(ii) What is the pitting factor?

(50 marks)

[b] Draw a sketch of the anodic polarization curve for a metal that exhibits active-passive behavior in an Evans diagram.

(i) Include a line for the cathodic process when the metal is 1) actively corroding, 2) borderline passive, and 3) stably passive.

(ii) Label the cathodic lines, the three polarization regions (active corrosion, passive and transpassive regions), and indicate the following electrochemical parameter in your sketch: equilibrium potential and exchange current density of anodic reaction, primary passive potential, passive current density, transpassive potential and critical current density. Also indicate $E_{cor}$ for each case (in question i).

(25 marks)

[c] Explain briefly how to construct experimental potential-pH diagram for iron in environment containing aggressive ions. You should show the sketch of the relationship between measured anodic polarization curves and experimental potential-pH diagram.

(25 marks)

...7/-

5. Type 304 stainless steel is susceptible to pitting, crevice, and intergranular corrosions as well as stress corrosion cracking.

   [a] Differentiate the mechanisms of pitting and crevice corrosion that may occur on the stainless steel. How do you avoid crevice corrosion? Explain.

   (30 marks)

   [b] Briefly discuss the mechanism of passive film breakdown that occurs on the stainless steel in a corrosive medium containing chloride ions, and then suggest how to increase the pitting corrosion resistance of the stainless steel.

   (30 marks)

   [c] Briefly discuss the mechanisms of intergranular corrosion and intergranular stress corrosion cracking that may occur on this stainless steel and then give the methods how to prevent against those corrosions.

   (40 marks)

6. [a] Design a sacrificial anode cathodic protection (SACP) system for a pipeline based on the following data and requirements.

Data: - Pipe dimension: diameter = 14 inches
thickness = 0.5 inches
length = 10km
- Coating : polyethylene tape, overlap 5cm
- Average resistivity of soil : 2000 ohm.cm
- Weight of one magnesium anode : 8kg
- Anode capacity of magnesium anode : K = 1200 Ah/kg
- Length of magnesium anode : 50cm
- Diameter of magnesium anode: 12 cm
- Length of backfill for the anode: 80 cm
- Diameter of backfill for the anode: 20 cm

Requirements:- Protection criteria :≤ -0.85 V vs. CSE
- Designed life time of CP: 20 years
- Protection current density requirement: 0.5 $mA/m^2$
- One ground bed must contains 4 magnesium anodes
- ΔE (maximum potential shift of anode) = 0.7 volt

(85 marks)

[b] Draw a sketch of the installation of anodes in one ground bed which includes the connection method between anodes and pipe through a test point terminal.

(15 marks)

7. [a] Explain why a galvanized steel structure is more resistant to atmospheric corrosion than a steel structure.

(15 marks)

[b] Describe briefly the hot dip galvanizing process of steel.

(15 marks)

[c] It is well known that zinc electroplating can also be applied to increase the corrosion resistance of small steel components especially for indoor applications. Describe briefly a zinc electroplating process in a sulfate bath. A zinc electroplating is done using current density 2 $A/dm^2$. The current efficiency of the process is 90 %. Estimate the electroplating time for producing 30μm zinc coating. The density of zinc is 7.14$g/cm^3$. Mol. wt. of zinc = 65.4.

(40 marks)

[d] Explain why galvanized coating does not give sufficient corrosion protection for reinforcing steel bars (rebars) embedded in a marine concrete structure.

(15 marks)

[e] Utilization of galvanized reinforcing steel bars might extend the durability of concrete structures exposed in environment in which carbonation of concrete cover can occur. However, the utilization of galvanized rebars requires the existing of inhibitor in the concrete mix. Suggest one inhibitor that can be utilized for this purpose and then explain its inhibition mechanism.

(15 marks)

- oooOooo -

## APPENDICES

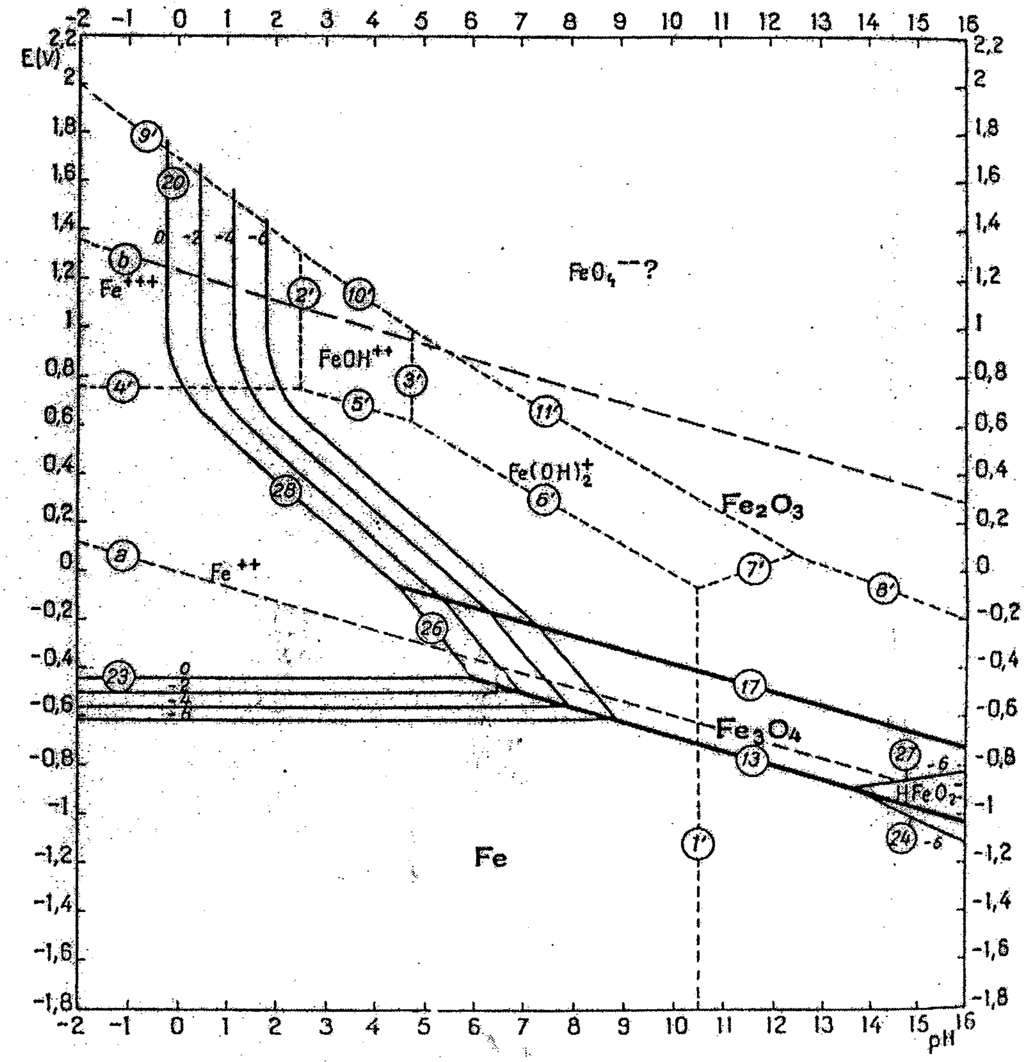


FIG. 4. Potential–pH equilibrium diagram for the system iron–water, at 25°C (considering as solid substances only Fe, $Fe_3O_4$ and $Fe_2O_3$).

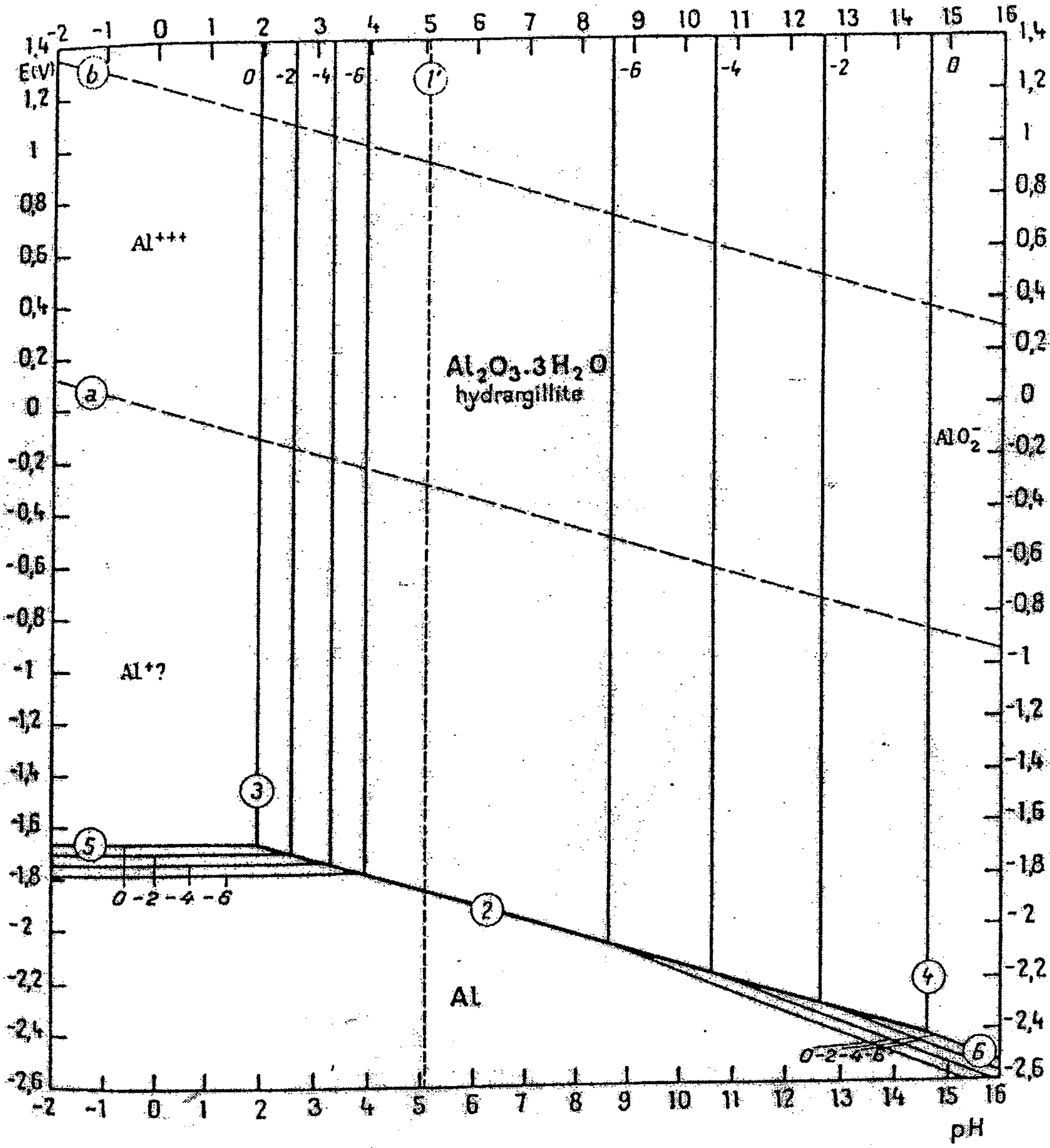


FIG. 1. Potential–pH equilibrium diagram for the system aluminium–water, at 25°C.

Below is a list of formulas that can be utilized to solve the exam questions

$$R_{v\,anode\,to\,backfill} = \frac{\rho_{backfill}}{2\pi l_{anode}}\left[\ln\frac{4l_{anode}}{r_{eff\,anode}} - 1\right]$$ ohm

$$R_{v\,backfill\,to\,soil} = \frac{\rho_{soil}}{2\pi l_{backfill}}\left[\ln\frac{4l_{backfill}}{r_{backfill}} - 1\right]$$ ohm

$$r_{eff} = \left[\frac{U\,x\,initial\,cross\,section\,area}{\pi}\right]^{1/2} = \left[\frac{U\,\pi\,r^2}{\pi}\right]^{1/2}$$ cm

$$F = 1 + \frac{\rho_{soil}}{\pi\, S_a\, R_{v\,total}}\ln(0.656\,x\,n)$$

$$W_0 = \frac{I_0\,x\,T\,x\,8760}{K\,x\,U}\,kg$$

$$R_{groundbed} = \frac{R_{v\,total}}{n}\,xF$$ Ohm

Butler – Volmer equation

$$i = i_a - i_c = i_0\left[\exp\left(\frac{\alpha_a F \eta_{act}}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta_{act}}{RT}\right)\right]$$

Linear Polarization Resistance

$$i_{corr} = \frac{B}{R_p} \qquad B = \frac{b_a b_c}{2.303(b_a + b_c)}$$

- At potentials around $E_{cor}$

$i_{applied} = i_{anodic\ process} - i_{cathodic\ process} =$

$$i_{0\,an}\exp\left(\frac{\alpha_{an}\eta_{an}F}{RT}\right) - i_{0\,cat}\exp\left(-\frac{\alpha_{cat}\eta_{cat}F}{RT}\right) = i_{0\,an}\exp\left(\frac{E - E_{an}}{b_{an}}\right) - i_{0\,cat}\exp\left(-\frac{E - E_{cat}}{b_{cat}}\right)$$

**Theoritical weight of metal deposit (g)** $= \dfrac{(I.t.)}{F}\dfrac{(atomic - weight)}{n}$

F = 96 487 A.sec./mol

R = 8.314 J/(mol.K) = 1.987 cal/(mol.K)

r = pipe radius

D = pipe diameter

t = pipe thickness

$r_{eff}$ = effective radius of anode

$R_V$ = resistance of vertical anode

ρ = resistivity of soil or backfill

$S_a$ = distance between two anodes

$i_T$ = total current density

$i_0$ = exchange current density

$\overleftarrow{i}$ = current density of oxidation

$\overrightarrow{i}$ = current density of reduction reaction

U = [initial cross section area + final cross section area]/2

U = utility factor

n = number of anodes in one ground bed

$W_0$ = total weight of anodes

Y = T = life time, years

K = anode capacity, Ah/kg

$\overleftarrow{\alpha}_{an}$ = charge transfer coefficient for anodic process

$\overrightarrow{\alpha}_{cat}$ = charge transfer coefficient for cathodic process

$\overleftarrow{\alpha}$ = charge transfer coefficient for deelectronation reaction

$\overrightarrow{\alpha}$ = charge transfer coefficient for electronation reaction

$\eta_{an}$ = activation overpotential for anodic reaction

$\eta_{cat}$ = activation overpotential for cathodic reaction

$\eta_{ac}$ = activation overpotential

$E_{an}$ = equilibrium potential for anodic reaction

$E_{cat}$ = equilibrium potential for cathodic reaction

$$\overleftarrow{b}'_{an} = \frac{RT}{\overleftarrow{\alpha}F} \quad ; \quad \overrightarrow{b}'_{cat} = \frac{RT}{\overrightarrow{\alpha}F}$$