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# **UNIVERSITI SAINS MALAYSIA**

First Semester Examination  
Academic Session of 2004/2005

October 2004

## **EBB 522 - Corrosions and Protection**

Time : 3 hours

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Please ensure that this paper consists of ELEVEN printed pages before you proceed with the examination.

This paper contains SEVEN questions.

Answer FIVE questions. Question number ONE is compulsory and answer any FOUR questions from the rest. 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 answered in English.

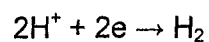
1. Circle the right statements/answers. There can be  $\geq 1$  right statements /answers in each number.
- (a) The difference between potential-pH diagrams for Fe-H<sub>2</sub>O and Al-H<sub>2</sub>O describes the difference in corrosion resistant behavior of these metals.
- (i) Steel/iron has an active-passive corrosion behavior but aluminium has not. Therefore, in alkaline solution anodic protection is effective to protect aluminium from corrosion attack.
- (ii) Aluminium can be used as a material for construction and utensil because this metal is passive in a neutral aqueous environment ( $4 < \text{pH} < 8.6$ ).
- (iii) Steel corrodes in seawater ( $\text{pH} = 7.8$ ) because its corrosion potential is in active corrosion domain. However it is used for ship hull because it can be protected by decreasing its interface potential close to/into its passivation domain (cathodic protection).
- (iv) Anodic protection is also recommended to protect steel exposed in sulphuric acid solution containing significant aggressive ions.
- (v) Reinforcing steel bars is passive in uncontaminated concrete environment ( $\text{pH} = 13.5$ ) while aluminium corrodes because in this pH passive film of Al hydroxide dissolves to  $\text{AlO}_2^-$ .

(20 marks)

(b) Anodic and cathodic reactions which can significantly occur on Fe in:

(i) Deaerated pH 2 are

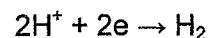
- cathodic reactions:  $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$  (when ferric ions is present)



- anodic reaction:  $\text{Fe} \rightarrow \text{Fe}^{++} + 2e$

(ii) Aerated pH 7 are

- cathodic reactions:  $\text{Fe}^{3+} + e \rightarrow \text{Fe}^{2+}$  (when ferric ions is present)



- anodic reaction:  $\text{Fe} \rightarrow \text{Fe}^{++} + 2e$  follows by rust formation reactions

(iii) Aerated pH 13.5 are

- cathodic reactions:  $1/2\text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow 2\text{OH}^-$

- anodic reaction:  $2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+$  (Fe becomes passive)

(20 marks)

- (c) Corrosion process of an active metal can be controlled by the rate of anodic and cathodic processes or the rate of mass transfer of oxidizer toward cathodic sites.
- (i) In case of the corrosion of a metal is controlled completely by the activation polarization for both anodic and cathodic reactions, solution stirring increases the corrosion rate.
  - (ii) Limiting current density of dissolved oxygen reduction can be increased by increasing temperature, oxygen partial pressure above the solution and stirring because the diffusion coefficient of oxygen and its concentration in the solution increases, and the thickness of stagnant layer on the metal surface decrease.
  - (iii) Corrosion of iron in an aqueous environment (pH 1.5) is controlled by the rate of mass transfer of hydrogen ions toward the cathodic sites while corrosion of iron in deaerated water is a mixed controlled process.
  - (iv) Increasing the velocity of ship will result in an increase of corrosion rate, this leads to reduce the need of protection current density supplied from a cathodic protection.
  - (v) Passivator (oxidizing inhibitor) is effective to reduce the corrosion rate of the steel in neutral solution because it will decrease the limiting current density of dissolved oxygen reduction.

(20 marks)

- (d) A passive metal might be susceptible to pitting and crevice corrosion in environment containing aggressive ions.
- (i) Crevice corrosion of stainless steel type 304 is initiated by passive film breakdown rather than dissolution process of passive film inside crevice.
  - (ii) Increasing nitrogen, molybdenum, chromium and nickel contents in an austenitic stainless steel will decrease the susceptibility of the material against crevice and pitting corrosion.
  - (iii) Pitting corrosion can be prevented by anodic protection.
  - (iv) Steel actively corrodes in water containing small amount of chloride ions, this material is not susceptible to crevice corrosion because it is not in passivation state.
  - (v) Similarly with pitting corrosion, intergranular corrosion of AISI 304 stainless steel is induced by passive film breakdown at potential  $\geq E_{\text{pit}}$ .

(20 marks)

- (e) There are two ways to cathodically protect a structure: (i) by external power supply or (ii) by appropriate galvanic coupling.
- (i) Impressed current cathodic protection (ICCP) is not recommended to protect steel ship hulls because they have already protected by organic coating.
  - (ii) Function of backfill is to decrease anode resistance therefore backfill is used in marine environment.
  - (iii) Increasing conductivity of environment and decreasing the conductivity of coating will result in a better protection current distribution.
  - (iv) Sacrificial anodes can be used together with ICCP when it is necessary. Magnesium anodes have been used for initial polarization of steel piles immersed in seawater. The objective is to reduce the needs of excessive current from rectifier/s.
  - (v) Area of external pipe that picks up high current density of stray current may be at a stage of over-protection while pipe location that supplies stray current corrodes with a significant rate.

(20 marks)

2. A metal is immersed in a solution where the oxidizer is dissolved oxygen gas coming from the atmosphere. The cathodic polarization curve for  $O_2$  reduction crossed the polarization curve for the metal in passive region and reaches a limiting current density of  $5 \times 10^{-3} A/cm^2$ . The corrosion potential at this limiting current density is  $-0.25V$  vs. SHE.

(a) What is the critical current density?

(40 marks)

(b) By what factor must  $O_2$  concentration in the solution be increased to achieve stable passivation. What partial pressure of  $O_2$  in the gas would be required?

(40 marks)

(c) What other strategies to achieve stable passivity could be used instead?

(20 marks)

Data :  $E_{pp} = -0.20 V$  vs. SHE

Tafel slope anodic ( $b_a$ ) =  $0.12V/decade$

3. Corrosion of Fe in aerated stagnant water at  $25^{\circ}C$  is controlled by a diffusion process of dissolved oxygen through a diffusion layer.

(a) Sketch the Evans diagram of the process.

(10 marks)

(b) Write the reduction and oxidation reactions as well as the rust formation reactions.

(10 marks)

(c) Calculate the initial penetration rate of Fe in mm/year.

(40 marks)

- [d] Predict the corrosion potential of Fe by assuming the resistivity of solution approaches zero.

(40 marks)

Data :

- ✓ Solubility of pure oxygen gas in water at 298K (25°C) is 41.5ppm.
  - ✓ Diffusion coefficient of dissolved oxygen in water at 25°C =  $0.2 \times 10^{-5} \text{ cm}^2/\text{sec}$ .
  - ✓ Diffusion layer thickness is 500 $\mu\text{m}$ .
  - ✓ Atomic weights of Fe and O are 55.85 and 16.0 respectively
  - ✓ Density of Fe =  $7.8 \text{ g/cm}^3$
  - ✓ Exchange current density of electronation/deelectronation reaction of Fe =  $1 \times 10^{-4.5} \text{ A/cm}^2$
  - ✓ Tafel slope of anodic reaction ( $b_a$ ) = 190mV/decade
  - ✓  $E^0_{\text{Fe}^{++}/\text{Fe}, 298\text{K}} = -440 \text{ mV}$
4. Corrosion in a storage tank was monitored by an electrical resistance probe consisting of a wire with a diameter of 0.2 inch and made of the same material as the tank. After 6 months usage, the measured resistance increased from 20.40 to 22.34 $\Omega$ , 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 inch.
- (i) What is the uniform corrosion rate in mpy?  
(60 marks)
- (ii) Calculate the pitting factor.  
(20 marks)
- (iii) Give 3 methods for controlling corrosion of the tank  
(20 marks)



5. Two types of polarization data obtained for mild steel in a chemical reactor environment at pH 6 and 25°C are given below. Figure (a) shows the potentiodynamics polarization curve while figure (b) is a plot of polarization resistance. Using this data and considering a steel surface of 1cm<sup>2</sup> answer the following:

(i) By drawing the cathodic and anodic Tafel lines on Figure (a) determine the values of anodic and cathodic Tafel slopes,  $E_{cor}$  and  $i_{cor}$ . (60 marks)

(ii) Determine the polarization resistance  $R_p$ , and the corrosion current using the data in Figure (b) and the Tafel slopes determined in part (a). (40 marks)

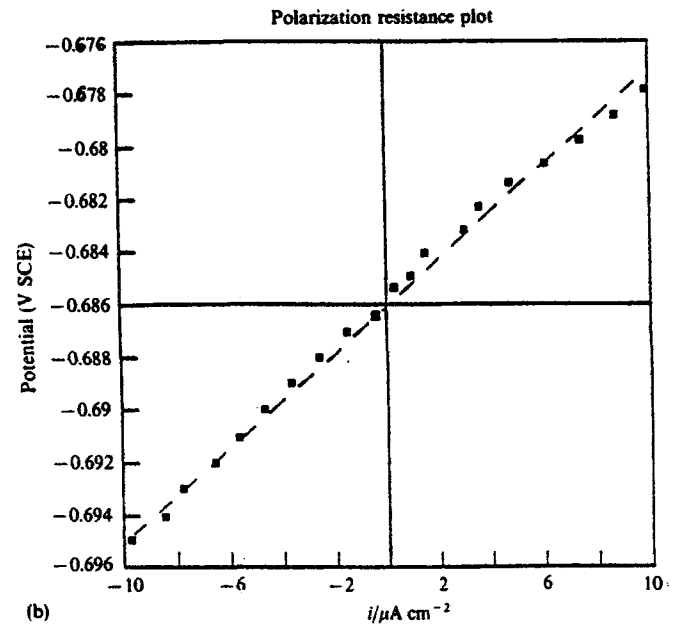
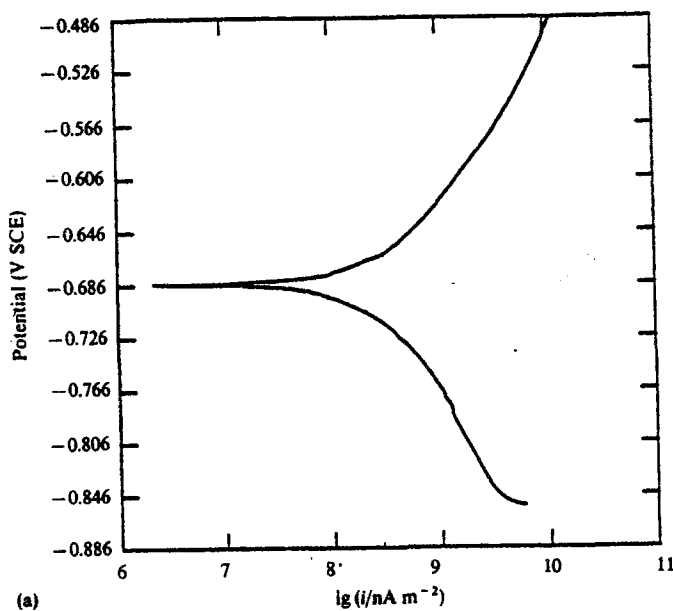


Figure 1

6. A cathodic protection using multiple sacrificial anodes is proposed to protect a coated steel pipeline having diameter 14 inches, thickness 0.5 inches and length 10km. Each groundbed will consist of 6 magnesium anodes and the spacing between two anodes is proposed to be 0.8 m.

Data :

- Soil resistivity = 2000  $\Omega$ cm
- Protection current density that has to be provided = 0.5mA/m<sup>2</sup>
- Magnesium anode capacity, K = 1200Ahr/kg
- Potential shift of anode ( $\Delta E$ ) is proposed to be 0.7volt
- Anode dimension: length = 50cm; diameter = 12 cm
- Backfill dimension (including anode): length = 80 cm; diameter = 20 cm
- Weight of an anode: 8 kg

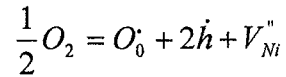
- (a) Calculate the resistance of each groundbed and examine the protection current that can be supplied by each groundbed. Is it sufficient enough to protect the pipeline?

(80 marks)

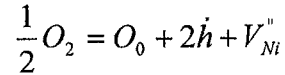
- (b) Give 3 methods that are able to increase the protection current from the ground bed.

(20 marks)

7. Consider following defect formation reaction of NiO:



and



The parabolic rate constant can be calculated from :

$$k' = \frac{1}{z_c^2 F^2 C_M} \int_{\mu_M}^{\mu_M'} \sigma_c d\mu_M \dots \dots \dots cm^2 / sec$$

- (a) Show using schematic figure that the NiO has a type P semiconductor properties and its growing rate is controlled by the diffusion-migration of Ni ions.

(35 marks)

- (b) Derive the equation in order to express the relationship between  $k'$  and  $p_{O_2}$  of environment.

(30 marks)

- (c) What will happen when the NiO contains a small amount of dissolved  $Cr_2O_3$ ?

(35 marks)