

National Exams December 2003
98-Met-B2, Hydrometallurgy

3 hours duration

NOTES:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.
2. Candidates may use one of two calculators, the Casio or Sharp approved models. This is a closed book exam.
3. Answer the first problem and chose any 5 out of the remaining 7 problems (i.e., problems 2-8).
4. All questions within a problem are of equal value.

Marking scheme

1. Problem 1: 10
2. Problems 2-8: 18

GIVEN:

Ideal gas constant: $R = 1.987 \text{ cal/mol/K} = 8.314 \text{ J/mol/K}$,

Absolute temperature $T = (^{\circ}\text{C} + 273) \text{ K}$,

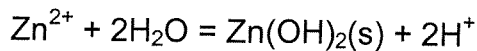
$F = 96,500 \text{ C/eq}$,

$K_w = 10^{-14}$ at 25°C

PFD: Process Flow Diagram

Problem 1

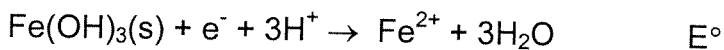
1,000 L of an aqueous solution at $\text{pH} = 1$ containing 1 mol/L Zn^{2+} enter a chemical reactor at 25°C and are subjected to neutralisation by the addition of CaO base. Given that the equilibrium constant is 1 for the following reaction



- Calculate the solubility product of $\text{Zn}(\text{OH})_2$.
- Calculate the target pH to precipitate 99% of Zn^{2+} .
- Calculate (approximately) the mass of base needed to arrive at this pH .

Problem 2

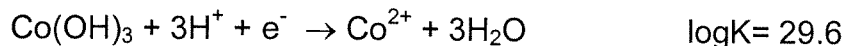
You are given that:



Prove that in a Eh-pH diagram, all three lines depicting the above three reactions will intersect at a common point. Initially, you may prove it for the limited case where all iron ions are in their standard states (i.e., activities = 1). However, you must also prove that this will be the case regardless of the dissolved iron ion activities, as long as they are all equal with each other.

Problem 3

We want to selectively dissolve electrochemically cobaltic hydroxide in order to recover cobalt metal. The acidic dissolution of cobaltic hydroxide at pH=2, $[Co^{2+}] = 0.1 M$ and $25^{\circ}C$ is described by the following reaction:

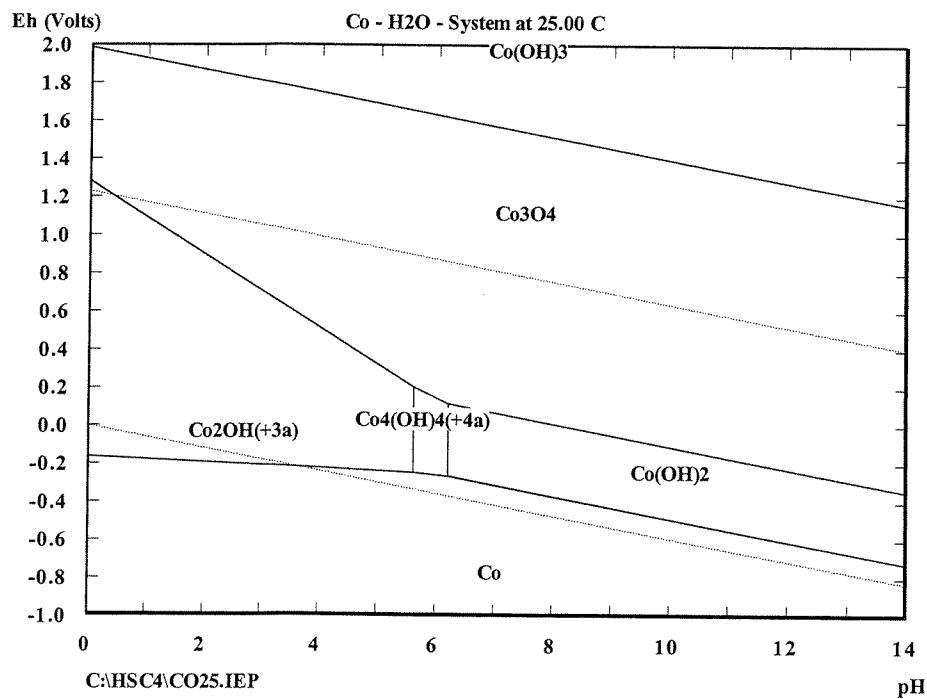


- (a) Which of the two couples Cu^{2+}/Cu^+ or Cu^{2+}/Cu can be used as a reducing agent in the reaction?
- (b) Calculate the equilibrium constant of the most spontaneous reaction.

Consult the attached Eh-pH diagram (aqueous species are shown with a small "a" in parenthesis) and answer the following:

- (c) Provide the pH range (if any) within which cobalt metal can be recovered by electrolysis of an aqueous solution on the basis of thermodynamic arguments only. Write the electrolysis reaction.
- (d) Provide the pH range (if any) within which cobalt metal can be recovered by a reduction with hydrogen gas under atmospheric pressure and at $25^{\circ}C$. Write the overall reaction of cobalt reduction by hydrogen gas.

Given:



ELEMENTS	Molality	Pressure
Co	1.000E-01	1.000E+00

Problem 4

- a.) Define the distribution coefficient D in a Solvent Extraction (SX) process, and sketch its variation with pH.
- b.) Calculate the fraction of a metal loaded in the organic phase for a SX system with $D=1$ and aqueous-to-organic (A/O) volume ratio of 5.
- c.) Describe the different extraction mechanisms in SX systems.
- d.) Describe the most common SX contactors that are used today by the industry
- e.) What are the criteria used in deciding whether solvent extraction or ion exchange is more suitable for metal ion separation in aqueous streams?

Problem 5

You are processing an acidic aqueous stream containing 1 M of dissolved nickel. You are asked to suggest chemical precipitation approaches to produce:

- (a) Fine powder of NiO with a narrow particle size distribution.
- (b) A clean solution that passes the government limits for environmental disposal, and a solid product that can be disposed safely.
- (c) A solid product of $\text{Ni}(\text{OH})_2$ that will be further treated for pure Ni production.

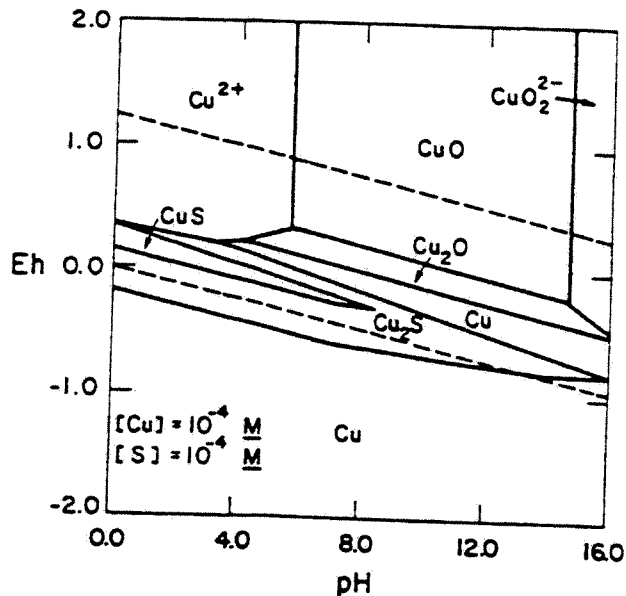
Describe in each step the precipitation approach, provide the respective PFD and explain briefly and clearly the reasoning for each process step employed.

- (d) Will it make any difference in the approach you take if the feed solution is a sulphate or a chloride one? Explain why.
- (e) Will it make any difference in the approach you take if the feed solution is considerably dilute in nickel? Explain why in qualitative terms.

Problem 6

It is desired to process a feed material of chalcocite (Cu_2S) to produce an aqueous Cu-containing solution, in order to produce copper. Based on the Eh-pH diagram for the Cu-S- H_2O system presented in the Figure below:

- (a) Identify all the possible chemical pre-treatment steps that can be used to produce a copper-containing product amenable to direct dissolution. For each such chemical reaction path, provide the corresponding balanced chemical equation.
- (b) Identify the several alternative process schemes that can be used to convert a feed material of chalcocite to an acidic Cu-containing solution.
- (c) For each process scheme, provide the relevant chemical equation for the dissolution step.
- (d) For each processing scheme, provide the corresponding well-labelled PFD.



Problem 7

The total hydrometallurgical route for zinc production involves direct treatment of zinc sulphide (sphalerite) by oxygen pressure leaching in sulphuric acid solution. The advantage of this process is due to the formation of elemental sulphur $\text{S}(\text{s})$ rather than $\text{SO}_2(\text{g})$ as in roasting, or $\text{SO}_4^{2-}(\text{aq})$ as when complex ores (that contain iron sulphides) are treated.

Assume that the laboratory experiment was performed in a batch autoclave in which O_2 partial pressure was maintained constant. The operating conditions of the autoclave were: 160°C , 10 atm O_2 pressure. The typical size distribution of sphalerite sample was as follows:

Particle radius	μm	-27+22	-22+18	-18+7	-7+4	-4+2
Fraction	wt%	20	16	22	27	15

Leaching of sphalerite is known to follow the shrinking core model for surface reaction control (even though sulphur forms) of the form $k_s t = 1 - (1 - f)^{1/3}$ where k_s is the apparent rate constant, t is the leaching time and f the particle conversion. Since the concentration of dissolved oxygen is proportional to the oxygen pressure, the apparent rate constant may be conveniently expressed as a function of oxygen pressure (rather than concentration) as follows:

$$k_s = 285 \cdot 10^4 \frac{P_{\text{O}_2}}{r_s} \exp\left[-\frac{7500}{T}\right] \text{ min}^{-1}$$

where P_{O_2} = partial oxygen pressure in atm; T = temperature in K; and $r_s = \sqrt{r_{s,\text{min}} r_{s,\text{max}}}$ is the geometric mean radius for each size fraction in μm .

1. Write the chemical reaction of sphalerite leaching and evaluate the conversion of zinc after 15 minutes of reactor operation.
2. The same zinc concentrate was leached in a continuous autoclave operated at steady-state under the same conditions (pressure and temperature) as in the batch reactor. The slurry flow rate was $80 \text{ m}^3/\text{h}$; the autoclave volume was 20 m^3 . Evaluate the mean residence time for that autoclave and the conversion of zinc at steady state.

Problem 8

A copper refinery is designed to operate at a current density of 280 A/m^2 . Permanent cathodes made of stainless steel are used measuring $150 \text{ cm} \times 150 \text{ cm}$. There are 800 tanks in total, each containing 44 anodes and 43 cathodes. Cathodes are pulled every 7 days from the tanks for stripping and washing before they are used again. The stripping/washing operation takes 1 day. At any time, 10% of the tanks are out of operation because of cleaning or general maintenance. Cathode current efficiency is 94 percent; anode efficiency is 100 percent. The voltage per tank is 0.30 Volts. The molar mass of Cu is 63.5.

Calculate:

- i) The electrical energy in kWh to electrorefine 1 kg of copper.
 - ii) The nominal annual capacity of the plant (in tonnes) operating 360 days.
- (b) Compare in terms of power requirements Cu electrowinning (EW) with Cu electrorefining (ER). Assume the same production capacity for both processes. The pertinent electrode reactions along with their applicable in each case reversible potentials and overpotentials are the following for the two electrolytic processes (state any additional assumptions implicit in your calculations):

	<u>Cu EW</u>	<u>Cu ER</u>
Cathodic reaction	$\text{Cu(II)} + 2\text{e}^- \rightarrow \text{Cu(s)}$ $e_{\text{rev}} = 0.33 \text{ V}$ $\eta_{\text{cath}} = 0.06 \text{ V}$	$\text{Cu(II)} + 2\text{e}^- \rightarrow \text{Cu(s)}$ $e_{\text{rev}} = 0.33 \text{ V}$ $\eta_{\text{cath}} = 0.06 \text{ V}$
Anodic reaction	$2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ $e_{\text{rev}} = 1.23 \text{ V}$ $\eta_{\text{an}} = 0.74 \text{ V}$	$\text{Cu(II)} + 2\text{e}^- \rightarrow \text{Cu(s)}$ $e_{\text{rev}} = 0.33 \text{ V}$ $\eta_{\text{an}} = 0.2 \text{ V}$
Potential drop due to electrolyte resistance	$IR = 0.3 \text{ V}$	$IR = 0.3 \text{ V}$

- (c) Why is it critical to remove impurities to below-ppm level prior to electrowinning of ZnSO_4 in the zinc industry?