GWANDA STATE UNIVERSITY

FACULTY OF ENGINEERING AND ENVIRONMENT

DEPARTMENT OF METALLURGICAL ENGINEERING

ADVANCED HYDROMETALLURGY

EMR5102/EMG 5102

Part IV First Semester Examination Paper

September 2024

This examination paper consists of 7 printed pages

Time Allowed: **3 hours**

Total Marks: **100**

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INSTRUCTIONS

1. Answer **any four questions**
2. Use of calculators is permissible

Additional Requirements

MARK ALLOCATION

Part Questions	As shown in each part question
Total Attainable	100

Question 1.

Mhangura copper mine has rich copper sulphide ores. It was closed mainly due to low copper prices. A hydrometallurgy processing route can be cheaper making copper mining viable for Mhangura again. The ore is composed of copper in the minerals, chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4). The ore at time of mine closure was processed via pyrometallurgical route. If the mine is to be revived and a hydrometallurgical route was to be used

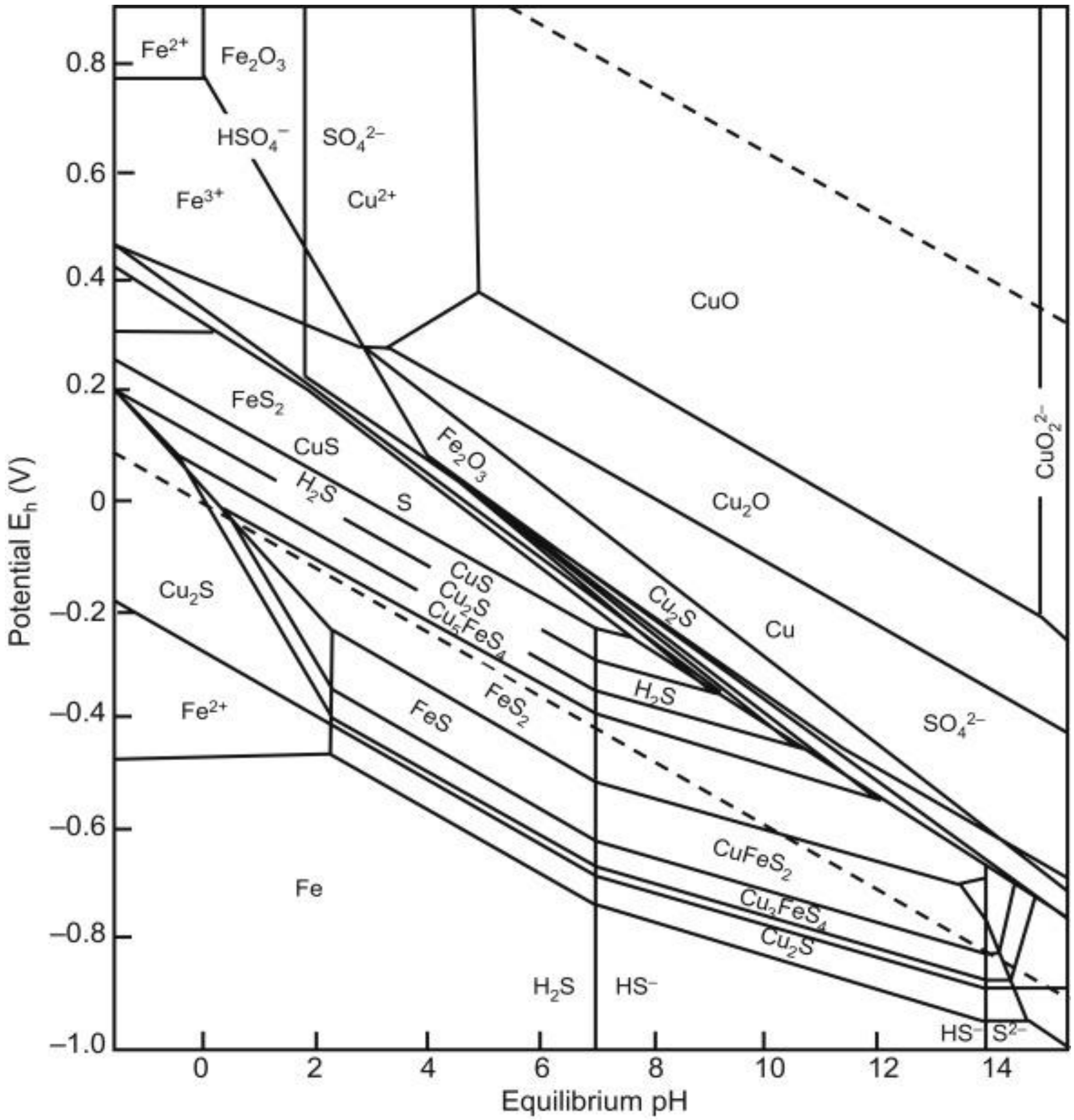


Fig 1. Pourbaix diagram of the Cu-Fe-S system

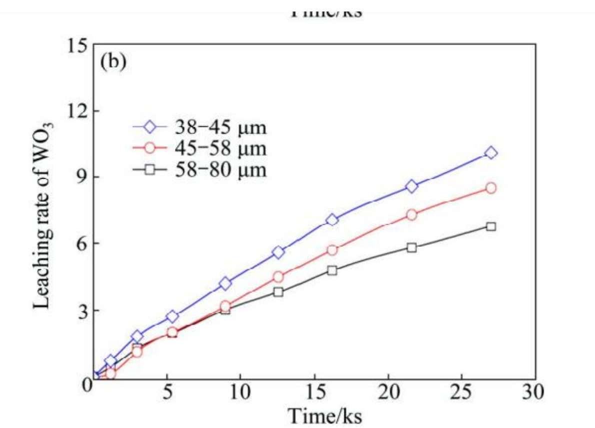
(a) Draw a flow-sheet of the process you would use to recover copper from Run Off Mine ore [5]
(b) Write down balanced chemical reactions where chemical reactions are involved in the above flowsheet [12]
(c) What pH and oxidizing potential would you use to leach the ore? [4]
(d) In what ways can the co-leaching of iron be reduced [4]

Question 2.

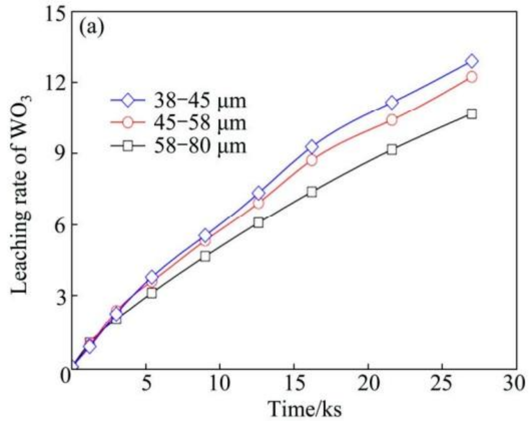
Tungsten is widely used in alloying and has reserves in Matabeleland South as scheelite $CaWO_4$. Currently, the main technologies for scheelite extraction are caustic and sodium carbonate decomposition. Carbonate decomposition is done in an autoclave at 230°C with three to four times the theoretical of Na_2CO_3.

The leaching reaction is:
CaWO4(s) + Na2CO3(aq) → CaCO3(s) + NaWO4(aq) Reaction Q2i

Trials are under study of ways to improve the rate of leaching using ultrasound, graphs Q2ii and Q2iii show the results.



Graph Q2ii Scheelite leaching rate without ultrasound



Graph Q2iii Scheelite leaching rate with ultrasound

(a) From the reaction equation and ultrasound trial results state and describe a model that can be used to describe the leaching kinetics of scheelite. [8]
(b) Using the graphs Q2ii and Q2iii discuss if the use of ultrasound is effective in improving leaching kinetics for scheelite [5]
(c) How does the effectiveness of ultrasound depend on the particle size? Explain the scientific basis of this observation. [6]
(d) Ultrasound trials are being carried out to improve the leaching kinetics of scheelite, state and explain other two techniques you can implement in a mechanically agitated autoclave with ultrasound. [6]

Question 3

Zimbabwe discovered Uranium deposits in Hwange and Binga districts. The country in 2019 joined the Atomic Energy Agency (IAEA) and partnered with Russian State Atomic Energy Cooperation to look into mining and beneficiation of these deposits.

Uranium ores can be acid leached by weak sulphuric acid. Ion exchange can then be used to recover Uranium from the pregnant solution.

(a) Considering the graphs below, which Dowex resin would choose for use amongst the three above? Give reasons for your choice [7]
(b) Give possible explanation for the variations in breakthrough capacities at different acid concentration for one type of resin with the same influent concentration. [6]
(c) What other three factors can affect the resin absorbance? Suggest how its capacity can be improved in operation. [6]
(d) What other three factors would you consider in resin selection over and above its breakaway capacity? [6]

Figure 3 shows a comparison of three different resins. C_0 is influent and C effluent concentration.

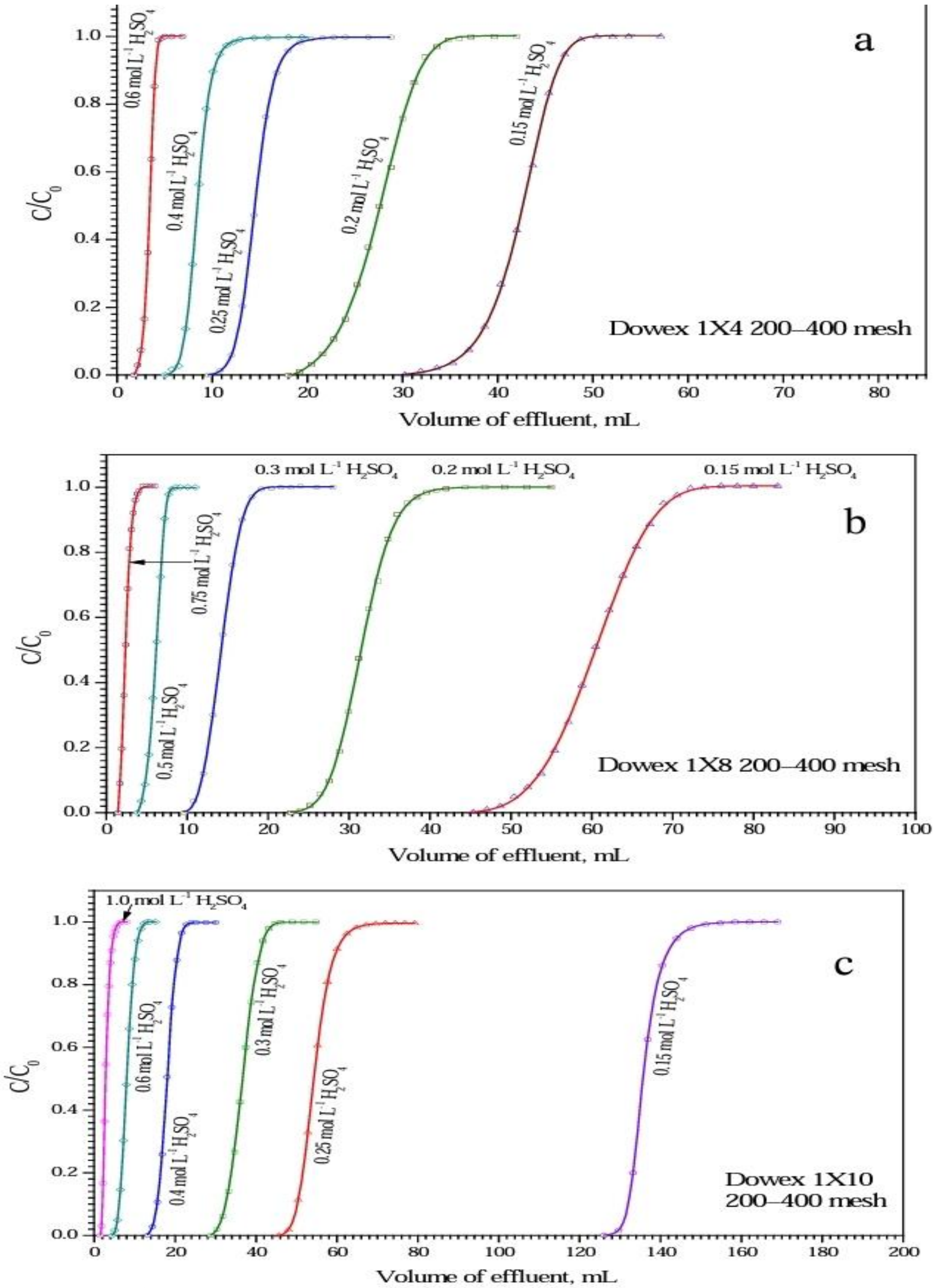


Fig. 3. The effect of H_2SO_4 concentration on the breakthrough curve of uranyl ions for resins of different cross-linking: X4 (a), X8 (b) and X10 (c). Concentration of the feed solution: 20 $\mu g \cdot mL^{-1}$ UO_2^{2-}. Column: 0.071 cm^2 × 5.0 cm; t = 20°C; u = 0.75 $cm \cdot min^{-1}$.

Question 4

As an engineer with expertise in hydrometallurgy designing a novel process for lead recovery from battery scrap involving the following steps:

Leaching – Insoluble lead (II) sulphate is converted to lead chloride by leaching in neutral sodium chloride brine solution

Purification – Milk of lime Ca(OH)2 and HCl is introduced to the leach solution to remove the dissolved sulphate as insoluble gypsum (calcium sulphate dehydrate) and keep the neutral pH

Electrowinning – finally the metallic lead and oxygen is produced by electrowinning from purified lead chloride solution.

(a) Provide the chemical reaction for each of the steps in the process [6]
(a) Draw a flowsheet for the process above. [4]
(a) On the flowsheet show areas of possible recycling of consumables [3]
(a) Calculate the minimum electrowinning potential to electro win lead at pH 7. Assuming one molar lead concentration. [5]
(a) Calculate the maximum electrowinning potential to avoid chloride gas evolution assuming one molar chloride concentration. [5]
(a) Explain why this process will not work efficiently under too acidic conditions and the process controls one need to put in place to ensure efficiency. [2]

Pb2+ + 2e-= Pb E^0 = -0.13V
½ Cl2 + e-= Cl E^0 = +1.36V

Question 5

Zimbabwe's platinum industry is not fully beneficiating its products locally. Some of the local mines export concentrates for smelting and some exports matte for refining. Understanding the platinum beneficiation and possibly improving it locally will help add local value to the precious finite resource to maximise local value. Platinum is leached by hydrochloric acid in PGM refining. Zinc cementation can be used to recover platinum from the solution.

$PtCl_6^{2-} + 4e^- = Pt + 6Cl^-$	E^θ +0.74V
$PdCl_4^{2-} + 2e^- = Pd + 4Cl^-$	E^θ 0.64V
$ZnCl_3^{4-} + 2e^- = Zn + 3Cl^-$	E^θ -0.78V

(a) Write balanced chemical equations for the cementation of Pt and Pd using Zn solids from the solution. Calculate the standard potential for the cementation. [4]
(b) Consider the typical pregnant solution concentration of Pt 59.4mg/l, Pd 37.2mg/l and Zn 7.7mg/l, and calculate the nonstandard potential for cementation on solid zinc. Atomic masses Pt 195 g/mol, Pd 106g/mol Zn 65 g/mol and Cl 35 g/mol, RT/F is 0.0592mV where R is the gas constant, T the temperature and F the Faraday constant. [6]

(c) What is the thermodynamics theoretically achievable recovery of platinum from solution using zinc cementation for batch pregnant solutions in (b)? [6]

(d) Nowadays resins are used to enrich the concentration of pregnant solution. Typical values would be Pt 2430 mg/l and Pd 499 mg/l. Discuss the effects of cementation on the lean pregnant solution or after resin concentration on the overall recovery, costs, reagent consumption and final product quality. [6]

(e) Another option for the recovery of Pt after ion exchange concentration is electrowinning. How does electrowinning compare to cementation in terms of costs, product quality and recovery? [3]

Additional Data

Standard Reduction Potentials in Aqueous Solutions at 25 °C

Oxidizing Agent				Reducing Agent	Reduction Potential (V)
F_2	+	$2e^-$	→	$2F^-$	2.87
H_2O_2	+	$2H^+ + 2e^-$	→	$2H_2O$	1.78
MnO_4^-	+	$8H^+ + 5e^-$	→	$Mn^{2+} + 4H_2O$	1.51
Au^{3+}	+	$3e^-$	→	Au	1.50
Cl_2	+	$2e^-$	→	$2Cl^-$	1.36
O_2	+	$4H^+ + 4e^-$	→	$2H_2O$	1.23
$Cr_2O_7^{2-}$	+	$14H^+ + 6e^-$	→	$2Cr^{3+} + 7H_2O$	1.23
Br_2	+	$2e^-$	→	$2Br^-$	1.07
NO_3^-	+	$4H^+ + 3e^-$	→	$NO + 2H_2O$	0.96
Ag^+	+	e^-	→	Ag	0.80
I_2	+	$2e^-$	→	$2I^-$	0.54
Cu^+	+	e^-	→	Cu	0.52
O_2	+	$2H_2O + 4e^-$	→	$4OH^-$	0.40
Cu^{2+}	+	$2e^-$	→	Cu	0.34
$2H_3O^+$	+	$2e^-$	→	$H_2 + 2H_2O$	0.00
Pb^{2+}	+	$2e^-$	→	Pb	−0.13
Sn^{2+}	+	$2e^-$	→	Sn	−0.14
Ni^{2+}	+	$2e^-$	→	Ni	−0.26
Fe^{2+}	+	$2e^-$	→	Fe	−0.45
Cr^{3+}	+	$3e^-$	→	Cr	−0.74
Zn^{2+}	+	$2e^-$	→	Zn	−0.76
$2H_2O$	+	$2e^-$	→	$H_2 + 2OH^-$	−0.83
Mn^{2+}	+	$2e^-$	→	Mn	−1.19
Al^{3+}	+	$3e^-$	→	Al	−1.66
Mg^{2+}	+	$2e^-$	→	Mg	−2.37
Na^+	+	e^-	→	Na	−2.71
Ca^{2+}	+	$2e^-$	→	Ca	−2.87
Ba^{2+}	+	$2e^-$	→	Ba	−2.91
K^+	+	e^-	→	K	−2.93
Li^+	+	e^-	→	Li	−3.04

Increasing Strength of Oxidizing Agent (↑)

Increasing Strength of Reducing Agent (↓)

Fig 4 SHE in aqueous solutions at 25 C.

END OF QUESTION PAPER