

# GWANDA STATE UNIVERSITY FACULTY OF ENGINEERING AND ENVIRONMENT DEPARTMENT OF METALLURGICAL ENGINEERING ADVANCED HYDROMETALLURGY EMR 5102 Part IV First Semester Examination Paper September 2023

This examination paper consists of 7 printed pages

Time Allowed: 3 hours

Total Marks: 100

Mr Tinashe Mabikire

#### **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

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#### Question 1.

Antimony Sb is used in the production of flame retardants, alloying, and brake pads. Zimbabwe has antimony found in sulphide minerals, mainly stibnite  $(Sb_2S_3)$ . Oxidative pyrometallurgical routes can recover antimony using the blast furnace (1200°C) or reverberatory furnace (1000°C). One of the hydrometallurgical routes that can be used to extract antimony includes leaching with a ferric chloride lixiviant in the following reaction Q1i.

$$Sb_2S_3 + 6Fe^{3+} \rightarrow 2Sb^{3+} + 6Fe^{2+} + 3S^0$$
 Reaction Q1i

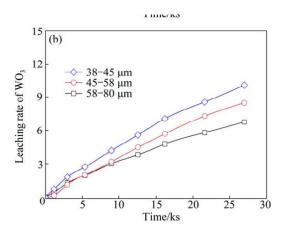
- a. State and briefly explain five possible advantages of the hydrometallurgical over pyrometallurgical process route in antimony extraction. [10]
- b. State and briefly explain five possible disadvantages of the hydrometallurgical route over the pyrometallurgical process route in antimony extraction. [10]
- c. State five ways the leaching of stibnite with ferric chloride can be accelerated. [5]

#### Question 2.

Tungsten is widely used in alloying and has reserves in Matabeleland South as scheelite CaWO<sub>4</sub>. 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<sub>2</sub>CO<sub>3</sub>. The leaching reaction is:

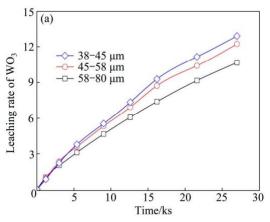
$$CaWO_4(s) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + NaWO_4(aq)$$
 Reaction Q2i

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

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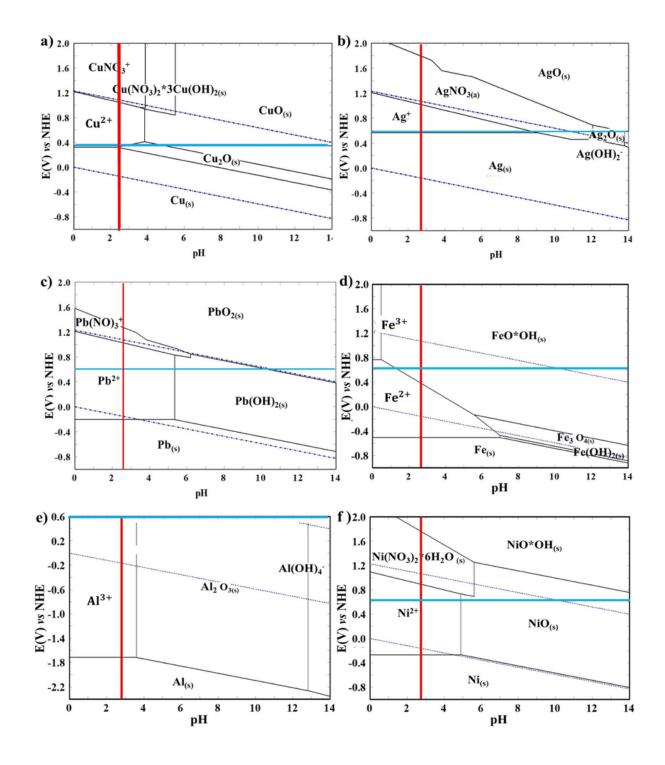


Graph Q2iii Scheelite leaching rate with ultrasound

- 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.

#### **Question 3**

With the accumulation of electronic waste, their disposal offers a source of metals from their recycling. Figure Q3i show the Eh-pH for most common metals found in electronic waste.



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Figure Q3i Pourbaix diagram for metals found in electronic waste leaching in 2 mol/dm<sup>3</sup> HNO<sub>3</sub> solution at 25°C, the vertical and horizontal bold lines represent the pH and potential restrictions for leaching. The concentration of metals is a) Cu 2.57M, b) Ag 0.16mM, c) Pb 9.54mM, d) 0.24M Fe, e) Al 0.32M, and f) Ni 0.24M

- a. What conditions of pH and Eh are ideal for the leaching of copper with nitric acid? [4]
- b. How will you control the pH to achieve your ideal leaching pH?
- c. Assuming complete dissociation what is the pH of 2 mol/dm<sup>-3</sup> HNO<sub>3</sub> solution at 25°C [5]

[2]

[2]

(4)

(4)

- d. How with you control the Eh to achieve the desired potential?
- e. What other metal will be leached at the same Eh-pH conditions? [4]
- f. How will you improve the selectivity of the leaching process to produce a pregnant solution rich only in copper?

#### **Question 4**

A gold miner uses vat or percolation leaching to recover gold using sodium cyanide. Residence time, cyanide concentration, tails grade and pH are some of the parameters they monitor in operation. However, they hardly measure the dissolved oxygen concentration, yet it is believed to be the rate-limiting factor.

The rate of oxygen consumption in a gold vat leaching operation is  $6.67 \times 10^{-6}$  /(m<sup>2</sup>s) at STP and only 3% of the oxygen is consumed in the gold dissolution reaction involving cyanide. The plant vat leach tanks have an ore profile 1.0\_m high, containing 1500\_kg/m<sup>3</sup> ore with 1.5g/ton gold. At STP molar volume is 22.4 litres.

- a. Estimate the rate of gold dissolution by cyanide leaching.
- b. How long will it take to extract 80% of the gold at that rate?
- c. How long will it take to extract 80% of the gold if only 0.45% of the oxygen were utilised for the cyanide gold reaction? (5)
- d. What two factors might cause different proportions of dissolved oxygen to be overly consumed by the cyanide gold reaction? (4)
- e. In what two different ways can the plant operator increase the rate of this gold dissolution reaction?
  (4)
- f. Explain how one of the factors you mentioned above will be better than the other in effectively increasing the rate of gold dissolution in cyanide. (4)

#### **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.

$PtCl_{6^2} + 4e = Pt + 6Cl$	$E^{\Theta}$ +0.74V		
$PdCl_{4^{2}} + 2e = Pd + 4Cl_{4^{2}}$	E <sup>θ</sup> 0.64V		
$\operatorname{ZnCl}_{3^{4}}$ + 2e = Zn + 3Cl	E <sup>θ</sup> -0.78V		
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- 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)
- 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)
- 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)

		A	queous sc	JILLIN	0115 at 25	C	
Oxidizing Agent			Reducing Agent			Reduction Potential (V)	
	F <sub>2</sub>	+	2e <sup>-</sup>	$\rightarrow$	2F-		2.87
Increasing Strength of Oxidizing Agent	$H_2O_2$	+	2H <sup>+</sup> + 2e <sup>-</sup>	$\rightarrow$	2H <sub>2</sub> O		1.78
	$MnO_4^-$	+	8H <sup>+</sup> + 5e <sup>-</sup>	$\rightarrow$	$Mn^{2+} + 4H_2O$		1.51
	Au <sup>3+</sup>	+	3e <sup>-</sup>	$\rightarrow$	Au		1.50
	Cl <sub>2</sub>	+	2e <sup>-</sup>	$\rightarrow$	2Cl <sup>-</sup>	gent	1.36
	O <sub>2</sub>	+	4H <sup>+</sup> + 4e <sup>-</sup>	$\rightarrow$	2H <sub>2</sub> O		1.23
	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	+	14H <sup>+</sup> + 6e <sup>-</sup>	$\rightarrow$	2Cr <sup>3+</sup> + 7H <sub>2</sub> O		1.23
	Br <sub>2</sub>	+	2e <sup>-</sup>	$\rightarrow$	2Br⁻	Ig Ag	1.07
	NO <sub>3</sub> <sup>-</sup>	+	4H <sup>+</sup> + 3e <sup>-</sup>	$\rightarrow$	NO + $2H_2O$	ducir	0.96
	Ag <sup>+</sup>	+	e <sup>-</sup>	$\rightarrow$	Ag	f Re(	0.80
	1 <sub>2</sub>	+	2e <sup>-</sup>	$\rightarrow$	21-	Increasing Strength of Reducing Agent	0.54
	Cu <sup>+</sup>	+	e <sup>-</sup>	$\rightarrow$	Cu		0.52
	O <sub>2</sub>	+	2H <sub>2</sub> O + 4e <sup>-</sup>	$\rightarrow$	40H-	ng S	0.40
	Cu <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Cu	reasi	0.34
	$2H_3O^+$	+	2e <sup>-</sup>	$\rightarrow$	$H_2 + 2H_2O$	Inci	0.00
	Pb <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Pb		-0.13
	Sn <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Sn		-0.14
engt	Ni <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Ni		-0.26
g Sti	Fe <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Fe		-0.45
asin	Cr <sup>3+</sup>	+	3e <sup>-</sup>	$\rightarrow$	Cr		-0.74
Incre	Zn <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Zn		-0.76
	2H <sub>2</sub> O	+	2e <sup>-</sup>	$\rightarrow$	H <sub>2</sub> + 20H <sup>-</sup>		-0.83
	Mn <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Mn		-1.19
	Al <sup>3+</sup>	+	3e <sup>-</sup>	$\rightarrow$	AI		-1.66
	Mg <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Mg		-2.37
	Na <sup>+</sup>	+	e	$\rightarrow$	Na		-2.71
	Ca <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Ca		-2.87
	Ba <sup>2+</sup>	+	2e <sup>-</sup>	$\rightarrow$	Ba		-2.91
	K+	+	e	$\rightarrow$	К		-2.93
	Li <sup>+</sup>	+	e <sup>-</sup>	$\rightarrow$	Li		-3.04

## Standard Reduction Potentials in Aqueous Solutions at 25 °C

Fig 4 SHE in aqueous solutions at 25 C.

### **END OF QUESTION PAPER**