National Exams May 2015

10-Met-B2, Hydrometallurgy and Electrometallurgy

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 two problems and chose any 3 out of the remaining 4 problems (i.e., problems 3-6).

4. All sub-questions within a problem are of equal value.

Marking scheme

Each problem is worth 20 marks

Given:
$R=8.314\ J\ mol^{-1}\ K^{-1}$
$F=96{,}485\ C\ g\text{-}eq^{-1}$
For all aqueous species, take activities = concentrations

Problem 1

Sketch a generic process flow diagram for a typical hydrometallurgical process and discuss the various unit operations associated with each step. Start with freshly excavated ore that contains a valuable metal A as well as impurities, and end with a finished product (metal or pure compound). Show liquid, solid, recycle and bleed streams, as well as effluents and residues produced. Try to be as detailed as possible.

Problem 2

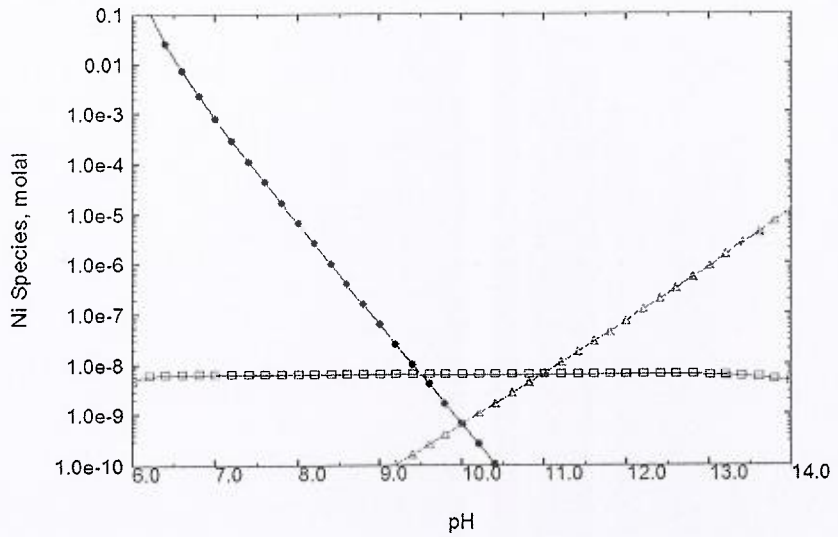
Define and identify the differences of the following terms briefly and concisely:

a) Hydrolysis and Hydration
b) Speciation Diagram and Distribution Diagram
c) Cementation and Precipitation
d) Anode and Cathode
e) Galvanic cell and electrolytic cell
f) Solubility and Dissolution
g) Saturation and supersaturation
h) Filtrate and raffinate
i) Ion exchange and solvent extraction
j) Electrowinning and electrorefining

Problem 3

The following graph is an idealised nickel hydroxide solubility diagram. The dominant Ni aqueous species considered in this diagram are Ni^{2+}, $Ni(OH)_{2(aq)}$, $Ni(OH)_3^-$.

a. Calculate the solubility product of nickel hydroxide
b. Label the Ni aqueous species (Ni^{2+}, $Ni(OH)_{2(aq)}$, $Ni(OH)_3^-$) on the graph.
c. Draw how the real solubility curve of Ni on this graph would look like using your pen or a highlighter.



Problem 4

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

a. *Leaching.* Insoluble lead(II) sulphate is converted to soluble lead chloride by leaching in a neutral (i.e., not acidic, nor alkaline) sodium chloride brine solution.
b. *Purification.* Milk of lime ($Ca(OH)_2$) and hydrochloric acid is introduced into the leach solution to remove the dissolved sulphate as insoluble gypsum (calcium sulphate dihydrate) and keep the pH neutral.
c. *Electrowinning.* Finally, metallic lead (and oxygen) is produced by electrowinning from the purified lead chloride solution (electrolysis).

1. Provide the relevant chemical reactions for each of the steps above.
2. Provide a fully labeled flowsheet for this process. Intermediate products must be recycled where possible.
3. Calculate the minimum electrowinning potential to electrowin lead at pH=7. Assume a reasonable lead concentration.
4. Calculate the maximum electrowinning potential to avoid chlorine gas evolution at pH=7. Assume a reasonable chloride concentration.
5. Explain why electrowinning may not work efficiently under very acidic conditions and what process controls one needs to put in place.

State any additional assumptions in any question above clearly.

$Pb^{2+} + 2e^- \rightarrow Pb$ $\quad e° = -0.13$ V

$\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-$ $\quad e° = +1.36$ V

Problem 5

Ni is electrodeposited from an aqueous sulphate solution that has a composition that fluctuates from 1 to 0.01 M due to changes in the feed composition of the process.

a) What is the pH range that this electrodeposition can be conducted in order to avoid hydrogen gas evolution and nickel hydroxide precipitation? Take activities equal to concentrations. Given:

$Ni^{2+} + 2\,e^- \leftrightarrow Ni$ $\quad e^\circ = -0.25$ V

$Ni^{2+} + 2H_2O \leftrightarrow Ni(OH)_2(s) + 2H^+$ $\quad \log K = -12.73$

b) Make a rough sketch of the electric circuit and mark the anode, cathode, positive electrode, negative electrode, and show the reactions at the cathode, reactions at the anode.

c) Regardless of the outcome of question a) above, one decides to electrowin Ni at pH=2. Assume that at this pH 30% of the charge is being used for hydrogen ion reduction. How many L of hydrogen gas are evolved per kg of Ni produced?

Problem 6

Referring to the Eh-pH diagram presented in the Figure below Co-H_2O system:

a) Identify all possible reaction paths (including combined thermochemical/hydrochemical treatment) that may be used to dissolve a feed material consisting of cobalt oxide (Co_3O_4).
b) For each reaction path, provide the relevant chemical equation.
c) Indicate whether each selected reaction path is non-oxidative, oxidative, or reductive.
d) For each dissolution scheme, provide a corresponding well-labelled simplified flow-diagram.