Lecture 11

Benefits of mass transport effect (hydrodynamic effect) on metal recovery by electrochemical methods

Goal of the Lecture

The goal of this lecture is to introduce students to the crucial role of mass transport and hydrodynamic enhancement in electrochemical metal recovery processes. Students will understand how forced convection, flow field design, and hydrodynamics influence limiting current, recovery efficiency, deposition quality, and energy consumption. The lecture also emphasizes modelling tools used to optimize these processes.

Lecture Objectives

By the end of this lecture, students will be able to:

1. ***Describe** mass transport mechanisms (diffusion, migration, convection) involved in metal recovery.*
2. ***Explain** the concept of limiting current and identify when metal recovery becomes mass-transport controlled.*
3. ***Apply** dimensionless groups (Sh, Re, Sc, Da) to analyze flow-enhanced transport in electrochemical recovery.*
4. ***Evaluate** the effects of hydrodynamic design (RDE, flow cells, turbulence) on deposition rate and efficiency.*
5. ***Construct** simplified coupled Nernst–Planck–Butler–Volmer models to simulate hydrodynamic enhancement in COMSOL Multiphysics.*

Metal recovery by electrochemical methods (such as electro-winning, electro-refining, and electro-recovery from waste streams) is increasingly important in circular economy and sustainable materials processing. In these processes, mass transport – i.e., the movement of ionic species from the bulk solution to the electrode – plays a decisive role in determining deposition rate, current efficiency, energy consumption, and deposit morphology. Hydrodynamic conditions (stirring, flow, turbulence) directly control mass transport, thus significantly influencing the overall recovery efficiency.

Mass Transport Mechanisms in Electrochemical Systems

The total flux J_i of an ionic species i is given by the Nernst–Planck equation:

$$J_i = -D_i \nabla c_i - z_i u_i c_i \nabla \phi + v c_i$$

where D_i - diffusion coefficient, u_i - ionic mobility, ϕ - potential, and v - velocity vector of solution.

In metal recovery, forced convection (hydrodynamics) is often the dominant term enhancing transport to the electrode.

Limiting Current and Mass Transport Control

When reduction of metal ions at the cathode is fast, the overall rate becomes limited by ion transport. The diffusion-limited current density is:

$$j_{lim} = nFk_m C_{bulk}$$

where k_m = D/δ is the mass-transfer coefficient, and δ is the diffusion layer thickness. A thinner diffusion layer increases k_m and enhances recovery rate.

Hydrodynamic Effects: Theory and Modelling

In quiescent solutions, the diffusion layer has δ ≈ 0.1–1 mm. Flow reduces δ, increasing the concentration gradient and deposition rate. The correlation between flow and mass transport can be expressed using dimensionless numbers:

$$Sh = \frac{k_m L}{D} = aRe^b Sc^c$$

where $Sh = k_m L / D$, $Re = \rho v L/\mu$, and $Sc = \mu/\rho D$. Where Re is Reynolds, Sc is Schmidt, Sh is Sherwood number.

Example: For a rotating disk electrode (RDE), $k_m = 0.62\ D^{2/3}\ v^{-1/6}\ \omega^{1/2}$.

Benefits of Enhanced Mass Transport

Enhanced hydrodynamics lead to several benefits:

- Increased deposition rate and faster metal recovery.
- Improved current efficiency by reducing competing reactions.
- Reduced energy consumption through lower overpotentials.
- Enhanced deposit quality (uniform, smooth, dense).
- Feasibility for recovery from dilute solutions.

Modelling Hydrodynamic Effects

A coupled transport–kinetic model combines Nernst–Planck and Butler–Volmer equations. The surface flux relates to current density as:

$$j = zFD\left.\frac{dc}{dy}\right|_{y=0}$$

and interfacial kinetics as:

$$j = j_0\left[\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(-\frac{\alpha_c F\eta}{RT}\right)\right]$$

Dimensionless analysis uses Sherwood (Sh), Reynolds (Re), and Damköhler (Da) numbers to identify control regimes. A high **Re** (strong flow) → high **Sh** → mass-transport enhancement. The interplay between **Da** and **Sh** indicates the controlling regime:

$Da \ll Sh$: kinetics-controlled,
$Da \gg Sh$: transport-controlled.

Example: Copper recovery from dilute $CuSO4$ solution. Given $c_{bulk} = 1\times10^{-3}$ mol/L, $D = 7\times10^{-10}$ m^2/s, δ = 1 mm (no flow), $k_m = 7\times10^{-7}$ m/s. For δ = 50 μm (flow), $k_m = 1.4\times10^{-5}$ m/s. Thus, $j_{lim(flow)}/j_{lim(static)} \approx 20$ ⇒ ~20× enhancement with flow.

Hydrodynamic enhancement of mass transport is a key factor in optimizing electrochemical metal recovery systems. Proper flow design enables faster deposition, better efficiency, improved quality, and sustainable recovery from dilute feeds. Model-based approaches allow scale-up from laboratory to industrial systems effectively.

Questions for Self-Examination

1. What is the role of mass transport in electrowinning, electrorefining, and metal recovery from waste streams?
2. Why does hydrodynamic flow reduce the diffusion-layer thickness?
3. Explain the terms in the Nernst–Planck equation and state when convection becomes dominant.
4. Define limiting current density. Under what conditions does metal recovery become diffusion-limited?
5. How do Reynolds (Re), Schmidt (Sc), and Sherwood (Sh) numbers relate to mass transport?
6. For a rotating disk electrode (RDE), why does the mass transfer coefficient scale as $\omega^{1/2}$?

7. What are the benefits of hydrodynamically enhanced mass transport in metal recovery?
8. Explain the concept of Damköhler number (Da) and its interpretation for kinetics vs transport control.
9. Why does increased flow improve current efficiency and reduce energy consumption?
10. How can modelling guide the design of hydrodynamic systems for sustainable metal recovery?

Self-Study Assignment

Assignment Title:

Simulation of Hydrodynamic Enhancement in Electrochemical Metal Recovery Using Coupled Transport–Kinetics Modelling

Objective:
To investigate how flow-induced mass transport enhancement affects metal recovery rate and limiting current by modelling forced-convection electrodeposition in COMSOL Multiphysics.

Tasks

1. Geometry and Physics Setup

Choose one of the following configurations:

- **Rotating Disk Electrode (RDE)** (2D axisymmetric), or
- **Flow-by Cell / Parallel Plate Cell** (2D laminar flow).

Add the following physics:

- **Laminar Flow (spf)** → hydrodynamics
- **Transport of Diluted Species (tds)** → Nernst–Planck diffusion + convection
- **Electrode Surface Reaction** → Butler–Volmer kinetics

2. Governing Equations

- Flux of metal ion M^{n+}:

$$\mathbf{N}_M = -D\nabla c_M - uzFc_M\nabla\phi + c_M\mathbf{v}$$

- Electrode kinetics:

$$i = i_0\left[e^{\alpha_a F\eta/RT} - e^{-\alpha_c F\eta/RT}\right]$$

- Ion flux–current relation:

$$N_M = -\frac{i}{nF}$$

3. Simulation Tasks

1. Apply a potential step sufficient to drive metal-ion reduction.
2. Simulate three flow velocities:
   - $v = 0$ (no convection)
   - $v = 0.01$ m/s
   - $v = 0.05$ m/s
3. Compare:
   - Concentration boundary-layer thickness
   - Local and total current densities
   - Deposition rates along electrode
4. Extract the mass-transfer coefficient k_m from concentration gradients.

4. Dimensionless Analysis

Compute:

- Reynolds number $Re = \frac{\rho v L}{\mu}$
- Schmidt number $Sc = \frac{\mu}{\rho D}$
- Sherwood number $Sh = \frac{k_m L}{D}$

Use results to evaluate transport enhancement.

5. Plot and Interpret

- Concentration profiles for each velocity

- Current density distributions
- Deposition flux
- Sh vs $Re^{1/2}$ or $Re^{0.8}Sc^{1/3}$ correlations

Explain why deposition rate increases with flow and how limiting current changes.

6. Report (2–3 pages)

Include:

- Full model description
- Dimensionless analysis tables
- Plots and interpretation
- Discussion of practical implications for metal recovery efficiency

Learning Outcomes

Learning Outcome (LO)	**Indicator of Achievement (ID)**	**Description**
LO 3: Explain the principles of key computational and numerical modeling techniques used in electrochemical science.	**ID 3.5:** Explain how improved metal deposition can be achieved via mass transport effects.	Students will analyze and model how hydrodynamic enhancement improves metal recovery efficiency and deposition quality.

References

1. Bard & Faulkner, *Electrochemical Methods*, 2001.
2. COMSOL Multiphysics examples on laminar flow + electrodeposition.