Lecture 11

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

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:

$$j = zFD\frac{dc}{dy}\bigg|_{y=0}$$

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, $\delta = 1$ mm (no flow), $k_m = 7\times10^{-7}$ m/s. For $\delta = 50$ µm (flow), $k_m = 1.4\times10^{-5}$ m/s. Thus, $j_{lim(flow)}/j_{lim(static)} \approx 20 \Rightarrow \sim20\times$ 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.