

Simulating the Effect of Forced Electrolyte Flow in Pyroprocessing with Liquid Cathodes

Applied Physics: Bachelor End Project
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Simulating the Effect of Forced Electrolyte Flow in Pyroprocessing with Liquid Cathodes

by

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to obtain the degree of Bachelor of Science

at the Delft University of Technology,

to be defended publicly on Thursday July 2nd, 2026 at 14:30.

Student number:	5848296
Project duration:	April 13th, 2026 - July 2nd, 2026
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Abstract

Molten salt reactors (MSRs) are well suited to a closed fuel cycle, in which actinides are recovered from spent fuel and recycled rather than discarded. This requires reprocessing the salt to recover fissile actinides and remove neutron-absorbing lanthanides. Pyroprocessing with a liquid metal cathode achieves this through electrowinning, depositing metal ions selectively by their reduction potentials. Forced electrolyte flow can enhance mass transfer to the cathode, but its hydrodynamics have not previously been combined with an electrochemical model of a liquid cathode.

This work investigates how forced flow of a NaCl–KCl electrolyte influences mass transfer to a liquid bismuth cathode, using CFD simulations in OpenFOAM. A zero-concentration boundary model (Part A.1), validated against the data of Pickett and Recio, reproduced the expected mass-transfer trends. A Butler–Volmer boundary model (Part A.2) showed that the cathode current density saturates at a transport-limited value near -0.4 V and rises with electrolyte velocity. A multiphase model (Part B) gave a critical velocity of 1.36 m/s for Kelvin–Helmholtz instabilities, well above the laminar limit of 0.11 m/s.

Increasing the electrolyte velocity is therefore an effective way to raise the limiting current density and throughput, with interfacial instabilities as the ultimate constraint.

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1

Introduction

With increasing energy demands worldwide, it remains challenging to transform all energy production into sustainable form. Nuclear energy provides a stable, sustainable solution for this challenge. After several generations of nuclear reactor designs, the Generation IV International Forum has selected six promising reactor technologies with improved safety, sustainability, efficiency and cost. One of these technologies is the molten salt reactor (MSR) [34].

1.1. Molten salt reactor

In general, MSRs are a class of nuclear reactors which uses molten salts as a coolant. While there exist many types of specific MSR designs, two categories can be distinguished [42]:

1. In a solid-fueled MSR design, the molten salt only serves as a low-pressure coolant. The nuclear fuel is still kept in a solid state. This type of reactor is often referred to as 'Fluoride salt-cooled High-temperature Reactor' (FHR).
2. In liquid-fueled MSR designs, the fissile materials are dissolved with the molten salt. The fission reaction occurs in the fuel salt, heating up the mixture. The molten salt then flows into a heat exchanger where heat is exchanged with a coolant salt (Figure 1.1). This coolant salt is then used to generate steam or gas, producing electricity.

In this report, the liquid-fueled MSR is considered, a design concept with the possibility of a closed fuel cycle. A closed fuel cycle means recovering the valuable actinides from spent fuel and feeding them back into the reactor, rather than discarding them as waste in a "once-through" cycle. MSRs are well suited to this because they can burn a wide range of actinides [15].

Advantages compared to a light water reactor

Currently, the most widely deployed reactor type is the light water reactor (LWR) [27], which uses ordinary water as both coolant and neutron moderator. Compared to these conventional reactors, MSRs offer several advantages.

Safety features MSRs have numerous inherent safety features. The primary systems operate at low pressure (< 5 bar), and since the boiling point of the fuel salt is much higher than the operating temperature of the reactor, it is essentially impossible for the pressure to increase with increasing temperature. Furthermore, if the fuel temperature rises, the molten salt expands, leading to a lower neutron flux, which creates a negative feedback loop and prevents criticality accidents [8].

Fuel cycle Conventional LWRs operate on a once-through, open fuel cycle (Figure 1.2a): uranium is burned once and the spent fuel, still containing significant unused fissile material, is stored as long-lived, high-level radioactive waste. While countries with abundant uranium reserves have generally accepted this approach, it leaves much of the fuel's energy potential unused and produces waste that

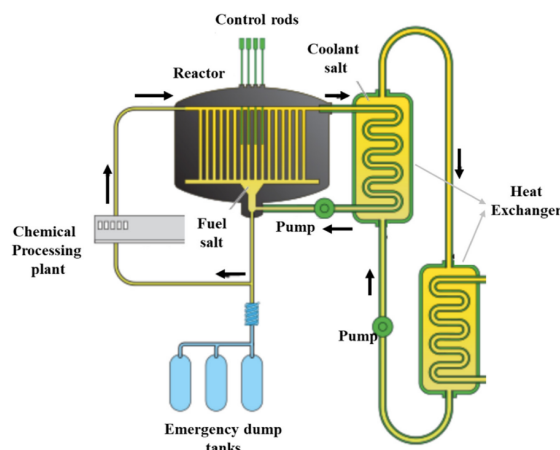


Figure 1.1: Schematic illustration of a liquid-fueled MSR design [42]. Pyroprocessing takes place in the ‘Chemical processing plant’.

remains radiotoxic for a very long time [46]. A closed fuel cycle (Figure 1.2b) addresses both issues by reprocessing spent fuel to recover and recycle its remaining uranium and plutonium, reducing waste volumes and making better use of the original resource. The molten salt reactor is particularly well-suited to closing the fuel cycle. By recycling actinides rather than discarding them, MSRs have the potential to both reduce the amount of produced nuclear waste and extract far more energy from the fuel than a conventional LWR reactor [34].

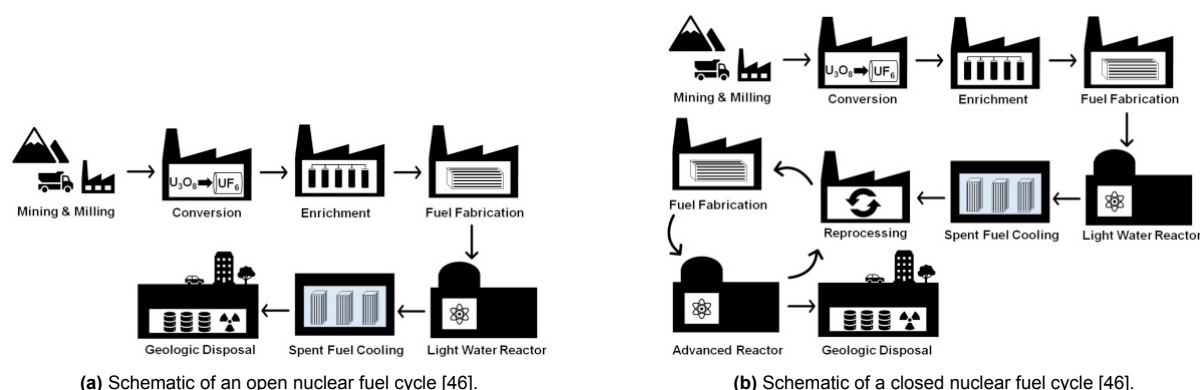


Figure 1.2: Schematics of open and closed nuclear fuel cycles

Refueling while operating An LWR uses solid fuel, so it must shut down periodically to replace the fuel assemblies, which lowers its availability [34]. In a liquid-fueled MSR the fuel is a flowing salt that can be added or removed while the reactor stays at power. This keeps the reactivity of the core nearly constant over time and allows fission products to be removed continuously instead of building up. This allows an MSR to operate continuously, providing more economic value [34].

1.2. Pyroprocessing

Despite the promising properties of MSRs, several challenges remain before widespread deployment is feasible. A key issue is the management of spent fuel and fission products that accumulate in the molten salt over time [34]. These must be continuously or periodically removed to maintain reactor performance and prevent the buildup of neutron-absorbing fission products. This requires dedicated reprocessing technologies capable of operating at high temperatures with highly radioactive materials [17].

Pyroprocessing is one technology being developed to address this need, being a collective term for sev-

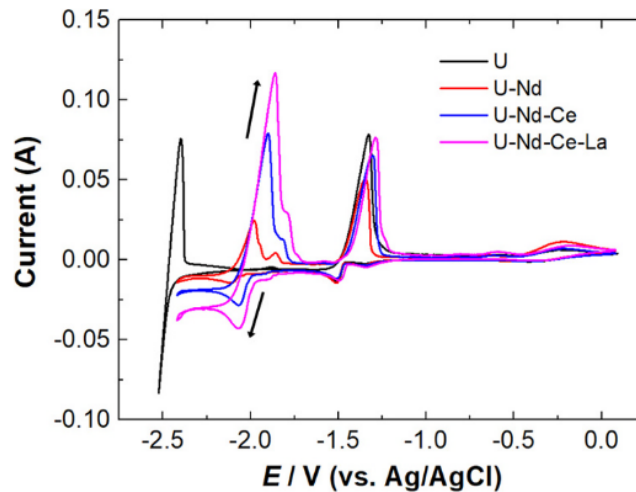


Figure 1.3: Cyclic voltammograms obtained at a tungsten working electrode in LiCl-KCl molten salt containing U and Ln elements (Nd, Ce, and La) at 723.15 K [17].

eral high-temperature methods used to reprocess spent nuclear fuel (SNF) in a molten salt electrolyte. The fact that pyroprocessing uses a molten salt electrolyte makes the process compatible with MSR fuel cycles [34]. In pyroprocessing, two main extraction routes can be distinguished. In reductive extraction, the separation is driven thermodynamically. In electrolytic extraction, the separation is instead driven electrochemically by an applied voltage. In this work, the electrolytic extraction is considered.

The materials targeted by this reprocessing can be divided into two groups, which are removed for different reasons. The actinides (e.g. uranium, plutonium), are valuable fissile materials. Recovering them from the spent fuel and feeding them back into the reactor is what enables the closed fuel cycle described above: it extracts more energy from the original resource and reduces the volume and long-term radiotoxicity of the remaining waste [34, 46]. The lanthanides, by contrast, are fission products that accumulate as the fuel is burned. Several of them are strong neutron absorbers, so their buildup captures neutrons and degrades the reactivity of the core [34]. A successful reprocessing technique must achieve both ends at once. This is only useful if the two groups can be cleanly separated from one another.

Selective deposition

Electrolytic extraction separates elements by exploiting differences in their reduction potentials [1]. Because each metal chloride has a distinct standard electrode potential, dissolved species are reduced at the cathode in a fixed order: the most readily reduced ions, such as uranium, deposit before the more stable fission-product chlorides, such as the lanthanides. Figure 1.3 shows a cyclic voltammogram of the electrochemical separation of uranium from lanthanides (Nd, Ce and La) [17]. The x-axis displays the voltage applied to the cell and the y-axis the resulting current, which serves as an indicator of how much material is being deposited. Uranium exhibits redox reactions at approximately -1.5 V, while the lanthanides only become electrochemically active near -2.0 V and beyond. This separation of roughly 0.5 V between the deposition potentials of uranium and the lanthanides means that, as the applied voltage is swept to more negative values, uranium deposits selectively before the lanthanides, providing a practical basis for their separation [17].

Solid and liquid metal cathodes

The choice of cathode strongly affects this selectivity. The cathode material plays an important role in determining which elements can be deposited and how they can be recovered afterwards. Two types of cathodes are commonly used: solid metal cathodes and liquid metal cathodes. A useful measure of selectivity is the potential gap between the most electronegative actinide and the least electronegative lanthanide: a larger gap means the two groups deposit at more clearly separated potentials and can

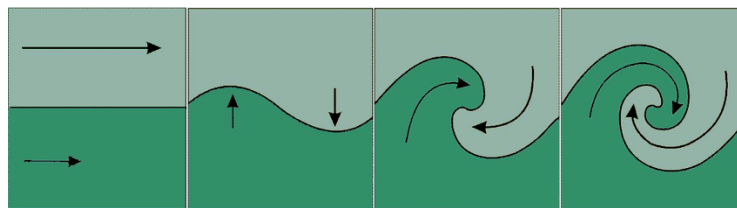


Figure 1.4: Kelvin-Helmholtz instability in shear flow. A small velocity perturbation, perpendicular to the shear flow direction, initiates a Kelvin-Helmholtz instability and causes roll up of the shear layers [25].

therefore be separated more cleanly [1].

Solid cathodes, typically made of steel, are simple to use but deposit the extracted material as a solid structure, making recovery difficult. In addition to this, solid cathodes suffer from limited reduction selectivity, since this potential gap is relatively small [17].

Liquid metal cathodes, such as cadmium or bismuth, offer several advantages over solid cathodes. Their low melting point allows them to remain liquid during operation, and their ability to form intermetallic compounds with uranium and transuranic elements (elements with an atomic number greater than 92) enables a higher selectivity in the deposition process [17, 42]. The formation of these intermetallic compounds lowers the activity coefficient of the deposited species, so that, as the Nernst equation (Equation 2.12) shows [2], a less electronegative potential is required to reduce the metallic ions. This shifts the deposition potentials of the actinides relative to the lanthanides, widening the potential gap between the most electronegative actinide and the least electronegative lanthanide and thereby improving the separation compared to a solid cathode [43].

Interfacial instabilities

Because the liquid metal cathode and the molten salt form two stratified, immiscible layers, the flowing electrolyte shears against the cathode surface. When the relative velocity between the two phases becomes sufficiently large, this shear triggers Kelvin-Helmholtz instabilities at the liquid-liquid interface [5], which grow into interfacial waves and can entrain droplets of the liquid metal into the electrolyte. Figure 1.4 presents a schematic representation of these waves. Such entrainment is undesirable for two reasons: it removes cathode material, reducing the amount available to capture the deposited actinides [17], and it contaminates the molten salt with the cathode metal. Since forced flow is introduced precisely to enhance mass transfer, the electrolyte velocity must remain below the threshold at which these instabilities set in, making interfacial stability an important design constraint for a liquid-cathode cell.

1.3. Literature

This work models electrolyte flow with an electrochemical model of a liquid-cathode electrowinning cell using a CFD simulation, and builds on prior research: experimental studies of mass transfer in flow cells used for validation, experimental and review work on pyroprocessing and liquid metal cathodes, and modelling studies of electrochemical cells.

Several studies of mass transfer in parallel-plate flow cells provide a basis for validating the CFD model. Although these studies do not concern pyroprocessing, their simple geometry makes them well suited for validating the CFD model. Pickett and Ong, hereafter Pickett [26] measured average mass transfer coefficients in a rectangular electrolytic cell over a range of electrode lengths and Reynolds numbers, characterising the hydrodynamic and mass-transfer entrance effects for both developing and fully developed flow. Because their geometry matches the duct studied here, their data form the primary benchmark for Part A.1. Recio et al. [28] examined the same geometry and showed that nanostructuring the cathode raises the mass transfer coefficient relative to a polished electrode. Their well-documented cell dimensions make them a well suited second benchmark.

On the application side, Koyama et al. [19] recovered uranium from a U–Pu–Zr alloy by molten-salt electrorefining in LiCl–KCl at high current efficiency: that work concerns electrorefining, whereas the electrowinning route is studied here. More directly related, Jung et al. [17] separated uranium and lan-

thanides from LiCl–KCl using bismuth and cadmium liquid cathodes. Their study supports the selective-deposition picture, motivates treating the deposited species as U^{3+} (since U^{4+} is first reduced to U^{3+}). The transport of metals once they enter the cathode has been reviewed by Wang et al. [43].

For the numerical treatment, several frameworks exist for modelling electrochemical cells [7, 40]. Van Soestbergen [40] couples Butler–Volmer kinetics with mass transport, as implemented in the Part A.2 boundary condition; Cumberland and Yim [7] provide an estimation for the exchange current density parameter in the Butler–Volmer equation. The zero-concentration boundary used in Part A.1 to isolate mass transport is itself well established, having been introduced for limiting currents by Rosenberg and Tirrell [30], by Tanaka [37], and Ge et al. [12]. Finally, the decision to neglect electromigration follows the established result that a supporting electrolyte reduces the limiting current to its diffusion-controlled value [31, 39].

1.4. Research question

Although the individual building blocks of this problem are well studied, they have not yet been combined. Mass transfer in parallel-plate flow cells has been thoroughly characterised [26, 28], but these studies concern neither pyroprocessing nor liquid cathodes. Experimental and review work on pyroprocessing with liquid metal cathodes [17, 19, 43], on the other hand, establishes the selective-deposition behaviour at the cathode, but does not investigate the hydrodynamics of the flowing electrolyte. Finally, existing numerical frameworks for electrochemical cells couple Butler–Volmer kinetics with mass transport [7, 40], but have not been applied to a molten salt flowing over a liquid cathode.

To close this research gap, the influence of electrolyte velocity is explored in this article, aiming to answer the research question: *How does forced flow of a liquid molten salt electrolyte influence the mass transfer between the molten salt and a liquid cathode during pyroprocessing, and what are the limitations in this process?*

This research question is divided into four sub-questions:

- What is the effect of forced electrolyte flow on the limiting current density?
- What is the effect of overpotential on the current density at the cathode surface?
- What are the limiting factors when increasing the electrolyte flow velocity?
- What is the appropriate velocity boundary condition for simulating liquid-liquid interfaces?

In reality, electrochemical systems are very complex to model. Therefore, to be able to model the system, a few assumptions are made. At first, only the laminar flow regime is considered. Additionally, the electrolyte is assumed to only contain one fission product or fissile material at a time, neglecting possible interactions between these materials. Finally, this report focuses on the transport phenomena of actinides and lanthanides in the molten salt electrolyte, while the transport phenomena of the extracted materials within the liquid cathode are intended to be included in future work; when the extracted materials enter the liquid cathode, they are assumed to be "recovered" from the electrolyte.

1.5. Thesis outline

In this chapter, a description of the molten salt reactor and the pyroprocessing technique was given, together with an overview of the existing literature and the relevance of the research with regard to the research questions. In order to answer these research questions, in chapter 2 an overview is given of the relevant theory, consisting of the fundamental fluid dynamics and dimensionless numbers governing flow and mass transfer, the electrowinning process described through the Nernst and Butler–Volmer equations, the transport mechanisms within the molten salt, and the Kelvin–Helmholtz criterion used to predict interfacial instability. In chapter 3, the simulated setup is described and the three evaluated cases are defined: a single-phase model with a zero-concentration cathode boundary (Part A.1), an extended single-phase model using the Butler–Volmer equation as boundary condition (Part A.2), and a multiphase model of the liquid-liquid interface (Part B), each with its numerical setup and validation method. In chapter 4, the results of the numerical simulations for the various cases are presented. In chapter 5, these results are interpreted and the assumptions underlying the model are discussed. The thesis is concluded and recommendations for further research are given in chapter 6.

2

Theory

This chapter sets out the physical and electrochemical principles needed to model the system. It covers the fundamental fluid dynamics and dimensionless numbers governing flow and mass transfer, the electrowinning process and its description through the Nernst and Butler-Volmer equations, and the transport mechanisms within the molten salt, before introducing the Kelvin-Helmholtz criterion used to predict interfacial instability.

2.1. Fundamental fluid dynamics

Navier-Stokes equation

The flow of the molten salt electrolyte is governed by the Navier-Stokes equations [6]. For an incompressible, Newtonian fluid, these consist of the continuity equation and the momentum equation. The continuity equation expresses conservation of mass:

$$\nabla \cdot \mathbf{v} = 0 \quad (2.1)$$

with $\mathbf{v}$ being the velocity; the divergence of the velocity field is zero. The momentum equation expresses conservation of momentum:

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g} \quad (2.2)$$

where $\mathbf{v}$ is the velocity field (m/s), ρ the fluid density (kg/m³), p the pressure (Pa), μ the dynamic viscosity (Pa · s), and $\mathbf{g}$ the gravitational acceleration (m/s²). The left-hand side represents the inertial forces, while the right-hand side contains the pressure gradient, viscous forces, and gravitational body force, respectively. In this work, the molten salt is treated as incompressible, so Equation 2.1 holds throughout the domain and Equation 2.2 fully describes the electrolyte flow [6].

Dimensionless numbers

Dimensionless numbers allow comparison of fluid behavior across different conditions by expressing complex interactions into a single ratio. In this article, several dimensionless numbers are of interest. The Reynolds number indicates the ratio between inertial and viscous forces. Based on this number, it can be determined if a flow is laminar or turbulent [36]:

$$\text{Re} = \frac{v d_e}{\nu} \quad (2.3)$$

where v is the flow velocity (m/s), d_e the equivalent diameter (m), and ν the kinematic viscosity (m²/s). A ‘fully developed’ laminar flow occurs when $\text{Re} < 2300$. When $\text{Re} > 2900$, the flow is generally considered

turbulent [32]. In these dimensionless numbers, a characteristic length d_e is used. For a rectangular duct, this parameter, being the equivalent diameter is defined as [44]:

$$d_e = \frac{4A_{cross}}{P} = \frac{4WS}{2(W+S)} \quad (2.4)$$

with A_{cross} being the cross-sectional area (m^2), P the perimeter (m), and W , S respectively being the width and height of the duct (m).

Another important dimensionless quantity, particularly of interest when investigating mass transfer, is the Sherwood number. This quantity is defined as the total mass transfer rate, divided by the diffusion rate:

$$Sh = \frac{k_m d_e}{D} \quad (2.5)$$

In this equation, k_m is the mass transfer coefficient (m/s), d_e the equivalent diameter (m) and D the diffusion coefficient (m^2/s).

Mass transport

Fick's law (Equation 2.6) states that the diffusion flux J of a substance is proportional to the concentration gradient dc/dx , with the diffusion coefficient D as proportionality constant. The steeper the concentration gradient, the faster the net movement of molecules diffusing from a high to low concentration:

$$J = \frac{\dot{n}_A}{A} = -D \frac{dc}{dx} \quad (2.6)$$

with J the diffusion flux (mol/m^2s), $\dot{n}_A$ the molar flow rate (mol/s), A the effective mass transfer area (m^2), D the diffusion coefficient (m^2/s), and dc/dx the concentration gradient (mol/m^4).

Equation 2.7 describes mass transfer in a simplified form: the rate is the driving force $c_b - c_s$ times an effective area and a single coefficient k_m . Here c_b is the bulk concentration in the fluid, and c_s the concentration at the surface, while k_m absorbs all the detail of how diffusion and convection move species across the boundary layer. Therefore, the mass transfer coefficient k_m is a measure of how efficient mass transfer occurs in a system:

$$\dot{n}_A = k_m A (c_b - c_s) \quad (2.7)$$

with $\dot{n}_A$ being molar flow rate (mol/s), k_m the mass transfer coefficient (m/s), A the effective mass transfer area (m^2), and c_b , c_s respectively the bulk and surface concentrations (mol/m^3).

2.2. The electrowinning process

The goal of electrowinning is extracting metallic ions that are dissolved in a solution. In this process, a voltage is applied over an inert anode (anode that does not consume itself during the reaction) and a cathode, causing the metallic ions to deposit onto the cathode.

A practical application of electrowinning is the conversion of impure metal ores (e.g. gold, copper, nickel) into pure metals [21]. In Figure 2.1, a schematic representation of the electrowinning of copper is displayed. In this process, the dissolved copper cations (positively charged ions) Cu^{2+} are reduced to form solid copper $Cu(s)$ which can then be recovered from the cathode.

In this report, the electrowinning of lanthanides and actinides from a NaCl-KCl molten salt is considered. After extraction, some of these materials can be reused as nuclear fuel [17]. This process can be described using two half-reactions that are combined into a total reaction.

Reduction half-reaction In the reduction half-reaction, metallic cations absorb electrons and are reduced into solid form. This chemical reaction takes place at the cathode surface:



where M represents any metallic ion. For the specific case of uranium, the reaction is:



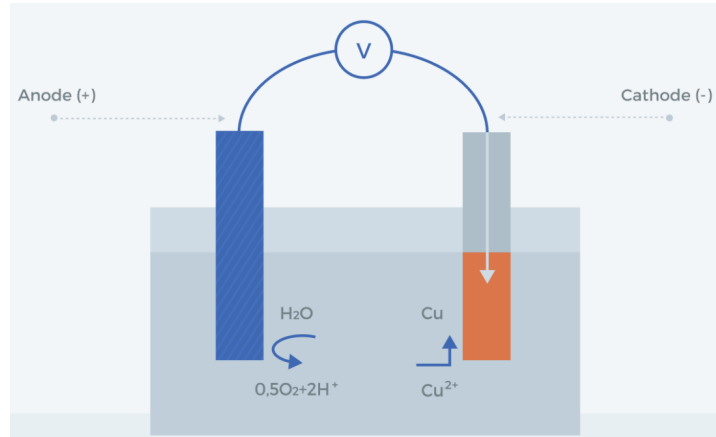


Figure 2.1: Electrowinning process of copper [45]. Copper cations are deposited onto the cathode (right).

Oxidation half-reaction As mentioned before, the anode itself is not consumed during the reaction. Instead, the chloride anions (negatively charged ions) are oxidized to form chloride gas:



Total reaction After equaling the number of electrons, these half-reactions can be combined into a total reaction. For the case of uranium, this results in:



The total reaction shows that, in the process of electrowinning uranium, the UCl_3 is converted into solid uranium and gaseous chloride. This process is similar for other actinides and lanthanides.

2.2.1. Butler-Volmer equation

The electrowinning process is carried out by applying a cell voltage over the anode and the cathode. When the applied cell voltage deviates from the equilibrium cell voltage, a net electrochemical reaction occurs and current flows through the cell. This current depends on the overpotential η , which is defined as the difference between the applied voltage and the equilibrium potential:

$$\eta = E - E_{eq} \quad (2.8)$$

where E is the applied voltage to the cell (V) and E_{eq} the equilibrium potential (V).

The simple Butler-Volmer (BV) equation (Equation 2.9) relates the amount of electrical current in an electrochemical cell to the applied overpotential [9]. This makes it a key tool for modeling the deposition rate of lanthanides and actinides at the cathode surface, and therefore central to understanding and optimizing the electrowinning process:

$$j = j_0 \cdot \left\{ \exp \left[\frac{\alpha_a z F \eta}{RT} \right] - \exp \left[-\frac{\alpha_c z F \eta}{RT} \right] \right\} \quad (2.9)$$

with j being the resulting current density at the cathode surface (A/m^2), j_0 the exchange current density (A/m^2), α_a and α_c the anodic and cathodic charge coefficients (dimensionless), z the number of electrons involved in the reaction, η the applied overpotential (V) and F , R , T being Faraday's constant (C/mol), the universal gas constant (J/Kmol) and temperature (K), respectively.

At low overpotential, the reaction consumes ions more slowly than they are resupplied, so the surface concentration stays close to the bulk value and the current is kinetically limited. As the overpotential increases, the reaction consumes ions faster than diffusion and convection can resupply them, and

the surface concentration drops. A more general form of the Butler-Volmer equation also takes into account this mass transport limitation [2]:

$$j = j_0 \cdot \left\{ \frac{c_o(0, t)}{c_{o,b}} \exp \left[\frac{\alpha_a z F \eta}{RT} \right] - \frac{c_r(0, t)}{c_{r,b}} \exp \left[-\frac{\alpha_c z F \eta}{RT} \right] \right\} \quad (2.10)$$

In this equation, $c_o(0, t)$ is the concentration of oxidized species at the cathode surface (mol/m³) and $c_{o,b}$ the bulk concentration of oxidized species (mol/m³). The same applies to $c_r(0, t)$ and $c_{r,b}$, representing the concentrations of the reduced species.

In CFD simulations, the Butler-Volmer equation can be used as a boundary for the cathode surface concentration. Using Faraday's law, the calculated current density from Equation 2.10 can be converted into a concentration flux at the cathode surface [2]:

$$\frac{\dot{n}_r}{A} = \frac{j}{zF} \quad (2.11)$$

with $\dot{n}_r$ the molar flow rate (mol/s), A the cathode area (m²), j the current density (A/m²), z the number of electrons involved in the reaction and F Faraday's constant (C/mol).

2.2.2. Nernst equation

For determining the appropriate equilibrium potential in Equation 2.8, the Nernst equation can be used. At 'standard conditions', meaning a temperature of 25°C, concentration of 1 mol/L and 1 atm pressure, the 'standard electrode potentials' are well-documented [1]. For non-standard conditions, the equilibrium potential can be determined using the Nernst equation [2]:

$$E_{eq} = E^\circ - \frac{RT}{zF} \ln Q \quad (2.12)$$

with E_{eq} being the resulting equilibrium potential (V), E° the standard electrode potential (V), T the temperature (K), z the number of electrons involved in the half-reaction, Q the reaction quotient of the cell reaction, and R , F respectively the gas constant (J/Kmol) and Faraday's constant (C/mol).

2.2.3. Transport mechanisms within the molten salt

In order to determine the maximum current density that can be reached in the electrochemical cell, it is important to understand the transport mechanisms of metallic ions within the molten salt. In general, the mass transfer of the metallic ions within an electrochemical cell is determined by [38]:

1. **Advection:** With the fluid flowing at a velocity v , it carries the metallic ions along with it
2. **Diffusion:** The diffusion of metallic ions is driven by the diffusion coefficient D and the concentration gradient dc/dy
3. **Electromigration:** The movement of charged ions due to an electric field. The electric field is caused by the voltage applied over the cathode and anode.

Combining these factors, the total rate of transfer can be expressed using the Nernst-Planck equation [18]:

$$\mathbf{J} = \underbrace{\mathbf{v}c}_{\text{Advection}} - \underbrace{D\nabla c}_{\text{Diffusion}} - \underbrace{Dc \frac{zF}{RT} \nabla \varphi}_{\text{Electromigration}}, \quad (2.13)$$

with $\mathbf{J}$ being the molar flux intensity (mol/m²s), $\mathbf{v}$ the velocity (m/s), c the species concentration (mol/m³), D the diffusion coefficient, z the charge number, T temperature (K), φ the electric potential field (V), and F , R respectively Faraday's constant (C/mol) and the gas constant (J/Kmol).

2.3. Estimating the ion transport number

To calculate the effect of electromigration on the results, it is useful to estimate the ion transport number. This number is defined as the fraction of total electric current carried by an ionic material:

$$t_i = \frac{j_i}{j_{total}} \quad (2.14)$$

The partial current density j_i (A/m²) can be expressed in terms of ion mobility [11]:

$$j_i = z_i F c_i \mu_i E \quad (2.15)$$

where z_i is the charge number, F Faraday's constant (C/mol), c_i the concentration (mol/m³), μ_i the ion mobility (m²/Vs) and E the electric field (V/m). When substituting Equation 2.15 in Equation 2.14, the electric field and Faraday's constant cancel out, resulting in:

$$t_i = \frac{z_i c_i \mu_i}{\sum_j z_j c_j \mu_j} \quad (2.16)$$

The Nernst-Einstein equation relates the ionic mobility μ to the diffusion coefficient [11, 13]:

$$\mu_i = \frac{D_i z_i F}{RT} \quad (2.17)$$

with D_i being the self-diffusion coefficient of the species (m²/s), T the temperature (K) and R the ideal gas constant (J/Kmol). This equation gives an upper bound for the ion mobility and is only valid for low ion concentrations, as the ion-ion interactions are not taken into account [41]. Using this relation, the ion transport number can be estimated, with again the constants canceling out:

$$t_i = \frac{z_i^2 c_i D_i}{\sum_j z_j^2 c_j D_j} \quad (2.18)$$

2.4. Kelvin-Helmholtz instabilities

The Kelvin-Helmholtz instability develops at the interface between two stratified, immiscible fluids moving relative to one another, here the molten salt flowing over the liquid bismuth cathode. Treating both fluids as incompressible and inviscid, a small wavy perturbation is applied to the flat interface and tracked to see whether it grows or decays [5].

The shear from the relative velocity Δv tends to amplify the wave, while gravity (acting on the density difference) and the interfacial surface tension σ tend to flatten it back out. The interface stays stable as long as the stabilizing effects dominate; once the shear is strong enough to overcome them, the wave grows and the interface rolls up, entraining droplets into the salt. Balancing these competing effects allows to calculate the critical velocity difference at which Kelvin-Helmholtz instabilities occur [5]:

$$\Delta v_c^2 = 2 \frac{\rho_b + \rho_s}{\rho_b \rho_s} \sqrt{\sigma g (\rho_b - \rho_s)} \quad (2.19)$$

where Δv_c is the critical velocity difference (m/s), ρ_b and ρ_s the densities of the liquid bismuth and molten salt (kg/m³) and σ the interfacial surface tension (N/m).

3

Methods

This chapter describes the simulated setup of a molten salt flowing over a liquid bismuth cathode and how it is implemented in OpenFOAM. The work is divided into three parts: a single-phase model with a zero-concentration cathode boundary (Part A.1), an extended single-phase model using the Butler-Volmer equation as boundary condition (Part A.2), and a multiphase model of the liquid-liquid interface (Part B), each with its numerical setup and validation strategy detailed here.

3.1. Setup of interest

In this report, the setup of interest is displayed in Figure 3.1. This setup consists of a NaCl-KCl molten salt flowing over a liquid bismuth cathode. With the density of bismuth being higher than the molten salt, the two liquids form naturally stratified (separated) layers. In the setup, a voltage is applied over the cathode and anode. Diffusion, advection and electromigration effects in the cell cause the metallic ions to be transported towards the cathode, eventually being dissolved into the liquid bismuth. The operating temperature for this cell is typically around 700-900 K [17].

The setup is simulated in OpenFOAM, a free open-source toolbox used in computational fluid dynamics [22]. In this report, a distinction is made between three parts:

- In part A.1, only the electrolyte domain is considered, while the liquid cathode is modeled using a boundary condition by setting $c = 0$ at the cathode surface. To verify this model, experimental data from Pickett [26] and Recio [28] will be compared to CFD results.
- Part A.2 still only considers the electrolyte domain, but replaces the boundary condition of $c = 0$ for the cathode surface of Part A.1 with the Butler-Volmer equation, giving the option to investigate the relation between overpotential and cathode current density.
- In part B, the liquid bismuth cathode is included in the domain. The forming of droplets caused by Kelvin-Helmholtz instabilities is visualized using a multiphase simulation. A maximum velocity is defined, above which instabilities and droplet forming occur.

3.2. Numerical framework: OpenFOAM

All simulations in this work are performed in OpenFOAM, an open-source C++ toolbox for computational fluid dynamics [22]. This section briefly describes how OpenFOAM solves the governing equations, so that the numerical setups of Parts A.1, A.2 and B can be understood in context. A detailed description of the simulation setup and mesh density can be found in Appendix C.

Finite volume discretisation

OpenFOAM solves the governing equations using the finite volume method (FVM) [10]. In this method, the computational domain is divided into a large number of control volumes (cells), and the governing equations are integrated over each cell. Volume integrals of divergence terms are converted into surface integrals over the cell faces using Gauss's divergence theorem, so that the convective and

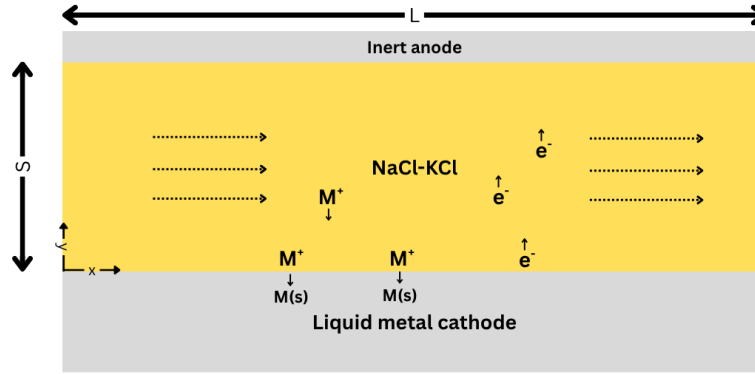


Figure 3.1: Setup of interest, molten salt flowing over a liquid bismuth cathode. After reduction, metallic cations (M^+) get deposited into the liquid metal cathode. The applied cell voltage drives a current of electrons (e^-) from the negative cathode towards the positive anode.

diffusive transport is expressed as a sum of fluxes through the faces of each cell. The field values are stored at the cell centres, and interpolation schemes are used to reconstruct the face values required to evaluate these fluxes. This converts the Navier-Stokes equations into algebraic equations, one per cell, which is then solved iteratively [10].

Pressure-velocity coupling

For an incompressible flow, velocity and pressure are linked, velocity depends on pressure, but pressure has no dedicated equation of its own, only appearing indirectly through mass conservation [10]. OpenFOAM handles this by solving the two fields in turns: guess the pressure, solve for velocity, correct the pressure to fix any mass imbalance, and repeat until both are consistent. SIMPLE does this for steady-state problems [patankar_numerical_nodate], PISO for transient ones [16], and PIMPLE combines the two to allow larger time steps.

Boundary conditions

In CFD simulations, boundary conditions define how a field variable behaves at the edges of the domain. A no-slip condition sets the fluid velocity to zero at a wall, reflecting the physical reality that viscous fluids “stick” to solid surfaces. A slip condition, by contrast, allows the fluid to move along the boundary without friction. A zero-gradient (or Neumann) condition sets the normal derivative of a variable to zero at the boundary. This is used at the outlets or walls where the field values naturally follow from the flow field inside the domain. For Part A, the boundary conditions for concentration, velocity and pressure used in the CFD simulation are listed in Table 3.1.

Application in this work

In Parts A.1 and A.2, the steady-state single-phase flow of the molten salt electrolyte is solved using the `simpleFoam` solver, which uses the SIMPLE algorithm for pressure-velocity coupling. This solver is combined with a transport equation for the concentration of the reacting species, with the cathode reaction entering through the boundary condition at the cathode surface. In Part B, the transient two-phase flow of the molten salt over the liquid bismuth is solved with the `interFoam` solver, which couples the pressure-velocity solution described above with the Volume of Fluid method to track the liquid-liquid interface [24].

3.3. Part A: Single-phase simulation

Part A considers a single-phase simulation of the electrolyte domain alone, with the liquid bismuth cathode represented through different boundary conditions in Parts A.1 and A.2. Across both parts, electromigration effects are neglected, a simplification supported by the calculation presented in Part A.2.

Table 3.1: CFD Boundary conditions for Part A.

Boundary	Concentration	Velocity	Pressure
Inlet	fixedValue: c_{inlet}	fixedValue: v_{inlet}	zeroGradient
Outlet	zeroGradient	zeroGradient	0
Upper wall	zeroGradient	noSlip	zeroGradient
Lower wall	0 (Part A.1) or BV-equation (Part A.2)	noSlip	zeroGradient

3.3.1. Part A.1: Limiting current behavior with zero-concentration boundary condition

In Part A.1, the limiting current density behavior is investigated by setting the concentration of metals at the cathode surface to zero. The current at the cathode is limited by two factors: how fast the reaction itself can run, and how fast ions can be supplied to the surface. At low overpotentials, the reaction rate is the limiting factor. As the overpotential increases, the reaction speeds up until it is consuming ions as fast as they arrive. At this point, supplying ions to the surface becomes the limiting factor instead, and the current stops increasing when increasing the overpotential. This maximum current is the limiting current density.

When the limiting current density is reached, every ion that reaches the cathode is dissolved into the cathode immediately, leaving no ions at the surface. Therefore, in this part of the experiment the concentration at the cathode surface can be assumed to be zero. By setting $c_s = 0$ and combining Equations 2.6 and 2.7, the mass transfer coefficient can be determined in terms of the concentration gradient at the cathode surface:

$$k_m = \frac{D}{c_b} \frac{dc}{dy} \Big|_{y=0} \quad (3.1)$$

Setting $c_s = 0$ therefore allows to ignore the reaction kinetics completely and focus only on mass transport, so the mass transfer coefficient can be calculated directly from the concentration gradient at the surface using Equation 3.1. This method of setting the surface concentration to zero to obtain the limiting current density is well known in literature [12, 30, 37].

Comparison with Pickett

To verify the CFD model, numerical results are compared with data from experimental studies, the first being Pickett [26]. In this study, a parallel plate electrochemical cell with a copper cathode and lead anode was investigated. The experimental setup consisted of separate anode and cathode compartments, with an equivalent diameter of $d_e = 11.9$ mm. The electrolyte was m-nitrobenzene sulphonic acid. After setting the desired electrolyte flow velocity, the cell potential was increased with step changes, after which the current was measured. The authors increased the voltage until the limiting current, I_L , was reached (i.e. the current is not further increasing). Using the measured limiting current density, the authors calculated the mass transfer coefficient:

$$k_m = \frac{I_L}{6Fc_bA} \quad (3.2)$$

where k_m is the mass transfer coefficient (m/s), I_L the limiting current (A), F Faraday's constant (C/mol), c_b the bulk species concentration (mol/m³) and A the electrode area (m²). Using this equation, mass transfer coefficients were determined for different electrode lengths, ranging from 10 mm to 150 mm.

In this paper, the diffusion coefficient of the reduced species, necessary for replicating the setup in a CFD simulation, was not directly provided. To estimate the diffusion coefficient, several measurement values for Sh were determined from Figure A.2, and their corresponding values for k_m were determined from Figure A.1. Using these data points for k_m and Sh with the provided value of the equivalent diameter, $d_e = 11.9$ mm, the diffusion coefficient was estimated with Equation 2.5 to be around 5×10^{-9} m²/s.

Comparison with Recio

To further validate the model, a study from Recio is replicated [28]. In this study, the influence of the effective surface area of the electrode on the mass transfer coefficient was determined, for a parallel-plate

geometry. As can be seen in Figure 3.2, two cathode configurations in this study are ‘Nanostructured’ and ‘Polished’. The authors used an undivided electrolyte compartment, with a nickel cathode and carbon anode. The exact cell dimensions and characteristics of the electrolyte are well-documented, making the study suitable for validating for the CFD model.

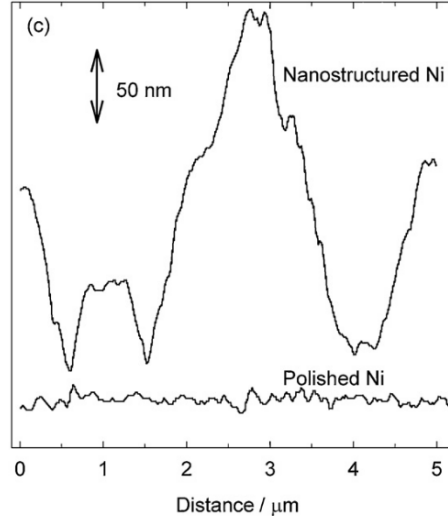


Figure 3.2: Polished vs. nanostructured cathode surface in Recio [28].

3.3.2. Part A.2: Extending the model with Butler-Volmer as cathode boundary condition

In Part A.2, the effect of overpotential on the current density at the cathode surface is investigated. Instead of setting the concentration boundary condition at the cathode surface to zero, the extended Butler-Volmer equation (Equation 2.10) is used as boundary condition.

For the parameters in the Butler-Volmer equation, two assumptions are made. First, $\frac{c_o(0,t)}{c_o^*} = 1$, i.e. the concentration of the oxidized chloride ions at the cathode surface is equal to the bulk concentration of chloride ions. This assumption is justified by the fact that the concentration of the investigated materials is low compared to the concentration of chloride, implying that concentration variations of chloride ions are neglected.

Second, $\alpha_c = \alpha_a = 0.5$, meaning the Butler-Volmer equation is symmetric with respect to overpotential. Similar assumptions were found in literature for electrorefining spent fuel [7], though these rely on the fact that the reaction is mass transfer limited. After setting the appropriate parameters, the calculated current density from Equation 2.10 is converted to mass flux at the boundary condition in OpenFOAM using Faraday’s law (Equation 2.11).

Choice of materials

The species investigated in Part A.2 (U^{3+} , Pu^{3+} , Ce^{3+} , La^{3+} and Zr^{4+}) were chosen to cover the groups of elements that occur in the molten salt during the pyroprocessing of spent fuel: the actinides that are to be recovered, the lanthanide fission products from which they must be separated, and zirconium as a fuel-alloy. Uranium and plutonium represent the actinides, the valuable fissile materials that can be reused to fuel MSRs [3, 34]. Cerium and lanthanum represent the lanthanide fission products that accumulate in the salt and must be separated from the actinides. The separation of these lanthanides has been studied experimentally by Jung et al. [17].

Zirconium is included because it is commonly present in the U–Pu–Zr spent fuel alloy [19], meaning that zirconium ions enter the salt alongside the actinides and lanthanides. A further practical reason for this choice of materials is that diffusion coefficients for all five ions in molten salt are reported in a single source [48] (Table 3.3), allowing the materials to be compared reliably.

The effect of electromigration

Similar to Part A.1, mass transport within the molten salt is assumed to be governed by the convection-diffusion equation, i.e. the electromigration term in Equation 2.13 is neglected. This is justified because the NaCl–KCl melt acts as a supporting electrolyte: the Na^+ , K^+ and Cl^- ions are present in large excess and are not consumed at the electrodes, meaning they carry almost all of the current. It is well established that when a supporting electrolyte dominates the conductivity, migration of the reacting ion becomes negligible [31, 39].

The ion transport number can be estimated using Equation 2.18, providing a means to quantify the effect of electromigration. Uranium extraction is considered for this calculation; since the diffusion coefficients of the other investigated materials vary by at most a factor of two (Table 3.3), the resulting ion transport numbers would be of the same order of magnitude for those materials as well. The charge numbers, concentrations and self-diffusion coefficients of all relevant ions are required for Equation 2.18.

Starting with the concentration. For an equimolar NaCl–KCl mixture (50 mol% each), the mean molar mass of the electrolyte is:

$$M = 0.5 \cdot M_{\text{NaCl}} + 0.5 \cdot M_{\text{KCl}} = 66.5 \text{ g/mol} \quad (3.3)$$

where the individual molar masses are obtained from the periodic table. Using the density of the NaCl–KCl molten salt electrolyte from Table 3.4, the molar concentration of the salt is:

$$c_{\text{salt}} = \frac{\rho}{M} = 2.44 \times 10^4 \text{ mol/m}^3 \quad (3.4)$$

where ρ is the density of the molten salt (g/m^3) and M is the mean molar mass (g/mol). Given the equimolar composition, this yields $c_{\text{Na}^+} = c_{\text{K}^+} = 1.22 \times 10^4 \text{ mol/m}^3$ and $c_{\text{Cl}^-} = 2.44 \times 10^4 \text{ mol/m}^3$.

The self-diffusion coefficients of the ions were taken from Xie et al. [47], who report values for Na^+ , K^+ and Cl^- at several CaCl_2 concentrations. The coefficients corresponding to the lowest CaCl_2 concentration investigated (20 mol%) were read from Figure B.1. These self-diffusion coefficients, together with the charge numbers and ion concentrations used in Equation 2.18, are listed in Table 3.2. Using these values, the ion transport number for U^{3+} is estimated to be $t_U = 7 \times 10^{-6}$.

Table 3.2: Charge number, self-diffusion coefficient and concentration of different species, used for estimating the ion transport number.

Species	Charge number z	Self-diffusion coefficient ($\times 10^{-9} \text{ m}^2/\text{s}$)	Concentration (mol/m^3)	c
U^{3+}	+3	0.992 [48]	0.25	
Na^+	+1	8 [47]	1.22×10^4	
K^+	+1	7 [47]	1.22×10^4	
Cl^-	-1	5.5 [47]	2.44×10^4	

Cell dimensions and constants

One of the parameters in the Butler-Volmer equation is the exchange current density j_0 . This parameter cannot be calculated directly, it needs to be experimentally determined. No specific literature for the exchange current density of uranium in NaCl–KCl has been found. Rose et al. [29] has determined the parameter j_0 for uranium in LiCl–KCl, which is used in this article:

$$j_0 = 20396e^{-4143/T} \quad (3.5)$$

For $T = 773 \text{ K}$, this yields an exchange current density of 959 A/m^2 , which is used in the Butler-Volmer equation. The dimensions of the cell are chosen to have an electrode spacing of 2 cm ($= S$), and a length of 5 cm . Using Equation 2.3, the maximum flow velocity to stay in the laminar regime is $v_{\text{max}} = 0.11 \text{ m/s}$, which is used as the maximum electrolyte flow velocity. The diffusion coefficients for the investigated materials are listed in Table 3.3. For all CFD simulations in Part A.2, an inlet concentration of $c = 0.25 \text{ mol/m}^3$ is considered.

Table 3.3: Diffusion coefficients in NaCl-KCl molten salt at $T = 773$ K for the investigated materials [48].

Material	D at 773 K ($\times 10^{-9} \text{m}^2/\text{s}$)
U^{3+}	0.992
Pu^{3+}	1.08
Ce^{3+}	1.7
La^{3+}	1.87
Zr^{4+}	1.13

Table 3.4: Properties for NaCl-KCl molten salt and liquid bismuth at $T = 900$ K.

Molten salt (NaCl-KCl)	
Density	$1.621 \times 10^3 \text{ kg/m}^3$ [20]
Dynamic viscosity	$2.231 \times 10^{-3} \text{ Pa} \cdot \text{s}$ [20]
Kinematic viscosity	$1.38 \times 10^{-6} \text{ m}^2/\text{s}$ [20]
Liquid bismuth	
Density	$9.60 \times 10^3 \text{ kg/m}^3$ [4]
Kinematic viscosity	$2.1 \times 10^{-7} \text{ m}^2/\text{s}$ [33]
Interfacial surface tension	0.24 N/m [35]

3.4. Part B: Multiphase simulation

With Part A.1 and A.2 only concerning the electrolyte domain, Part B includes the liquid bismuth into the simulation. To investigate the behavior of the liquid-liquid interface and determine the appropriate velocity boundary condition for the single-phase simulations, a two-phase simulation was performed using OpenFOAM's *interFoam* solver. The *interFoam* solver is designed for two incompressible, isothermal, immiscible fluids and uses the Volume of Fluid (VOF) method to track the interface between the two phases [23].

The two phases in the simulation are the molten salt (NaCl-KCl) as top layer and the liquid bismuth cathode as bottom layer, with material properties listed in Table 3.4. As literature values for the interfacial surface tension between the NaCl-KCl molten salt electrolyte and liquid bismuth cathode are only available at $T = 900$ K, this temperature was adopted for this part of the simulation. The liquid bismuth is initialized as a stratified layer at the bottom of the domain, with the molten salt flowing over it. The inlet velocity is prescribed for the molten salt phase only, while the bismuth is initially at rest. A no-slip condition is applied at the top and bottom walls of the duct. The detailed simulation setup is described in section C.2.

Using Equation 2.19, the predicted critical velocity at which Kelvin-Helmholtz instabilities occur is $v_c = 1.36 \text{ m/s}$. The simulation was run at several inlet velocities, ranging from below to above the theoretically predicted critical velocity. This allows direct comparison between the CFD and analytical results. Additionally, the velocity profile near the liquid-liquid interface was extracted from the multiphase simulation at a low, stable inlet velocity of 0.1 m/s , in order to determine the physically appropriate velocity boundary condition (slip or no-slip) to apply at the cathode surface in the single-phase simulations of Parts A and B.

4

Results

This chapter presents the outcomes of the three simulation parts. It reports the validation of the zero-concentration model against the experimental data of Pickett and Recio, the dependence of cathode current density on overpotential and electrolyte velocity from the Butler-Volmer model, and the behavior of the liquid-liquid interface, including the occurrence of Kelvin-Helmholtz instabilities and the resulting velocity boundary condition.

4.1. Part A.1: Single-phase simulation with zero concentration at cathode surface

In this section, the single-phase model with a zero-concentration cathode boundary is validated against experimental data. By fixing the surface concentration at zero, the cathode is treated as a perfect sink. The CFD results are first compared with the parallel-plate flow-cell measurements of Pickett [26], investigating the dependence of the mass transfer coefficient on electrode length and Reynolds number, and with the data of Recio [28].

Comparison with Pickett

In Figure 4.1, the relationship between the mass transfer coefficient and electrode length for various flow conditions is investigated. Figure 4.1a shows the original experimental data from Pickett, which serves as the basis for comparison with the CFD results. In this figure, the colored data points were measured using an electrolyte entrance length of 925 mm, meaning the electrolyte had traveled this distance before reaching the electrochemical cell, ensuring a fully developed flow profile. In contrast, the outlined data points correspond to an entrance length of 95 mm, which represents a developing flow condition.

In Figure 4.1b, the average mass transfer coefficient from the CFD simulation at the cathode surface is plotted against the electrode length, for various electrolyte flow velocities ($Re = 100$ and $Re = 2000$) and both developing and fully developing electrolyte velocity profiles. The results demonstrate a decline in the overall mass transfer coefficient as electrode length increases, a trend also observed in Pickett's experimental data. This behavior is physically expected: the solute concentration is at its highest at the inlet and decreases along the electrode as species are reduced at the cathode surface. As a result, the diffusion layer is thinnest near the electrode entrance, resulting in a high local mass transfer coefficient, which decreases when averaged over a longer electrode.

Furthermore, consistent with Pickett's experimental observations, Figure 4.1b shows the mass transfer coefficient for developing flow to be persistently higher than that for fully developed flow across all electrode lengths considered. From Figure 4.2, showing the velocity profile at the entrance of the cell for various flow conditions, it can be observed that the electrolyte velocity in the x-direction near the cathode surface is higher for a developing flow compared to a fully developed flow. Therefore, the mass transfer coefficient being higher for developing flow is an expected result, as the electrolyte velocity is higher, leading to a thinner diffusion layer.

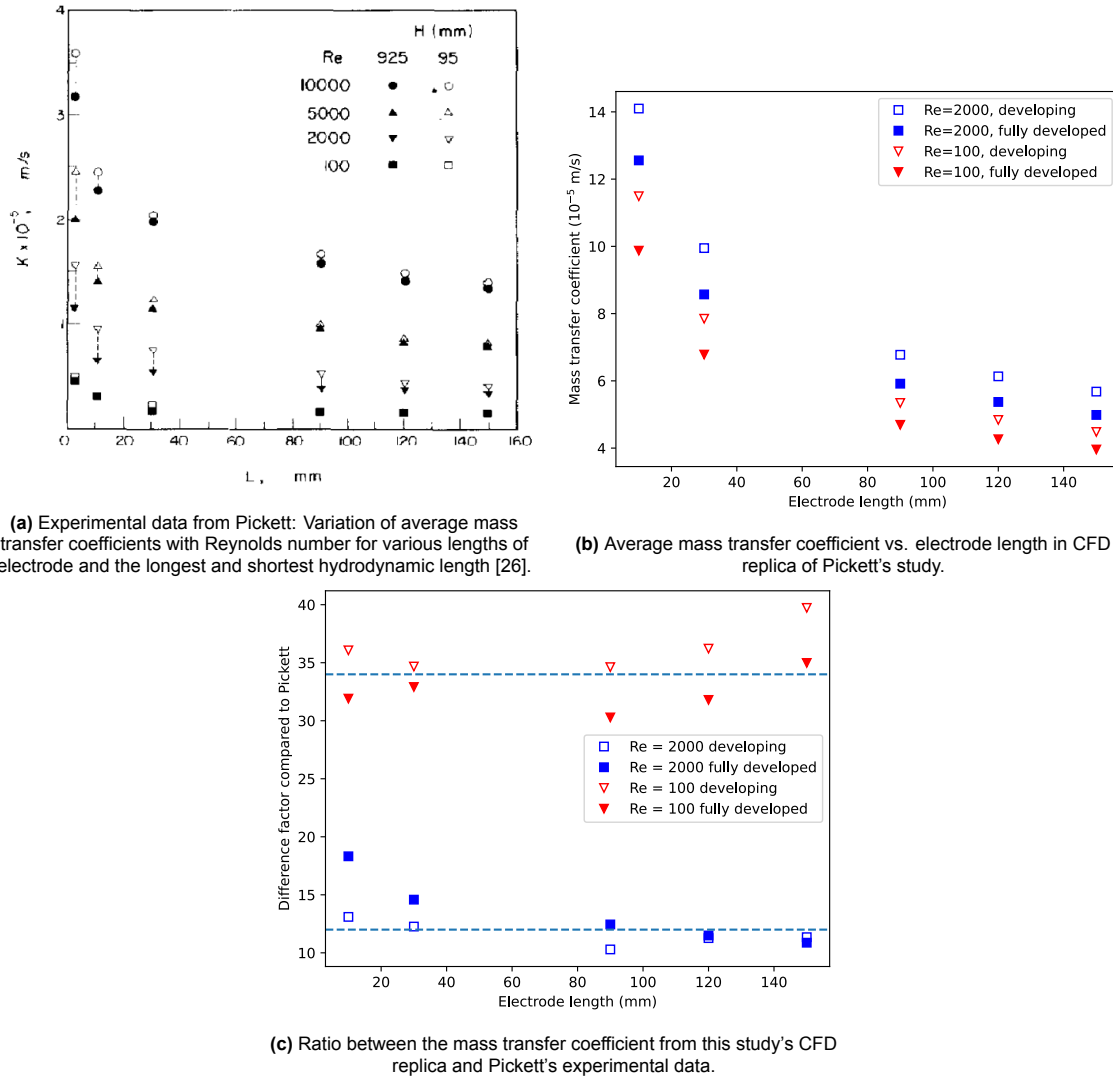


Figure 4.1: Results for the CFD model validation with Pickett's experimental data.

Figure 4.1c shows the ratio of the mass transfer coefficient obtained in this study (CFD results) to that reported in Pickett's experimental data. For $Re = 2000$, the CFD simulation yields mass transfer coefficients approximately 12 times greater than the experimentally measured values, while at $Re = 100$ this factor increases to approximately 34.

Comparison with Recio

Figure 4.3 compares the Sherwood number from the CFD model with the experimental correlations of Recio [28] for the mirror polished and the nanostructured nickel cathode, plotted against the Reynolds number on logarithmic axes. A power-law fit of the simulated data, $Sh = a \cdot Re^b$, gives $a = 4.08$ and $b = 0.32$. Two features are apparent. First, in absolute magnitude the CFD results lie closer to the mirror polished cathode than to the nanostructured one, the latter sitting well above both across the entire Reynolds range considered. Second, the CFD curve is flatter than the mirror polished curve: the fitted exponent of 0.32 is below the value of 0.71 reported by Recio for the polished electrode [28].

4.2. Part A.2: Single-phase with Butler-Volmer as boundary condition

The results for the extended model, which uses the Butler-Volmer equation as boundary condition at the cathode surface, are presented in Figure 4.4. The figure shows several relations between electrolyte

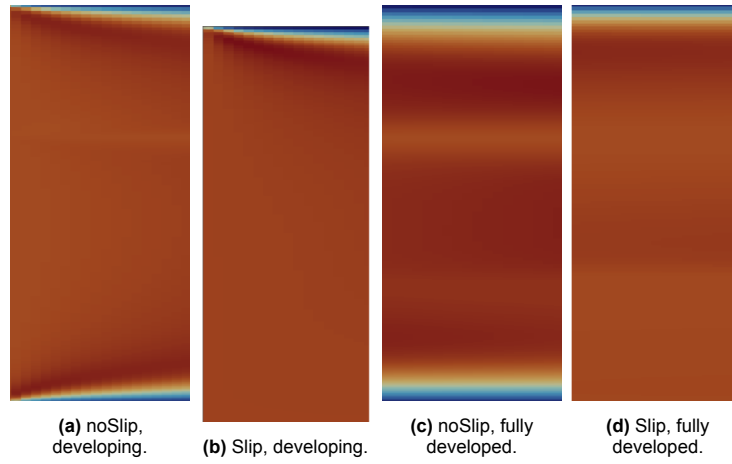


Figure 4.2: Velocity profile (x-direction) for Part A at various flow conditions. Blue color corresponds to $v_x = 0$, red to $v_x = 0.1$ m/s.

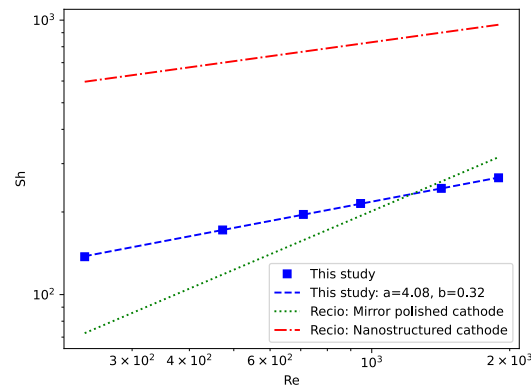


Figure 4.3: Log-log plot of the Sherwood number vs. Reynolds number for the CFD model (this study) compared with the experimental correlations of Recio [28] for a mirror polished nickel cathode and a nanostructured nickel cathode.

velocity, overpotential, current density and concentration values for various materials.

Current density behavior for different extracted materials

Figure 4.4a shows the average current density at the cathode surface for different extracted materials, as a function of the overpotential. The figure shows that, for an overpotential lower than -0.4 V, the current density at the cathode surface does not further increase. Figure 4.4b shows current densities plotted against the electrolyte velocity, with a constant overpotential of -0.5 V. The figure shows that the magnitude of the current density at the cathode surface increases as the electrolyte velocity increases. This is an expected result, as a higher electrolyte velocity reduces the thickness of the concentration boundary layer near the cathode surface, steepening the concentration gradient and increasing the diffusive flux of ions to the surface, which raises the achievable current density.

Limiting current density

In Figure 4.4c, the average current density at the cathode surface is plotted against overpotential, for various electrolyte velocities ranging from 0 to 10 cm/s. Similar to Figure 4.4a comparing different materials, Figure 4.4c shows that the magnitude of the current density does not further increase after a certain overpotential value. The current density at this overpotential value is the limiting current density. Again, the figure shows that the magnitude of the limiting current density increases for higher electrolyte flow velocities.

The effect of velocity flow conditions on the current density

While the concentration flux boundary condition at the cathode surface is still calculated using the Butler-Volmer equation, the effect of setting different velocity flow conditions on the current density is now explored. These various conditions include a noSlip and slip velocity boundary condition for the cathode surface, and a developing and fully developed flow. In Figure 4.4d, the average current density at the cathode surface is plotted against the electrolyte velocity for these conditions. From the figure, it can be observed that the 'noSlip fully developed' cathode boundary condition results in the lowest magnitude current density, followed by the 'noSlip developing' and the highest magnitude is observed for the 'Slip developed' and 'Slip fully developed'. Both the cases for 'Slip developed' and 'Slip fully developed' resulted in the same average current density.

These results are physically expected: a noSlip condition forces the fluid velocity to zero at the cathode surface, thickening the concentration boundary layer and reducing the mass transfer coefficient, while a slip condition allows the fluid at the cathode surface to achieve a higher velocity (Figure 4.2), thinning the boundary layer and raising the current density. The identical results for the slip developing and slip fully developed cases can be explained by the identical velocity profile near the cathode surface for both cases, as can be seen in Figures 4.2b and 4.2d.

Concentration profile at cathode surface

The concentration profile of U^{3+} near the cathode surface is shown in Figure 4.4e. For a low overpotential, the concentration U^{3+} at the cathode surface is close to the bulk concentration. When increasing the overpotential, the concentration at the cathode surface decreases, and the concentration slope at the cathode surface $dc/dy|_{y=0}$ increases, leading to a thinner diffusion layer and high mass transfer coefficient.

4.3. Part B: Multiphase simulation

In this section, the liquid bismuth cathode is included through a two-phase simulation of the liquid-liquid interface. The goal is to determine the velocity at which Kelvin-Helmholtz instabilities occur and to establish the appropriate velocity boundary condition for the single-phase simulations of Parts A.1 and A.2.

Calculated critical velocity for Kelvin-Helmholtz instabilities

To verify the CFD results, the theoretical critical velocity where Kelvin-Helmholtz instabilities occur can be calculated using Equation 2.19. Using the data from Table 3.4, this gives a critical velocity of 1.36 m/s, which corresponds to a Reynolds number of around 28000 — well into the turbulent regime.

Droplet forming

The simulation was executed at velocities near the calculated critical velocity for instability. In Figure 4.5, the droplet forming phenomenon is shown. As can be seen in Figure 4.5a, for velocities lower than the critical velocity, the liquid cathode and electrolyte remain stratified. Just above the critical velocity, some Kelvin-Helmholtz waves were observed. In the video simulation, some of the bismuth showed to be 'captured' from the stratified flow, and transported along with the electrolyte. The strength of this effect increases for higher velocities (Figure 4.5c) where a distinct droplet of bismuth being dragged along the electrolyte can be seen in the figure.

Velocity profile near the cathode surface

To determine the appropriate velocity boundary condition for the single-phase simulation, it is useful to plot the velocity profile near the cathode surface in the multi-phase simulation. This data is visible in Figure 4.6. From the figure, it can be observed that the velocity in the x-direction near the cathode surface is zero, indicating that the noSlip velocity boundary condition used in part A.2 of this article is appropriate for modeling the liquid-liquid interface. For higher inlet velocities, the viscosity of the electrolyte might cause the liquid bismuth to move along with it. With the density of the liquid bismuth being much higher, at low speeds these effects are apparently negligible.

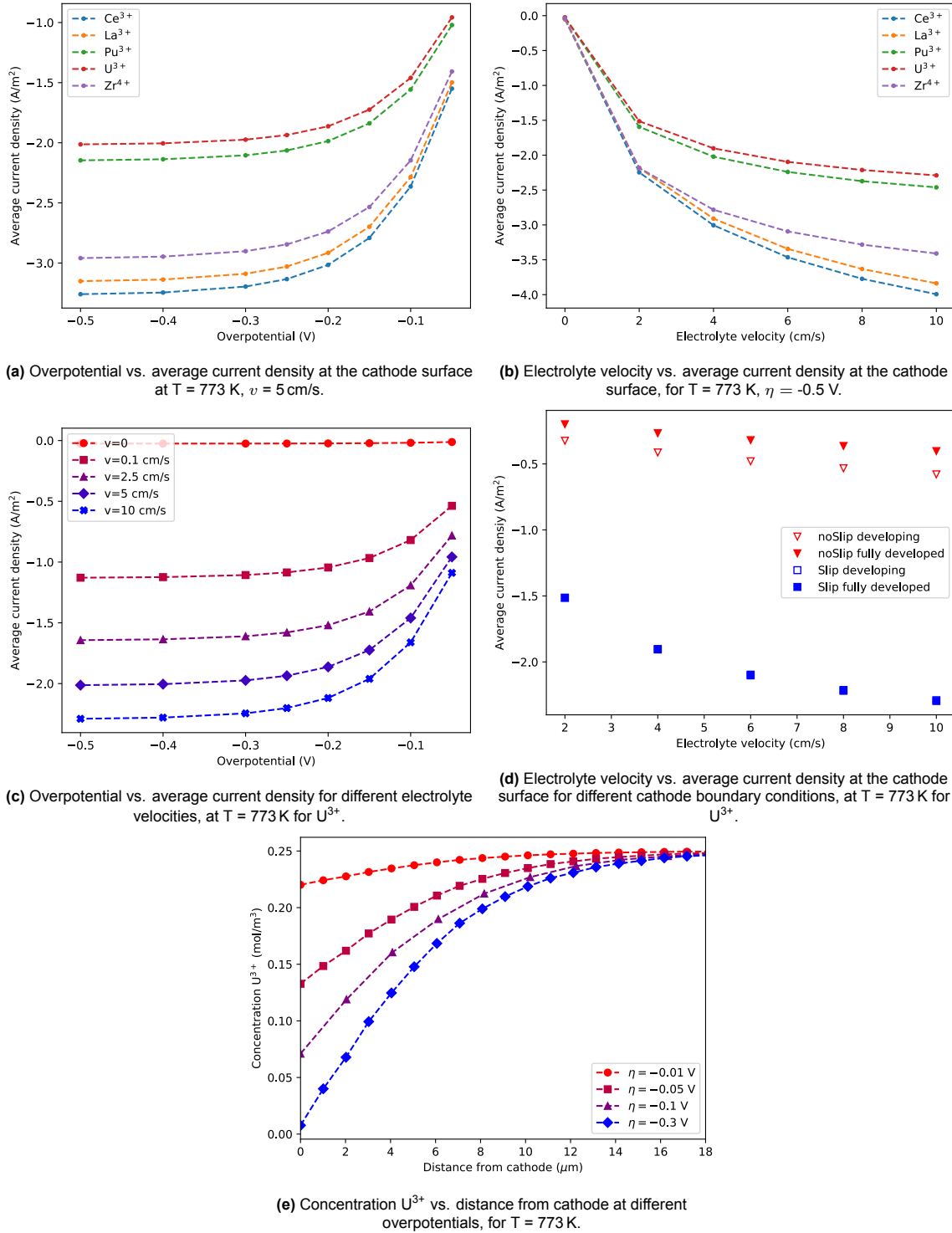


Figure 4.4: Results of the Butler-Volmer simulation.

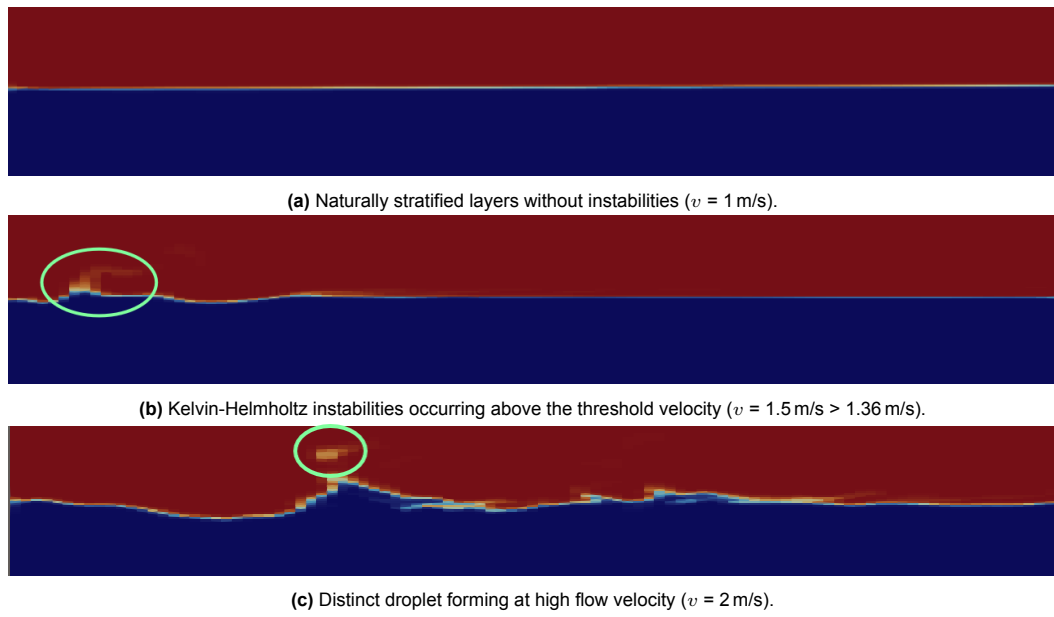


Figure 4.5: Multiphase simulation, with the molten salt at the top (red) and the liquid bismuth at the bottom (blue).

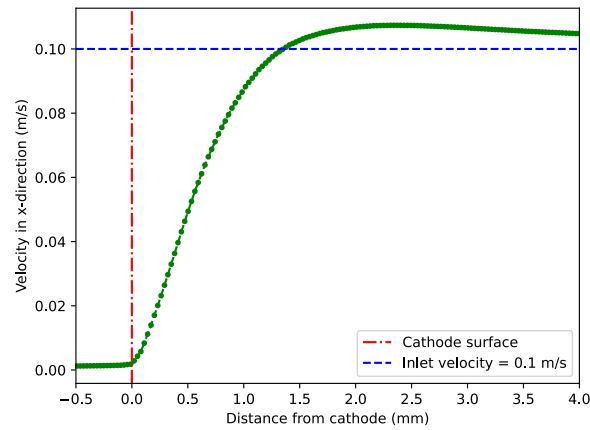


Figure 4.6: Multiphase simulation: velocity profile at liquid-liquid interface for $v_{inlet} = 0.1$ m/s.

5

Discussion

This chapter interprets the results and examines the assumptions underlying the model. It addresses the discrepancies between the CFD and experimental mass transfer coefficients, the consequences of treating the cathode as a perfect sink, the justification for neglecting electromigration, and the relevance of droplet formation and the electrical double layer, and directions for future research.

5.1. Explaining the differences with experimental data

Pickett study

Despite reproducing the qualitative trends, a declining mass transfer coefficient with electrode length and higher values for developing than for fully developed flow, the CFD results overestimate the experimentally measured mass transfer coefficients by a factor of 12 at $Re = 2000$ and up to 34 at $Re = 100$. The most likely explanation lies in the diffusion coefficient, which Pickett did not report directly and was estimated here at $5 \times 10^{-9} \text{ m}^2/\text{s}$ from the published Sherwood and mass-transfer data. Since the mass transfer coefficient scales linearly with D through Equation 3.1, an overestimated diffusion coefficient propagates directly into an overestimated k_m . Obtaining an independently measured diffusion coefficient for the Pickett electrolyte would be the most direct way to resolve the discrepancy.

Recio study

The comparison with Recio reveals two distinct discrepancies. In absolute magnitude, the CFD Sherwood numbers align reasonably well with the mirror-polished cathode, which is the most appropriate benchmark since the model assumes a smooth cathode surface. The nanostructured cathode sits well above both, as the increased effective surface area and surface roughness enhance mass transfer. There is a discrepancy in the Reynolds number correlation: the fitted exponent from the CFD results is 0.32, considerably lower than the value of 0.71 reported by Recio for the polished electrode. This flatter response suggests that the CFD model underestimates how strongly convection enhances mass transfer as flow rate increases. For future research, the CFD model can be extended into 3D to determine if this is able to reproduce the experimental data more accurately.

5.2. Mass transport limitations within the cathode

In this study, the liquid cathode is treated as a perfect sink: once a metal ion reaches the interface and is reduced, it is assumed to be instantly removed from the system. In reality, the reduced metal must still be transported away from the interface into the bulk of the liquid cathode, and this transport can itself become rate-limiting. The metal dissolves into the liquid bismuth and either diffuses with a finite diffusion coefficient or is transported by convection with a finite velocity, while the formation of intermetallic compounds and local saturation near the interface can reduce the effective driving gradient [43]. When transport within the cathode is slower than supply through the electrolyte, the metal concentration at the interface rises rather than staying near zero, lowering the achievable current density below the value predicted by the present model. The mass transport behavior of metals inside liquid

metal cathodes has been reviewed in detail by Wang et al. [43], and the limiting role of intermetallic compound formation for uranium and lanthanides in bismuth and cadmium has been observed experimentally [17]. Incorporating this second resistance would therefore be a useful extension of the model, possibly leading to lower values for the mass transfer coefficient and limiting current density.

5.3. The effect of electromigration

The migration term of Equation 2.13 was neglected on the grounds that the NaCl–KCl melt acts as a supporting electrolyte. The ion transport number estimated in subsection 3.3.2 makes this argument quantitative. For U^{3+} , the transport number was found to be $t_U \approx 7 \times 10^{-6}$, meaning that uranium ions carry only about seven millionths of the total current passing through the cell. This is a consequence of the large excess of supporting electrolyte: with Na^+ , K^+ and Cl^- present at concentrations nearly five orders of magnitude higher than that of U^{3+} (Table 3.2), these inert ions carry practically all of the migration current. Since the fraction of the U^{3+} flux to the cathode that is delivered by migration is equal to t_U , electromigration accounts for a negligible part of the uranium transport, while diffusion and advection account for essentially all of it. This justifies dropping the migration term from the Nernst–Planck equation (Equation 2.13) and modeling mass transport in the electrolyte with the convection–diffusion equation alone, as was done in both Part A.1 and Part A.2. This assumption becomes invalid as the U^{3+} concentration increases. In future research, to provide more accurate simulations with a high concentration of solutes, the electromigration term should be included into the model.

5.4. Droplet forming

Using Equation 2.19, the critical velocity for the onset of Kelvin–Helmholtz instabilities was found to be 1.36 m/s, and the multiphase simulation reproduced this transition qualitatively: the interface remained stratified below the critical velocity (Figure 4.5a), developed interfacial waves just above it (Figure 4.5b), and produced distinct bismuth droplets at higher velocities (Figure 4.5c). Within the laminar operating regime considered in this work, however, the electrolyte velocity is capped at roughly 0.11 m/s, which is well below the critical velocity of 1.36 m/s. Under the conditions studied, the liquid–liquid interface therefore stays stable and no entrainment of cathode material occurs, which also justifies treating the interface as a no-slip boundary in the single-phase simulations of Parts A.1 and A.2.

This does not mean droplet forming can be neglected in general. The critical velocity in Equation 2.19 depends on the fluid properties (the density difference between the two phases and the interfacial surface tension) and on the cell geometry. When the setup is scaled up, the larger dimensions can bring the operating velocities closer to the instability threshold. In that regime, entrainment of bismuth into the flowing electrolyte would represent both a loss of cathode material and a contamination of the salt, so droplet forming becomes a relevant design constraint.

5.5. Electrical double layer

In the present model, the cathode reaction is described by the Butler–Volmer equation, which assumes that the full applied overpotential is available to drive the charge-transfer reaction. In reality, a thin region of charge separation forms at the electrode surface, known as the electrical double layer [14]: ions of opposite charge arrange themselves close to the charged cathode, and part of the potential drop occurs across this layer rather than driving the reaction directly. A more complete description, the Frumkin–Butler–Volmer model, corrects for this effect by accounting for the potential drop across the diffuse part of the double layer [40]. Integrating this effect into the model would lead to a slightly lower achievable limiting current density.

5.6. Experimental verification for Part A.2

The simplified model of Part A.1 was compared to experimental data. Part A.2, with the implementation of the Butler–Volmer equation as boundary condition, was however not experimentally verified, due to a lack of available literature on the exact setup. Dedicated experiments on the actual NaCl–KCl and liquid bismuth system would allow the model to be properly validated, and allows the exact determination of model parameters such as the exchange current density j_0 .

6

Conclusion

This work investigated how forced flow of a molten salt electrolyte influences the mass transfer to a liquid bismuth cathode in a pyroprocessing cell, using CFD simulations in OpenFOAM.

The single-phase model with a zero-concentration cathode boundary (Part A.1) reproduced the expected mass-transfer behavior: the mass transfer coefficient decreased with electrode length and was higher for developing than for fully developed flow, in qualitative agreement with the experimental data of Pickett [26] and Recio [28].

Regarding the effect of overpotential, the Butler–Volmer model (Part A.2) showed that the current density at the cathode increases with overpotential until it saturates at a limiting current density, reached at an overpotential of roughly -0.4 V. Beyond this point the current is no longer reaction-limited but transport-limited, as confirmed by the concentration profiles, where the surface concentration of U^{3+} drops.

The result is that forced electrolyte flow enhances mass transfer. Increasing the flow velocity is therefore an effective method of raising the throughput of the cell. The limiting factor in this geometry is the occurrence of Kelvin–Helmholtz instabilities at the liquid–liquid interface. The multiphase simulation (Part B) showed no instabilities at a velocity of 1 m/s, and droplet forming at 1.5 m/s. This is in agreement with the prediction of Equation 2.19 which yielded a critical velocity of 1.36 m/s, above which the interface becomes unstable and bismuth is entrained into the electrolyte. Within the laminar regime considered here (velocities up to 0.11 m/s) this threshold is not approached, so the interface remains stratified.

Finally, the appropriate velocity boundary condition for the liquid–liquid interface was identified. The multiphase simulation showed that the velocity in the flow direction vanishes at the interface, so a no-slip condition is the appropriate choice for the single-phase simulations, rather than a slip condition.

In conclusion, the limiting current density of a liquid-cathode pyroprocessing cell can be increased by increasing the electrolyte velocity, with the limiting factor being Kelvin-Helmholtz instabilities. The model still requires experimental calibration of the diffusion coefficient, and could be extended to include transport within the cathode, electromigration, and operation beyond the laminar regime.

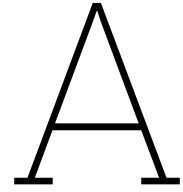
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Mass transfer relations from Pickett

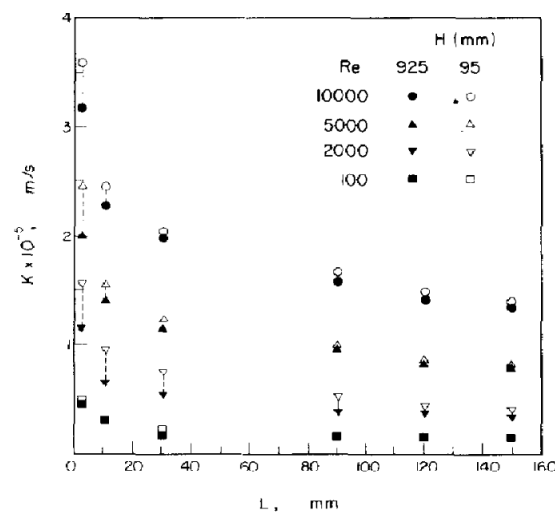


Figure A.1: Variation of average mass transfer coefficients with Reynolds number for various lengths of electrode and the longest and shortest hydrodynamic length [26]

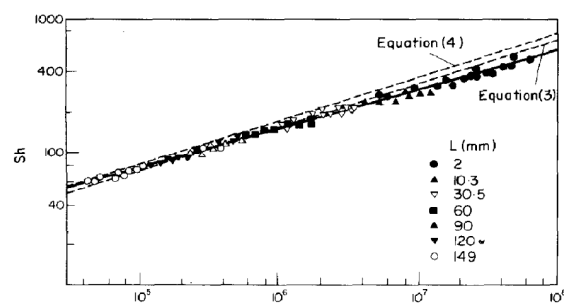


Figure A.2: Variation of Sherwood number with Graetz number for fully developed laminar flow [26]

B

NaCl-KCl ion self-diffusion coefficients from Xie et al.

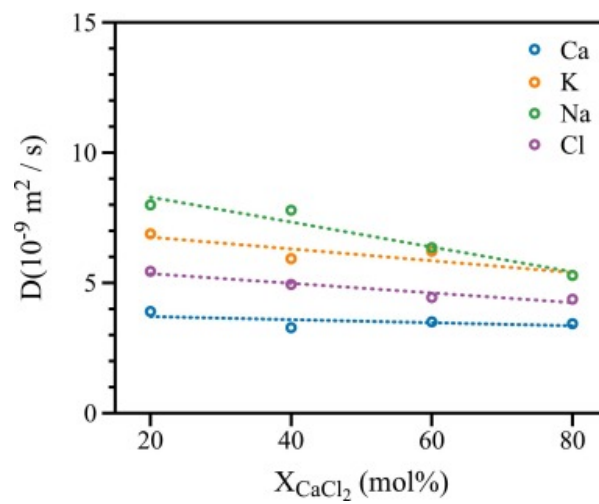
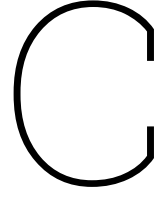


Figure B.1: The variation of self-diffusion coefficients for different ions in relation to concentration of CaCl_2 [47].



Detailed OpenFOAM setup

C.1. Single-phase simulations (Part A.1 and A.2)

The computational mesh for the single-phase simulations consists of 100 uniformly distributed cells in the x -direction and 500 cells in the wall-normal y -direction. The mesh in the y -direction is graded such that, starting from the channel midpoint, the cell size decreases by a factor of 100 towards both the upper and lower walls. This ensures sufficient resolution of the concentration boundary layer that develops near the cathode surface.

Parts A.1 and A.2 are simulated using `simpleFoam`, the steady-state incompressible flow solver in OpenFOAM v2012 [23]. The solver uses the SIMPLE algorithm to iteratively solve the Navier–Stokes equations until convergence. The run is set to a maximum of 150 iterations with fields written every 10 steps.

Since only the laminar regime is considered, no turbulence model is active. The concentration field c is solved as a scalar using the `scalarTransport` function object. The diffusion coefficient D is set according to the material being simulated, as listed in Table 3.3. The difference between Parts A.1 and A.2 lies only in the boundary condition applied to c at the cathode surface: a fixed value of $c = 0$ in Part A.1, and a Butler–Volmer flux (Equation 2.10) in Part A.2.

The divergence schemes control how convective transport is discretised on the mesh. Momentum convection `div(phi,U)` uses `bounded Gauss linearUpwind`, a second-order scheme that estimates face values using the upstream cell and its local velocity gradient, with `bounded` adding stability during early iterations. For scalar convection `div(phi,c)`, first-order `Gauss upwind` is chosen instead. This takes the upstream cell value directly as the face value.

The mass transfer coefficient is extracted using the `surfaceFieldValue` function object, which computes the area-averaged concentration gradient $dc/dy|_{y=0}$ at the cathode surface. This is then used in Equation 3.1 to obtain k_m . Additionally, the concentration profile normal to the cathode is sampled using the `sets` function object, providing the boundary layer profiles shown in Figure 4.4e.

C.2. Multiphase simulation (Part B)

The domain of the multiphase simulation consists of two rectangles, each 0.050 m long and 0.020 m high, giving a total height of 0.040 m. The liquid–liquid interface is initialised at the midplane ($y = 0.020$ m). Each block contains 100×60 cells. The y -direction grading is set to 0.1 in the lower block and 10 in the upper block, so that in both blocks the cells become progressively finer towards the central interface. The domain is one cell thick in the z -direction with `empty` front and back patches, making the simulation effectively two-dimensional.

Phase initialisation

The initial condition is set using `setFields`. The lower block ($0 \leq y \leq 0.020$ m) is assigned a salt volume fraction $\alpha_{\text{salt}} = 0$ and zero velocity, representing the bismuth layer at rest. The upper block ($0.020 \leq y \leq 0.040$ m) is assigned $\alpha_{\text{salt}} = 1$ and the prescribed inlet velocity U_{inlet} in the x -direction, representing the flowing molten salt.

Solver and time-stepping

The simulation uses `interFoam`, which solves the momentum equation for a mixture of two fluids and solves the phase fraction field α . The pressure-velocity coupling is handled by the PIMPLE algorithm, with 4 outer correctors (`nOuterCorrectors 4`) and 3 inner pressure correctors (`nCorrectors 3`).

The Courant number expresses how far a fluid parcel travels relative to the local cell size in a single time step [23]. Keeping the courant number below 1 ensures that information propagates no faster than one cell per time step, which is important for numerical stability. The time step is adjusted automatically at every step to keep both the flow Courant number and the interface Courant number below 0.5 (`maxCo 0.5`, `maxAlphaCo 0.5`), with a maximum physical run time of 1 s and fields written every 100 time steps.

Linear solvers

The phase fraction α is solved with a `smoothSolver` using Gauss–Seidel smoothing to a tolerance of 10^{-7} . The modified pressure p_{rgh} uses GAMG with Gauss–Seidel smoothing. Velocity is solved with `smoothSolver` to a tolerance of 10^{-7} .

Post-processing

The velocity profile across the liquid–liquid interface is sampled at the end of the run along a wall-normal line at $x = 0.025$ m, from $y = 0.018$ m to $y = 0.024$ m, using 200 points. This covers the region immediately around the interface and provides the profile shown in Figure 4.6.