

CFD Investigation on Free Surface of Immiscible Molten LiCl-KCl/Cd System

Kwangrag Kim*, Si-Hyung Kim, Jun-Bo Shim, Seungwoo Paek, In-Tae Kim

Korea Atomic Energy Research Institute, 1045 Daedeokdaero, Yuseong-gu, Daejeon, 305-353, Republic of Korea

*Corresponding author: krkim1@kaeri.re.kr

1. Introduction

Molten-salt mixing in stirred electrolytic cells is a common operation in many pyrochemical processes. In an electro-winning cell, two immiscible liquids of molten LiCl-KCl/Cd are in place and contact with free surface each other for an electrochemical reaction. LiCl-KCl eutectic serves as an electrolyte, and liquid cadmium serves as a cathode material.

Therefore, the electro-winning reactors need to be designed to provide high mass transfer and electrode surface area between the electrode and bulk electrolyte. The efficiency of the electro-winning cell is largely affected by its geometric configuration and electrolyte turbulence. The influence of electrolyte flow on the performance can be evaluated using a CFD model.

However, the hydrodynamic behavior in the molten state is not well understood in this system. Therefore, a computational method has been developed to investigate the hydrodynamic behavior of immiscible phases in an electro-winning cell.

This paper presents an interface tracking method for modeling the flow of immiscible liquids of LiCl-KCl/Cd in the electrolytic processes. An approach was proposed to provide an insight into the behaviors of free electrode surface in an electro-winning cell.

2. Methods and Results

2.1 Immiscible liquid layer system

To understand the mechanism of the mass transfer effect across the free surface, a simple liquid layer system is suitable for the interface simulation of immiscible liquids.

The following assumptions are made in formulating the viscous flow in both liquid phases as sketched in Fig. 1: (1) the fluids are incompressible, viscous and Newtonian, (2) the flow is turbulent and isothermal, (3) the physical properties of liquids are constant despite the change in solute concentration, and (4) the interface is a free surface so that the gravity becomes irrelevant in the momentum equations.

2.2 CFD Model

The dynamics of two (or more) immiscible fluids are governed by the Navier-Stokes and continuity equations [1,2]. The homogeneous multiphase model is described by these equations.

The numerical model directly solves the equations governing an incompressible isothermal multi-fluid flow within a CFD platform.

$$\nabla \cdot U = 0 \quad (1)$$

$$\frac{\partial U}{\partial t} + \nabla \cdot UU = -\frac{1}{\rho} \nabla P + \frac{1}{\rho} \nabla \cdot \tau + g + \frac{1}{\rho} S \quad (2)$$

Volume tracking methods represent two immiscible fluids with a characteristic function C :

$$C = \begin{cases} 1 & \text{in cells full of a particular fluid} \\ 0 & \text{in cells devoid of that particular fluid} \end{cases} \quad (3)$$

The location of the interface is not explicitly tracked, but is instead captured by the distribution of C , since C takes the values $0 \leq C \leq 1$ on the interfaces. The species mass transfer in each liquid phase is governed by the convective diffusion equation:

$$\frac{\partial c}{\partial t} + \nabla \cdot (Uc) = D \nabla^2 c \quad (4)$$

A simulation of the free surface flows usually requires defining the boundary and initial conditions to set up the appropriate pressure profile and volume fraction fields.

2.3 Free surface simulation

The simulation is made for a simple case of geometry with $L=0.1$ m, $d=0.05$ m, $U_{\max}=0.1$ m/s, $C_{\max}=50$ mol/m³ and $C_{\min}=0$ mol/m³ as shown in Fig. 1. The properties of each phase are listed in Table I.

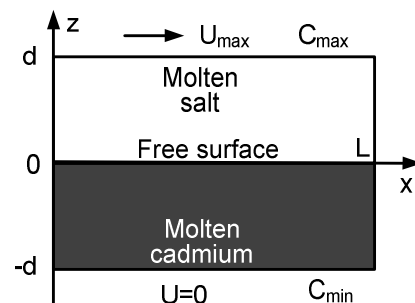


Fig. 1. Schematic of the system with two immiscible liquid layers with mass transfer from top to bottom phase.

For this analysis, computational hexahedra meshes up to a resolution of 5000 elements were used. The standard k-epsilon model is used for the free surface simulation of the immiscible LiCl-KCl/Cd system.

Table I: Properties of molten phase for simulation [3,4]

	LiCl-KCl	Cadmium
Solute diffusion coefficient (m ² /s)	1.03×10 ⁻⁹	1.45×10 ⁻⁹
Surface tension (mN/m)	125.33	600
Viscosity (mN s/m ²)	2.23	1.84
Density (kg/m ³)	1621	7820

In this study, we focused on a specialized interface arising between two immiscible solutions of electrolyte and liquid electrode. An electrolyte, a medium with ionic conductivity and mobile charge carriers, provides ion transport through the immiscible interface with the liquid metal electrode. An interface is defined as a free surface boundary between the electrolyte and liquid electrode held in a crucible container.

The volume of fraction model is used and is a surface tracking technique applied to a fixed Eulerian mesh. It is designed for two or more immiscible fluids where the position of the interface between the fluids is of interest. In this model, a single set of momentum equation is shared by the fluid and the volume fraction of each of the fluids in each computational cell is tracked throughout the domain.

Fig. 2 shows the typical evolution of the velocity streamlines and free surface *versus* time, where the circulation patterns are observed. The local circulation pattern is not stabilized and changes constantly, suggesting that the random fluctuations in the surface concentration may play a significant role even after the convection has been developed. This situation is more realistic in practical liquid electrode system; in which the free surface is formed between the immiscible phases with sharing convection of the bulk flow parallel to the interface.

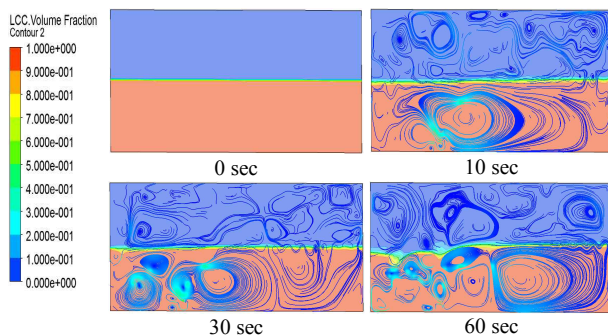


Fig. 2. Figures showing the progression of free surface evolution and streamline map as a function of time.

3. Conclusions

A numerical model has been developed to simulate complex free surface flows in an immiscible molten LiCl-KCl/Cd system. It was found that this method was capable of tracking a contorting free surface as well as interface mass transfer in the multi-phase flow fields. The approach can provide an insight into the behaviors of free electrode surface in an electro-winning cell.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (2012M2A8A5025699)

REFERENCES

- [1] Z. Mao, P. Lu, G. Zhang, and C. Yang, Numerical Simulation of the Marangoni Effect with Interphase Mass Transfer between Two Planar Liquid Layers, Chinese Journal of Chemical Engineering, Vol.16(2), p. 161, 2008.
- [2] V. G. Levich, Physicochemical Hydrodynamics, Prentice Hall, Englewood Cliffs, New Jersey, USA, 1962.
- [3] Y. H. Kang et al., Pyrometallurgical Data Book, KAERI Report, KAERI/TS-110/99, 1999.
- [4] G. J. Janz et al., Physical Properties Data Compilations Relevant to Energy storage-II. Molten salts: Data on single and Multicomponent Salt System, Molten Salts Data Center, Cogswell Laboratory, Rensselaer Polytechnic Institute, Troy, New York, 1979.