A numerical study on electrochemical transport of ions in calcium fluoride slag

E Karimi-Sibaki, A Kharicha, M Wu, and A Ludwig

Christian-Doppler Lab for Adv. Process Simulation of Solidification & Melting,
Chair of Simulation and Modeling of Metallurgical Processes,
University of Leoben, Franz-Josef-Str. 18, A-8700 Leoben, Austria

E-mail: abdellah.kharicha@unileoben.ac.at

Abstract. Electrically resistive \( \text{CaF}_2 \)-based slags are widely used in electroslag remelting (ESR) process to generate Joule heat for the melting of electrode. The electric current is conducted by ions (electrolyte) such as \( \text{Ca}^{+2} \) or \( \text{F}^- \), thus it is necessary to establish electrochemical models to study electrical behavior of slag. This paper presents a numerical model on electrochemical transport of ions in an arbitrary symmetrical (ZZ) and non-symmetrical (\( \text{CaF}_2 \)) stagnant electrolytes blocked by two parallel, planar electrodes. The dimensionless Poisson-Nernst-Planck (PNP) equations are solved to model electro-migration and diffusion of ions. The ions are considered to be inert that no Faradic reactions occur. Spatial variations of concentrations of ions, charge density and electric potential across the electrolyte are analyzed. It is shown that the applied potential has significant influence on the system response. At high applied voltage, the anodic potential drop near the electrode is significantly larger than cathodic potential drop in fully dissociated \( \text{CaF}_2 \) electrolyte.

1. Introduction

In many metallurgical processes such as electroslag remelting (ESR), the slag is core compound served to clean the metal by removing sulfur and non-metallic inclusions. In general, \( \text{CaF}_2 \)-based slags are used since they have high degree of chemical reactivity and low electrical conductivity. The heat required to supply into the process is obtained by passing electric current through the resistive slag layer. The mode of current conduction in the slag is either ionic or a mixed ionic/electronic process [1]. Mitchell et al used a galvanostatic pulsing technique to measure magnitudes of overpotentials resulting from concentration polarization at the interface between iron and \( \text{CaF}_2 \)-based slags in an electrolytic cell [2]. They found that potentials observed on the ESR electrode agreed with the results from the electrolytic cell. Furthermore, addition of a relatively small amount of \( \text{Al}_2\text{O}_3 \) to \( \text{CaF}_2 \) substantially decreases electric conductivity of liquid slag [3]. As a consequence of formation of complex ions such as \( \text{AlOF}_2 \), the mobility of \( \text{F}^- \) reduces [3]. Kojima studied the effect of mode of current (DC or AC) on electrochemical behavior of oxygen in a small scale ESR unit [4]. The distribution of oxygen in ingot was influenced by mode of current and electrode polarity. Kharicha et al [5] addressed possible effects of electrochemical reactions on formation of droplets at an ESR electrode. Metallic droplets which are surrounded by resistive slag can conduct an electric current when the potential drop at their extremities exceeds the sum of anodic and cathodic overpotential. As a consequence of ionic conduction of slag, dependences of melt rate of electrode and ingot composition on the electrode polarity were observed in DC operation of the ESR process [4]. Kawakami et al...
reported that electrode with positive polarity has higher melt rate compared to electrode with negative polarity [6]. The roles of electrochemical reactions occur in the slag-metal interface are well known. Loss of alloy elements such as Ti and Al by oxidation is reported as a significant issue during DC operation of ESR process [7-8]. Furthermore, the efficiency of sulphur removal in ESR process was reported to be dependent on the condition of applied electric current (AC or DC) [9]. In fact, the aforementioned phenomena are as a result of the ionic character of slag. As such, it is essential to develop an electrochemical model to investigate the electrical behavior of slag. The model must take into account ions response to the applied electric field.

In the current study, a typical electrochemical cell is considered including two parallel, planar electrodes and a completely dissociated electrolyte. The Finite Volume Method (FVM) is used to model the ions transfer under the applied electric potential. No Faradaic reaction is modeled. Mass conservations of inert ions are automatically satisfied that is the advantage of using FVM method. First, an arbitrary binary symmetric electrolyte (\(Z^+Z^-\)) is investigated in which diffusion coefficients and concentrations of \(Z^+\) and \(Z^-\) ions are equal. Then, \(CaF_2\) is considered as a fully dissociated electrolyte consisted of \(Ca^{2+}\) and \(F^-\) ions where the diffusion coefficients and concentrations are different. The effect of applied potential and electrolyte properties such as concentrations of ions on the system response is discussed. The goal is to achieve some fundamental understanding of electrochemical behavior of \(CaF_2\) slag under the influence of applied electric field.

2. Transport of ions

For an electrolyte subjected to an electric field, the Poisson-Nernst-Planck (PNP) equations describe the flux of ions through the electrolyte.

\[-\nabla \cdot (\varepsilon \nabla \phi) = F \sum z_i c_i = \rho \]  \hspace{1cm} (1)

\[\frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{N}_i \]  \hspace{1cm} (2)

\[\vec{N}_i = \bar{u} c_i - D_i \nabla c_i - \frac{Fz_i D_i \nabla \phi}{RT} c_i \]  \hspace{1cm} (3)

The net flux of ions \((N_i)\) including convection, diffusion, and electro-migration must be conserved as described in Eq. (2) where \((c_i)\) is the concentration of \(i\)-th ion. According to Eq. (3), the convection and diffusion fluxes are dependent on velocity \((u)\) and diffusion respectively where \((D_i)\) is diffusion coefficient of \(i\)-th ion. Furthermore, the electro-migration flux of ions is included in Eq. (3) where \((z_i)\) is the charge number of \(i\)-th ion, \((F)\) is Faraday constant, \((R)\) is the universal gas constant, \((T)\) is temperature, and \((\phi)\) is electric potential. The Poisson equation, Eq. (1), relates the electric potential to the charge density \((\rho)\) of system where \((\varepsilon)\) is the electric permittivity constant of the electrolyte.

The steady state solution of the PNP equations for a symmetrical binary electrolyte was given in terms of Jacobi elliptic functions by Golovnev [10]. It was shown that the net charge density exists in a very thin boundary layer (diffuse charge layer) near the electrode (~1-100 nm). The length of diffuse charge layer is called Debye screening length \((\lambda_D)\) in electrochemical systems.

\[\lambda_D = \sqrt{\frac{\varepsilon \varepsilon_0 RT}{2z_i^2 F^2 C_0}} \]  \hspace{1cm} (4)

where \((C_0)\) is the bulk concentration of electrolyte.

The specific interfacial region formed near the electrode where the charge is separated is called electric double layer. As illustrated in Fig. 1, the double layer is composed of a diffusion layer, diffuse charge layer, and the compact stern layer (~0.5 nm) where ions are attracted to the surface. The diffuse charge layer is not electrically neutral as it has a net charge. However, the diffusion layer is
electrically neutral where a non-uniform concentration of electrolyte may exist [11]. The definition of thickness of diffusion layer is arbitrary because the concentration reaches asymptotically to the bulk concentration [12]. For instance in cyclic voltammetry, the thickness is considered as: \((D, t)^{0.5}\) where \((I/t)\) is the scan rate. As such, the thickness can be large (order of micrometer) at slow scan rate or small (order of nanometer) at fast scan rate [12].

![Diagram of electric double layer](image)

**Fig.1. Structure of electric double layer.**

3. **Modeling**

Configuration of the computational domain including liquid electrolyte blocked by electrodes (anode and cathode) is illustrated in Fig 2. A variable sized mesh is used applying a very fine mesh near the electrodes to resolve the boundary layer where the gradient is large. The mesh element size is gradually increased away from boundaries. The domain size is 1 mm and the total number of mesh elements is 1000. The simulation is performed with the commercial CFD software FLUENT-ANSYS v.14.5. The required transport equations are specified using User-Defined Scalars (UDS).

![Diagram of computational domain and mesh](image)

**Fig.2. Configuration of computational domain and the mesh.**

Applying numerical methods to model the problem requires extremely fine mesh to resolve the boundary layer adjacent to the electrode. As stated by Bazant [13], the investigation of electrochemical systems is significantly simplified using dimensionless formulations of PNP equations. This is the main step to study the asymptotic behavior of an electrochemical system in order to get physical insight into the problem.
Here, a one dimensional model is considered in which the parameter variation is only in one direction across the electrolyte. Furthermore, the electrolyte is assumed to be stagnant ($u=0$). Resultantly, the dimensionless form of PNP equations for the binary electrolyte is expressed as:

\[-\nabla \cdot (\xi^2 \nabla \phi^*) = z_+ C_+ + z_- C_- \quad (5)\]

\[\frac{\partial C_+}{\partial t} = \nabla \cdot \left( D_+ \nabla C_+ + z_+ D_+ \nabla \phi^* C_+ \right) \quad (6)\]

\[\frac{\partial C_-}{\partial t} = \nabla \cdot \left( D_- \nabla C_- + z_- D_- \nabla \phi^* C_- \right) \quad (7)\]

The basic variables in PNP equations are scaled as follow:

\[\phi^* = \frac{F \phi}{RT}, \quad C_z = \frac{c_z}{c_{ref}}, \quad \xi = \frac{\lambda_D}{L_{ref}}\]

Where $C_z$ denotes the dimensionless concentration of cation (+) or anion (-), and $c_{ref}$ is the reference concentration which is typically in the same order as bulk concentration of ions. The electric potential is scaled using thermal voltage ($RT/F$) since diffusion and chemical reactions are thermally activated processes. Furthermore, $\xi$ is the ratio of Debye screening length ($\lambda_D$) to the reference length ($L_{ref}$) which is typically considered as the distance between electrodes or the size of electrode.

Ions are considered to be inert and subsequently no faradaic reactions occur in our system. Thus the boundary conditions for Eq. (6) and Eq. (7) are zero total flux of ion (including electro-migration and diffusion fluxes). Additionally, Eq. (5) is used to determine the electric potential in the system. For the latter, a fixed value ($\pm FV/2RT$) is considered at the anode (+) and cathode (-) where ($V$) is the operating electric potential of the electrolytic cell. As described by Bazant [13], it is impossible to satisfy all the boundary conditions assuming a negligible screening length compared to the system size ($\xi~0$). Physically, this assumption is corresponding to electro neutrality ($\rho=0$) which is always violated at electrochemical interfaces. A numerical solution can only be achieved using a rather larger value of $\xi$ to emphasize the importance of diffuse charge near the electrodes where the electro neutrality condition is not valid. For instance, the value of $\xi$ can be chosen as large as 0.05 for a micro electrochemical system [13]. In this way, the asymptotic behavior of an electrochemical system can be captured.

Simulations are executed unsteadily, but only final steady state results are analyzed. Initial concentrations of ions are calculated assuming a fully dissociated electrolyte. The concentration of $\text{CaF}_2$ is the ratio of density ($\sim 2600 \text{ kg.m}^{-3}$) to molecular weight ($\sim 78.07 \text{ g.mol}^{-1}$). The fully dissociated $\text{CaF}_2$ electrolyte ($\text{CaF}_2 \leftrightarrow Ca^{2+} + 2F^-$) is consisted of $Ca^{2+}$ and $F^-$ ions in which the concentration of $F^-$ is twice larger than the concentration of $Ca^{2+}$. The electric permittivity of electrolyte is assumed to be the same as permittivity of free space since that is unknown for $\text{CaF}_2$ at elevated temperature. Table 1 lists all physical properties required for our calculations.
Table 1. Properties of the system.

| Property               | Value                  |
|------------------------|------------------------|
| $T$: Bulk temperature (K) | 1773                   |
| $R$: Universal gas constant (J·mol⁻¹·K⁻¹) | 8.314546               |
| $F$: Faraday constant (Amp·s·mol⁻¹) | 96485                  |
| $\varepsilon_s$: Electric permittivity (F·m⁻¹) | 8.85418x10⁻¹²          |
| $V$: Low applied voltage (V) | 0.005                  |
| $V$: High applied voltage (V) | 2                      |
| $C_{\text{ref}}$: Reference concentration (mol·m⁻³) | 1x10⁵                   |
| $L_{\text{ref}}$: Reference length (m) | 1x10⁻⁶                 |
| $\lambda_D$: Debye length (m) | 1x10⁻⁹                 |
| $\zeta$ | 0.01                   |

**ZZ electrolyte**
- $Z^+$: Concentration (mol·m⁻³) | 3.33x10⁵
- $Z^+$: Diffusion coefficient (m²·s⁻¹) | 4x10⁻⁹
- $Z^+$: Charge number | +1

**CaF₂ electrolyte**
- Ca²⁺: Concentration (mol·m⁻³) | 3.33x10⁵
- Ca²⁺: Diffusion coefficient (m²·s⁻¹) | 5.66x10⁻⁹ [14]
- Ca²⁺: Charge number | +2
- F⁻: Concentration (mol·m⁻³) | 0.666x10⁵
- F⁻: Diffusion coefficient (m²·s⁻¹) | 4.12x10⁻⁹ [14]
- F⁻: Charge number | -1

4. Results and discussions
A number of simulations were performed by considering two different operating applied potentials. Additionally, two different electrolytes are investigated. Firstly, an arbitrary binary symmetric electrolyte (ZZ) is studied in which diffusion coefficients, concentrations, and charge numbers of ions are identical. Secondly, the fully dissociated CaF₂ which is a non-symmetrical binary electrolyte is investigated. Furthermore, responses of electrolytes to the applied potential are compared. Fig. 3 shows the normalized concentration profile of cations ($Z^+$ or Ca²⁺) and anions ($Z^-$ or F⁻) across the electrolyte at low applied voltage. Note that, initial concentrations of anions are not the same in Fig. 3(b). As expected, cations move toward the cathode ($X=0$) and anions accumulate near the anode ($X=1$). Once the voltage is applied, ions move to screen the electric field originated from electrodes. Therefore counter-ions (relative to electrode) entering to double layers by electro-migration from the bulk. Concurrently, co-ions leave the double layer entering to the bulk. Due to excess of counter-ions in the double layer, diffusion competes against electro-migration until a uniform equilibrium state is reached. In this way, diffusion layers spread across the electrolytic cell from electrodes. As illustrated in Fig. 3 (c-d), the thickness of diffusion layer can significantly decrease by applying a larger voltage in the system. Here, the electro-migration is dominant that results in double layers filled only with counter-ions. In other words, bulk concentrations of ions significantly decrease so that co-ions completely leave diffusion layers.
Fig. 3. Normalized concentrations of ions are plotted across the electrolyte blocked by cathode ($x=0$) and anode ($x=1$). (a) Cations ($Z^+$ and $Ca^{2+}$) at low applied potential ($0.005 \text{ V}$), (b) Anions ($Z^-$ and $F^-$) at low applied potential ($0.005 \text{ V}$), (c) Cations ($Z^+$ and $Ca^{2+}$) at high applied potential ($2 \text{ V}$), (d) Anions ($Z^-$ and $F^-$) at high applied potential ($2 \text{ V}$).

As illustrated in Fig. 4 (a-b), charge density is divided in three regions: neutral region in the bulk and two electrically charged boundary layers near electrodes. The net bulk charge density remains very small ($\rho \sim 0$) that is known as electro-neutrality condition. Most often, electro-neutrality assumption is used for large scale electrochemical systems. This is an excellent assumption that can significantly simplify investigation of large scale systems. However, it is essential to incorporate the effect of double layers into boundary conditions [12]. As shown in Fig. 4 (b), the thickness of diffusion layer is significantly decreased by applying larger voltage which is consistent with Gouy-Chapman theory [12, 15]. According to the theory, counter-ions have higher tendency to be absorbed than co-ions to be pushed out of the double layer once the electric field is applied. As such, the total charge density of ions increases near the electrode and depletes in the bulk [12]. Furthermore, the charge density remains symmetrical for both $ZZ$ and $CaF_2$ at low applied voltage as indicated in Fig. 4(a). However, the symmetry breaks strongly applying large voltage for $CaF_2$ electrolyte due to difference in initial concentrations of ions ($F^-$ and $Ca^{2+}$) as shown in Fig. 4(b).

The spatial variation of electric potential is controlled by charge density distribution through Poisson’s equation (Eq. 1). Nevertheless, changes in bulk concentration of ions influence the electric...
potential through the whole electrolyte. In other words, variation in electric potential is not limited near electrodes due to evolution of diffusion layers. The thicknesses of diffusion layers are dependent on the applied potential since electro-migration and diffusion are competing. As shown in Fig. 4(c), the diffusion layer is a narrow region near diffuse charge layer at low applied voltage. Consequently, the potential drop is only near electrodes and the bulk variation of electric potential is negligible. Furthermore, the symmetry of electric potential through the electrolyte is kept independent of electrolyte whether ZZ or CaF$_2$. In contrast, strong breaking of symmetry in electric potential profile is observed for CaF$_2$ at large applied potential as illustrated in Fig. 4(d). Additionally, the spatial variation of electric potential is extended to the bulk. The interfacial potential difference near the anode is significantly larger than near the cathode for the CaF$_2$ electrolyte.

![Graphs](image)

Fig. 4. The following parameters are plotted across the electrolytes (ZZ or CaF$_2$) blocked by cathode ($x=0$) and anode ($x=1$), (a) Normalized charge density at low applied voltage (0.005 V), (b) Normalized charge density at high applied voltage (2 V), (c) Electric potential at low applied voltage (0.005 V), (d) Electric potential at high applied voltage (2 V).
It must be noted that a conventional slag is typically composed of $\text{CaF}_2$, $\text{Al}_2\text{O}_3$, $\text{CaO}$, $\text{SiO}_2$, and $\text{MgO}$. Therefore, a number of other ions such as $\text{O}^{2-}$, $\text{Al}^{3+}$, $\text{Mg}^{2+}$, and $\text{Si}^{4+}$ can play role in electrochemical behavior of the slag. Furthermore, they can participate in Faradaic reactions at electrode surface. Therefore, the model must be further developed to take into account effects of other ions as well as Faradaic reactions on electrical behavior of a conventional slag.

5. Summary
A numerical study is performed to investigate electrochemical transport of ions in $\text{CaF}_2$ slag as a non-symmetrical binary electrolyte. The behavior of system is compared to an arbitrary binary symmetrical electrolyte (ZZ) in which concentration, charge number and diffusion coefficients of ions are identical. Furthermore, the influence of applied potential is studied. The Poisson-Nernst-Planck (PNP) equations considering convection, diffusion, and electro-migration of ions through the electrolyte are solved. The effect of Faradic reactions is not included in the current study. Spatial variations of concentrations of ions, charge density, and electric potential across the electrolyte are compared for ZZ and $\text{CaF}_2$ electrolytes. At low applied voltage, the interfacial potential difference near electrodes remains just about the same. Additionally, the diffusion layer is thin resulting in uniform concentration of ions in the bulk. In contrast, the diffusion layer is extended to the bulk of electrolytes at high applied voltage. The symmetrical electrolyte (ZZ) has identical potential drop near electrodes independent of magnitude of operating potential. However, significant difference of interfacial potential drop is observed for non-symmetrical electrolyte ($\text{CaF}_2$). For the latter, the anodic interfacial potential drop is much larger than the cathodic one.

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7. References
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