PH MODELING DURING ELECTROCHEMICAL TRANSFORMATION IN GROUNDWATER

A Thesis Presented

by

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Abstract

A theoretical model is developed in this research to predict the change of pH during electrochemical remediation process. During electrochemical remediation process electrolyte will experience an alteration in pH due to water electrolysis reaction. The resulted pH change can cause a significant deviation in existed reactions or create new pathways. The reactive solute can be subjected to a variety of chemical changes including reactions such as acid-base reaction, oxidation-reduction, and dissolution-precipitation. Having a mathematical model will create a better understanding of multicomponent species transport mechanisms which is needed to develop the necessary design or analysis tools for engineering the implementation.

Development of the model is based on two type of reactors, completely stirred batch reactor and flow-through reactor. This model accounts for transport mechanisms as well as chemical and electrochemical reactions. A two-step iterative finite difference method is adopted to solve for all the available species in the system. The concentration variables consist of are $H^+$, $OH^-$, $CO_3^{2-}$, $HCO_3^-$, $H_2CO_3$, and $CaCO_3$ for the flow through reactor and are $H^+$, $OH^-$, $SO_4^{2-}$, $HSO_4^-$ for the batch reactor. The result of this study is compared to the obtained experimental data by Ciblak et al [12] for batch reactor and Rajic et al [36] for flow-through reactor. The model predicts the pH change resulted by the electrochemical process and shows a good correlation in comparison to experimental data.
Chapter 1  Introduction

1-1 Introduction

Groundwater is an essential source of drinking water because of its availability as well as its reliability and good quality [28]. More than 1.5 billion people worldwide and more than 50% of the population of the United States rely on groundwater as their primary source of drinking water [5]. Concern about the health risks associated with groundwater pollution have led to the enactment of federal and state laws regulating the use, storage and transport of hazardous substances, as well as establishing human exposure limits [18]. The Safe Drinking Water Act (SDWA) amendments of 1986 established the Wellhead Protection Program in an effort to protect the recharge areas of public water system wells from all sources of contamination [1]. Therefore, it has been recognized that the quality of groundwater is just as important as its quantity where this required quality depends on the usage purpose of water as well as the environmental impacts of contamination [47]. Furthermore, intensive use of groundwater has been causing difficulties with resource depletion and additional effects such as saltwater intrusion, base-flow and wetland impacts involving further complications with environment and its ecosystems. In the United States, more than 17,000 square miles in 45 states have been directly affected by subsidence and more than 80% of the identified subsidence is due to pumping of groundwater [14]. Therefore, the impact of soil and water contamination of groundwater resources is becoming increasingly significant as the disclosed number of un-engineered waste contaminant facilities and contaminated sites grow and remediation costs increases. Prior
to urbanization, natural groundwater recharge resulted from infiltration of precipitation through upper layers. The remaining contamination which finds its way into aquifer would be mostly eliminated by environment’s self-purification capability. With the growth of urbanization, the permeable soil surface area through which recharge by infiltration could occur was reduced which resulted in much less groundwater recharge as well as increase in contamination [33]. Therefore, the subsurface water is vulnerable to pollution. Groundwater has been polluted by contaminants from storage tanks, septic systems, hazardous waste sites, landfills, mine waste, and the widespread use of road salts, fertilizer and pesticide in farming, and other chemicals all over the world for decades. Once contaminated, it is difficult and expensive to clean-up the contaminated site including soil and water. Of the various organic contaminants found in groundwater, the widely used industrial solvents and aromatic hydrocarbons from petroleum products are the most common [25].

A variety of options may exist to select a cleanup remedy at a site, however the efficiency and cost of these options may vary widely. Conventional treatment programs for groundwater contamination have involved pumping groundwater to the land surface followed by treatment and engineered disposal [9]. Pump-and-treat groundwater remediation methods have proved to be expensive and in many cases ineffective at achieving the proposed level of cleanup [25]. An alternative to pump-and-treat groundwater remediation is the use of reactive barriers. These reactive barriers are installed in the path of flowing groundwater, either as horizontal treatment layers or as vertical treatment walls [9]. Although conventional ground burial and land disposal are often economical, they do not provide the best solution, and in some cases they are not
necessarily the most effective solution. Removal and remediation are different since the removal refers to an immediate, short-term action whereas remediation is a long-term decontamination which is a more expensive solution for a complex problem. Therefore, a demand for an efficient and cost effective remediation technique has led to the innovative method of using low electric current for oxidation/reduction of contamination as well as to expedite of the ion movement through fine grained sites. Electrokinetie remediation is a controlled application of electrical migration and electroosmosis together with the electrolysis reactions at the electrodes [2].

Electrochemical mechanisms are gaining increasing attention and interest because of their low energy consumption accompanied by low required maintenance. Consequently, they are one of the most promising in-situ soil and groundwater decontamination methods, particularly for contaminated fine grained sites. Therefore, the opportunity of substituting the conventional remediation energy source with a renewable source of energy is of interest because of the method’s low energy consumption. Electroremediation involves using direct current across porous electrodes to intercept and transform contamination in groundwater through direct and indirect electrolysis mechanisms [31]. Conceptually, in direct electrolysis mechanism, the contaminants exchange electrons directly at the electrode surface. This mechanism is theoretically possible in systems with low dissolved oxygen at low potentials. However, direct electrolysis has low kinetic rate but could be increased by using catalyst deposited electrodes since it depends on anode electrocatalytic activity. Alternatively, metal oxide electrodes (MMOs) are used typically for indirect electrochemical oxidation [24]; here, contaminants do not exchange electrons directly with
the anode surface but rather through an intermediate compound which can be electro-generated by either anodic or cathodic processes.

In an unenhanced electrochemical remediation process, the applied current produces an acidic and basic region in anode and cathode compartments, respectively [2]. The produced acidic and basic fronts will spread through the soil due to different transport mechanisms caused by hydraulic, concentration, and charge gradient. Since chemical species can exist in different forms depending on the pH of the aqueous environment, the resulted pH alteration can cause a great change in existed reactions or create new pathways. The reactive solute can be subjected to a variety of chemical changes including reactions such as acid-base reaction, oxidation-reduction, and dissolution-precipitation [50]. Therefore, the transport mechanisms can be accompanied by one or more of these chemical processes depending on the chemical solution and aquifer constituents [6].

Furthermore, Acar et al. came to the conclusion that the efficiency of the remediation processes strongly depends on the ionic mobility and the concentration of the species. Therefore, pH monitoring is needed to advance the transport of contaminants to prevent precipitation and induce depolarization [2, 40, 41].

Electrochemical remediation can be optimized by integrating it with other remediation methods such as the Fenton process or adding zero valent metal to the system [38]. They have mainly described the advection and dispersion of conservative solutes.

Groundwater flow models have been used to design the groundwater monitoring networks, evaluate the local and regional groundwater resources, predict the effect of future groundwater withdrawals on groundwater levels, estimate the aquifer parameters and boundary conditions, design the dewatering system for underground structure construction
and maintenance, etc. [39]. Groundwater models have been integral tools for groundwater water contamination investigation, remediation design and optimization. Solute transport models based on water flow models have been used in studies of salt-water intrusion, leachate movement from landfills and other waste-disposal sites, contamination plumes from seepage ponds, radionuclide movement from radioactive waste sites, movement of fertilizers and pesticides from agricultural fields, and other types of groundwater pollution problems. Having a mathematical model will create a better understanding of multicomponent species transport mechanisms which is needed to develop the necessary design or analysis tools for engineering the implementation. Moreover, the mathematical model provides a good estimate of energy use, and therefore will play an important role in evaluating the cost efficiency of the remediation process.

The combined effect of aforementioned physical and chemical processes will lead to developing N number of partial differential equations (PDEs) for N number of species existing in the solution. One of the important considerations in developing the model is the assumption of chemical equilibrium versus kinetic formulation. Although the local equilibrium model particularly reduces the number of unknowns in the system and has a significant computational advantage, it is only valid under specific assumptions, such as the fast rate of reaction in respect to species transport [46]. Even though this implies that a kinetic formulation is always the more general approach in describing the reactions as opposed to equilibrium formulation, the kinetic rate constants for fast equilibrium reactions have uncertainty due to their fast nature [46].

Although analytical solutions are accurate and efficient for a variety of problems, as the system gets complicated and the impacts of more variables are considered in the model,
they are not easily available. For a nonlinear system of PDEs with N number of unknowns, analytical or approximate analytical solutions are limited. For general heterogeneous porous media, numerical solutions are more commonly used since they are more convenient to manipulate for heterogeneous cases as well as complicated boundary conditions. Numerical solutions usually involve spatial discretization to approximate the partial differential equations by a system of ordinary differential equations, temporal discretization to approximate the ordinary differential equations to a system of algebraic equations. Eventually, the partial differential equations are approximated by a set of algebraic equations in a number of time steps. For the accuracy and stability of the solution, the spatial and temporal grid sizes must be fine enough depending upon the spatial and temporal heterogeneity. Otherwise, approximation errors and truncation errors can accumulate in each time step and the solution can be inaccurate or diverge. But fine grid size in space means very large scale model; and fine grid size in time suggests a large number of time steps. This combination makes the computation requirements for some groundwater flow models infeasible even by today’s most powerful computers with parallel algorithms.

The combination of transport mechanisms and reaction of the species is numerically intensive due to the small time steps required, the number of ion fluxes to be calculated, and the iterative method to solve the partial differential equations implicitly. Until now, most of the studies are based on precipitation and sorption of the species and include the water association/dissociation reaction, since the method is mostly used in the sites with fine grained soil where electro-migration has more impact in the system than reactions [6, 20, 37].
1-2 Objectives

The objectives of this study are:

- To provide a theoretical model and the numerical solution to describe the transport mechanisms of fluid, charge and molecular species coupled with aqueous reactions of chemically reactive species under hydraulic and chemical gradients
- To identify related techniques to increase the modeling accuracy and efficiency
- To evaluate the developed theoretical model for electrochemical remediation process in batch reactor as well as a flow-through reactor with experimental measurements
- To investigate possibility of enhancing the model to further discussion of change of concentration of species outside the electrodes’ boundaries.

1-3 Scope of the study

This study is aimed to develop a theoretical model as a tool to explain the complex identity of changes in chemical and electrical potentials by the application of a small direct current through electrodes. The presented model includes electrochemical reactions, water auto-ionization, precipitation reactions, as well as acid-base reactions in addition to transport mechanisms such as advection and diffusion processes. One dimensional conditions are adopted in this study since two dimensional system makes the system unnecessarily complicated and more difficult to compare with experimental data.

The main focus in this study is on hydrogen and hydroxide ion movement to evaluate the current understanding of the technology as well as the validation of the presented
theoretical model. Although various number of ions are present in the solution but to simplify the modeling and the experimental verification effort necessary, reaction and transportation of species which are not contributing much to the result are being neglected. The predominant species in the model predictions are $H^+, OH^-, CO_3^{2-}, HCO_3^-, H_2CO_3$, and $CaCO_3$. The first two species, $H^+, OH^-$, are the most dominantly produced ions on the electrodes’ surfaces and the carbonate related species are the most important ions in the buffered environments. The chemical reactions associated with these species such as acid/base reactions, water association/dissociation reaction, and precipitation/dissolution reactions are considered to be relatively fast therefore an equilibrium model has been adopted as opposed to kinetics approach. The constant current condition is being employed in the model, therefore the production rates are assumed to stay constant during the process, even though it might slightly change due to double layer appearance around the electrodes and limiting the mass flux to the electrode surface.

Predictions from the result of this model are compared to the obtained experimental data from another study. The model developed herein consists of two parts: one on a batch reactor where the reactions are mostly under investigation, and the results are used to develop the second part of the study on flow-through reactor where the combination of transport and reactions are considered.
1-4 Organization of the report

The second chapter presents an overview of electrochemical remediation method as well as the treatment mechanisms. The chapter is continued with describing the mechanisms of solute transport. In the end the need for further theoretical studies in this area is explained and the base for the theoretical development chapter is provided.

A brief summary of governing equations fluid and contaminant transport model is described in chapter 3. Moreover, in the second part of chapter 3, the developed partial differential equations for developing the intended model are specified. As a supplementary chapter, the numerical solving method is described and personalized for this specific research problem in chapter 4. Chapters 5 contains the results of the developed and in the last chapter, chapter 6, a summary and a discussion of future work is included.
Chapter 2  Background

2-1 Introduction

Electrochemical mechanisms are gaining increasing attention and interest because of their low energy consumption accompanied by low required maintenance. Consequently, they are one of the most promising in-situ soil and groundwater decontamination methods, particularly for contaminated fine grained sites. Even though field investigation is important for management of contaminated soil and groundwater, it is usually expensive and the data is sparse and has uncertainty. Developing a model which combines the transport mechanisms of species with aqueous reactions will explain this remediation technique which is needed to develop the necessary design or analysis tools for engineering the implementation. In this chapter a general description of the electrochemical remediation method accompanied by a discussion of its advantages and limitations as well as a more in depth description of electrochemical reactions is provided.

2-2 Principles of electrochemical remediation

Electrochemical remediation is commonly used as an in-situ groundwater remediation method to extract heavy metals, organic and inorganic compounds by applying low direct current or a low potential gradient across the electrodes. This application of an electric field in the system will cause different phenomena such as electrochemical and chemical reactions as well as hydrological changes which leads to decontamination of water. Electroremediation involves using direct current across porous electrodes to intercept and
transform contamination in groundwater through direct and indirect electrolysis mechanisms [31]. In this section a more in depth description of each on-going phenomena is provided.

2-2.1 Electrolysis Reactions

Electrochemcial decontamination can be through direct or indirect electrolysis. In a direct electrolysis pathway contaminants exchange electrons directly at the surface of the electrodes, whereas in an indirect electrolysis, the reduction or oxidation of the pollutants occurs through mediation of a reagent. This electrogenerated reagent can be produced by either an anodic or a cathodic process. Depending on the characteristics of the system, which includes electrolyte concentration, transport mechanisms, and applied direct current or potential gradient onto the electrodes, these decontamination processes can be through reduction or oxidation pathways.

2-2.1.1 Direct electrolysis

Conceptually, direct electrolysis occurs at the surface of the electrodes. Species that find their way to the electrodes’ surfaces can undergo either direct oxidation or reduction [35]. From the thermodynamic point of view, the estimation of direct electrolysis starts from analyzing the electrodes’ potentials in addition to reactions’ potentials based on the electrolyte’s composition. These potentials,$E^\circ$, are variously known as redox potentials, oxidation-reduction potentials and standard electrode potentials.

\[
\text{Oxidized} + n \text{e}^- \rightarrow \text{Reduced} \quad E^\circ \text{ at } 25^\circ\text{C} \quad (2-1)
\]

$E^\circ$ is the standard redox potential, which indicates the tendency of the reactants to proceed towards their products under the standard state condition.

11
Table 2-1 presents standard redox electrochemical potentials for different electrolysis reactions in aqueous solution at 25°C.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2 + 2e^- \rightarrow 2F^-$</td>
<td>2.87</td>
</tr>
<tr>
<td>$Cl_2 + 2e^- \rightarrow 2Cl^-$</td>
<td>1.358</td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$</td>
<td>1.229</td>
</tr>
<tr>
<td>$Hg^{2+} + 2e^- \rightarrow Hg$</td>
<td>0.851</td>
</tr>
<tr>
<td>$Ag^+ + e^- \rightarrow Ag$</td>
<td>0.799</td>
</tr>
<tr>
<td>$Fe^{3+} + e^- \rightarrow Fe^{2+}$</td>
<td>0.771</td>
</tr>
<tr>
<td>$Zn^{2+} + 2e^- \rightarrow Zn$</td>
<td>0.763</td>
</tr>
<tr>
<td>$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$</td>
<td>0.682</td>
</tr>
<tr>
<td>$Cu^{2+} + 2e^- \rightarrow Cu$</td>
<td>0.340</td>
</tr>
<tr>
<td>$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + 2e^- \rightarrow H_2SO_3 + H_2O$</td>
<td>0.20</td>
</tr>
<tr>
<td>$Pb^{2+} + 2e^- \rightarrow Pb$</td>
<td>0.126</td>
</tr>
<tr>
<td>$2H^+ + 2e^- \rightarrow H_2$</td>
<td>0.000</td>
</tr>
<tr>
<td>$Cd^{2+} + 2e^- \rightarrow Cd$</td>
<td>-0.403</td>
</tr>
<tr>
<td>$Fe^{2+} + 2e^- \rightarrow Fe$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$</td>
<td>-0.56</td>
</tr>
<tr>
<td>$Cr^{3+} + 3e^- \rightarrow Cr$</td>
<td>-0.744</td>
</tr>
<tr>
<td>$2H_2O + 2e^- \rightarrow 2OH^- + H_2$</td>
<td>-0.828</td>
</tr>
<tr>
<td>$Mn^{2+} + 2e^- \rightarrow Mn$</td>
<td>-1.029</td>
</tr>
<tr>
<td>$Al^{3+} + 3e^- \rightarrow Al$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$Mg^{2+} + 2e^- \rightarrow Mg$</td>
<td>-2.375</td>
</tr>
</tbody>
</table>
If the system is assumed to be operating under constant temperature and pressure as a closed system, a thermodynamic analysis can be carried out. A closed system is defined as one where transport of mass and energy between the system and the surroundings is not permitted. As the first law of thermodynamics states, the total change in internal energy, $\Delta U$, of a closed system is defined by the energy exchange of work done by the system, $W$, and heat transferred to the system, $Q$, where work includes both mechanical and non-mechanical works (Eqn. 2-2). Hence, the first law of thermodynamics illustrates both conversion and conservation of energy.

$$\Delta U = Q - W$$  \hspace{1cm} (2-2)

Assuming the non-mechanical work done by the system is due to maximum available electrical energy:

$$w_e = nFE$$  \hspace{1cm} (2-3)

where $w_e$ is the electrical contribution to the work, $n$ is the number of exchanged charge, $F$ is the Faraday’s constant, and $E$ is the electrical potential applied to the system.

A natural state variable for an operating system at a constant temperature, $T$, and pressure, $P$, is the change in Gibbs free energy, $\Delta G$, which is dependent of change in enthalpy, $\Delta H$, as well as change of entropy, $\Delta S$.

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (2-4)

Therefore, considering the enthalpy change which is defined as the total change of internal energy, $\Delta U$, plus the mechanical work done by the system which is due to volume change, $P\Delta V$, change in Gibbs free energy will be defined as the electrical work done on the system (Eqn. 2-5) [27].

$$\Delta G = -nFE$$  \hspace{1cm} (2-5)
To calculate the changes in reversible potential when the system is not being operated at the standard condition, the considered thermodynamic relation is:

\[
\Delta G = \Delta G^\circ + RT \ln \left( \prod a_i^{v_i} \right) \quad (2-6)
\]

where \( \Delta G^\circ \) is the change of Gibbs free energy under standard condition, and \( a_i \) is the activity of species \( i \), \( v_i \) is the stoichiometric coefficient of species \( i \), and \( R \) is the gas constant. Consequently, equations 2-5 and 2-6 result in governing Nernst equation, which by assuming an activity coefficient of 1 for all species, gives an estimate of the thermodynamic electrode potential (Eqn. 2-7).

\[
E = E^\circ - \frac{RT}{nF} \ln \left( \prod a_i^{v_i} \right) \quad (2-7)
\]

If the electrode potential is being held higher that the redox potential, oxidation of the species is favored at that electrode’s surface and reverse for reduction of species [34]. Therefore, the oxidation or reduction occur directly on inert electrodes’ surfaces without the involvement of other substances such as electron mediators or biological species [35]. In this case in addition to the electrode potential criteria, which defines if a reaction is possible to proceed, in some cases the transport mechanisms limit the reaction by constraining the mass diffusion to the electrodes’ surface. As a result, the side reactions are almost always the dominant direct electrolysis reactions; especially solvent break down rather than the removal of unwanted species [35]. As Acar et al reported, particularly at the early stages of the process, water electrolysis (Eq. 2-8 and 2-9) is the dominant reaction which causes a significant alteration in pH in the range of 2 to 12 [2]. Therefore, in low concentrated electrolytes, the dominant electrochemical reaction is water electrolysis as it is abundantly available at the surface of the electrodes.
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = -1.229\, V \]  
\[ 2H_2O + 4e^- \rightarrow H_2 + 2OH^- \quad E^0 = -0.822\, V \]  

Direct electrochemical oxidation is mainly used for degrading organic and inorganic compounds [35]. Although direct oxidation electrolysis is theoretically possible at low potentials, before oxygen evolution, the reaction rate usually has low kinetics, which depends on anode electrocatalytic activity [31]. However using platinum, palladium, or mixed metal oxide anodes increases the electrochemical rates [31].

In effluent of chemical industries, the concentration of metal ions, \([M^{n+}]\), can be as high as \(10^5\) \(ppm\), whereas the maximum permitted concentrations are typically in the range of 0.05 and 5 \(ppm\) [35]. Electrochemical direct reduction is a commonly used method for removal of toxic metals to reduce them into their elemental states. As the metal ion concentration gets smaller, mass transport enhancement to the electrode becomes more essential [35]. Moreover, direct reduction electrolysis can be used for dechlorination of organic compounds [26]. To increase the efficiency of dechlorination, electrolytic reduction can be combined with other processes such as adding zero valent iron [26].

2-2.1.2 Indirect electrolysis

Indirect electrolysis electrochemically generates redox reagents, as a chemical reactant or catalyst for water decontamination. There is no need for addition of chemical reactants in the system, therefore the reduced cost of chemicals and their storage facilities on site is one of the great advantages of this method. For many years, there has been considerable interest in mediated or indirect electrolytic oxidation for both the synthesis of organic compounds and the treatment of effluents and destruction of organic wastes. Hydrogen peroxide, \(H_2O_2\), is a redox mediation in indirect electrolysis which is one of the strongest oxidizing agents.
It is already recognized as an environmentally friendly chemical for organic oxidation with no harmful residual after the reaction.

Hydrogen peroxide is produced at the cathode’s surface by reduction of oxygen (*Eqn. 2-11*), which is one of the products of water electrolysis reaction at the anode’s surface (*Eqn. 2-10*). Being a strong oxidizing agent, hydrogen peroxide is unstable and will get reduced in electrolyte; participating in an oxidation-reduction reaction which leads to water and the contamination oxidation.

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = -1.229 \, V \quad (2-10)
\]
\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^0 = 0.682 \, V \quad (2-11)
\]

Short-lived intermediates that have been reported to be present in the electrochemical destruction of pollutants include \(OH^*, O_2^- \) and \(HO_2^-\) [35]. For instance, in the presence of iron, hydroxyl radical will be produced (*Eqn. 2-12*). An oxidizing agent which is extremely unstable so that in some cases it cannot be measured [35].

\[
Fe^{2+} + H_2O_2 \rightleftharpoons OH^- + OH^* + Fe^{3+} \quad (2-12)
\]

Figure - 2-1 shows the schematic overview of direct and indirect oxidation processes. In a direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by anodic electron transfer reaction. On the other hand, in an indirect oxidation process, a strong oxidant such as hydrogen peroxide, Fenton’s reagent, or hypochlorite can be regenerated by the electrochemical reactions during electrolysis. The pollutants are then destroyed in the bulk solution by oxidation reaction of regenerated oxidant [11].
2-2.2 Chemical reactions

As the current passes through the reactor, causing electrochemical reactions to take place, the system experiences a deviation from its equilibrium state. Therefore, a number of chemical reactions are bound to happen in order for the system to bounce back to its lowest possible energy level. These reactions strongly depend upon the electrolyte composition as well as the material and the coating of the electrodes. The possible chemical reactions that can occur within this process include, but are not limited to, water association/dissociation reaction, acid-base reaction, sorption reactions, and precipitation/dissolution. In this section a more in depth description of these phenomena will be discussed.

2-2.2.3 Aqueous phase reactions

Electrochemical reactions, which cause the change of concentration in the system, will ultimately result in other aqueous phase chemical reactions. System experiences additional changes depending on the electrolyte composition to reach the equilibrium state once more. For instance, production of $H^+$ and $OH^-$ as the result of solvent direct electrolysis on the electrodes’ surfaces are the dominant electrochemical reactions; particularly in the early stages of the process. The produced $H^+$ tends to advance through the system towards the
cathode due to different transport mechanisms. In parallel to hydrogen ion advance across the reactor, $OH^-$ is being produced at the cathode surface which similarly heads towards anode. As these two fronts meet one another, the excess hydrogen and hydroxide ions participate in a relatively fast chemical reaction which results to water as its product. As this reaction, which is well known as water association/dissociation reaction ($Eqn. \ 2-13$), reaches the equilibrium state, hydrogen ion, hydroxide, and water come to a more stable concentration which illustrates a lower energy level of the system.

$$H_2O \rightleftharpoons H^+ + OH^- \quad K_w = 10^{-14} \ \text{mole}^2/\text{lit}^2 \quad (2-13)$$

Accounting for water association/dissociation reaction is inevitable since it is one of the most important factors of pH calculation. Thermodynamically speaking, this reaction has high kinetic rates, therefore it is safe to assume that it reaches local equilibrium before more production happens.

There are other aqueous based reactions in the system such as acid-base reactions. These reactions will increase the buffering capacity of the system; therefore, the change of pH is relatively limited. These reaction occurrences strongly depend on the composition of electrolyte as well as the characteristics of the reaction. For example, having carbonate in the system will cause higher buffering capacity than sulfate in the electrolyte. These reactions also have been known for fast kinetic rates as well as having elementary kinetics. Consequently, the kinetic expression of these reactions depend on the stoichiometric coefficients of the reactant and products as opposed to non-elementary reactions; which are a set of elementary reactions and the kinetic rates are more complicated to define [13].
Figure 2-2 A schematic configuration of ion movement due to transport mechanisms present in the system [2]

Figure 2-3 a) consecutive reactions; b) parallel reaction
In the case of indirect electrolysis, aqueous phase reactions play an important role in decontaminating the influent. These reactions may either be elementary or non-elementary and can happen in parallel, consecutive or even a mixture of both.

In a set of parallel simultaneous coupled reactions, the competition over the reactant(s) is unavoidable; thus, desired product may be formed less than a condition where there are no competing reactions [13]. Direct electrolysis which is defined on the electrodes’ surfaces is a practical example of parallel simultaneous reactions.

On the other hand, the formation rate of desired product(s) in consecutive set of reactions depends on the reaction rate of each step [13]. Formation of mediator reagents within the indirect electrolysis pathway is an applicable example of consecutive reactions in electrochemical remediation process. Figure 2-3 illustrates the difference between parallel and consecutive reactions.

In addition, if there is metal presence in the electrolyte composition, sometimes other reactions such as complexation which is between a ligand and a metal ion is probable to happen. Ligand is an ion or molecule that has electron pair available, so they can form a complex with metal atoms. For instance, presence of chromium in water will result in complexes with water or chloride, if available [43]. These reactions can highly change the characteristics of the contaminants as well as changing the efficiency of the system for remediation of metal ions.

### 2-2.2.4 Sorption reactions

Heavy metals and other positively charged species are highly attracted and adsorbed on the negatively charged surfaces. In the presence of clay in the system, the sorption reaction changes the transport characteristics of the ions. Thus, the contaminants can accumulate in
part of the aquifer and act as a source of contamination as the pH changes and causes a change in zeta potential of clay’s particles. The zeta potential of a particle (i.e. the potential difference between the outer Helmholtz plane of the electrical double layer formed at the particle/fluid interface and the bulk fluid) is a measure of its surface charge [19].

Metals have different sorption characteristics and mechanisms that can change due to different adsorbents. Sorption mechanisms include surface complication and ion exchange. The adsorbents show differences in selectivity sequences for different metals.

The surface charge of metal oxide particles, which are widely used as inert electrode material, plays an important role in their activity towards dissolved ions electrolysis [22]. Thus, the characterization of the surface charge or the surface potential is useful in the prediction of deposition of particles on the electrodes’ surface.

![Figure 2-4 surface charge of cobalt ferrite with titration curve 25°C](22)
As figure 2-4 illustrates for cobalt ferrite, as the pH changes, surface charge will change significantly or even can change sign. Therefore, the mobility of ions can strongly depend on pH change within the process.

2-2.2.5 Precipitation/dissolution

Sudden alteration in water pH throughout the electrochemical process will cause chemical reactions including precipitation/dissolution of species; therefore, species transport will be influenced by formation and dissolution of precipitants. Some salts and minerals form precipitations. The precipitation amount differs from one species to another but what they all have in common is that they are highly dependent on electrolyte’s pH. Different enhancement techniques have been recommended to maintain the system and prevent clogging in the porous electrodes as well as the reactor [2]. In more recent literature, polarity reversal is being proposed to enhance the movement of ions as well as to achieve higher removal efficiency by producing more intermediate oxidizing reagents throughout the remediation process [36].

2-2.3 Electrochemically driven transport mechanisms

As the potential gradient is applied to the reactor, free chemical species that are present in the electrolyte, will advance towards the electrodes depending on their surface charge; as was mentioned previously in Figure 2-2. The primary driving mechanism of species transport is the same as non-reactive flow in groundwater. Although in this system reactive species are being produced and a more complicated system of equations is developed to define the interaction, transport mechanisms due to hydraulic and concentration gradient are the same. Ion migration in the electrolyte is the new transport mechanism that is
introduced in the electrochemical systems due to the potential gradient applied to the electrodes. Ion migration is based on their mobility coefficient, which depends on ion’s size and charge. For example, hydrogen ion due to its small diameter and therefore high charge density will advance through the system by migration mechanism with relatively higher speed than hydroxide.

2-3 Essential role of modeling

As mentioned before, mathematical models have been used to help us understand the subsurface water flow and contaminant transport phenomena. A mathematical model could be the key to the management of contaminated soils and groundwater. Concerns on groundwater contamination has motivated the development of numerous simulation models for groundwater quality management in the recent years. To engineer the implementation of developed electrochemical remediation technology, there is an essential need to better understand the phenomena. Therefore, modeling coupled and uncoupled transport mechanisms of non-reactive as well as reactive species within the electroremediation process is a must.

As was aforementioned, as potential gradient is applied, an unenhanced electrochemical remediation system experiences a change in pH. The current produces an acidic and basic region in anode and cathode compartments, respectively. The produced acidic and basic fronts will spread through the soil due to different transport mechanisms caused by hydraulic, concentration, and charge gradient. The resulted pH alteration can cause a great change in existed reactions or create new pathways since chemical species can exist in different forms depending on the pH of the aqueous environment.
Decreasing the pH, which happens during the unenhanced process, can decrease the removal efficiency of the species [2]. Consequently, pH monitoring and controlling is needed to advance the transport of contaminants to prevent precipitation and induce depolarization [2, 40, 41]. There are a number of studies on removal efficiency of electrochemical process for different compounds, where pH plays an important role causing an alteration in exchange capacity and zeta potential of the soil [16, 21, 30, 32, 48]. Moreover, a number of studies have included the use of pH control on the efficiency of the remediation process [16, 32, 37, 40]. Electrochemical remediation can be optimized by integrating it with other remediation methods such as the Fenton process or adding zero valent metal to the system [10, 17, 49].

There has been a number of studies developing a design tool for electrochemical remediation processes. The missing part of most studies is the complication of adding aqueous and non-aqueous phase reactions to the system as it gets more computationally heavy and complicated. Yeh and Tripathi (1991), Acar and Haider (1990), and Alshawabkeh and Acar (1994) are of the originators of this field.

Acar and Haider (1990) developed a one-dimensional advective-dispersive-reactive model for transport of solutes in saturated fine-grained soils which was expanded for saturated earthen barriers in transport of low-concentration contaminants.

Yeh and Tripathi (1991) have developed a detailed model of transport for reactive multispecies. The described model accounts for variety of chemical processes such as complexation, dissolution/precipitation, adsorption/desorption, ion exchange, and acid-base reactions.

This research is focusing on development of a multi-species model is based on the possible
transport mechanisms combined with the aqueous and non-aqueous chemical reactions. As a result, a system of partial differential equations is governed to maintain the conservation of mass and energy. The chemical reactions are considered in the system by set of nonlinear algebraic equations which are solved in sequence with the transport defining PDEs.

A comprehensive theoretical model is required for electrochemical remediation process. This model accounts for coupled multicomponent species transport as well as chemical and electrochemical reactions such as water association/dissociation reaction, acid-base reactions, precipitation/dissolution, electrolysis reactions accompanied by other aqueous phase reactions depending on the electrolyte composition. It is expected that the model provides the basis for a comprehensive design tool for engineering a full scale implementation.
Chapter 3 Theoretical Development

3-1 Introduction

Hydraulic, electric, chemical, and thermal gradients in an electrolyte system result in the transport of the matter and energy. The resulting fluxes of fluid, charge, mass, and heat through the system and their variation in time effect the properties and composition of the system. Furthermore, electrochemical reactions will cause the system to deviate from its equilibrium condition, therefore, system will undergo a set of chemical reactions in order to bounce back to its lowest energy level. Developing a theoretical model means defining a set of linear and non-linear differential equation as well as algebraic equations in order to predict the system’s output.

3-2 Transport mechanisms

A system subjected to any sort of gradient will experience deviation from its equilibrium including transport of matter and energy. Hydraulic, electric, thermal, or chemical gradients will induce transport mechanisms. The resulted flux of matter and energy through the electrolyte could be categorized into two general types of coupled and un-coupled fluxes [2].

Un-coupled fluxes are results of the application of a potential gradient of the same type of matter transported. Darcy’s law introduces the transport of fluid due to hydraulic gradient as Ohm’s law defines charge transport caused by applied electric gradient. Moreover,
chemical gradient induces mass transport is expressed by Fick’s law, whereas the heat transport ascribed to thermal gradient is stated by Fourier’s law.

On the other hand, coupled fluxes define the transport of mass and energy due to non-similar applied potential. For example, as hydraulic gradient primarily causes fluid flux, it inevitably creates mass flux as well as charge flux alongside the bulk fluid movement. Charge flux and mass flux in electrolyte systems are bonded; as ionized particles move through the reactor and carry the charge to close the circuit. Therefore, almost always electrolyte systems will experience coupled fluxes as well as un-coupled fluxes. The following sections will describe each phenomenon in a more in depth fashion.

3-2.1 Fluid flux

Fluid flux is caused by application of a hydraulic gradient, an electric gradient as well as a chemical gradient. In the presence of fine-grained media in the reactor, fluid flow due to electric gradient, electroosmotic flow, is applicable due to Helmholtz-Smoluchowski theory. As fluid passes through micro-channels, electroosmotic fluid flow is a result of electric double layer formed on the micro-channel’s wall. In reactors without packed media the effect of capillarity is negligible. Moreover, chemicoosmosis is defined as fluid flux due to chemical gradient. In the presence of large chain molecules, as chemical gradient is applied, fluid transport is significant in the reverse direction of mass transport by diffusion. In conclusion, an existing hydraulic gradient in the system will cause a convective flux affecting the bulk fluid.

Advection is defined as the fluid flux due to hydraulic gradient. This flux is expressed through Darcy’s law (Eq. 3-1), where $J^a$ is the bulk fluid flux $[LT^{-1}]$; $k_h$ is the hydraulic conductivity $[LT^{-1}]$; $h$ is the hydraulic head $[L]$; and $v$ is the overall fluid velocity $[LT^{-1}]$.
in the system. The hydraulic conductivity can be used in the systems with packed media, since it can change during the remediation process due to precipitation/dissolution of species as well as the effects of consolidation. Moreover, while using electrochemistry for soil remediation, hydraulic conductivity is subjected to change due to alteration in pore fluid chemistry, diffusion double layer, soil fabric and consolidation. In system with constant applied velocity without media, using the overall velocity is a more common approach.

\[ J^a = k_h \nabla (-h) = v \]  \hspace{1cm} (3-1)

### 3-2.2 Mass Flux

As was mentioned previously, mass flux can be due to different coupled and un-coupled phenomena. The coupled mass transport is due to concentration gradient which is expressed by Fick’s first law, where \( J^d_i, c_i, \) and \( D_i \) are respectively the diffusive mass flux \([ML^{-2}T^{-1}]\), the chemical concentration \([ML^{-3}]\), and the diffusion coefficient \([L^2T^{-1}]\) of the \(i\)th chemical species.

\[ J^d_i = D_i \nabla (-c_i) \]  \hspace{1cm} (3-2)

The diffusion coefficient of ions in infinite dilution can be found in numerous studies [6, 23, 42, 44]. However, it should be noted that diffusion can get affected by the effects of electroneutrality, concentration, and electrolyte strength [6, 44]. Hydrogen and hydroxyl ions have relatively large diffusion coefficients because of their fast dissociation/association reaction with water molecules [2].

Mechanical dispersion effect is significant in contaminant transport in groundwater because of the relatively high hydraulic conductivity and advective flow in such
environments. Packed bed reactors experience local mixing and recirculation of fluid as the fluid flux through tortuous paths [7]. This effect can be neglected in reactors without packed media and with the assumption of an ideal plug flow in the system.

Mass flux by ion migration is due to the electrical gradient applied to the system and is defined by equation 3-3, where \( J_i^e \) is the migrational mass flux of the \( i \)th ionic species \([ML^{-2}T^{-1}]\); \( u_i \) is the ionic mobility of the species \( i \) at infinite dilution \([L^2T^{-1}V^{-1}]\).

\[
J_i^e = u_i c_i \nabla (-E)
\]  
(3-3)

The ionic mobility defines the velocity of the ion in the electrolyte due to applied electric field, which can be estimated from diffusion coefficient (Eq. 3-4) [34]. In this equation \( z_i \) is the charge of the \( i \)th ionic species, \( F \) is the Faraday’s constant, \( R \) is the gas constant, and \( T \) is the absolute temperature.

\[
u_i = \frac{D_i z_i F}{RT}
\]  
(3-4)

Table 3-1 presents values of diffusion coefficients for a number of cations and anions at infinite dilution.

Finally, another dominant mass transport mechanism is the advective mass flux of the \( i \)th species, \( J_i^a \) \([ML^{-2}T^{-1}]\), which is defined by the bulk fluid flux (Eqn. 3-5). To illustrate, as the hydraulic gradient causes fluid flux throughout the system, mass transport is inevitable due to bulk fluid movement.

\[
J_i^a = -c_i J_a
\]  
(3-5)

In conclusion, the total mass flux of the \( i \)th species in a flow through reactor without bed media, \( J_i \), is defined as the summation of aforementioned phenomena.

\[
J_i = -c_i k_h \nabla (-h) + D_i \nabla (-c_i) + u_i c_i \nabla (-E)
\]  
(3-6)
### Table 3-1 Values of diffusion coefficients of selected ions at infinite dilution in water at 25°C [29]

<table>
<thead>
<tr>
<th>specie</th>
<th>$D_j$ [cm²/sec × 10⁻⁵]</th>
<th>specie</th>
<th>$D_j$ [cm²/sec × 10⁻⁵]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>1.618</td>
<td>Cl⁻</td>
<td>2.032</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.541</td>
<td>CN⁻</td>
<td>2.077</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.792</td>
<td>CO₃²⁻</td>
<td>0.923</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.72</td>
<td>CrO₄²⁻</td>
<td>1.132</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.719</td>
<td>F⁻</td>
<td>1.475</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.604</td>
<td>HCO₃⁻</td>
<td>1.105</td>
</tr>
<tr>
<td>H⁺</td>
<td>9.312</td>
<td>HPO₄²⁻</td>
<td>4.39</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>0.847</td>
<td>H₂PO₄⁻</td>
<td>0.879</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.957</td>
<td>HSO₃⁻</td>
<td>1.331</td>
</tr>
<tr>
<td>Li⁺</td>
<td>1.030</td>
<td>HSO₄⁻</td>
<td>1.33</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.7063</td>
<td>I⁻</td>
<td>2.045</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.712</td>
<td>NO₂⁻</td>
<td>1.912</td>
</tr>
<tr>
<td>NH₄⁺</td>
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<td>NO₃⁻</td>
<td>1.902</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.334</td>
<td>OH⁻</td>
<td>5.260</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.661</td>
<td>PO₄³⁻</td>
<td>0.612</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0.945</td>
<td>ClO₄⁻</td>
<td>1.792</td>
</tr>
</tbody>
</table>

#### 3-2.3 Charge Flux

Application of charge gradient to the electrodes by either low direct current or low voltage gradient will initiate the electrochemical process. Conceptually, electrons moving through the external circuit are transferred to/from the electrodes from/to the electrolyte, by direct electrochemical reactions on the surface of the electrodes. To close the electrical circuit, charge transfer through the electrolyte is due to movement of ions towards the opposite charged electrodes. Figure 3-1 defines the electric circuit of the system. In this circuit model, $C_{dl}$ defines the capacitance of the double layer.

$$i_{dt} = C_{dl} \frac{dE}{dt} \quad (3-7)$$
Right when the current source is turned on, before double layer is formed, the capacitor acts as a closed switch, which allows the electrons to pass without having to react at the electrode’s surface. As time goes on and the double layer is fully formed, capacitor acts as a closed switch and causes the charge transfer through electrochemical reactions in the electrode/electrolyte junction (Figure 3-2).

Figure 3-1 Randels Model; Randels Model defines the electric circuit at the electrode surface with a capacitor to define the double layer and a resistance which expresses the direct electrolysis reaction, charge transfer.

Figure 3-2 (a), (b), and (c) show the equivalent electric circuit of electrode/electrolyte junction at general form, at the beginning of the process, and after double layer is charged.
Meanwhile the double layer is charging up, the total current density passing through the system is a combination of both circuit elements (Eqn. 3-8)

\[
i = \frac{I}{A} = i_{dl} + i_F
\]  

(3-8)

The charge migration within the electrolyte is defined by Ohm’s law (Eqn. 3-9). Conductance of the solution, \( \sigma \), depends on the ions concentrations and composition of the electrolyte.

\[
i_{\Omega} = \sigma \nabla (-E)
\]  

(3-9)

Charge migration can also be defined by migration of the ions. The migrational mass flux was defined in the section 3-2.2. Using the Faraday’s law, the migrational charge flux can be related to the migrational mass flux of species (Eqn. 3-10).

\[
i^e = \sum_{j=1}^{N} z_j F J^e_j \quad \therefore \quad i^e = \sum_{j=1}^{N} z_j F u_j c_j \nabla (-E)
\]  

(3-10)

To separate the contribution of each species in the total current density (Eqn. 3-10), transport number, \( t_i \), is defined.

\[
t_i = \frac{F z_i u_i c_i}{\sigma} = \frac{F z_i u_i c_i}{\sum F z_j u_j c_j}
\]  

(3-11)

The transport number of a specific species will increase as the ionic concentration of that species rise. This implies that as the concentration of \( i \)th species decreases, removal under electric currents will be less efficient.

Similar to the migrational charge flux, the diffusional charge flux (Eqn. 3-12) and advective charge flux (Eqn. 3-13) are evaluated using Faraday’s law.

\[
i^d = \sum_{j=1}^{N} z_j F J^d_j \quad \therefore \quad i^d = \sum_{j=1}^{N} z_j F D_j \nabla (-c_j)
\]  

(3-12)

\[
i^a = \sum_{j}^{N} z_j F \frac{c_j}{c_a} J^a
\]  

(3-13)

Due to electroneutrality in the system, equation (3-14) illustrates that the total current density is a result of migration and diffusion only.
3-3 Chemical Reactions

As was in section 2-2.2 was described, a number of chemical reactions must happen in order for the system to bounce back to its lowest possible energy level after an electrical gradient is applied to the system. These reactions strongly depend upon the electrolyte composition as well as the material and the coating of the electrodes. The possible chemical reactions that can occur within this process include, but are not limited to, water association/dissociation reaction, acid-base reaction, sorption reactions, and precipitation/dissolution.

Two approaches have been developed and used in literature to describe chemical reactions; instantaneous equilibrium approach and kinetics approach. In local equilibrium models, concentrations of species are assumed to reach equilibrium faster than the rate of transport whereby in kinetic reactions, approach the rate of reactions is slower than the rate of transport [50]. Even though this implies that a kinetic formulation is always the more general approach in describing the reactions as opposed to equilibrium formulation, the kinetic rate constants for fast equilibrium reactions have uncertainty due to their fast nature [46]. Furthermore, chemical reactions involved in this study are expected to reach local equilibrium at a very short time.
3-3.1 Aqueous Phase Reactions

Aqueous phase reactions contain all reactions including acid-base reactions as well as more complicated ones like complexation. In this model the only applicable aqueous phase reactions to include are water electrolysis as well as acid-base reactions which account for the buffering capacity of the system.

Conservation of mass in the unit volume of the solution can be written as equation (3-16).
\[
\frac{\partial c_i}{\partial t} = -\nabla j_i \pm R_{ci}
\]  
(3-16)

\( R_{ci} \) is the chemical reaction kinetics occurring within the system, which will be further expanded for aqueous phase reactions. \( R_{ci} \), which is better defined in Eqn. (3-17) includes reactions such as precipitation-dissolution, oxidation-reduction, acid-base reactions and other aqueous phase reactions.

\[
\frac{\partial c_i}{\partial t} = \pm R_{ci} = \pm \sum k_j \prod c_R^a
\]  
(3-17)

\( k_j \) is the kinetic rate constant of the \( j \)th reaction and \( c_R^a \) is the reactants of the \( j \)th reaction in the system.

Equation (3-18) describes the \( j \)th chemical reaction
\[
x_j = K_{j}^{eq} \prod c_i^{a_{ji}}
\]  
(3-18)

where \( c_i \) is the chemical formula for component \( i \), \( x_j \) is the chemical formula for the complex \( j \), \( a_{ji} \) is the stoichiometric coefficient in complex \( j \) for component \( i \), and \( K_{j}^{aq} \) is the equilibrium constant for aqueous reaction \( j \) [46].
3-3.2 Sorption Reactions

Assuming instantaneous equilibrium in sorption reactions and linear isotherms, the change in concentration of the adsorbed phase of species \( i \) is linearly related to the change in concentration of the aqueous phase (Eqn. 3-19).

\[
\frac{\partial s_i}{\partial c_i} = K_{d_i}
\]  (3-19)

where \( s_i \) is the adsorbed concentration of the component \( i \) per unit mass of the soil solids (mole/M). \( K_{d_i} \) is called the distribution coefficient, \( K_d \) of species \( i \). A retardation factor, \( R_{d_i} \), which defines the relative rate of transport of a non-adsorbed species to that of a adsorbed species, has been introduced and used in modeling species transport accounting for linear sorption as equation (3-20) where \( \rho \) is the bulk dry density of the soil.

\[
R_{d_i} = 1 + \frac{\rho K_{d_i}}{n}
\]  (3-20)

For a non-adsorbed species, \( R_{d_i} = 1 \).

3-3.3 Precipitation/ Dissolution Reactions

It is necessary to account for the precipitation/dissolution reaction in the formulation of mass transport equations. In precipitation reactions, the chemical components are assumed to be composed of products. Knowing that the production of the precipitate will not occur until the solution is saturated and using the solubility product equilibrium constants \( K_{j}^{sp} \), the equilibrium reaction can be written as equation (3-21).

\[
K_{j}^{sp} \geq \prod c_{i}^{a_{ji}}
\]  (3-21)
In this study, the electrochemical reactions that are accounted for are only direct electrolysis at the surface of the electrodes. Assuming the effects of double layer and diffusion to the surface of the electrodes are negligible due to duration of electrolysis and advection in the column, respectively, the production rates of species can be defined by Faraday’s law.

The electrochemical reactions are determined by Faraday’s law’ assuming the charge transfer through the electrode/electrolyte surface is 100% faradaic process, the current efficiency of the system is 100%, hence all the applied electric current is expected to participate in the electrochemical reactions and not to dissipate heat. Although, depending on the conductivity of the electrolyte, portion of the applied current will be used to develop a thermal gradient in the system, the study is under an isothermal condition assumption, therefore this portion can be neglected. The electrolysis rate on the electrodes’ surfaces are expressed by Faraday’s law under a constant current condition within the system where the total produced mass is correlated to the applied current as well as the number of electrons transferred (Eqn. 3-22).

\[
\frac{\partial c_l}{\partial t} = \frac{\alpha I}{nF}
\]  

(3-22)

In equation (3-22), \( n \) is the number of transferred charges, \( \alpha \) is the current efficiency, and \( I \) is the current density of the electrode \((ml/l)\).
3-5 The Final System of Equations

Hydraulic, electric, chemical, and thermal gradients in an electrolyte system result in the transport of the matter and energy. The resulting fluxes of fluid, charge, mass, and heat through the system and their variation in time affect the properties and composition of the system. The model equations are developed assuming that the fluxes are linear and homogenous functions of their causing phenomena.

In this study the models are to describe a completely stirred batch reactor and a flow-through reactor without media, separately.

3-5.1 Batch Reactor

The batch model was defined for divided and mixed electrolyte batch reactors using inert electrodes. The results of laboratory scale test reported by Ciblak et al.[12] are compared with the model prediction, therefore the initial conditions of the model was adopted from the presented laboratory scale test.

3-5.1.1 Laboratory Setup

The considered setup is a glass electrochemical cell with two compartments for anolyte and catholyte, which have a liquid volume of 200mL and a headspace of 100mL. The area of the submerged part of electrodes are 7 cm² with a length of 7 cm and a center to center distance of 13 cm. The anolyte and catholyte are assumed to be continuously stirred with a constant speed during the remediation process to simulate a well stirred batch system and to avoid developing a considerable double layer on the electrodes’ surfaces (Figure - 3-3).
3-5.1.2 Model development

As was mentioned previously, the system is defined under a constant current condition using a DC power supply where having constant electrolysis rates on the electrodes’ surfaces is a reasonable assumption. As discussed, supposing the charge transfer through the electrode/electrolyte surface is 100% faradaic process, the current efficiency of the system is 100%, hence all the applied electric current is expended in generation of $H^+$ at the anode and $OH^-$ at the cathode and $\nu_0$ can be determined by Faraday’s law (Eqn. 3-22) [8]. Although, depending on the conductivity of the electrolyte, portion of the applied current will be used to develop a thermal gradient in the system and since the study is under an isothermal condition, this amount can be neglected.

The electrolyte consists of $0.02\ M\ Na_2SO_4$, where the initial solution has a $pH$ of 5.4. Although there are several number of species present in the system, to simplify the modeling, this part of the study focuses on the two main variables present in the system, $H^+$ and $OH^-$ and their changes within the process. Additionally, to account for the small
buffering capacity of sulfate in the system, the species associated with sulfate, like \(SO_4^{2-}\) and \(HSO_4^-\), as well as their correlated reactions are being considered in the model.

Acar et al. demonstrated that for currents on the order of milliamperes used in experimental cells, there is a sufficient supply of \(H_2O\), and adequate local convection is present at the electrodes to sustain the electrolysis [4]. The considered applied current to the system is 22.5 \(mA\) and was kept constant within the process, therefore it’s a reasonable assumption to say that the electrolysis reaction occurring in the system is primarily water electrolysis (Eqn. 3-23 and 3-24). The dominant aqueous phase reactions in the electrolyte, which also affect the pH change throughout the system, can be safely considered as water association/dissociation and acid/base reactions of sulfate (Eqn. 3-25 and 3-26).

\[
2H_2O - 4e^- \xrightarrow{r_{anode}} O_2 \uparrow +4H^+, \text{ where } E_0 = -1.229 \, V \quad (3-23)
\]
\[
2H_2O + 2e^- \xrightarrow{r_{cathode}} H_2 \uparrow +2OH^-, \text{ where } E_0 = -0.828 \, V \quad (3-24)
\]
\[
H_2O \rightleftharpoons H^+ + OH^-, \text{ where } K_w = 10^{-14} \left[\frac{mol^2}{l^2}\right] \quad (3-25)
\]
\[
HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}, \text{ where } K_{a1} = 1.2 \times 10^{-2} \left[\frac{mol}{l}\right] \quad (3-26)
\]

Since the completely stirred condition is applied in the batch reactor, the total amount of charge transferred to the electrolyte from the DC power supply is defining the amount of electrolysis that is occurring at each time step.

An equilibrium model is used for the batch model where the reactions are the model’s variables. The model is treating the electrochemical reactions as a titration into the system. Therefore, the sources of productions are calculated as the transfer of charge into or out of the system (Eqn. 3-27 and 3-28).

\[
\frac{dc_H}{dt} = \frac{1}{FV} \quad (3-27)
\]
\[
\frac{dc_{OH}}{dt} = \frac{1}{FV} \quad (3-28)
\]
As was mentioned, the equilibrium reactions in this part of the research are water association/dissociation and acid/base reactions (Eqn. 3-29 and 3-30).

\[
K_w = c_H c_{OH} \quad (3-29)
\]

\[
K_{a1} = \frac{c_H c_{SO_4^{2-}}}{c_{HSO_4^-}} \quad (3-30)
\]

The solving methods and the adopted formulation would be discussed in section 4-3.

3-5.2 Flow-through Reactor

Moreover, adding the transport mechanism effects for the flow-through reactor will alter the perspective of the model. The mass flux of the species in the system is a combination of transport mechanisms as well as the reactions. The results of laboratory scale test reported by Rajic et al. [36] are compared with the model predictions.

3-5.2.1 Laboratory Setup

The electrochemical setup considered for treatment is a vertical cylindrical column with diameter of 3.8 cm and height of 10 cm. Two Ti/MMO electrodes are placed with 2.5 cm spacing connected to a DC power source operating in a constant current mode of 60 mA (Figure - 3-4).

![Electrochemical flow-through reactor: (1) DC source; (2) PR device; (3) synthetic groundwater reservoir; (4) peristaltic pump and (5) effluent; E1, E2 and E3 are MMO mesh electrodes; P0, P1, P2 and P3 are sampling ports.](image-url)
3-5.2.2 Model Development

This study was on two different electrolytes with different compositions and concentrations; first the effect of polarity reversal on a non-containing bicarbonate system with $0.172 \text{ g/l}$ calcium sulfate in deionized water as electrolyte, second, the system with higher buffering capacity with $0.413 \text{ g/l}$ sodium bicarbonate as well as $0.172 \text{ g/l}$ calcium sulfate in deionized water as electrolyte to explore the effects of polarity reversal in a highly buffered system. In this case the study from the batch reactor was carried out to this part and continued with the introduced transport mechanisms, polarity reversal effects, as well as the additional aqueous reactions in the system.

Polarity reversal applies in the reaction rates of electrolysis reactions, $r_{0, \text{electrode}}$, as the cathode and anode are reversed. Although various number of ions are present in the solution, to simplify the modeling and the necessary experimental verification effort, reaction and transportation of species which are not contributing much to the result are being neglected. The predominant species in the model predictions are $H^+, OH^-, CO_3^{2-}, HCO_3^-, H_2CO_3$, and CaCO$_3$. The first two species, $H^+, OH^-$, are the most dominant produced ions on the electrodes’ surfaces and the carbonate related species are the most important ions in the buffered environments. The constant current condition is being employed in the model, therefore the production rates are assumed to stay constant during the process, even though it might slightly change due to double layer appearance around the electrodes, as the polarity reversal is applied and limits the mass flux to the electrode surface. The effects of charging the double layer is not accounted for since the frequency of polarity reversal is low relative to the average time for the double layer to charge up.
(~10 ms). Accounting for diffusivity on the electrode surface is also not applicable since the system is under hydraulic gradient and mass transport to the electrodes’ surfaces are not the limiting criteria.

Having no media in the reactor as well as having a relatively high advective flow in the system, result in advection and diffusion being two sets of dominant transport mechanisms. Therefore, the mass flux equation is described as follow:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x} \pm R_{c_i} \quad (3-31)$$

The considered applied current to the system is 60 mA and was kept constant within the process, therefore it’s a reasonable assumption that, as before, the electrolysis reaction occurring in the system is primarily water electrolysis (Eqn. 3-23 and 3-24). The dominant aqueous phase reactions in the electrolyte, which also affect the pH change throughout the system, can be safely considered as previously used, water association/dissociation as well as acidic and basic reactions involving sulfate and bicarbonate (Eqn. 2-13, 3-32 and 3-33). To account for the precipitation of the calcium carbonate particles, additionally the solution/dissolution reaction is considered in the model (Eqn. 3-34).

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}, \text{ where } K_{a2} = 4.68 \times 10^{-11} \left[ \text{mol/l} \right] \quad (3-32)$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3, \text{ where } K_{b3} = 2.34 \times 10^6 \left[ l/mol \right] \quad (3-33)$$

$$CaCO_3 \rightleftharpoons Ca^+ + CO_3^{2-}, \text{ where } K_{sp} = 8.7 \times 10^{-9} \left[ \text{mol}^2/l^2 \right] \quad (3-34)$$

Therefore, the system of partial differential equations contributing to the model is mentioned in equation 3-31.
Therefore, for 7 unknown concentrations in the system, there are 7 equations describing the transport mechanisms (Eqn. 3-31) separately. The 4 reaction equations (Eqn. 3-35 to 3-38) are added to the system after each time-step (See section 4-3).

\[
K_w = c_H c_{OH} \quad (3-35)
\]

\[
K_{a2} = \frac{c_{Hc}c_{CO_2^-}}{c_{Hc}c_{HCO_3^-}} \quad (3-36)
\]

\[
K_{b2} = \frac{c_{H_2CO_3}}{c_{H}c_{HCO_3^-}} \quad (3-37)
\]

\[
K_{sp} = c_{CO_3^{2-}}c_{Ca^+} \quad (3-38)
\]

The initial condition of the electrolyte for the column is assumed to be homogenous over the reactor therefore there is a constant pH and a global equilibrium for the species in the column. The initial species’ concentrations are calculated for each model based on the equilibrium reaction presented. The fluid flow rate is kept constant within the remediation process at the rate of 0.25 \( cm/min \).

\[
C_i(x,0) = C_{i,0} \quad (3-39)
\]

A constant current of 60 mA is applied across the electrodes which results in constant flux boundary condition for the electric potential at electrodes.

\[
- \sum_j z_j F D_j \frac{\partial C_j}{\partial x} - \sigma \frac{\partial E}{\partial x} \bigg|_{at\ anode} = I \quad (3-40)
\]

\[
E|_{at\ cathode} = 0 \quad (3-41)
\]

Boundary conditions for the partial differential equations describing species transport were evaluated based on species flux and electrolysis reactions at the electrodes. Therefore, flux type boundary is considered for the upper bound of the reactor since the system is going to be continuously fed with the known and constant concentrations of species. This will lead to conservation of mass inside the column.
\[-D_l \frac{\partial c_l}{\partial x} + v c_l \bigg|_{x=0} = c_l^0(t) v \quad (3-42)\]

And for the lower bound assuming a finite column with zero concentration gradient, we can say:

\[
\frac{\partial c_l}{\partial x} (L, t) = 0 \quad (3-43)
\]

This condition leads to a continuous concentration distribution at \(x=L\).

The mass fluxes of \(H^+\) and \(OH^-\) at the electrodes’ location are considered as

\[
-D_{H^+} \frac{\partial c_{H^+}}{\partial x} + v c_{H^+} \bigg|_{x=electrode} = c_{H^+}^{electrode} + \frac{I}{F} \quad (3-44)
\]

\[
-D_{OH^-} \frac{\partial c_{OH^-}}{\partial x} + v c_{OH^-} \bigg|_{x=electrode} = c_{OH^-}^{electrode} + \frac{I}{F} \quad (3-45)
\]

The adopted solving approach is described at section 4-3.
Chapter 4 Numerical Calculation

4-1 Introduction

Obtaining accurate numerical solution to differential equations describing physical systems is of an importance. Although analytical solutions are accurate and efficient for a variety of problems, as the system gets complicated and the impacts of more variables are considered in the model, they are not easily available. For nonlinear system of PDEs with N number of unknowns, analytical or approximate analytical solutions are limited. For general heterogeneous systems, numerical solutions are more commonly used since they are more convenient to manipulate for heterogeneous cases as well as complicated boundary conditions. In this study, a finite difference approach is used to find the approximate numerical solution for these set of equations.

4-2 Finite Difference Method

The adopted approach to modeling the defined electrochemical remediation reactor is the finite difference method. Numerical solutions are preferred to obtain results for systems with complicated boundaries or systems that analytical solution is not available for them. Finite difference method discretizes the time and space domain into blocks (Figure - 4-1). These blocks can either have the same dimensions or not. Discretizing the domain in respect to space, reduces the partial differential equations to ordinary differential equations.
Consequently, time discretization changes the system of ordinary differential equations to a system of algebraic equations. The accuracy of the solution strongly relates to these block sizes, as they get larger, the assumption of constant value within the block is less reliable.

\[ h = \frac{x_L - x_0}{m} \quad \therefore x_i = x_0 + ih, \quad i = 0,1,2, \ldots, m \]  

(4-1)

\[ k = \frac{t_{\text{final}} - t_0}{n} \quad \therefore t_i = t_0 + jk, \quad j = 0,1,2, \ldots, n \]  

(4-2)

With this approach each differential equation is replaced by a set of difference equations.

For example, for a first order derivative using a forward difference setup:

\[ \left( \frac{\partial u}{\partial x} \right)_i \approx \frac{u_{i+1} - u_i}{\Delta x} \]  

(4-3)

Therefore, to solve \( N \) number of equations for \( N \) number of variables, each variable should be obtained in each block. Hence, if \( M = n \times m \) is the total number of blocks, the minimum number of equations to be solved is \( N \times M \). This is why finite difference method is slow and not used widely. The advantage of this method is that it can be easily derived for boundary conditions in transient models.
These difference equations are governed using Taylor series. For example, for first order derivative, if it is assumed that the function \( y(t) \) can be expanded in Taylor series in the closed interval of \( t - k \leq t \leq t + k \):

\[
y(t \pm k) = y(t) \pm ky'(t) + \frac{k^2}{2!} y''(t) \ldots + \frac{(\pm 1)^n}{n!} k^n y^{(n)}(t) + \ldots
\]

Therefore,

\[
\frac{y(t+k)-y(t)}{k} = y'(t) + O(k) \tag{4-5}
\]

In this equation, \( O(k) \) means that the first term neglected is of order \( k \). Hence, forward and backward difference are accurate to order \( k \). To reach a more accurate solution higher order terms should be accounted for. Although for central difference where the first order differential equation is described by (Eqn. 4-6) the accuracy is in order of \( k^2, O(k^2) \).

\[
\frac{\partial y}{\partial t} \approx \frac{y(t+k/2)-y(t-k/2)}{k} \tag{4-6}
\]

### 4-2.1 Explicit versus Implicit Finite Difference Schemes

For transient models, the partial differential equations are defined in respect to time and space. If \( u^j_i \) is defined as variable \( u \) at time \( j \) and location \( i \) for a one dimensional system, first order partial differential equation (Eqn. 4-7) explicit finite difference scheme for space and forward finite difference scheme for time, using a central differentiation technique, is as defined in equation (4-8).

\[
\frac{\partial u}{\partial t} = A \frac{\partial u}{\partial x} \tag{4-7}
\]

\[
\frac{u^{j+1}_i-u^j_i}{\Delta t} = A \frac{u^{j+1}_{i+1}-u^{j+1}_{i-1}}{2\Delta x} \tag{4-8}
\]

Therefore, explicit finite difference method, approximates the variable at time \( j + 1 \), using the known variable at time \( j \) (Eqn. 4-9).
\[ u_i^{j+1} = u_i^j + A \frac{\Delta t}{2\Delta x} (u_{i+1}^j - u_{i-1}^j) \]  

(4-9)

However, the major advantage of explicit finite difference method is its relative simple and fast computation, the downside is the stability problem accompanied with the method. Explicit method, strongly depends on the block sizes as well as the constants in the original partial differential equation. As the partial differential equation gets more complicated with accounting for more phenomena, this method needs a specific attention for the choice of grid sizes. Therefore, an alternative and more complicated scheme is introduced, implicit finite difference scheme.

In implicit finite difference, the spatial derivatives are assessed in the new time step (Eqn. 4-10).

\[ \frac{u_i^{j+1} - u_i^j}{\Delta t} = A \frac{u_{i+1}^{j+1} - u_{i-1}^{j+1}}{2\Delta x} \]  

(4-10)

Consequently, a more complicated solution is being provided for the variable at time \((j + 1)\) (Eqn. 4-11).

\[ \left( A \frac{\Delta t}{2\Delta x} \right) u_{i-1}^{j+1} + u_i^{j+1} - \left( A \frac{\Delta t}{2\Delta x} \right) u_{i+1}^{j+1} = u_i^j \]  

(4-11)

Equation (4-11) can be solved using its matrix formation (Eqn. 4-12).

\[
\begin{bmatrix}
A \frac{\Delta t}{2\Delta x} & 1 & -A \frac{\Delta t}{2\Delta x} \\
A \frac{\Delta t}{2\Delta x} & 1 & -A \frac{\Delta t}{2\Delta x}
\end{bmatrix}
\begin{bmatrix}
u_{i-1}^{j+1} \\
u_i^{j+1} \\
u_{i+1}^{j+1}
\end{bmatrix}
= 
\begin{bmatrix}
u_i^j \\
u_i^j \\
u_i^j
\end{bmatrix}
\]  

(4-12)

The advantage of using implicit method is that there is no restriction on the grid and step sizes, although choosing large time-steps can result in less accurate result.
Figure 4-2 implicit versus explicit finite difference method; (a) explicit method; (b) implicit method
4-2.2 One-step versus Two-step Scheme

One of the most important decisions in solving partial differential equations is between one-step scheme versus two-step scheme.

One-step method solves the complete partial differential equation simultaneously whereas the two-step method separates the solutions for zero-order part of the equation and higher order parts in respect to space. To illustrate, if equation (4-13) is the intended partial differential equation that needs to be solved, one-step method solves it as (Eqn. 4-14), whereas the two-step approach separates the equations and solves it in sequence (Eqn. 4-15 and 4-16) and needs an additional iteration between the two steps.

\[
\frac{\partial u}{\partial t} = A \frac{\partial u}{\partial x} + Bu + C \tag{4-13}
\]

\[
\frac{u_i^{j+1} - u_i^j}{\Delta t} = A \frac{u_i^{j+1} - u_i^{j+1}}{2\Delta x} + Bu_i^{j+1} + C \tag{4-14}
\]

\[
\frac{u_i^{j+1} - u_i^j}{\Delta t} = A \frac{u_i^{j+1} - u_i^{j+1}}{2\Delta x} \text{ first step} \tag{4-15}
\]

\[
\frac{u_i^{j+1} - u_i^j}{\Delta t} = Bu_i^{j+1} + C \text{ second step} \tag{4-16}
\]

The accuracy of two-step approach depends on the degree of coupling between the terms. Therefore, if the time-steps are small or the terms are weakly coupled, the two-step method is a reliable solving method [46].
4-3 Adopted solving approach

The one-dimensional axisymmetric analysis is unnecessarily complicated for this setup, both for experimental measurement and for numerical modeling effort, therefore, a uniform one-dimensional flow is considered to be reasonable for a preliminary assessment of the validity of the presented mathematical model considering the assumption of homogenous species concentration.

4-3.1 Batch Reactor

In the batch reactor, the stirring rate is assumed to be significantly higher than the rate of mass transport by diffusion and migration, therefore, a well stirred condition is applied and the concentrations within the reactor are homogeneous.

Therefore, to have a time dependent simulation, at each time step it is assumed that the concentrations reach equilibrium.

\[
\frac{dc_i}{dt} = R_i \quad (4-17)
\]

Therefore, by defining the system numerically,

\[
\frac{c_{i}^{t+1} - c_{i}^{t}}{\Delta t} = R_i \quad (4-18)
\]

Therefore, in each time step, the change of concentration for all the species are calculated and iterated to find the equilibrium concentrations.
4-3.2 Flow-through Reactor

The general form of the partial differential equation in one dimension for a coupled model for transport and chemical reaction of multiple chemical species is given by equation (4-19).

To solve the equation for time differentiation first order error and for the space differentiation second order error is adopted (Eqn. 4-19). first step solves the transport mechanism.

\[ D_i \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x} + R_i = \frac{\partial c_i}{\partial t} \]  \hspace{1cm} (4-19)

The electrodes are adding additional boundary conditions to the system since each electrode is producing at least one chemical on the electrode surface. For the species that are produced via direct electrolysis, the reactor is divided into two sub-domains to solve the transport equation.

4-3.2.1 Transport of $H^+$ and $OH^-$

As was mentioned, the electrode surface adds more boundary conditions to the system, and makes the system over constrained. To implement the boundary conditions, the reactor is divided into two subdomains to solve for transport of $H^+$ and $OH^-$ (Figure - 4-3).

Depending on the configuration of the system, cathode/anode or anode/cathode setup, the length of the subdomains for each of species change, but to generalize the code for implementing polarity reversal in the system a general set of equations are obtained for $H^+$ and $OH^-$ specifically.
Each electrode has two surfaces, where the electrochemical reactions take place, therefore there are two boundary conditions defined by each electrode.

The mass transport equation is developed in previous section and is presented once more in here (Eqn. 4-19). The inflow boundary condition is a flux type boundary, as the system is continuously fed with constant concentrations (Eqn. 4-20). For the first subdomain, the outlet boundary condition, where there is $H^+/OH^-$ production at the first surface of the first/second electrode is defined as flux type boundary as well (Eqn. 4-21).

$$v c_i - D_i \left. \frac{dc_i}{dx} \right|_{x=0} = v c_i^0$$  \hspace{1cm} (4-20)

$$v c_i - D_i \left. \frac{dc_i}{dx} \right|_{x=x_1} = v c_i - \frac{l}{AF}$$  \hspace{1cm} (4-21)

where $A$ defines the electrode surface area $[cm^2]$.

![Figure 4-3 schematic view of the flow-through reactor and the chosen subdomains for $H^+$ and $OH^-$ transport calculation](image)
Moreover, for the second subdomain, the inlet boundary condition is defined at the second surface of the same electrode (Eqn. 4-22), and the outlet boundary is at the end of the reactor where it is assumed as a semi-infinite boundary condition (Eqn. 4-23).

\[
vc_i - D_i \frac{dc_i}{dx}_{x=x_i} = vc_i^{x=x_i} + \frac{l}{AF} \quad (4-22)
\]

\[
\left. \frac{dc_i}{dx} \right|_{x=L} = 0 \quad (4-23)
\]

4.3.2.2 Transport of other species

For other species that the production rate is not applicable to, the solution is over the whole domain (Figure - 4-4). Similarly, the boundary conditions at the inflow are defined as a flux type boundary and for the outflow it is assumed a semi-infinite condition, as was for the transport of \( H^+ \) and \( OH^- \) (Eqn. 4-24 and 4-25).

\[
v c_i - D_i \frac{dc_i}{dx}_{x=0} = vc_i^0 \quad (4-24)
\]

\[
\left. \frac{dc_i}{dx} \right|_{x=L} = 0 \quad (4-25)
\]

\[\text{Figure 4-4 Schematic view of the flow-through reactor for all species}\]
4-3.2.3 Reaction terms

As was mentioned before, the model calculates the equations in two sequential steps. Therefore, after transport of species, a local equilibrium model is defined for each species. The same concept for the batch reactor is applied here for flow through reactor, but instead of defining the equilibrium in the whole reactor, a local equilibrium is considered in each discrete by iteration. After local equilibrium is reached, the reaction term is updated in the transport mechanism and solved once again until it reaches conversion.
Chapter 5 Results and Discussion

This study is on modeling electrochemical remediation process with direct electrolysis in a batch and a flow-through reactor. The focus of the study was on equation development and numerical calculations as was stated in the previous chapters. In this chapter a number of comparisons between the model predictions and experimental data is presented.

5-1 Batch Reactor

The results of laboratory scale test reported by Ciblak et al.[12] is compared to the model prediction of batch reactor. The results are discussed under two conditions of mixed-electrolyte and divided-electrolyte.

It is assumed that the stirring in the reactor is high enough to simulate a homogenous environment. Therefore, as described earlier, an equilibrium reaction model is defined. The effects of diffusion and migration mass transfer is neglected in this part of the study since a completely stirred reactor is provided.

The direct electrochemical reactions in the system are water oxidation and reduction. The diffusion of ions to the surface of the electrodes, as well as the double layer effects are neglected due to the noted assumptions.
Figure 5-1 shows the pH change within a divided-electrolyte batch reactor. Completely stirred condition provides a fully homogenous concentration level in each compartments while they are connected using a 112 Nafion membrane as was reported in experimental work done by Ciblak et al.[12]. Knowing that the completely stirred condition was approved in the mixed-electrolyte, the model predicts a rapid decrease in anolyte pH to 2 and an increase in catholyte to 12 in less than half an hour of reaction. Ultimately, the pH in both anolyte and catholyte will reach stability. As was reported previously, pH value over time in the unenhanced electrochemical reactor can change between 2 and 12 [3], which validates the results from the model. As the anolyte and catholyte are not connected directly and just a limited number of ions can move past the membrane, the hydroxide and hydrogen ions are not provided for water association/dissociation reaction. As a result, an extremely acidic and basic condition develops in anolyte and catholyte, respectively.
Comparing the results of experimental data [12] and the model prediction, an insignificant mismatch is observed in catholyte, specifically. This can be explained by getting into more detail about the separating membrane used in this study, which allows sodium and hydrogen ions to migrate between two separated reactors and not negatively charged ions. Furthermore, Springer et al. mentioned in their research on the polymer fuel cells that there is an increase on proton conductivity of Nafion membranes with increase of water content [15, 45].

The extreme change in pH can only be observed in electrolytes with low buffering capacity. In this model, the electrolyte consists of calcium sulfate, which has a low buffering capacity, therefore it lets the electrolyte change pH with no resistance.

*Figure 5-2 pH change in the mixed-electrolyte batch reactor*
Figure 5-2 shows the results in a completely stirred batch reactor. The pH stays constant within the process since the produced hydroxide and hydrogen ion neutralize each other in a completely stirred condition. As was expected, due to the similar production rates of hydrogen ion and hydroxide ion in the system, the pH of the experiment stays constant throughout the process. The experimental data shows a close result comparing to the model prediction which verifies the completely stirred condition as well as the assumed chemical and electrochemical reactions defined in Chapter 3.

5-2 Flow-through Reactor

The results of laboratory scale test reported by Rajic et al. [36] are compared with the model predictions. Therefore, the initial and boundary conditions pertinent to the laboratory scale test are used in the solutions which are described along with each model setup in Chapter 3 and 4.

To calibrate the reaction kinetics of the model a study on batch reactor was preliminary presented and compared to the test report by Ciblak et al [12] in the previous section.

5-2.1 Effects of transport mechanisms

The effect of transport mechanisms can be illustrated by comparing the model prediction from the batch reactor and the flow-through reactor with same electrolyte composition. The electrochemical reactions create the same anolyte and catholyte pH in the system which can be altered by changing the current density in each of these systems. The pH changes in the range of 2 to 12 in both setups, however in the flow-through reactor, the pH after the second electrode, which in this case is anode, will head towards neutral.
Eliminating the hydraulic head difference from the flow-through reactor will result in higher backflow caused by diffusion of ions (Figure 5-4). Additionally, the effect of diffusion coefficient for acidic and basic fronts in backward and forward directions can be observed. The acidic front moves faster and spreads faster in the system than basic front which is because of higher diffusion coefficient of hydrogen ion. Keeping that in mind, increasing the velocity in the system will cause further transport of ions in the forward direction and therefore, the second electrode will be neutralized (Figure 5-4).
Figure 5.4 pH profile along the length of the reactor; (a) no hydraulic head gradient, velocity = 0; (b) velocity = 0.25 cm/min
Including carbonate in the system shows smaller pH alteration as it was expected. The trend of decrease in pH is lower since there is no sudden change in the system. The impact of sudden decrease and increase will be lowered by the buffering reactions in the system.

5-2.2 Polarity Reversal Effects

The effects of polarity reversal is added to the model. The experimental data are showing the effects 6cycles/hour with anode/cathode configuration in the beginning of the process. Figure 5-6 shows the comparison of the model prediction with the experimental obtained by Rajic et al [36] after the first electrode. The model estimate shows an alteration between 2 and 12 throughout the process whereas the experimental data is more stable and shows a consistent low pH during the electrochemical remediation process, Figure 5-6.
The possible explanation is the time of measurements; the measurements are right at the time and position where the chosen electrode is always an anode at the sampling times. Additionally the polarity reversal is introduced to the model as a sudden change of current direction. Even though a small period after each cycle, which is for appearance of the double layer after each cycle, is introduced to the model but the effects of direct electrolysis of hydroxide ion and oxygen gas on the surface of the anode and electrolysis of hydrogen ion at the surface of cathode is not accounted for. Therefore, each change of current direction results in sudden change in pH.
Although the aforementioned effects might result in less fluctuation within a smaller range in the reactor, model prediction and experimental data comparison show a good correlation at the measured points throughout the reactor (Figure 5-7). Figure 5-7 is obtained by comparing the experimental data and the model prediction at three different sampling port. As is shown in Figure 3-4, the sampling ports are after each electrode as well as one in the end of the reactor.

*Figure 5-7 Correlation Scatter plot between the polarity reversal model and experiment reported by Rajic et al. [36]*
Chapter 6 Summary and Conclusion

The model is to predict the concentration of species during the electrochemical remediation process. The initial step of this goal is modeling the pH change during the electrochemical process as a dominant factor affecting the efficiency of the system. Therefore, a set of direct electrolysis reactions as well as the possible chemical reactions are introduced to the model. The transport mechanisms of species are solved along the reactions in a two-step finite difference method. The considered reactors in this study are batch reactor, as a calibration for reactions, and flow-through reactor to account for transport of species. This model is introduced in a volume limited system, solving for continuously fed reactive flow reactor. In this approach time is divided into discrete intervals, time steps, and space as well, spatial grid. The solution of the system was coded using a finite difference approximation in MATLAB platform. Regarding the dependence of the concentration of each specie on one another, the system was not stable using an explicit solving method since there are a number of stiff terms in the calculations, hence an implicit method was carried out through the solving sequence. Hence, for every time step, the values of each species is calculated using the previous time step’s concentrations. Numerical solution used in this study is centered finite difference method with second order magnitude of error. At the lower boundary where a constant derivative condition, a backward finite difference approximation is used, as oppose to the upper boundary, where a forward difference scheme is more appropriate.

The model for batch reactor consists of a low buffered electrolyte, where a sudden change in anolyte and catholyte is observed. However, in the mixed electrolyte the hydroxide and
hydrogen ion participate in a neutralizing reaction and therefore a more stable concentration is obtained.

The flow-through reactor modeling starts with a system with low buffering capacity to carry on the results of the batch reactor. Modifying the model for the transport mechanisms resulted in a more comprehensive and more time consuming calculations. Having transport mechanisms in the system did not affect the extreme change of pH at the anode and the cathode positions. Therefore, the model predicted the pH to rise at cathode to 12 and decrease to 2 at the anode compartment. The transport mechanisms forced the acidic and basic fronts to advance and not accumulate. In the absence of hydraulic head difference in the system, diffusion mass transport observed to be the key transport mechanism so that the transport of the acidic and basic front in the reverse direction was higher. Additionally, the effect of diffusion coefficient for acidic and basic fronts in backward and forward directions was illustrated as the acidic front moves faster and spreads faster in the system than basic front which is due to higher diffusion coefficient of hydrogen ion.

The polarity reversal effect was added to the model as it is one of the important methods of electrochemical decontamination. The effects of polarity reversal were observed in a non-buffered electrolyte. Even-though, as the polarity reversal frequency increases, the effluent’s pH alters and experiences instability until the change of polarity does not let the system to experience any change in the effluent.

The final step of completing the study was to add buffering capacity to eliminate the extreme pH experiences as well as the cyclic change while having polarity reversal. As was expected, the buffering reactions prohibit the extreme change and make the overall system more stable. But around the electrodes, still a highly acidic or basic front is observed.
6-1 Future works

Study of transport mechanisms coupled with reaction of reactive species is a growing study area. There are still many uncertainties about the reaction mechanisms. Besides, developing a tool to predict the results of decontamination methods can reduce the cost of implementation as well as increasing the efficiency of the system.

Electrochemical remediation methods are significantly unique because of their low energy consumption as well as the ability of their in-situ application. Therefore, the effort is to combine the reactions in the system to have a more comprehensive perspective of the system.

The possible following subjects can be added to the models:

- Investigation of the possibility of modeling indirect electrolysis reactions
- To investigate the parallel indirect and direct electrolysis reactions to evaluate the concentration of unstable species to optimize the electrochemical remediation reactor
- Investigation of lowering the computation time of the coupled multicomponent transport and reaction model
Chapter 7 References


