

PART V: CONCLUDING REMARKS

Chapter XII. Conclusions and Recommendations

12.1 Introduction

In the study of electrokinetic applications of soil remediation, this research effort has focused on different aspects that directly affect, among others, the hydrodynamic component of an electrokinetic remediation cell. To this extent, the undertaken approach is based on fundamental and modeling principles as the key tools to satisfy the needs for more understanding of the different phenomena occurring during electroremediation operations.

In order to capture the most important features of the electroremediation process as well as to maintain a systematic theoretical approach, this thesis has been organized in parts composed by chapters. The idea behind this organization is to correctly address three research questions:

- A.** What are the chances to obtain reversal electroosmotic flow and how to avoid it?
- B.** What are the primary mechanisms involved?
- C.** What are the optimal arrangement of the electrodes and cell in geometry, shape, and orientation? (Vertical, horizontal, tubular, plate, cylindrical)

From the first to the preceding chapter of this thesis, these research questions have been systematically responded through documented information, simulation of different case scenarios, graphical illustrations and several forms of analysis and interpretation of results.

These chapters not only answer the above research questions but also embrace the study of higher issues in electroremediation. In fact, four major topic areas of contributions can be identified in the present thesis. Those specific areas are:

- Development of a hierarchically structured database for electroremediation and electrokinetic published information.
- A Novel Algorithmic Approach to Solve Poisson-Boltzmann Equations.
- Hydrodynamics in the treatment zone under the stress of electrostatic forces with Joule heating generation.
- Hydrodynamics in near the electrode zone under the influence of Joule heating generation.

The summary of conclusive results and addressed topics for each of these areas of contributions are further discussed in the following sub-sections.

12.2 Electroremediation Hierarchical Database

Considering the published information that reviews the electrokinetic remediation technology, no effort has been made to classify or organize the main topics of published researches in this subject matter. The need for developing a hierarchically structured database of electroremediation is in demand to provide scientists with the proper information about current and past research efforts. The present thesis has presented a simple but useful classification of topics undertaken by the many articles published in the last ten years. Although, on-line databases provide a screening process through “Key words,” they do not necessarily capture the main research topics of an article and no analysis is performed after the screening process is executed. Such analysis has been presented in a form of a hierarchical database with the main topics that have occupied the scientific community for the last decade. From the omissions of specific topics, research opportunities can be easily identified.

12.3 A Novel Algorithmic Approach to Solve Poisson-Boltzmann Equations

Nonlinear ordinary differential equations lack methods to derive analytical solutions. This is particularly critical with ODE of second and superior orders. Based on the facts, this study has focused on developing a simple procedure to obtain an explicit analytical solution for nonlinear ordinary differential equations. A simple predictor-corrector algorithm has been developed and is introduced as an alternative tool to solve differential equations with nonlinear source terms. The proposed method involves the use of a recursive function, f_{AO} , of the nonlinear dependable variable. The procedure converts the nonlinear ordinary differential equation to a simpler linear ordinary differential equation for its analytical solution. The resulting analytical expression is modified by means of the f_{AO} correction function yielding the nonlinear solution. The approach can be used as a fully developed numerical method or as an analytical algorithm of three steps because of its convergence goodness. Test examples performed in a highly nonlinear source term suggests that this new approach could be applied successfully in solving nonlinear ODE from different disciplines, such as hydrodynamics, electrostatics, mass and heat transfer, as well as different geometries of interest, such as planar, cylindrical and annular.

An analysis of predictions of the electrostatic potential based on the use of the Poisson-Boltzmann equation with the typical approximations for the free charge density modeled by the hyperbolic sine function has been performed. As a result, a correction function, f_{AO} , has been introduced to enhance the predictions of the electrostatic potential based on the use of the Debye-Hückel approximation. The f_{AO} correction function has a polynomial form whose coefficients are adjusted to predict the correct values of the hyperbolic sine function; moreover, this approach has the advantage that these coefficients can be modified to better represent the electrostatic potential. The value reported in this research yielded values of the polynomial function in excellent agreement with the original hyperbolic function. The function f_{AO} is used to correct the Debye length value, λ , in order to improve the predictions of the linear solution based on the Debye-Hückel approximation. Three completely different geometries have been used as examples to illustrate the wide range of validity of this approach and it has been successfully demonstrated that the proposed

modified solution substantially enhanced the Debye-Hückel approximation. In fact, the same form of the solution, based on the Debye-Hückel approximation, is used to predict the solution of the Poisson-Boltzmann equation. The only difference is that the target inverse Debye length, λ , must be modified using the correction function, f_{AO} . Another important characteristic of this approach is that it is simple to use and it does not required a large number of equations and decision tables to be more accurate. In this sense, if a coupling with other transport or hydrodynamics equation is needed, this proposed approach is mathematically and computationally friendly. Additionally, the solution approach introduced in this contribution does not required specific and intermediate values of electrostatic potential to obtain the full range of the electrostatic potential profile within the domain $-1 \leq \xi \leq +1$. Finally, the introduction of the correction function, f_{AO} , is a powerful concept that can be further applied in other transport or hydrodynamic models.

12.4 Hydrodynamics in the Treatment Zone

Rectangular Model

In this thesis, the combined effect of pressure driven, electroosmosis, and buoyancy on determining the different types of flow regimes in a capillary channel has been examined. Notably, the parameter values generate a family of pressure-driven flow regimes and an electroosmotic dominated family of flow regimes. These flow situations are modified by the buoyancy when the values of the Grashoff number, Gr , and Joule heating number, ϕ^2 , collaborate to significantly change the values of the mean temperature, θ_m , in the system. Furthermore, the presence of different temperature values at the walls of the capillary generates a non-symmetry effect in the temperature profile. In order to identify the role of this effect, a skew or an asymmetric factor, W_∞ , has been introduced. Two distinct values of this factor generate two different qualitative situations: the symmetric case, $W_\infty=0$, and the non-symmetric case, i.e., $W_\infty \neq 0$. Significant changes in both the temperature and the velocity profiles are noticed when a comparison between the two cases is made. This effect strongly affects the different flow regimes and could not be overlooked in an eventual application to processes such as soil remediation near the surface and bio-enhancement that involve the

three driving forces mentioned above. The symmetric case, as expected, generates a much simpler function for both the temperature as well as the hydrodynamic velocity profiles. For example, the maximum value of the system temperature is a simple function of the parameters Nu and ϕ^2 and it always occurs at the center of the capillary.

Another important aspect addressed in this thesis is the fact that, for the first time, several design criteria that constrain the values of the parameter space are reported. These criteria are useful to prepare efficient cleaning protocols in, for example, soils and in the interpretation of experimental results related to electrokinetic remediation processes. The criteria seem to be a tool currently missing in the literature.

Although the geometry adopted in this work may not fully describe field conditions, the obtained results have important practical implications that must be considered in a scale up operation as to avoid the usual pitfalls of electrokinetic remediation processes. Perhaps, the most important lesson to be learned is that, under certain conditions, different types of flow reversals occur and, therefore, mixing. As this phenomenon affects the efficiency of the process, practitioners may now optimize their designs using the knowledge herein provided.

Cylindrical Model

The effect of a combination of three different forces has been analyzed, i.e. pressure driven, electroosmosis, and buoyancy, to determine the different types of flow regimes that may occur in a cylindrical capillary channel. The adopted geometry is considered to describe more closely field conditions in that cylindrical channels emulate porous media. A remarkable family of flow regimes has been identified for characteristic parameter values of the system. For example, competing buoyancy forces with electroosmotic forces yield *single flow reversal* to *double flow reversal regimes* as buoyancy becomes the most important driving force. Also, collaborating buoyancy and electroosmotic forces against pressure driven forces generate a single flow reversal regime. And, when the buoyancy force is negligible electroosmosis competes with pressure driven forces yielding *flow reversal regimes*. From this analysis, the most important practical implication that must be considered in a scale up

operation to avoid the usual pitfalls of electrokinetic remediation processes is that, under certain conditions, different types of flow reversals occur and, therefore, mixing takes place.

Another contribution of this thesis is that a number of design criteria that constrain the values of the parameter space are reported. For example, limiting case expressions have been obtained for temperature and total hydraulic head gradient. As the mixing, caused by flow reversals, reduces the efficiency of the electrokinetic operation, these criteria may be found useful to prepare efficient cleaning protocols in, for example, soils. In addition, the interpretation of experimental results related to electrokinetic remediation processes may be carried out more accurately using these criteria as simulation tools.

Annular Model

The effect of a combination of three different forces has been analyzed, i.e. pressure driven, electroosmosis, and buoyancy, to determine the different types of flow regimes that may occur in an annular capillary channel. This particular geometry is considered to be the one that more closely describes porous media in that variations of the annular area can be related to porosity. Moreover, soil temperature development under field condition can be associated to resistive heating of the annular core and Joule heating effect. In consequence, the analysis of the role of the main driving forces on the hydrodynamic of electrokinetic processes has been enriched by the adopted geometry.

A non-trivial modeling, coupling, and solution of the proposed system have been accomplished with two significant results, as next described.

First, a family of flow regimes has been identified for characteristic parameter values of the system under study. For example, competing buoyancy forces with electroosmotic forces change the flow direction and yield *flow reversal regimes*. As any of these two forces becomes the more important driving force, the flow reversal effect vanishes and yields pressure driven type of flows. Also, when the buoyancy force is negligible electroosmosis competes with pressure driven forces; however, electroosmosis seems to be stronger and therefore no *flow reversal regimes* are observed. In addition, temperature development due to

resistive heating induces buoyancy driven flows near the walls. A similar effect is observed when the electrical potential at the inner wall is a maximum. For the analysis of porosity, higher values of the dimensionless core radius (lower porosity values) favor electroosmotic driven flows, diminishing *flow reversal regimes* and pressure driven flows.

Second, a number of design criteria that constrain the values of the parameter space are reported based on the model equations developed in this study. For example, limiting case expressions have been obtained for temperature and total hydraulic head gradient. As the mixing, caused by flow reversals, reduces the efficiency of the electrokinetic operation, these criteria may be found useful to prepare efficient cleaning protocols in soil remediation. In addition, the interpretation of experimental results related to electro-remediation processes may be carried out more accurately using these criteria as simulation tools.

From a practical point of view, this analysis has important implications that must be considered in a scale up operation. The dimensionless analysis of the typical conditions of an electro-remediation process has revealed that, under certain conditions, different types of *flow reversal regimes* occur and, therefore, mixing. For example, porosity plays an important role changing the hydrodynamic of the system in direct relationship with electroosmosis. The usual uncertainties of electrokinetic remediation processes may be avoided if these findings are considered.

Finally, and accordingly with the goal of this work, a manageable description of the system from an analytical point of view has been obtained. Further efforts to covert simplifying assumptions are currently made to promote more understanding of the dominating aspects on electrokinetic applications.

Comparison of Porous Media Geometrical Aspect

The role of soil's physical aspect has been analyzed by comparison of three geometrical models for capillary systems, i.e. planar, cylindrical and annular, in conjunction with three different forces, i.e. pressure driven, electroosmosis, and buoyancy. In this study, the most important hydrodynamic variables are analyzed and compared, across the

geometrical aspects, under the most typical stress scenarios. The transport forces considered in this analysis are the most realistic set for an electroremediation process.

Important criteria may arise from the comparison of results. Furthermore, interpretation of experimental results related to electrokinetic remediation processes may be conducted based on these first principles to improve process efficiency. Such a tool is currently missing in the literature.

For the first time, considering the available published information, three hydrodynamic models, including the heat transfer and electrostatic field components, have been put together for comparison. The summary of analytical expressions is presented in table forms with their respective nomenclature.

A significant number of illustrative results have been presented in a 3D fashion to demonstrate the actual form of flow regimes that may be expected under different conditions of geometry and physical constraints. Additionally, similar illustrations have been presented for cases of temperature and electrostatic potential.

12.5 Hydrodynamics in the Near the Electrode Zone

Rectangular Aspect

A study has been conducted on the hydrodynamic taking place near the electrode zone for devices of rectangular aspects. Natural convection and Joule heating generation are the main driving forces considered in the analysis with application in electrokinetic remediation. The Von Karman integral approximation approach was used to invert the boundary layer model in order to derive a simpler, two-first order, differential equation model. The effects of the heat generation in temperature, boundary layer thickness, and velocity profiles have been studied. When the adopted strategy is compared with previous works, the addition of the Joule heating generation term and the changing of the Dirichlet boundary conditions (to wall condition instead of fluid) lead to important modifications whose solution is not trivial. The

assumption that the heat generation follows a similarity type of function does not yield an analytical solution and therefore a numerical solution is forced. In other words, the source generation term, ϕ^2 , shows a constant value along ξ , the axial- coordinate of the system which is not obtained when a similarity solution is assumed. The final system model has been solved to portray dimensionless temperature, boundary layer thickness and velocity profiles as functions of ξ and η , dimensionless coordinates.

A major finding is that Joule heating generation affects considerably the value of the temperature, the boundary thickness and both velocities components of the hydrodynamic field. These findings could be either useful or detrimental for the electrokinetic remediation system depending upon the application under consideration. For example the increase in the velocity magnitudes may lead to important mixing conditions near the electrode surface that, for relatively small cells will decrease the treatment efficiency of the process. On the other hand, the increase in the velocity magnitude may, actually, help to transport pollutants in the direction of the flow and, therefore, increase the overall cleaning efficiency of the process.

Cylindrical Aspect

The hydrodynamic near the electrode zone has been modeled and analyzed for the case of cylindrical shape electrodes. The study has considered natural convection and Joule heating effect as the main driving forces in the system as it occurs in an electrokinetic remediation cell. A boundary layer approach was used to develop the primary model for the heat transfer and hydrodynamic components of the system under study. The integral approximation, proposed by Von Karman and applied to rectangular systems, was utilized to derive a simpler, two-first order, differential equation model. The Dirichlet boundary conditions, fluid at wall conditions, lead to a non-trivial solution, as the assumption of a similarity type of function cannot be applied to heat generation. In other words, the source generation term, ϕ^2 , shows a constant value along ξ , the axial- coordinate of the system which is not obtained when a similarity solution is assumed. Consequently, the simplified system model has been solved numerically. The final system model has been solved to portray dimensionless temperature, boundary layer thickness and velocity profiles as functions of ξ

and η , dimensionless coordinates. The effects of the heat generation in temperature, boundary layer thickness, and velocity profiles have been studied.

On cylindrical electrode aspect, two major findings are reported for the effect of Joule heating generation on the temperature, the boundary thickness and both velocities components of the hydrodynamic field. The first finding is that free convection is considerably affected by the fluid electric resistance. A cooling effect on temperature profiles is observed as a thinner boundary layer exchanges heat with free fluid. The second result deals with the radius aspect of the electrode. In this case, longer electrodes retract the boundary layer thickness as well as the axial velocity field. These effects could be used in favor of fluid collection in the electrokinetic remediation cell. However, a system based on a different approach may be affected by experiencing decrease on efficiency. Therefore, a set of illustrations has been presented to assess the possibilities of increasing the overall cleaning efficiency of the process for any electroremediation technology.

Comparison of Electrodes Geometrical Aspect

The role of electrode shape has been studied by comparison of the two most used electrode geometrical aspects, i.e. rectangular and cylindrical. These particular electrode designs characterize distinct electroremediation technologies and they may affect the efficiency of the intended removal process. In particular, the electrode shape promotes specific flow regimes in the near zone that may influence the delivery and/or collection of fluids from the electroremediation cell.

One important finding is that Joule heating has the opposite effect on temperature and boundary layer profiles. This phenomenon has a larger impact on boundary layer profiles where, for rectangular electrodes, the boundary layer significantly grows while in cylindrical electrodes the boundary layer reduces in thickness. The practical implication is that rectangular electrodes under the effect of Joule heating may offer a smaller effective treating zone than cylindrical electrodes. The same effect has been observed when different cylindrical radiuses are used. In other words, shorter cylindrical electrodes offer smaller effective treating zones than larger ones.

Finally, for the hydrodynamic part, the major finding is that buoyancy influences both geometrical aspects changing mainly the ascending axial flow stream. In the comparison, rectangular electrodes promote larger values of axial velocity reaching further in the transversal direction. In contrast, cylindrical electrodes develop larger axial velocity with shorter spreading. However the spreading can reach further using shorter electrodes. The implication here is that more restricted and easier to control collection of fluid can be accomplished near the electrode region with cylindrical type of devices.