Chapter II. Review of the Relevant Literature

2.1 Introduction

A comprehensive literature review, concerning the main research efforts on electrokinetic remediation, was conducted to gain a better view of past and current trends on this subject matter. In developing this task, primary sources considered were journal articles, government and private institutions reports that dealt with key issues of electrokinetic. In addition, a reasonable time frame for survey was assigned considering a horizon of ten years until date. In other words, relevant technical and scientific information, published between the years of 1994 and early 2004, was reviewed and analyzed to give support to this thesis. In order to find such information from primary sources on-line databases were consulted and used as search engines.

The number of contributions that could be found inquiring on-line databases can be quite large. In fact, a significant amount of time is required to select only the most relevant literature by either reading the complete article or the abstract when only this is available. In this case and after exhaustive screenings, five main topics have been identified among the collected journal articles and reports. Accordingly, the following flowchart has been prepared, Figure 2.1, to illustrate those topics within the context of electroremediation. The proposed database structure is not only a mere classification of available information but also a tool that could allow researchers to better orient their future efforts.

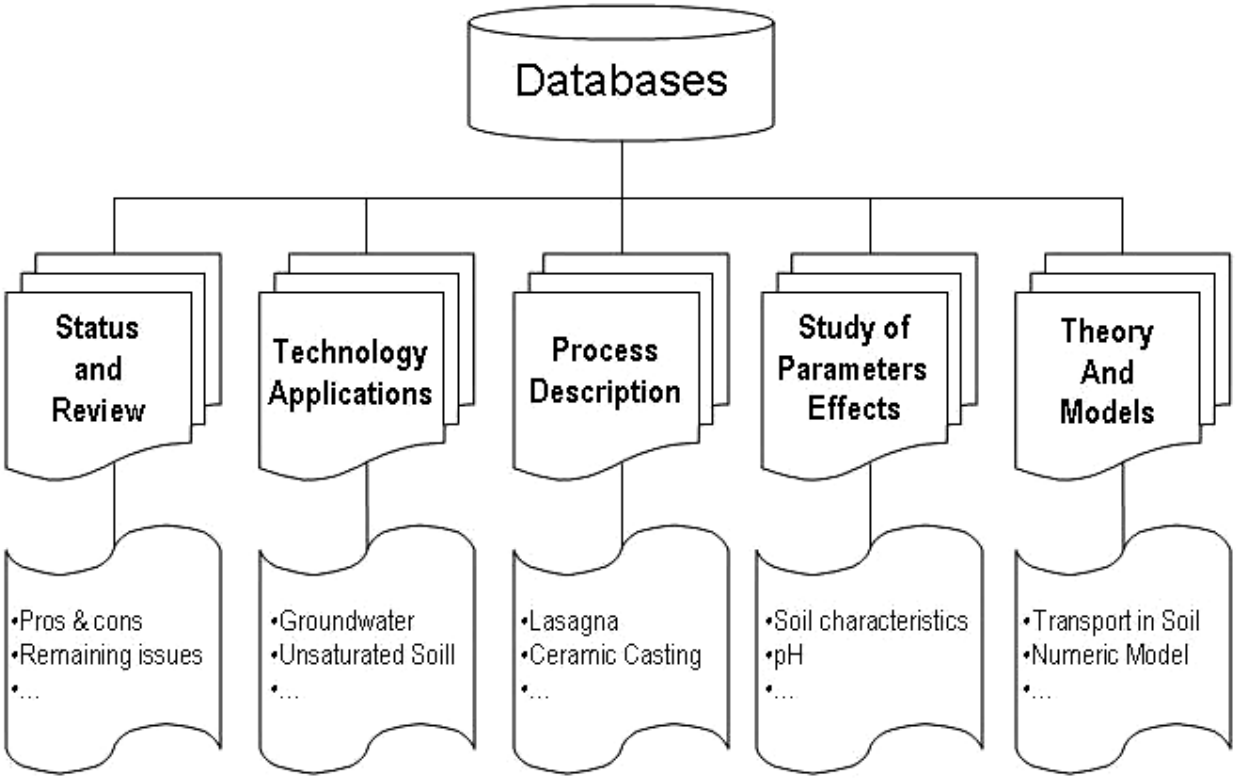

Figure 2.1 Tentative database structure of electroremediation information.

Figure 2.1 shows that the available information on proprietary databases can be classified or structured in topics such as a) Status and review, b) Technology applications, c) Process description, d) Study of parameters effects, and e) Theory and models. Specific examples, of each of these five topics, are listed to illustrate the issues being discussed; however, more detailed information will be given in next sections. A priori, subjects such as a) Status and review and e) Theory and models should be recognized as key topics for the development of this work; although, this last one is far more important.

The next sections will focus on the discussion of contributions within each of the five identified topics. A more general approach is adopted with those topics that provide background information and support to the addressed research questions. However, a

comprehensive analysis is devoted to topic c) Theory and models as it is the foundation for the present research effort.

2.2 Discussion of General Topics

2.2.1 Status and review

The current status of electrokinetic remediation was examined to provide background information on this matter. In addition, the evaluation of the current status was conducted to justify engaging the present research effort. Although, not many authors have dedicated their research to review the electrokinetic technology, there exists robust published information that provides solid grounds for further investigation.

As early as 1993, the first effort for describing the principles and status of electrokinetic was made. The latest effort in that direction was completed in 2002. Since then, no other contributions have been reported according to this study.

Table 2.1 Chronological list of contributions on status and review

Authors	Years
Acar, Yalcin B.; Alshawabkeh, Akram N.	1993
Acar, Yalcin B.; Gale, Robert .; Alshawabkeh, Akram N.; and others	1995
Childress, Vincent W.	2002
Virkutyte, Jurate; Sillanpaa, Mika; Latostenmaa, Petri	2002
Van Cauwenberghe, Liesbet	1997
Geokinetics International, Inc.	1999
U.S. EPA	2000

Table 2.1 presents the list of authors whose work has been important in documenting the main aspects of electrokinetics and its status through the years (Complete citations are given in the references at the end of this thesis). In particular, two types of information have been found, this is, technical articles and technology reports, as shown. As might be expected, the latest publication is the best written document as it covers in detail ten years of research. In fact, most of the previous years' sources are cited by the 2002 review.

Considering the excellent work of Virkutyte, Sillanpaa and Latostenmaa (2002), the first chapter of this thesis includes and follows the most relevant findings presented by these authors. Within this conclusive article is highlighted the discussion of the technology advantages and disadvantages, history of application, operational aspects, technology version and enhancements, and others. Although this document does not present explicitly the research questions compiled in the first chapter, the issues therein addressed are sources for their formulation.

2.2.2 Technology applications

The second entry to the proposed database structure corresponds to those journal articles whose main subject is the report and assessment electrokinetic applications. Several contributions have been dedicated to report the successful application of electroremediation on different type of porous matrices with different type of contaminant agent. The names of authors that have published their research are listed in Table 2.2. Among the many applications of electroremediation can be listed soil and sludge; enhancement on high sorption capacity soil; marine clay; metal contaminated groundwater; enhancement of reactive barriers; metal contaminated sediments; and VOCs, PBCs, and Pb removal. The first contribution was made on 1991 mostly reporting field data. The latest works published in 2002 deal with the use of electroremediation in contaminated groundwater and applications of electroremediation to metal and organic contaminated soils. It is interesting to know that no work has been published since 2003 under this particular classification.

Table 2.2 Chronological list of contributions on practical applications

Authors	Years
Acar, Yalcin B.; Hamed, Jihad	1991
Lindgren, E. R.; Mattson, E. D.; Kozak, M. W.	1994
Reddy, Krishna R.; Donahue, Matthew; saichek, Richard	1995
Kelsh, Dennis J.; Parsons, Michael W.	1997
Puppala, Susheel; Alshawabkeh, Akram N.; Acar, Yalcin B.; and others	1997
Chung H.I.; Kang B.H.	1999
Wills M.A.; Haley J.C.; Fabian G.L.; Bricka R.M.	1999
Yang, Gordon C. C.; Long, Y-W.	1999
Maini, G.; Sharman, A. K.; Knowles, C. J., and others	2000
Shiba, S.; Hirata, Y.	2000
Azzam R.; Oey W.	2001
Mulligan, C. N.; Yong, R. N.; Gibbs, B. F.	2001
Czurda, K. A.; Haus, R.	2002
Reddy, K.; Kumar, S.	2002

The collected information, coming from the listed sources, suggests at least three general conclusive ideas about electroremediation. First, the technology is applicable to metal and organic contaminants removal. Second, it indicates that electrokinetic works well under unsaturated and saturated soil conditions. Third, low permeability soil can be treated successfully by this technology. This conclusive information was included in the first chapter of this thesis. Specifically, these ideas have been used as history of applications.

2.2.3 Process description

The number of articles that refers to the description of different electrokinetic remediation processes obligates the inclusion of the process description category. Under this classification, several researchers (see Table 2.3) have reported new technologies or modification to the existing ones; control methods; monitoring techniques; process scaling up; enhancement by introducing supplementary chemicals; and description of specific methods. These different types of research efforts represent almost ten years of work, with the last publications made in the year of 2003. Having five published articles, this particular year is the most productive in comparison to the previous ones.

No matter what the year of publication is, every contribution has a tremendous value for the development of this work. One of the reasons is that any given description of process is like the enunciation of an engineering problem that can be modeled. In fact, this concept is used throughout this work. Another reason is that the most significant information has been included in the first chapter as description of electrokinetic technology.

Table 2.3 Chronological list of contributions on process and technology

Authors	Years
Wilson, D J; Rodriguez-Maroto, J M; Gomez-Lahoz, C	1995
Acar, Yalcin B; Alshawabkeh, Akram N	1996
LaBrecque D.J.; Ramirez A.L.; Daily W.D.; Binley A.M.; Schima S.A.	1996
Li, Zhogming;Yu, Ji-Wei ; Neretnieks, Ivars	1996
Leinz, R. W.; Hoover, D. B.; Meier, A. L.	1998
Sogorka, D. B.; Gabert, H.; Sogorka, B.	1998
Kim, S. O.; Moon, S. H.; Kim, K. W.	2000
Mattson, Earl D; Bowman, Robert S; Lindgren, Eric R	2000
Iyer, Ramasubramania	2001
Lee, Hyun-Ho; Yang, Ji-Won	2001
Reddy, Krishna R.; Xu, Charlie Y.; Chinthamreddy, Supraja	2001
Roulier, Mike; Kemper, Mark; Al-Abed, Souhail, and others	2001
Arnerdal, K; Neretnieks, I	2002
Niinae, M.; Aoki, K.	2003
O'Connor, C. Sidoli ; Lepp, N. W. ; Edwards, R. , and others	2003
Reddy, K. R.; Chinthamreddy, S.	2003
Sawada, Akira; Tanaka, Shunitz; Fukushima, Masami, and others	2003
Suèr, Pascal ; Allard, Bert	2003

2.2.4 Study of parameters effects

An important number of contributions have been devoted to identify driving parameters in electroremediation. The most common approach is to study the effect of a suspect parameter on the process. Table 2.4 shows the list of contributions that have been

made in that specific direction. For instance, saturation, electrolysis, fracturing, composition, redox conditions, electric potential, soil nature, and soil mineralogy could be found among the studied parameters. Perhaps the most interesting characteristic of the cited contributions is that none of them addresses the same issue. This fact creates an excellent opportunity for further research. The ten years of time frame, as presented in Table 2.4, clearly suggests that validation of published results is required. Considering only that the effect of hydrolysis was last reported in 1994, ten years of research is missing to validate or to extend the findings reported by Ugaz and collaborators (1994).

With respect to the objectives of this work, there has been no published study on the effects of electrode shape and the role of hydrodynamics. This conclusive information justifies the effort being made on the present thesis.

Table 2.4 Chronological list of contributions on the study of different effects

Authors	Years
Ugaz, A.; Puppala, S.; Gale, R. J., and others	1994
Krause, T R; Tarman, B	1995
Ramsey, J.; Reed, B.	1995
Reddy, K. R.; Parupudi, U. S.; Devulapalli, S. N.; Xu, C. Y.	1997
Murdoch L.C.; Chen J.-L.	1999
Pomès, V.; Fernandez A.; Costarramone N.; Grano B.; Houi D.	1999
Reddy, K. R.; Chinthamreddy, S.	1999
Yang, G. C. C.; Long, Y-W.	1999
Prozorov L.B.; Shcheglov M.Y.; Nikolaevsky V.B.; Shevtsova E.V.; Korneva S.A.	2000
Akretche, D. E.	2002
Darmawan; Wada, S-I.	2002
Fava, G; Fratesi, R; Ruello, M L, and others	2002
Ottosen, L M.; Erikson, T.; Hansen, H. K.; Ribeiro, A. B.	2002
Pomès, V.; Fernández, A.; Houi, D.	2002
Rohrs J.; Ludwig G.; Rahner D.	2002

2.3 Discussion of Theory and Models

As previously anticipated, this section concentrates in a more comprehensive discussion of contributions under the category of theory and models. The nature of the present study makes the subject of primary interest. In general terms, it is observed that different approaches have been adopted in seeking mathematical expressions for the electrokinetic problem. Table 2.5 presents a list of contributions from different authors that have been made over the last nine years. These contributions primarily deal with macroscopic and molar species mass balances; simplified cases of electroosmosis and electromigration; heat transfer; electric current; electrostatic potential; and momentum for different geometries. This brief view allowed the selection of the most relevant articles to this research.

After meticulous screenings have been performed, as suggested, the most important differences between these contributions and the present work can be established and discussed. The objective in this case is to demonstrate the originality of this investigation. Following this idea is that the next paragraphs state the contributions expected from this thesis in comparison with the selected published works, when pertinent.

For the given ten year horizon of published scientific information, the first contribution found was made by Choi and Lui (1995). Their approach is for the treatment zone and multi-component species. As modeling for several species complicate the mathematical solution, the authors simplified the hydrodynamic part of the problem considering only the electromigration phenomenon. The same year 1995, a second publication appeared by Wilson, Rodriguez-Maroto and Gomez-Lahoz (1995). These authors presented a transient state analysis of the treatment zone acknowledging only electromigration combined with hydrolysis. Both contributions differ from the present work in that the simplification of considering only electromigration, as the main transport mechanism, is not made to preserve the integrity of a more realistic hydrodynamic. A more accurate description of the hydrodynamic problem may lead to a more precise description of the distribution of species as they both are intimately related.

Table 2.5 Chronological list of contributions on theory and modeling

Authors	Years
Choi, Y S; Lui, R	1995
Wilson, D J; Rodriguez-Maroto, J M; Gomez-Lahoz, C	1995
Choi, Y S; Lui, R	1995
Alshawabkeh, Akram N; Acar, Yalcin B	1996
Wilson, D J	1996
Choi, Y S; Lui, R	1996
Yu J.-W.; Neretnieks I.	1996
Baraud F.; Tellier S.; Astruc M.	1997
Harris, M T; DePaoli, D W; Ally, M R	1997
Ho S.V.; Athmer C.J.; Sheridan P.W.; Shapiro A.P.	1997
Liu, B; Lui, R	1997
Yu J.-W.; Neretnieks I.	1997
Yang, C.; Li, D.; Masliyah, J. H.	1998
Alshawabkeh, Akram N; Gale, Robert J; Ozsu-Acar, Elif, and others	1999
Baraud F.; Tellier S.; Astruc M.	1999
Jennings, A. A.; Mansharamani, P.	1999
Bosse, M. A., and P. Arce	2000
Narasimhan B.; Sri Ranjan R.	2000
Wu, R. C.; Papadopoulos, K. D.	2000
Dukhin, S. S.; Zimmermann, R. and Werner, C.	2001
Wada, Shin-Ichiro; Umegaki, Yuki	2001
Hsu, J-P.; Kao, C-Y.; Tseng, S.; and Chen, C-J.	2002
Mattson, Earl D; Bowman, Robert S; Lindgren, Eric R	2002
Mattson, Earl D; Bowman, Robert S; Lindgren, Eric R	2002
Pomès, V.; Fernández, A.; Houi, D.	2002
Titov, K.; Ilyin, Y.; Konosavski, P; and Levitski, A.	2002
Musso, G.	2003
Vereda-Alonso, C.; Rodriguez-Maroto, J.; García-Delgado, R. A., and others	2004

During the next year, four new contributions were made. Alshawabkeh and Acar (1996) developed a one-dimensional model for the hydrodynamic and dispersive part of an electrokinetics cell. The approach does not considered the important effect of temperature on the flow regime. Later Wilson (1996) extended the pervious effort of 1995 including redox reactions for As and Zn; however, no changes were introduced on the hydrodynamic part. In other words, the key element of system description still presents the limitations that were

mentioned in the paragraph above. Choi and Lui (1996) republished their 1995's work adding more data but maintaining the same approach. Yu and Neretnieks (1996) developed a numerical model that discretizes the treatment zone into compartments. Each compartment follows a transient state molar material balance that describes the macroscopic system. The approach for the hydrodynamic part considers the hydraulic advection and the electroosmotic terms. These driving forces are directly inserted in the molar mass balance equation. It should be pointed out that the expressions for these terms correspond to isolated cases of electroosmosis and the real effect of combined pressure driving and electroosmotic forces over dispersion has not been described. On the contrary, the present work makes clear difference on the hydraulic forces involved in the electrokinetic process and the interactions that may occur among them. Particular attention should be given to the introduction of the joule heating effect in the study.

In 1997, the number of published articles reached the highest peak with five contributions. The first one by Baraud, Tellier and Astruc (1997) is to some extend similar to the research presented by Yu and Neretnieks (1996). The main difference is that the diffusion/dispersion mechanism has been neglected to introduce electrophoresis. These modifications do not outperform the research herein conducted. A second work by Harris, DePaoli, and Ally (1997) analyzed the electrokinetic problem in concrete type of porous media. In this approach the authors used the convective diffusion equation assuming electromigration and electroosmosis (although the authors called it convection). As in many other cases buoyancy is not included and the electroosmotic flow is considered constant. In another effort, Ho, Athmer, Sheridan and Shapiro (1997) considered electroosmosis as the main driving force. This approach as in previous cases is not accurate as it ignores other forces. However, they intended to model thermal effect using the energy conservation equation. As presented, the theoretical analysis is correct and perhaps more complex than the analysis developed in this thesis. Nevertheless, it has to be taken into account that the analysis of thermal effects is influenced by the hydrodynamic of the system; and therefore, hydrodynamic simplifications may lead to erroneous conclusions. The fourth article in the list (Liu and Lui, 1997) presented a modeling approach oriented to redox reactions. Electroosmosis, electromigration and molecular diffusion are considered as the main transport

forces. The approach is mathematically original although the model does not represent a real system as it ignores dispersion among others. This is not the type of approach engaged in the present work. Finally, Yu and Neretnieks (1997) presented their 1996 work with new features such as the introduction of adsorption but maintaining the already described principles. In consequence, argument also remains as in the previous paragraph.

The year of 1998 only registered one publication (Yang, Li and Masliyah, 1998). This single effort is one of the closest related to the present work. Comparatively, Yang and colleges study a rectangular microchannel in 2D while this work refers to 1D. In addition, these authors simplified the hydrodynamic and neglected the joule heating effect which is a fundamental part of the present effort.

In 1999, three contributions were made by the scientific community. The first, leaded by Alshawabkeh and collaborators (1999), referred to one and two dimensional analysis of an electrokinetics cell considering electroosmosis and electromigration. The main focus of the analysis is the cost problem more that the fundamental analysis. The second work, presented by Baraud, Tellier and Astruc (1999), intended the modeling of electromigration influenced by temperature. The approach is rather experimental than theoretical, and therefore, it has no real connection to this thesis, except perhaps with future efforts. The last publication, by Jennings and Mansharamani (1999), analyzed the enhancement of aggregate remediation by electrokinetic. The approach is rather interesting but different to the general process that is being studied herein.

The following year brought three new contributions with two important ideas for this research. Bosse and Arce (2000) studied the free convection phenomenon in a rectangular channel. The electroosmotic flow and further study of the electrostatic potential were not included. On the contrary, Wu and Papadopoulos (2000) presented a study for the cylindrical and annular geometries of electroosmotic force in a capillary. The general principles of these two combined contributions are the basis of the present work for the treatment zone. Furthermore, a significant improvement in the prediction of electrostatic potential is achieved. The third contribution of this year, presented by Narasimhan and Sri Ranjan (2000), intended

the modeling of groundwater flow near an electrokinetic barrier. The approach assumed that Darcy's velocity can be added to electroosmotic flow to obtain the net flow. This is not the decomposition of forces that is performed in this work.

During the year of 2001, the two registered publications presented information that only confirmed the need for further research. Dukhin, Zimmermann and Werner (2001), for example, studied boundary double layer around charged ions. The approach is simple but escapes from the scope of this work. In fact, the main concern for research is the boundary layer formed at the electrodes. The other work, presented by Wada and Umegaki (2001), developed an interesting expression for the flow density term of a single specie. The expression considers temperature changes but neglects pressure driven forces.

The second highest peak of published articles occurred in 2002 with five contributions as well. The first one, by Hsu, Kao, Tseng and Chen (2002), modeled the electroosmotic flow and hydraulic pressure on an elliptic channel. The study of the ratio aspect yielded by this geometry does not consider the relevance of cylindrical and annular channels which are focus of this work. The other contribution, presented by Mattson, Bowman and Lindgren (2002a, 2002b), intended the description of the treating zone by composing the net flux expression with the main transport terms. The approach acknowledged the dispersive effect of tortuosity but ignored the role of the effective velocity. A rather completely different approach was intended by Pomès, Fernández and Houi (2002) for the time of treatment in electroremediation. The authors presented a macroscopic mass balance that led to a partial differential equation of second order. The coefficients of this resulting equation are related to resident time and system response. Both can be easily computed without really solving the differential equation. The pressure driven force is not included although new fluid is pumped in at constant rate. The approach results are interesting and can be modified to be more realistic; however, the present work is more oriented to the study of micro-channels. The last contribution of this year dealt with the numerical modeling of the role of fractures in porous media (Titov, Ilyin, Konosavski and Levitski, 2002). This approach does not intend to answer the research questions herein proposed. Therefore, no argument will be presented.

In 2003 only one article was dedicated to electrokinetic modeling. Musso (2003) invoked the modeling approach presented by Alshawabkeh and Acar (1996) and conducted a series of experiments to determine electroosmotic parameters. The procedure might be correct although the model simplifications clearly have an effect on the results. The arguments were introduced when the original 1996 work was discussed.

For the present year, only one entry has been registered, on the proposed database, under the theory and modeling category. Vereda-Alonso and collaborators (Vereda-Alonso et al., 2004) proposed an electromigration model for the treatment zone based on the Kirchoff's law. The methodology is original in that converted a 2D system in complex network of electrical resistances. Although very appealing, the approach requires mayor modification to fit the study herein devoted. This is, it would require the inclusion of the hydrodynamic part, thermal effect of Joule heating, and the dispersion transport mechanism.

2.4 Summary of the Chapter

The literature review shows that a certain number of key issues have been investigated with regard to the electrokinetic remediation process during the last decade. A database structure has been proposed to organize the collected scientific information as well as to facilitate the discussion of issues. In particular, five primary topics of research have been identified: (a) Status and review, (b) Technology applications, (c) Process description, (d) Study of parameters effects, and (e) Theory and models. Although, other classifications may apply, the available information fits satisfactorily within these five topics.

For the first four topics, this chapter dedicates a section to describe the main sub-issues that have captured the attention of the scientific community. The use of these sources of information has been placed into context and how they give support to the first chapter has been explained. The unbalance number of issues and research efforts found within these first topics has allowed identifying research questions.

Finally, this chapter discusses in detail the most relevant aspects of all the contributions found under the last classification, theory and models. The author's contributions that closely relate to the present work are identified and the necessary improvements are enunciated.