THE POTENTIAL OF USING ELECTRO-MIGRATION FENCES AGAINST SEAWATER INTRUSION

Shadi HAMDAN

Supervisor:
Prof. dr. ir. Bart Van der Bruggen

Members of the Examination Committee:
Prof. dr. ir. H. Van Brussel (Chairman)
Prof. dr. S. Waldherr (Secretary)
Prof. dr. ir. T. Van Gerven (KU Leuven)
Prof. dr. ir. J. Vanderborght (KU Leuven)
Prof. dr. A. Alshawabkeh (Northeastern University)

Dissertation presented in partial
fulfillment of the requirements for the
degree of Doctor of Engineering Science
(PhD): Chemical Engineering

February 2019

Uitgegeven in eigen beheer, SHADI HAMDAN, FONTEINSTRAAT 113, 3000 Leuven, Belgium

ACKNOWLEDGEMENTS

After a long journey, I finally reached the final stage of my Ph.D., a ride full of bumps, jumps, twists, and turns. The driving forces have been my dedication and sacrifices, which propelled me to my final destination. This Ph.D. has been an intense process, a trip filled with life learning experiences, trials and errors coupled with failed tests and frustrating experimental results. It was a tough research with a shortage of successes sometimes, nevertheless, it was worth the effort to get to the end of this academic and personal adventure.

I come from Palestine, a region under political and economic struggles, with shortage of essential resources; a war zone, where people have difficulties to secure their basic needs. While living there I had the opportunity to work with multiple NGOs and got into contact with persons from many different parts of the world. My interaction with those people and my fellow Palestinians, who were in dire need for basic needs, such as access to drinking water and sanitation, opened my eyes and made me realize the importance of access to drinking water. This is so because in Palestine, the water quality is in such a bad state to an extent that farmers cannot even use it for irrigation or for their stock/cattle, and causing serious health and sanitary issues among the community members, meanwhile just few meters away from their places of residence, the occupier settlers are using and abusing the water and other natural resources.

This unbalanced and unfair situation has reached disproportionate level where the most vulnerable ones have to deal with the consequences caused by the poor quality of the water. Even those who are in a slightly better situation still do not have access to water of the same quality as the one supplied to the occupiers for their use, for example, wash their cars. To this day, these individual occupiers are wasting good quality water suitable for humans for less than moral and other despicable uses, without attaching any sustainability element to the manner in which they use the water.

This fact, as strange as it may appear to most of those living in developed countries, is what made me realize the huge disadvantage that people are facing in their day to day lives just because of their place of origin. As a young engineer who was faced with this situation, I played my small role and contributed towards helping to build infrastructure that would support Palestinian farmers and provide water to the most depressed areas.

However, it soon became clear to me that the root cause of the problem would not be solved just by these initiatives, and at that time I did not have enough knowledge nor the necessary capability to contribute in a more meaningful or impactful way. The question on how we could solve or improve the situation remained unanswered at that point.

It was in 2006 when I arrived in Belgium to pursue my Master in 'Water Resources Engineering' at high quality university, KU Leuven, that I got the opportunity of acquiring the right tools and means that I could use to address the problems of water quality back in Palestine.

After finishing this program, my knowledge and understanding of water quality management had gone higher up the ladder, which then became the reflection point and a driving force in my endeavor to try and find answers for the water quality challenges my people and I were still faced with in Palestine. This knowledge refined my thought on what technologies could be applied to mitigate this problem and provide a sustainable solution that would ensure access to clean water supply to my fellow Palestinians, particularly in Gaza.

The main problem around this fact is that in Gaza, groundwater is severely affected by seawater intrusion, now the question for me was what could be the solution to this difficult circumstances and what contribution should I make to change the situation around.

This quest and search for answers and possible solutions to remedy this situation is what gave birth to the idea of starting my Ph.D., focusing on the issue of seawater intrusion. This was because, if I continued with my Masters research study, I would have arrived at the same conclusion as those existing methods identified and applied by researchers and industries, respectively. However, though proven successful in other areas, those methods could not really be applicable to the water problem in Gaza.

I then contacted Prof. Bart Van der Bruggen who encouraged me to pursue a way forward with this track of thought and together we toiled around this topic. He helped me give shape and form to this initial idea until I developed a good proposal which was submitted for my admission to the Doctoral School of Engineering and Technology (CIT).

I remember vividly his responses to the first communications we exchanged, because it gave me the guidance and motivation I needed to start this research journey. The support and constant efforts that came from him from the very beginning were key for me to be able to initiate my investigation despite the financial constraints I had at the time. Nevertheless, he remained the pillar of my strength and the force behind my determination to pursuing this search. Without him and his unwavering mentorship, I would not have been able to achieve this. However, no tons of words can explicitly indicate my deepest gratitude for all his support. I want to thank him once again for being there for me from the very first day, for supporting me through and through, during the difficult times and low moments I endured during the different stages of my research journey. He was able to give me the space and time I needed to overcome the challenges all the way until today, a quality you don’t easily find in the academic world, for that I am truly grateful. I feel honored and lucky for having had the opportunity to work under his supervision.

I would also like to express my sincere gratitude to Prof. Akram Alshawabkeh, for giving me the opportunity to join his research team in the USA, at a critical time of my Ph.D. We always mention the importance of moral support, however nuance, the logistics around a Ph.D. journey also require a strong financial support, which Prof. Akram offered me and granted me the possibility to work for an extended period of time with an experienced and well recognized group of professionals, from which I learned a great deal. Him and his team welcomed me and made me an integral part of that cohort and never made me feel like an outsider.

Concerning the members of the Ph.D. examination committee, I would like to thank Prof. Hendrik Van Brussel, who accepted the invitation for chairing my Ph.D. Thank you to Prof. Tom Van Gerven, Prof. Jan Vanderborght, and Prof. Steffen Waldherr, as well as Prof. Akram Alshawabkeh for the time they spent in evaluating my dissertation and providing suggestions to improve it. Their critical questions and valuable comments pushed me to remain focused during the finalization of this dissertation.

I would like to acknowledge the Interfaculty Council for Development Cooperation (IRO) for the scholarship that they granted me, which allowed me to continue with this journey. In the same vein, I would to acknowledge FWO and the Junior Mobility Programme (JuMo) for the travel grant they gave to travel to the USA and join the research group of Prof. Akram Alshawabkeh.

My special thanks are extended to the administrative staff of *Chemische Ingenieurstechnieken* (CIT): Alena Vaes, Marie-Claude Deflem and Beatrice De Geest, for always being ready for solving any administrative matter pertain to my research. I also like to offer my gratitude to the technical staff of CIT: Hanne Geunes and Michèle Vanroelen, for the interventions they offered and ensuring that the machines they I used

at CIT were in good working conditions. A special thank you to Herman Tollet for his close follow-up and support. I appreciate his camaraderie and the late hours we spent together in the laboratory fixing the machines.

A particular acknowledgement goes to Valentijn Tuts, who helped me during the build-up of my setup and the manufacturing of my experimental prototype. I respect him for his technical skills and hands-on experience and advice. I could not have run some of my experiments without the first prototype he built for me.

I thank Prof. Jiangnan Shen for his scientific advice and deep knowledge. Furthermore, I thank him for having built and sent a prototype all the way from China to Belgium at a crucial time of my research, thus allowing me to continue with my work.

During my experience at CIT, I have been in contact with quite a large number of people that have been great colleagues to me, some of them even became good friends. I would like to acknowledge some of them: Nora, Priyanka, Anh, Ruixin, Alemayehu, Abdellah, Siavash, Dessalegn, Carlos, Antonio, Wenyuan, Jiuyang, Hasan, Mokgadi and many more for their contribution to a pleasant working atmosphere and helping to build a friendly international environment.

This experience would have never been the same without Giuseppe Genduso, Saeed Mazinani, and Fred Molelekwa. To Giuseppe thank you for the laughter, coffee discussions and critical arguments around work and personal lives, this made my experience more human and fun.

I want to heartily thank Saeed and Fred for being more than colleagues and friends but for being like “family” from the first day we met, thank you for always being there for me no matter where we were.

It has been my pleasure and luxury to get the opportunity to work with the group of PROTECT Center at Northeastern University in Boston, USA, which has also allowed me to participate in several academic events. I would like to particularly thank some of the members of the group: Ljiljana Rajic for being the first person to welcome and help me during my stay there. To all the team members: for all the scientific discussions and fruitful arguments we had during our time together, a special thank you to my office-mates: Shirin, Amir, Koosha, Roza, Noushin, Reza, Wei, Yuwei, Xue, Harshi, Hadi, Kim, Yunfei and Long.

As part of the long hours I spent in the laboratory, I will always remember the countless moments I had with Zhijia Xue in the laboratory and his sense of humor. Thank you also for the shared moments that made the atmosphere feel like home, also the laughter in the driest moments.

Extended thank you to the administrative staff of PROTECT Center: Lura, Elli and Dana, for helping with expediting the bureaucracy tasks.

Certainly an important part of this Ph.D. journey happened in Boston, which at the beginning was a big challenge and not easy, however, I was fortunate enough to soon encounter wonderful people which made my stay there enjoyable. A large part of my thesis was actually written in the Andala Coffee House, where the owner Sami Herbawi treated me as his son from the beginning and made an effort to ensure I was always feeling good. I will always remember his delicious dishes with fondness. I also want to thank the manager Qais "Leo" who always made me laugh, especially during hard moments, as he was always there for me to encourage, support and willing to help me move forward, I will always miss your best "Kunafah" ever. They both cared for me and showed me their friendship.

While in USA I made fantastic friends, with whom I spent the craziest and most fun times during this journey, the list is long and although each and every one would deserve a chapter of their own, I would like to acknowledge them here: Imen, David, Mehrdad, Ahmed, Valentina, Andres, Martha, Rania, Charlotte, Dea, Julien, Marc, Kevin, Sam, Jennifer, Stephen, Yanis and the little Hasan Herbawi. Thank you all for the love and care you always gave me.

The highlight of this adventure was definitely meeting the best friends one could ever hope for; I would even say they are like brothers to me: Armano Zona, Heyaw Abebe, and Fekadu Yilma. I truly love and care for every one of them, they gained a space in my life, even now with the distance between us, they still write to me making me feel as if we are still together sharing crazy moments. You guys are truly nice and beautiful souls, I wish you the best and you deserve all possible good things. I will treasure the memories of those long freezing nights in Cambridge, MA, which together we made them more bearable and warmer. Those that do not have the luck to know you like I did will miss the fact that you are not just normal people, but actually wonderfully patient human beings filled with incredible hopes and amazing dreams. Leaving you guys was one of the hardest parts of this trip, but you know guys that we will meet again, "the legend" will be back, but this time without engaging in any fights. Please keep taking care of each other and caring for one another now that I am not there.

The other people that made this journey memorable are my friends in Leuven, those whom I met when I had just arrived: Dr. Muath Sabha, Dr. Jamal Rabaia, Dr. Shadi Alkhatib, Amid Elzayegh and Juma Aqel, all of whom came from Palestine. They understood better than anyone the challenges I faced when I moving abroad, so I want to thank them for providing me with the strength and encouragement I needed at that time.

I want to take this opportunity to acknowledge my language teacher Det Deprez who treated me like her son and for providing me with the motherly love I needed sometimes while helping me adapt and understand better the Belgian culture.

I want to thank Tess Dekeyser and her family for being there over many years I spent in Belgium. They were so kind and they took care of me and gave me the support, I will always be truly grateful.

In the last sprint of this long journey, I crossed paths with Bárbara Cano, with whom it felt we had known each other for a long time, even though we had just met, I am truly thankful to her for being there for me when I needed someone to talk to; and for the positive messages she kept sending me especially at the time when my morale was at a low, filled with stress and for being patient with me.

When you are away from your family there are moments in which some friends become dearer to you and shower you with their constant support and honest care. In my case, this was done by Dr. Ashraf Tayh and Kirollos Meguid. I am expressing a special word of thanks to both of them.

Those of you who know me understand how significant and important is my family in my life, even though I have been far from them for so long, I have always felt their presence, they have sent me their love and encouragement to continue with this adventurous journey. I want to thank my older brothers Feras and Fadi for their guidance and setting an example for me to follow. I have to thank my sisters: Reem, Rana, Hanadi and Fatemah "Fefe" for the caring love and support they have shown me, in a way that only sisters can provide. I would like to say thank you to my younger brothers Mahammed "Hamada" and Faisal for making me feel proud of their accomplishments and successes, it has been a fresh source of inspiration and motivation.

Coming from a large family, the relationship that you establish with your siblings is different from one sibling to another, and in this regard I want to mention Almohannad and Abdallah “Abood” for being the spices of the family.

Thank you to Abood who is the last of the bunch but definitely not the least, who has always been my eyes and ears, sharing with me everything that is important to our lives, and also made me not to feel distant from the family, nothing made me happier than having you close when you moved to Germany. Thank you Mohannad for being a true partner and helping me with those very nice figures and designs, which I used as part of my dissertation.

The pillar of my family is my parents, to whom I hold the most profound love and respect. I want to deeply thank my mother Suhaila for all the love and prayers she continued sending my way. I know that my departure was very hard for you, but I truly hope that with this Ph.D., I have made you proud and I promise to continue doing so in this journey of life. To my late father Dr. Hamdan, you were always my example and ideal to follow, losing you was one of the most difficult moments for me, even though you are not here with us anymore, you are still the source of my strength and I will always be grateful for that. I only wish to one day have an impact in society and those around me in the same way you did as a medical doctor by making the community a better place, saving many lives and helping others, which was the seed to the original idea of this Ph.D. May your eternal soul rest in peace.

Now that I have reached the final stop of my Ph.D. journey, I hope I have not forgotten any of the travel mates I encountered through the years, if I have not mentioned you, please know that it is also thanks to you that I am here today.

Shadi Hamdan

Leuven, February 2019

ABSTRACT

The application of electrokinetic remediation as a novel alternative technique for controlling seawater intrusion into groundwater aquifers in coastal areas is demonstrated in this dissertation. Initial experiments were conducted by using a sodium chloride model solution, followed by experiments carried out using a sea salts model solution. However, the intention of the study was not to necessarily remove all chloride and/or sodium but to efficiently capture the Cl^- and/or Na^+ concentration of the water to the extent that the quality of the water meets the standards for potable and/or irrigation water, respectively. Laboratory experiments were carried out to investigate the fundamental electromigration behavior of soluble salts ions under the influence of an electrical gradient when coarse grained soil is used. The experiments were performed without applying any enhancement process. This was done in order to enable a better understanding of the actual physiochemical reaction occurring during electrokinetic remediation, and to identify the most important contributing parameters in the removal mechanisms. The results show that the development of potential gradients and current of the three group experiments was in agreement within the first 24 *h* or 72 *h*, indicating a good experimental reproducibility. Additionally, the current trace shows an increase within the first 24 *hour*s after reaching a maximum value of approximately 180 *mA*. The current dropped to 40 *mA* after 48 *hours* and continued to decrease to a steady state at around 20 *mA* after 72 *hours*, which is an evidence of the removal of dissolved ions from the specimen. At the very beginning of the experiments, the electrical potential was linearly distributed. In this instance, the constituents in the specimen were uniformly distributed and the conductivity in each section was almost identical. A lower conductivity was observed near the anode with respect to the initial value and it reflects the removal of the ionic species near the anode. Alternatively, a higher conductivity was observed closer to the cathode as sodium ions were migrating and accumulating in the cathodes. A steep electrical conductivity gradient has also been developed in line with the potential gradient, which is attributed to the formation of the reaction plane between the two binary zones formed in the cell, reflecting a sudden drop of electrical conductivity between the two zones. As time progressed, a large voltage drop developed within a small zone, while across the rest of the soil core gradients, a smaller voltage drop was observed.

A very low reversed electroosmotic flow moving towards the anode was observed. This could be attributed to the characteristics of sandy soil. Additionally, this reversed electroosmotic flow is contrary to the known direction of the electroosmotic flow (i.e., flowing towards the cathode), which could be influenced by the surface charge of the solid matrix, represented by the zeta potential. More chloride ions were removed and more sodium ions migrated towards the cathode when the experiments were carried out for a longer time (168 *hours*); however, the difference was not significant when comparing the results of experiments carried out for 72 *hours* with experiments carried out for 168 *hours*. An average of 73% of chloride was removed during experiment group 1, which was carried out for only 24 *hours*. Most of the sodium from the sections near the anode and from the anodic electrolyte solution was removed and migrated towards the cathode: more than 90% of dissolved sodium from those sections was removed, the migrated sodium accumulated gradually from the third section (in the middle of the soil specimen) and started to build up near the cathode and in the cathodic electrolyte. Experimental group 2 and 3 were running for 72 *hours* and 168 *hours*, respectively. They show better removal efficiencies under the same condition. In those cases, more than 85% of chloride was removed from the system, and more sodium migrated towards the cathode.

When using a sea salt solution as the model solution, two series of tests were carried out under the same experimental conditions. In the first series a voltage of 0.5 $V\ cm^{-1}$ was applied, while an applied voltage of 1 $V\ cm^{-1}$ was used in the second series. The results regarding the development of current, potential gradients, change in ions concentration, and pH absolutely coincided with the NaCl experiment.

Considering these data, it can be concluded that the electrokinetic configuration in this study efficiently removed chloride and forced sodium to migrate towards the cathode, which could also be removed from the system by pumping out electrolytes in the cathode compartments. As a result, the objective of this study has been achieved.

SAMENVATTING

De toepassing van elektrokinetische remediëdering als een alternatieve techniek voor het controleren van insijpelen van het zeewater in kustgebieden wordt aangetoond in deze dissertatie.

De eerste experimenten werden uitgevoerd met behulp van een natriumchloride model oplossing alleen en vervolgens door experimenten uitgevoerd met behulp van een model oplossing van zeezouten. De bedoeling van de studie was echter niet noodzakelijkerwijs alle chloride en/of natrium te verwijderen, maar om de Cl^- en/of Na^+ concentratie van het water efficiënt vast te leggen voor zover de kwaliteit van het water voldoet aan de normen voor drinkbaar/of irrigatiewater, respectievelijk. Laboratoriumexperimenten werden uitgevoerd om het fundamentele electro-migratiegedrag van oplosbare zoutionen te onderzoeken onder invloed van een elektrische gradiënt wanneer grof gekorrelde grond wordt gebruikt. De experimenten werden uitgevoerd zonder toepassing van een verbeteringsproces. Dit werd gedaan om een beter inzicht te krijgen in de feitelijke fysiochemische reactie tijdens electrokinetische sanering en om de meest bijdragende parameters in de verwijderingsmechanismen te identificeren. De resultaten tonen aan dat de ontwikkeling van potentiële gradiënten en stroom van de drie groepsexperimenten in overeenstemming was binnen de eerste 24 of 72 *uur*, met een goede experimentele reproduceerbaarheid. Bovendien toont het stroomverloop een verhoging binnen de eerste 24 *uur* na het bereiken van een maximumwaarde van ongeveer 180 *mA*. De stroom daalde tot 40 *mA* na 48 *uur* en bleef dalen tot een constante waarde op ongeveer 20 *mA* na 72 *uur*. Dit is een bewijs van de verwijdering van opgeloste ionen uit het specimen. Aan het begin van de experimenten werd het elektrisch potentieel lineair verdeeld. In dit geval werden de bestanddelen in het specimen gelijkmatig verdeeld en de geleidbaarheid in elke sectie was bijna identiek. De lagere geleidbaarheid werd waargenomen dichtbij de anode met betrekking tot de aanvankelijke waarde en het wijst op de verwijdering van de ionische soorten dichtbij de anode. Als alternatief werd een hogere geleidbaarheid waargenomen dichter bij de kathode als natriumionen migreerden en accumuleerden in de kathode. Een steile elektrische geleidbaarheidsgradiënt is ook ontwikkeld in lijn met de potentiële gradiënt, die wordt toegeschreven aan de vorming van de reactieszone tussen de twee binaire zones gevormd in de cel, als gevolg van een plotselinge daling van de elektrische geleidbaarheid tussen de twee zones. Naarmate de tijd vorderde, ontwikkelde zich een

grote spanningsdaling binnen een kleine zone, terwijl in de rest van de bodem een kleinere spanningsdaling werd waargenomen.

Een zeer lage omgekeerde electro-osmotische stroom die naar de anode beweegt werd waargenomen. Dit zou aan de kenmerken van zandige grond kunnen worden toegeschreven. Bovendien is deze omgekeerde electro-osmotische stroom strijdig met de bekende richting van de electro-osmotische stroom (d.w.z., stromend naar de kathode), die door de oppervlaktelading van de solide matrix zou kunnen worden beïnvloed, weergegeven door de zeta potentiaal.

Meer chloride-ionen werden verwijderd en meer natrium-ionen migreerden naar de kathode toen de experimenten voor een langere tijd werden uitgevoerd (168 *uur*); echter, het verschil was niet significant bij het vergelijken van de resultaten van experimenten uitgevoerd voor 72 *uur* met experimenten uitgevoerd voor 168 *uur*. Een gemiddelde van 73% van chloride werd verwijderd tijdens experimentgroep 1, die slechts 24 *uur* werd uitgevoerd. Het merendeel van de natrium uit de secties in de buurt van de anode en van de anodische elektrolytische oplossing werd verwijderd en migreerde naar de kathode: meer dan 90% van de opgeloste natrium uit deze secties werd verwijderd, de gemigreerde natrium accumuleerde geleidelijk uit de derde sectie (in het midden van het bodem specimen) en begon op te bouwen in de buurt van de kathode en in de kathode elektrolyse. De experimentele groepen 2 en 3 liepen voor 72 *uur* en 168 *uur*, respectievelijk. Zij tonen een betere verwijdering onder de zelfde voorwaarde. In die gevallen, meer dan 85% van chloride werd verwijderd uit het systeem, en meer natrium gemigreerd naar de kathode.

Bij het gebruik van een zeezout oplossing als de model oplossing, werden twee series van tests uitgevoerd onder dezelfde experimentele voorwaarden. De eerste reeks werd een spanning van 0.5 $V\,cm^{-1}$ toegepast, terwijl een spanning van 1 $V\,cm^{-1}$ in de tweede reeks werd gebruikt. De resultaten betreffende de ontwikkeling van huidige, potentiële gradiënten verandering in ionenconcentratie en pH bevestigden de bevindingen van het NaCl experiment.

Gezien deze gegevens, kan worden geconcludeerd dat de electrokinetische configuratie in deze studie chloride efficiënt verwijderde en dat natrium gedwongen werd naar de kathode. Deze natrium kan ook worden verwijderd uit het systeem door het verpompen van elektrolyten in de kathode compartimenten. Het doel van deze studie is dus bereikt.

LIST OF ABBREVIATIONS AND SYMBOLS

1D	One-dimensional
2D	Two-dimensional
Al_2O	Aluminum Oxide
Ca^{2+}	Calcium
$CaCl_2$	Calcium Chloride
CaO	Calcium Oxide
CER	Chlorine Evolution Reaction
Cl_2	Chlorine
Cl^-	Chloride
Cl_2	Molecular Chlorine
Cl_{ad}	Adsorbed Chlorine Species
DC	Direct Current
DSA	Dimensionally-Stable Anode
DTPA	Diethylenetriamine Pentaacetic Acid
E	Electric Field
EBF	Electrokinetic Bio-Fence
EC	Electrical Conductivity
ECe	Electrical Conductivity at Saturation Paste
EDTA	Ethylenediaminetetraacetic Acid
EKR	Electrochemical Remediation
ESP	Exchangeable Sodium Percentage
F	Faraday Constant
Fe	Iron
Fe_2O_3	Iron Oxide
H	Hydrogen
H_2O_2	Hydrogen Peroxide
H_3BO_3	Boric Acid

HAA’s	Halo Acetic Acids
HAN’s	Haloacetonitriles
HK’s	Haloketones
HNO_3	Nitric Acid
HOCl	Hypochlorous Acid
HSCl	High-Cast Silicon Iron
I^-	Iodide
IrO_2/Ti	Iridium Oxide Coated Titanium Electrodes
K^+	Potassium
K_2O	Potassium Oxide
KBr	Potassium Bromide
KCl	Potassium Chloride
$KMnO_4$	Potassium Permanganate
Mg^{2+}	Magnesium
MgCl	Magnesium Chloride
MgO	Magnesium Oxide
Na^+	Sodium
Na_2O	Sodium Oxide
Na_2S0_4	Sodium Sulfate
NaCl	Sodium Chloride
NaF	Sodium Fluoride
$NaHCO_3$	Sodium Bicarbonate
$NaMnO_4$	Sodium Permanganate
NH_3^-	Ammonia
NO_3^-	Nitrate
$NS/IrO_2/Ti$	Nafion Solution Coated Iridium Oxide Coated Titanium Electrode
OCl^-	Hypochlorite Ion
OER	Oxygen Evolution Reaction

OH^-	Hydroxyl
pH_{PZC}	Point of Zero Charge
R	Universal Gas Constant
RTO	Ruthenium-Titanium Oxide
RuO_2	Ruthenium Oxide
SAR	Sodium Absorption Ratio
SiO_2	Silica
SO_4^{2-}	Sulfate
SP	Saturation Paste
$SrCl_2$	Strontium Chloride
SWI	Seawater Intrusion
T	Absolute Temperature
THM’s	Trihalomethanes
TiO_2	Titanium Dioxide
V_{Anode}	Anode Voltage
$V_{Cathode}$	Cathode Voltage

LIST OF SYMBOLS

A	Cross Sectional Area
B	The Saturated Thickness of The Aquifer (L)
D	Dielectric Constant
E^0	Standard Reduction Potential (V)
E_z	Voltage Gradient ($V\ L^{-1}$)
g	The Acceleration of Gravity (ms^{-2})
h_f	Fresh Water Head Above The Saltwater (L)
h_s	The Distance From The Saltwater Surface (mean sea level) to The Interface (L)
k_{eo}	Electroosmotic Permeability Coefficient ($cm^2\ s^{-1}\ V^{-1}$)
k_h	Hydraulic Conductivity ($cm\ s^{-1}$)
n	Porosity
n_e	Effective Porosity
q_{eo}	Electroosmotic Flow ($L^3\ T^{-1}$)
Q_f	The Discharge ($L^3\ T^{-1}$)
R	Recharge Coefficient ($L\ T^{-1}$)
t	Tortuosity
u_i	Ion mobility ($m^2\ V^{-1}\ s^{-1}$)
u_i^*	Effective ion mobility
v_{eo}	Electromigration velocity
ζ	Zeta Potential (V)
z_i	Ionic Valance
ρ_f	Fresh Water Density ($g\ cm^{-3}$)
ρ_s	Seawater Density ($g\ cm^{-3}$)

TABLE OF CONTENTS

1 INTRODUCTION

The beginning of 21^{st} century is marked by global scarcity of water resources, environmental pollution and increased salinization of water and soil [1]. Two major sources of salinity are soil salinity and seawater intrusion into groundwater aquifers, which threaten crop production and the availability of freshwater in coastal areas, respectively. Salinity can develop naturally (primary salinity) or be human-induced (secondary salinity) [2]. Primary salinity is mainly caused by natural processes, owing to a high salt content of the parent material or in groundwater, whereas secondary salinity occurs as a result of anthropogenic activities such as irrigation practices [3, 4], which account for about 20 % of the world's irrigated areas [5], and over extraction of groundwater, especially from coastal aquifers [5]. Salinization is affecting almost 1 billion ha worldwide, representing about 7% of earth's continental extent or approximately 10 times the size of a country like Venezuela and even 20 times the size of France [1, 6, 7]. Szabolcs reiterated that about 100,000 km^2 of irrigated land are abandoned each year, mainly owing to the adverse effects of secondary salinization and alkalinization. This clearly suggests that secondary salinity is more problematic [8]. The two major sources of salinization, soil salinity and seawater intrusion, are discussed hereunder.

1.1 Soil salinity

Saline soils refer to soils in which an electrical conductivity (EC) of the saturation soil extract (EC_e) in the root zone of more than 4 $dS\ m^{-1}$ is measured at 25°C, which is equivalent to approximately 40 mM NaCl [1, 9] and generate an osmotic pressure of approximately 0.2 *MPa* [9], and has an exchangeable sodium of 15% [1]. Salts generally found in saline soils include anions (chloride, nitrate and sulfate) and cations (sodium, calcium, magnesium, and potassium) [10]. Salinization of soil is a major problem in arid and semi-arid regions with saline shallow water table [11]. Soil salinity develops as excess water from well-drained recharge zones moves to and collects in imperfectly to poorly drained discharge zones. In essence, soils that were previously non-saline have become saline due to changes in saline groundwater discharge [2]. Climate, soil type, crop, irrigation water quality and management practice, depth and salinity of the water table are some of the main drivers of soil salinity [11].

In irrigated condition, soil salinity may be increased by applying saline irrigation water on surface soil layers and if this is excessively applied, it may lead to salt leaching. More importantly, when applied water is higher than the field capacity of the first layer, the excess water will leach the salt in the first layer. This process is continued for the other layers, and may increase the salt content in the second layer, if the infiltration in the second layer is less than required water for field capacity of the second layer [11]. It is important to contextualize the extent of soil salinity by highlighting the following facts: (a) salt-affected soils cover about 800 million ha of land, which accounts for more than 6% of the total land area in the world [9]. (b) Moreover, about 20% of total cultivated and 33% of irrigated agricultural lands globally are afflicted by high salinity [1]. (c) Furthermore, the salinized areas are increasing at a rate of 10% annually for various reasons, including low precipitation, high surface evaporation, weathering of native rocks, irrigation with saline water, and poor agricultural practices [1]. (d) It has been estimated that more than 50% of the arable land would be salinized by the year 2050 [1, 12]. (e) soil salinity that occurs as a result of anthropogenic activities [3, 4], account for about 20% of the world’s irrigated areas and in countries such as Egypt, Iran, and Argentina, this figure increases to more than 30% [4]. This is a huge threat to human wellbeing that cannot be left unchallenged.

The harmful effects of soil salinity include lost agricultural production, stream salinity and damage to infrastructure, urban households and environmental costs [13]. In terms of its effects on the agricultural sector, soil salinity is a major limiting factor that endangers the capacity of agricultural crops to sustain the growing human. Moreover, it is characterized by a high concentration of soluble salts that significantly reduces the yield of most crops [9]. There are no quick or easy solutions to soil salinity [1]. There was once a belief that *“the only real reclamation procedure for saline soils is to drain* *the excess water off the bottom and pour fresh water on the top to flush the salts out and away."* [2]. However, this is not always feasible, as alternative water volumes, such as reclaimed wastewater, and land-use changes may be required, or the water demand cannot be fulfilled from other areas or sources [14] and may perpetuate overexploitation of freshwater groundwater resources [11]. Moreover, reclamation of salt-affected soils requires an integrated management approach, including consideration of socioeconomic aspects, mapping, monitoring and maintenance of irrigation schemes and reuse and/or safe disposal of drainage water [15]. Implementation of efficient irrigation, drainage tillage operation, and good farming practices can prevent and, in some cases, reverse salinization. However, if appropriate management practices are not applied in time, the land may be degraded and crop production deteriorated [15]. Seawater intrusion, which is another source of salinity in low-lying areas along the coast [9], is discussed in the following section.

1.2 Seawater intrusion at a glance

Coastal aquifers are principal sources of fresh water in various parts of the world due to their groundwater quantity and quality, suitable to cover water needs of cities, rural villages, and agricultural and industrial activities [16]. However, fresh groundwater along densely populated coastlines is vulnerable to seawater intrusion (SWI) either laterally due to sea-level rise or vertically from land surface due to ocean-surge inundation [17]. Seawater intrusion is a phenomenon whereby fresh water is mixed with seawater through seepage of saline water from the seas and oceans into the inland aquifers, especially those adjacent or in close proximity to the shores [18]. Seawater intrusion and deterioration in water level create a serious threat to current groundwater quality for human consumption [19] and agriculture. This problem is intensified by large population growth, notably, because 70% of the world population occupies coastal areas [3] and in most cases embark on over-exploitation of coastal aquifers [16], thus giving rise to lowered groundwater levels and reduced freshwater flux [20]. Moreover, seawater intrusions induced by the over-exploitation of groundwater may severely damage the balance between water resources and ecosystems [14]. Consequently, seawater intrusion has challenged the sustainable development of coastal areas [14]. Seawater intrusion obliges all coastal areas to search for alternative resources while aquifers recover, if possible, their quality. These alternatives usually involve long-distance water transfers between basins, finding deeper good-quality groundwater levels (which may also be vulnerable to future salinization), or building desalination plants. However, while the latter partially solve the problem of freshwater availability, they raise other issues regarding water prices, energy costs and environmental concerns [14].

The level in which and the speed by which salt water intrusion occurs can be illustrated by an example from China. In 1971 and 1979, researchers from the coastal towns of Laizou and Lonkou have shown that the excessive (pumping) of groundwater in those areas resulted in a distinguished salt water intrusion. It concerned a transition area of 1.5 to 1.6 *km* and an aquifer surface of more than 580 *km*. In the beginning, the observations came from specific isolated areas with a total surface of 0.5 km^2. In the subsequent years, the saline affected area increased in size, which was attributed to more pumping up of groundwater for agriculture and industrial use. In 1979, the saline affected area covered an area of 16 km^2; in 1982 it expanded to 39 m^2. The area kept expanding to 71 km^2 in 1984 and to 196 km^2 in 1987. In 1989, the situation reached a significant magnitude, whereby the entire coast up to Laizou was a continuous saline affected area, spanning 238 km^2. It was discovered that the average yearly expansion increased from 4 km^2 in 1970 to 30 km^2 in 1989. This represents more than 7 folds expansion in just under two decades [21]. As a result, the control of seawater intrusion is a top priority in order to protect human health and environment [21].

The management of seawater intrusion into coastal aquifers is one of the most challenging environmental management problems faced by water resource planners worldwide [20]. This is because seawater enters easily into the groundwater regime and it is difficult to push back. Moreover, it is hard to select the optimal control measures because of the many limitations associated with the conventional control measures, which could be linked to performance efficiency, cost, etc. For instance, drilling of capture wells is an expensive exercise, since many wells need to be drills very close to each other [14].

Various intervention mechanisms and management strategies with different principles [22] have been implemented to control seawater intrusion. They include (1) rising groundwater level by reducing groundwater extraction or altering pumping patterns; (2) maintaining the freshwater ridge along the coast above the sea level by artificial recharge; and (3) development of barriers against seawater intrusion [23-25]. However, the overriding principle of these control measures is to increase the volume of fresh groundwater water and / or reducing the volume of saltwater [26] which in most instances could be inefficient, time consuming, cost prohibitive and sometimes not feasible. For instance, in countries characterized by low rainfall with limited resources of freshwater such as the United Arab Emirates, pump and treat will deplete those resources [27]. The cost of providing high quality water (e.g., desalinated water) and its in-situ delivery for recharging purpose is among the main limitations to the recharge barriers. In addition, unavailability of such water locally, especially in dry years or in the regions that suffer from scarcity of water, also restricts the use of hydraulic barriers [27]. The artificial surface recharge of the aquifer with ponded treated wastewater would need construction and maintenance of several surface recharge basins in different locations of the affected area [27]. Regarding flow barriers, a study [28] found that flow barriers showed that more effective saltwater repulsion is achieved with deeper barrier penetration and with barriers located closer to the coast. Conversely, when the barrier is installed landward of the original toe position, saltwater intrusion increases as barrier depth increases. These remediation methods involves the excavation of soil, which is time consuming and costly process [29]. Furthermore, there are situations in which this is not possible. In this case, attempts should be made to search for alternative technologies and electrokinetic remediation is a potential candidate.

1.3 Electrokinetic application as an electromigration fencing against seawater intrusion

Recently, the research community has been focused on developing cost-effective treatment technologies for controlling seawater intrusion, and electrokinetic remediation is one such technology that has significant potential to effectively and economically to remove contaminants from soil or to fence off the spread of pollutants plumes from spreading into groundwater [29]. Electrokinetic barriers represent a promising option to control seawater intrusion. Electrokinetic processing of soil involves the application of a low-density direct current through a wet-soil mass, resulting in the development of electrical, hydraulic, and chemical gradients. An electric field is created by inserting electrodes into the contaminated site and passing the current through it, making the contaminant particles mobile in the soil media [30, 31]. This technology has been explored for many decades to understand the various aspects of soil remediation [32]. The first electrokinetic remediation configuration was used in a field trial by Puri and Anand in 1936 for the removal of sodium hydroxide from soil [33]. The technique can enable and control the flow of water and contaminants and efficiently extract contaminants [34]. Moreover, this technique can be used to treat inaccessible areas that cannot be excavated, and to treat the entire soil mass between the electrodes. This technology can act as a barrier preventing seawater from flowing inland, thereby protecting the groundwater pumping zone. Furthermore, it can be deployed as a means to capture the major salts constituent of the seawater such as sodium (Na^+) and chloride (Cl^-) ions present in the interface of fresh-brackish water. Lageman and Pool simulated the deployment of an electric fence as a means to intercept sodium and chloride ions at the front edge of an advancing fresh-saline water interphase [21]. The action of electrical direct current (DC) field influences transportation/migration of Na^+ and Cl^- ions towards the cathodes and anodes in the fence zone, respectively. The captured ions are removed regularly until the Na^+ and Cl^- ions concentrations in groundwater that passed through the fence have met the irrigation or potable water standards [21].

Numerous laboratory studies and a very few field applications have been conducted to investigate the electrokinetic processes to date. The areas in which electrokinetic have been applied successfully to some extent include increasing pile strength, stability of soil during excavation and embankments, increasing flow rate of petroleum production, removal of salts from agricultural soils, removal of metallic objects from the ocean bottom, injection of grouts, microorganisms and nutrients into the subsoil strata of low permeability. Other areas include the removal of gasoline hydrocarbons and trichloroethylene from clay and the removal or separation of inorganic and organic contaminants and radionuclides, barriers and leak detection systems in clay liners, dewatering of clayey formations during excavation, control and decontamination of hazardous wastes, removal of chemical species from saturated and unsaturated porous medium [35]. Despite these advantages, however, this technology has not been fully exploited, particularly in controlling seawater intrusion.

1.4 The feasibility of electrochemical fencing

Economic consideration of remediation techniques is a crucial aspect in the application and sustaining its implementation, especially when considering the fact that the management of soil pollution is a major economic challenge worldwide. In addition to social and environmental acceptability aspects, cost involved is the key factor in determining the success and practical application of remediation technique in the field conditions. Literature capturing economic aspect of electrokinetic remediation technique generally is scarce and the one that focuses specifically on agriculture is non-existent. Generally, various factors which contribute to cost pertaining to remediation of polluted site include those related to contaminated site (such as type and depth of soil, depth of groundwater, possible migration pathways and purpose of remediation), the contaminant(s) (such as type/nature of contaminant, and concentration of contaminant(s) in soil) and the remediation technology (various technologies have different requirements and cost of action) [36]. Electrokinetic remediation method is economically effective because it is easy to install and operate [36, 37], moreover, electrokinetic remediation does not destroy the original nature of the soil [38]. In comparison with other remediation technologies, electrochemical remediation method is inherently or could be adapted to be green and sustainable because the technology uses fewer chemicals and can be powered by renewable energy sources. For instance, electrokinetic fencing can be applied against seawater intrusion along the coastal lines using renewable energy because coastal regions are considered perfect and suitable locations to harvest both solar and wind energy. This would result in significant reduction of energy cost when the technology is implemented. This technology could therefore be regarded as green remediation methods, since green remediation requires more use of renewable energy and less use of natural resources to minimize the environmental footprints [39]. Despite these positive aspects related to this method, one of the drawbacks of using electrokinetic at field scale is that specially developed tools for field-scale implementation, design, and testing are still lacking [40, 41]. Another limiting factor for direct electrokinetic remediation is fluctuation in soil pH because it cannot maintain soil pH value [36]. Additionally, very low pH environment can be developed during the remediation process which may impact the environment adversely and render the remediated soil not readily arable afterwards [42]. In some cases, soil pH is controlled by adding buffer solutions in cathode and anode, using complexant or ion exchange membrane [36, 43]. Apart from the applied voltage, there are additional significant parameters which are governing the efficacy and the technical-economical aspects of an electrokinetic/electromigration fence against seawater intrusion [44], namely: Groundwater velocity, Electrokinetic mobility, Specific electrical conductivity of the soil, Resistivity of the soil, Length of the electrodes (depth of the fence), Length of the fence, Distance between the electrodes, Radius of the electrodes. Groundwater velocity (hydraulic conductivity) is one of the major factors in determining whether an electrokinetic fence can be economically feasible or even possible, the challenge is more severe in sandy aquifers where there is higher groundwater velocity. This scenario requires a higher voltage between electrodes and a higher current per meter electrode, which obviously means higher operating cost [44]. However, there is a limit to the current which can be supplied by the electrodes. For instance a higher conductive medium (i.e., high salinity level) returns a higher electric current flow, which could lead to excessive heat generation, boiling of electrolytes and system getting out of control, respectively. These challenges would be more pronounced in sandy and high conductive soil medium, which is the focus of this research work [44]. On the other hand, decreasing the distance between electrodes would help to diminish the necessary electric potential needed to operate the electrical fence because the smaller the distance between electrodes the less potential is needed to deflect and capture the ions at the electrode reservoirs, and thus less electrical current would be needed and supplied. However, a smaller distance between electrodes means more electrodes and higher initial capital cost of the fence infrastructure [44].

The extent of seawater intrusion differs among regions and hydro-geologic characteristics. Seawater intrusion may affect small parts of the aquifer, resulting in negligible impact on the wells pumped for groundwater supply [36, 45]. Contamination may also be of regional extent resulting in substantial effect on groundwater supplies [46, 47]. Efforts to ameliorate seawater intrusion fall into three overarching categories: (1) modified groundwater and surface water withdrawals, (2) modified groundwater and surface water deliveries, and (3) the use of engineered structures [48]. Electrochemical fencing falls under the last category whereas *ex-situ* desalination could be linked with categories 2 and 3, respectively.

Additionally, electrokinetic fencing is a direct water pollution prevention technique against seawater intrusion, whereas desalination is an indirect measure to provide high quality water that could be injected into the aquifers to maintain hydraulic gradient and push back seawater intrusion. Notably, electrokinetic remediation technique is at the development stage [49] whereas desalination has been extensively practiced at full field scales in many countries, including Australia, Singapore and USA [50].

However, *ex-situ* desalination may not be feasible where seawater intrusion is concerned because it is a non-point source pollution which happens underground across the geological profile and can be over a vastly wide area. Moreover, the practice of using fresh water (i.e., fresh water well injection) to reduce salt concentration of the water may work against logic particularly in regions which struggle to provide sufficient water for human consumption [47], especially in dry years [51, 52] and with the ever growing population and increasing demand for water [53, 54]. Furthermore, maintaining the hydraulic gradient by way of injecting freshwater into an aquifer and push back saline water from the sea could prove effective however, the setback of this method is the cost factor involved in the construction and maintenance of the wells [47] as well as the cost of providing high quality water, its delivery and injection in the aquifer [52]. This is influenced by the fact that, before any water could be injected in the aquifer, many crucial factors should be considered. These include but not limited to: the hydraulic properties of aquifer systems, pumping rate and duration, initial position of the interface, density contrast between freshwater and saltwater, dispersion and sorption effects, groundwater recharge, regional flow rate, and the well and aquifer geometries [55-57]. Additionally, research has shown that desalination needs to be used in collaboration with other treatment processes in order for it to be relevant for controlling seawater intrusion. For instance, Abdelhamid and Javadi proposed a technique called Abstraction, Desalination and Recharge as an efficient method to control saltwater intrusion [51]. The process consists of three steps; abstraction of brackish water from the saltwater, desalination of the abstracted brackish water using treatment process, and recharge of the treated water into the aquifer [51]. This method combines the advantages of these three components; abstraction of brackish water helps to reduce the volume of saline water in the aquifer and reduce the intrusion of saltwater; recharge of treated water helps to increase the fresh groundwater volume to prevent the intrusion of saltwater; and desalination of abstracted brackish water helps to produce fresh water for recharge, beside it is generally less expensive than other sources of freshwater for injection. For example, desalination of seawater has a lot of problems such as; high cost, high pollution (mainly carbon emission), and disposal of the brine. Desalinating brackish water would be more efficient alternative to seawater desalination, because the salinity of brackish water is less than one-third of that of seawater. Therefore, brackish water can be desalinated at a significantly lower cost than seawater. Abstraction-Recharge process helps to move freshwater/saltwater interface towards the sea. However, this may not be relevant in regions where there is water scarcity [47].

Although many different seawater control methodologies are available, electrokinetic remediation offers many advantages. Being easy to operate, it is economically viable and applicable for a variety of contaminants. However, the technology is reported to be efficient when the cation exchange capacity (CEC) and the salinity are low [58]. This leads to a main question of this study, whether the application of electrochemical technique as seawater fencing would also be efficient, and energy feasible in medium with high salinity.

1.5 Aim of the study

The application of electromigration barriers along the coast to fence off the migration of sodium chloride ions was investigated in this work as a new measure to lessen the impact of salinity problem caused by seawater intrusion into groundwater aquifers. As a result, the research hypothesis for this research is that “Electrokinetic technique can be as efficient in terms of energy consumption and in removing salts in high permeability sandy soil and high conductivity media (i.e., high salt concentration) as in low permeability clay soil and low conductivity media (i.e., low salt concentration)”. Moreover, the aim of this research is to demonstrate the feasibility and relevance of electrokinetic (electromigration) fencing in the control of seawater intrusion at a laboratory scale with a view to redirect the attention of the research community towards the re-application of electrokinetic in the treatment of saline water since Puri and Anand applied it in 1936. Currently the focus is on the use of electrokinetic for remediation of soils contaminated with heavy metals, whereby it proved efficient, therefore there is a knowledge gap in terms of the application of electrokinetic phenomena in high conductivity media. Furthermore, the goal of the study is to demonstrate the feasibility of using electrokinetic fencing to capture Cl^- and/or Na^+ that is present in the soil media in relatively high concentrations, which is known to be a difficult process, without compromising the operational efficiency of the electrokinetic system. This was investigated by laboratory experiments in a high conductivity soil media.

The gain of applying the electromigration fence for the control of seawater intrusion might include: (a) reduction of the groundwater and soil salinity, and (b) re-use of treated seawater that has intruded the aquifer as a source of fresh water. However, it is important to mention upfront that the intention of the study was not to necessarily remove all chloride and/or sodium but to efficiently capture the Cl^- and/or Na^+ concentration of the water to the extent that the quality of the water meets the standards for potable and/or irrigation water, respectively. The basic principles and application of electrokinetic remediation are discussed in detail in Chapter 2.

The objectives of the research study are to:

- Conduct experiments to assess the migration of sodium chloride in a high conductivity soil media;
- Conduct experiments in clean artificial silica soil in order to determine the efficiency of electrokinetic without potential influence of external factors;
- Assess the influence of physiochemical processes, particularly pH gradient, dominant transport process, influence of possible electroosmotic flow on the efficiency of electrokinetic in salt removal;
- Assess the influence of Anode on the efficiency of the electrokinetic system in addressing competition between oxygen and chlorine; and addressing new approaching for enhancing electrokinetic treatment process in saline media.

1.6 Dissertation outline

The rest of the contents of this dissertation are provided below in relation to its five chapters.

Chapter 2. This chapter consists of two parts which provides a literature review of the two major aspects of this study. In the first part, the theoretical background of electrokinetic remediation is described in detail in terms of its application, its strength and limitations. The second part focusses on seawater intrusion, whereby it describes seawater intrusion phenomena and also covers the control measures of seawater intrusion. The advantages and drawbacks of those control measures are addressed.

Chapter 3. This chapter covers the common aspects of chlorine electro catalysis and electrokinetic remediation. Specific aspects that are presented include chlorine evolution reaction, oxygen evolution reaction, as well as the surface chemistry of the electrodes. These are electrochemical aspects which are directly related to the behavior of the anodic reaction under the application of electrochemical treatment to control seawater intrusion, or when applying electrokinetic remediation in saline groundwater aquifers, whereby oxygen is produced and competes with chlorine for dominance in the saline water. The chapter also focusses on toxicity of chlorine on soil, plants, and humans; as well as on the Influence of electrode selectivity on oxygen evolution reaction and chlorine evolution reaction, and its relevance to electrokinetic remediation.

Chapter 4. The application of electrokinetic remediation for treating high saline water was investigated in a laboratory using a self-assembled set up. This chapter provides a detailed explanation of the materials and methods, as well as schematic diagrams of the set-up. At first, optimum parameters for treating high saline water using electrokinetic remediation are studied. Then, self-assembled electrokinetic remediation set-up is applied.

Chapter 5. The effect of sandy soil, duration of treatment, pH, and the effect of the different ionic salts on the efficiency of the set-up to treat the water are the parameters which were studied in detail. Eventually, the observed performance of the set-up is discussed in relation to the theoretical background of electrokinetic remediation and in relation to its performance in treating contaminated sandy soil.

Chapter 6. The general conclusion of the study is described in this chapter. Moreover, recommendations for future perspective on the use of electrokinetic remediation to treat high salinity water and its possible application in controlling seawater intrusion are indicated.

1.7 References

1. Shrivastava, P. and R. Kumar, *Soil salinity: A serious environmental issue and plant growth promoting bacteria as one of the tools for its alleviation*. Saudi J Biol Sci, 2015. **22**(2): p. 123-31.

2. Agriculture, M. and F.a.R. Initiatives, *Soil Management Guide*. 2008.

3. Podmore, C., *Irrigation salinity–causes and impacts*. Primefact, 2009. **937**(1): p. 1-4.

4. CSIRO. *Salinity fact sheet*. 2010 [cited 2017; Available from: http://www.watersciencelab.com.au/assets/teacher_ref/SalinityFactsheet_CSIRO.pdf.

5. Ghassemi, F., A.J. Jakeman, and H.A. Nix, *Salinisation of land and water resources: human causes, extent, management and case studies*. 1995: CAB international.

6. Yensen, N.P. *Halophyte Uses For The Twenty-First Century*. in *Ecophysiology of High Salinity Tolerant Plants*. 2006. Dordrecht: Springer Netherlands.

7. Metternicht, G.I. and J.A. Zinck, *Remote sensing of soil salinity: potentials and constraints*. Remote Sensing of Environment, 2003. **85**(1): p. 1-20.

8. Szabolcs, I., *global problems of salt-affected soils*. Acta Agronomica Hungarica, 1987.

9. Sharma, A., et al., *Soil Salinity Causes, Effects, and Management in Cucurbits*, in *Handbook of Cucurbits: Growth, Cultural Practices, and Physiology*. 2016, CRC Press: Boca Raton. p. 419-439.

10. Sonon, L.S., U. Saha, and D. Kissel, *Soil salinity testing, data interpretation and recommendations*. C. o. A. a. ES The University of Georgia Cooperative Extension, College of Family and Consumer Sciences, editor. University of Georgia. UG, Atlanta, Georgia, USA, 2012: p. 1-6.

11. Jorenush, M.H. and A.R. Sepaskhah, *Modelling capillary rise and soil salinity for shallow saline water table under irrigated and non-irrigated conditions*. Agricultural Water Management, 2003. **61**(2): p. 125-141.

12. Jamil, A., et al., *Gene Expression Profiling of Plants under Salt Stress*. Critical Reviews in Plant Sciences, 2011. **30**(5): p. 435-458.

13. Government, Q. *Types of salinity*. 2017 [cited 2018 02 April]; Available from: https://www.qld.gov.au/environment/land/soil/salinity/types.

14. i Pla, J.M., G. Ghiglieri, and G. Uras, *Seawater intrusion and coastal groundwater resources management. Examples from two Mediterranean regions: Catalonia and Sardinia*. Contributions to science, 2014: p. 171-184.

15. Mohamed, H., et al., *Improving the properties of saline and sodic soils through integrated management practices*. Global Journal of Plant Ecophysiolgy, 2012. **2**(1): p. 44-53.

16. Botero-Acosta, A. and L.D. Donado, *Laboratory Scale Simulation of Hydraulic Barriers to Seawater Intrusion in Confined Coastal Aquifers Considering the Effects of Stratification*. Procedia Environmental Sciences, 2015. **25**: p. 36-43.

17. Yang, J., et al., *Impact of hydrogeological factors on groundwater salinization due to ocean-surge inundation*. Advances in Water Resources, 2018. **111**: p. 423-434.

18. Kumar, K.S.A., C.P. Priju, and N.B.N. Prasad, *Study on Saline Water intrusion into the Shallow Coastal Aquifers of Periyar River Basin, Kerala using Hydrochemical and Electrical Resistivity Methods.* International Conference on Water Resources, Coastal and Ocean Engineering (Icwrcoe'15), 2015. **4**: p. 32-40.

19. Gopinath, S. and K. Srinivasamoorthy, *Application of Geophysical and Hydrogeochemical Tracers to Investigate Salinisation Sources in Nagapatinam and Karaikal Coastal Aquifers, South India.* Aquatic Procedia, 2015. **4**: p. 65-71.

20. Goswami, R.R. and T.P. Clement, *Laboratory-scale investigation of saltwater intrusion dynamics.* Water Resources Research, 2007. **43**(4).

21. Lageman, R. and W. Pool, *Elektrokinetische schermen tegen intrusie zout water.* H 2 O, 2011. **44**(21): p. 45.

22. Todd, D.K., *Salt-Water Intrusion and Its Control.* American Water Works Association, 1974. **66**(3): p. 180-187.

23. Pool, M. and J. Carrera, *Dynamics of negative hydraulic barriers to prevent seawater intrusion.* Hydrogeology Journal, 2009. **18**(1): p. 95-105.

24. Tsanis, I.K. and L.-F. Song, *Remediation of Sea Water Intrusion: A Case Study.* Ground Water Monitoring & Remediation, 2001. **21**(3): p. 152-161.

25. Todd, D.K., *Salt-Water Intrusion and Its Control.* Journal - American Water Works Association, 1974. **66**(3): p. 180-187.

26. Allow, K.A., *The use of injection wells and a subsurface barrier in the prevention of seawater intrusion: a modelling approach.* Arabian Journal of Geosciences, 2011. **5**(5): p. 1151-1161.

27. Hussain, M.S., A.A. Javadi, and M.M. Sherif, *Three Dimensional Simulation of Seawater Intrusion in a Regional Coastal Aquifer in UAE.* Procedia Engineering, 2015. **119**: p. 1153-1160.

28. Luyun, R., K. Momii, and K. Nakagawa, *Effects of Recharge Wells and Flow Barriers on Seawater Intrusion.* Groundwater, 2011. **49**(2): p. 239-249.

29. Reddy, K.R., et al., *Effects of soil composition on the removal of chromium by electrokinetics.* Journal of Hazardous Materials, 1997. **55**(1): p. 135-158.

30. Acar, Y.B. and R.J. Gale, *Electrochemical decontamination of soils or slurries.* 1992, Google Patents.

31. Acar, Y.B., et al., *Removal of cadmium (II) from saturated kaolinite by the application of electrical current.* Géotechnique, 1994. **44**(2): p. 239-254.

32. Hamdan Shadi, H., F. Molelekwa Gomotsegang, and B. Van der Bruggen, *Electrokinetic Remediation Technique: An Integrated Approach to Finding New Strategies for Restoration of Saline Soil and to Control Seawater Intrusion.* ChemElectroChem, 2014. **1**(7): p. 1104-1117.

33. PURI, A.N. and B. ANAND, *Reclamation of Alkali Soils by Electrodialysis.* Soil Science, 1936. **42**(1): p. 23-28.

34. Alshawabkeh, A.N. and R.M. Bricka, *Basics and applications of electrokinetic remediation.* Environmental Science and Pollution Control Series, 2000: p. 95-112.

35. Karim, M.A., *Electrokinetics and soil decontamination: concepts and overview.* Journal of Electrochemical Science and Engineering, 2014. **4**(4): p. 297-313.

36. Khalid, S., et al., *A comparison of technologies for remediation of heavy metal contaminated soils.* Journal of Geochemical Exploration, 2017. **182**: p. 247-268.

37. Virkutyte, J., M. Sillanpää, and P. Latostenmaa, *Electrokinetic soil remediation — critical overview.* Science of The Total Environment, 2002. **289**(1-3): p. 97-121.

38. Page, M.M. and C.L. Page, *Electroremediation of contaminated soils.* Journal of Environmental Engineering-Asce, 2002. **128**(3): p. 208-219.

39. Baek, K., et al., *Green Remediation of Soil and Groundwater by Electrochemical Methods*, in *GeoCongress 2012*. 2012.

40. MASI, M., *Electrokinetic remediation of heavy metal-contaminated marine sediments: experiments and modelling*. 2017, University of Pisa.

41. Reddy Krishna, R. and C. Cameselle, *Overview of Electrochemical Remediation Technologies*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*. 2009, John Wiley & Sons, Inc.

42. Yeung, A.T. and Y.Y. Gu, *A review on techniques to enhance electrochemical remediation of contaminated soils.* J Hazard Mater, 2011. **195**: p. 11-29.

43. Wang, H., J. Ma, and X. Fan, *Research progress on enhancement of in situ remediation of heavy metal by electrokinitics. Ecol.* Environ. Sci, 2007. **16**(1): p. 223-227.

44. Lageman, R., *Preliminary assessment of the application of an electrokinetic ring fence for the removal of radionuclides from groundwater at fukushima daiichi nuclear power plant*. 2015.

45. Felisa, G., V. Ciriello, and V. Di Federico, *Saltwater Intrusion in Coastal Aquifers: A Primary Case Study along the Adriatic Coast Investigated within a Probabilistic Framework.* Water, 2013. **5**(4): p. 1830.

46. Eissa, M.A., et al., *Geophysical and geochemical studies to delineate seawater intrusion in Bagoush area, Northwestern coast, Egypt.* Journal of African Earth Sciences, 2016. **121**: p. 365-381.

47. Kayode, O.T., A.M. Odukoya, and T.A. Adagunodo, *Saline Water Intrusion: Its Management and Control*. Vol. 9. 2017.

48. White, E. and D. Kaplan, *Restore or retreat? Saltwater intrusion and water management in coastal wetlands.* Ecosystem Health and Sustainability, 2017. **3**(1): p. e01258.

49. Liu, L., et al., *Remediation techniques for heavy metal-contaminated soils: Principles and applicability.* Sci Total Environ, 2018. **633**: p. 206-219.

50. Bienkowski, B., *can saltwater quench our growing thirst?* 2015.

51. Abd-Elhamid, H.F. and A.A. Javadi, *A Cost-Effective Method to Control Seawater Intrusion in Coastal Aquifers.* Water Resources Management, 2011. **25**(11): p. 2755-2780.

52. Mohammed, H., J. Akbar, and S. Mohsen, *Cost-efficient management of coastal aquifers by recharging with treated wastewater.* International Journal of Hydrology, 2017. **1**(6): p. 183-185.

53. Kazakis, N., et al., *Seawater intrusion mapping using electrical resistivity tomography and hydrochemical data. An application in the coastal area of eastern Thermaikos Gulf, Greece.* Science of The Total Environment, 2016. **543**: p. 373-387.

54. Colón-Rivera, R.J., et al., *Hydrological modification, saltwater intrusion, and tree water use of a Pterocarpus officinalis swamp in Puerto Rico.* Estuarine, Coastal and Shelf Science, 2014. **147**: p. 156-167.

55. Wirojanagud, P. and J. Charbeneau Randall, *Saltwater Upconing in Unconfined Aquifers.* Journal of Hydraulic Engineering, 1985. **111**(3): p. 417-434.

56. Saeed, M.M., M. Bruen, and M.N. Asghar, *A Review of Modeling Approaches to Simulate Saline-Upconing under Skimming Wells.* Hydrology Research, 2002. **33**(2-3): p. 165-188.

57. Reilly, T.E. and A.S. Goodman, *Analysis of saltwater upconing beneath a pumping well.* Journal of Hydrology, 1987. **89**(3): p. 169-204.

58. Shenbagavalli, S. and S. Mahimairaja, *Electro kinetic remediation of contaminated habitats.* African Journal of Environmental Science and Technology, 2010. **4**(13): p. 930-935.

2 LITERATURE REVIEW

This chapter comprises the relevant background and a review of the literature in the area of electrokinetic remediation technology.

Adapted from : Hamdan, S. H., Molelekwa, G. F. and Van der Bruggen, B. (2014), Electrokinetic Remediation Technique: An Integrated Approach to Finding New Strategies for Restoration of Saline Soil and to Control Seawater Intrusion. CHEMELECTROCHEM, 1: 1104-1117. doi:*10.1002/celc.201402071*

2.1 Introduction

It is to be noted that the focus of this research is on controlling seawater intrusion and therefore electrokinetic method is tested to establish if it could serve as an alternative control measure thereof. For decades, electrokinetic method has been touted as an environmentally friendly technology that uses low DC to clean up contaminated soils, particularly low permeability soils and the main contaminant is heavy metals. Literature documented the performance of electrokinetic in less conductive media whereby low current was used. Furthermore, the focus was on the transportation of pollutants across the soil matrix (i.e., to anodes and cathodes). For instance, Yeung and Mitchel investigated the potential of electrokinetic fencing as an effective measure to stop migration of contaminants under a hydraulic gradient [1]. They applied it on clay with experiments aimed at mobilizing sodium chloride [1, 2]. Additionally, Lynch et al. evaluated the application of electrokinetic fence in one and two-dimensional (1D and 2D) configurations. Their results showed that such an application can significantly reduce heavy-metal contamination spreading against a hydraulic gradient [3].

Electrokinetic fences have been successfully applied in a coupled configuration, in which an electric field is applied perpendicular to the main direction of groundwater flow and contaminants can be removed at the electrodes solution [3, 4]. However, this study investigated the feasibility and the performance of electrokinetic fencing when it is applied in more severe conditions such as high salinity level, also in more permeable soil. It is anticipated that the results would lead to a broader understanding of the conditions under which electrokinetic remediation would be most effective in controlling seawater intrusion.

There are very few studies conducted to study the efficiency of electrokinetic remediation in removing salt from saline soil. Moreover, these studies have not been focused on the chemical reactions at the electrodes and even how these chemical reactions are affecting the performance of electrokinetic, especially when one was to consider the types and materials of the electrodes. The reaction kinetics, or the rate of electrolysis reactions at the electrodes, may also affect the generation and movement of ions [5]. This research study is an attempt to fill the knowledge gaps on the chemical reactions and their influence on the performance of electrokinetic in high conductive media and in sandy soil, which has high permeability. Moreover, this research study demonstrated the energy efficiency of electrokinetic, when subjected to high conductive media, whereby less energy was used. The research also determined the effect of electrokinetic on soil conditions when high conductive media was used. The research results have shown an insignificant heating up of the soil, which is an indication that the ecosystem where electrokinetic system is installed would not be adversely affected. This study also addressed the knowledge gaps in as far as geochemical processes are concerned when electrokinetic is applied in high conductivity media. This is important given the fact that geochemical processes may enhance or retard electrokinetic remediation processes. The geochemical processes include the generation of a pH gradient; change in the zeta potential of soil particle surfaces; change in direction of electro-osmotic flow, sorption, and desorption of contaminants onto/from soil particle surfaces; buffer capacity of soil; complexation; redox reactions; and interactions of these processes [6].

2.2 Theoretical background of electrokinetic remediation

2.2.1 Electrokinetic remediation process

Electrochemical remediation (EKR) of the environment is gaining widespread acceptance due to the mild conditions used, the cleanliness of the electron as a reagent, the easiness for automation, and its versatility [7]. Electrokinetic remediation is a technology that has been applied in soil decontamination processes [8, 9]. The technology dates back to the seventeenth century [10] and it involves installation of electrodes placed at the end of the contaminated soil sample and application of a low dc voltage gradient [5], in the range of 20-200 $V\ m^{-1}$ [10, 11] or, alternatively, a constant current density in the range of 0.025-5 $A\ m^{-2}$ [10, 12] between the electrodes to transport pore fluid and ions or charged species, particularly contaminants, through the soil sample [13]. Freundlich and Neumann provided the general name "electrokinetic phenomena" to refer to the electrically driven mass flow of dissolved contaminants and pore fluid transport in soils induced by an applied dc voltage [13, 14]. However, this phenomenon was first described by Reuss in Russia in 1808 and first treated analytically by Helmholtz in 1879. Subsequently, the electrokinetic phenomenon was modified by Pellat in 1903 and Smoluchowski in 1921, resulted in it being universally known as the Helmholtz-Smoluchowski model [10]. The important parameters of electrokinetic remediation processes are electrode reactions [15], electric gradient, system pH, electroosmotic flow, ion-migration, zeta potential, electroosmotic permeability, and current density. All of these parameters play an important role in the process efficiency, soil decontamination and remediation cost [10, 16].

When the electrokinetic technique is applied without conditioning of the process fluid at the electrodes (i.e., unenhanced electrokinetic remediation), the applied electric current leads to electrolysis reactions at the electrodes, generating an acidic medium at the anode and an alkaline medium at the cathode [17, 18]. Basically, H^+ and the OH^- ions are generated at the electrodes, and then move across the pore fluid within soil particles towards the cathode and the anode, respectively. Moreover, the H^+ cations generated at the anode enhance desorption of the adsorbed metals on the soil surface and at the same time promote the dissolution of precipitated contaminants. Similarly, the production of OH^- ions at the cathode increases the pH, which causes the precipitation of the metals, thus preventing their movement and reducing the treatment efficiency [19, 20].

Electrolysis of water occurs at the electrodes according to the following reactions:

at the anode

$$O_{2(g)} + 4H^{+} + 4e^{-} \rightarrow 2H_2O \qquad E^0 = 1.229V \tag{2.1}$$

at the cathode

$$4H_2O + 4e^{-} \rightarrow 2H_{2(g)} + 4OH^{-} \quad E^0 = -0.828V \tag{2.2}$$

A typical *in-situ* application of electrokinetic decontamination technology is shown in Figure 2.1. Depending on the approach as shown in Figure 2.2, the first approach is the removal of electrically charged ions by electro-migration in which ions deflected under an applied electric direct current field towards the oppositely charges electrode. Lageman et.al. developed this approach commercially for practical applications in the late 1980s [21]. The concept of this approach relies on circulating electrolytes by inducing an electrical dc into the soil through a row of anodes and cathodes placed across salt-fresh water interface along the shore line in the areas affected by seawater intrusion. The electrodes are not in direct contact with the soil but hang in ion-permeable wells in which the contaminants are removed as they approach the fence.

The second approach can act as a barrier, and it relies on the movement of pore water through the electrical double layer created on porous media by creating a counter gradient flow (electroosmotic) to stop the migration of contaminant under the hydraulic flow, this could be done by installing two parallel rows of electrodes, one row represents the positive electrodes (anode) and the second row represents the negative electrodes (cathode) [22].

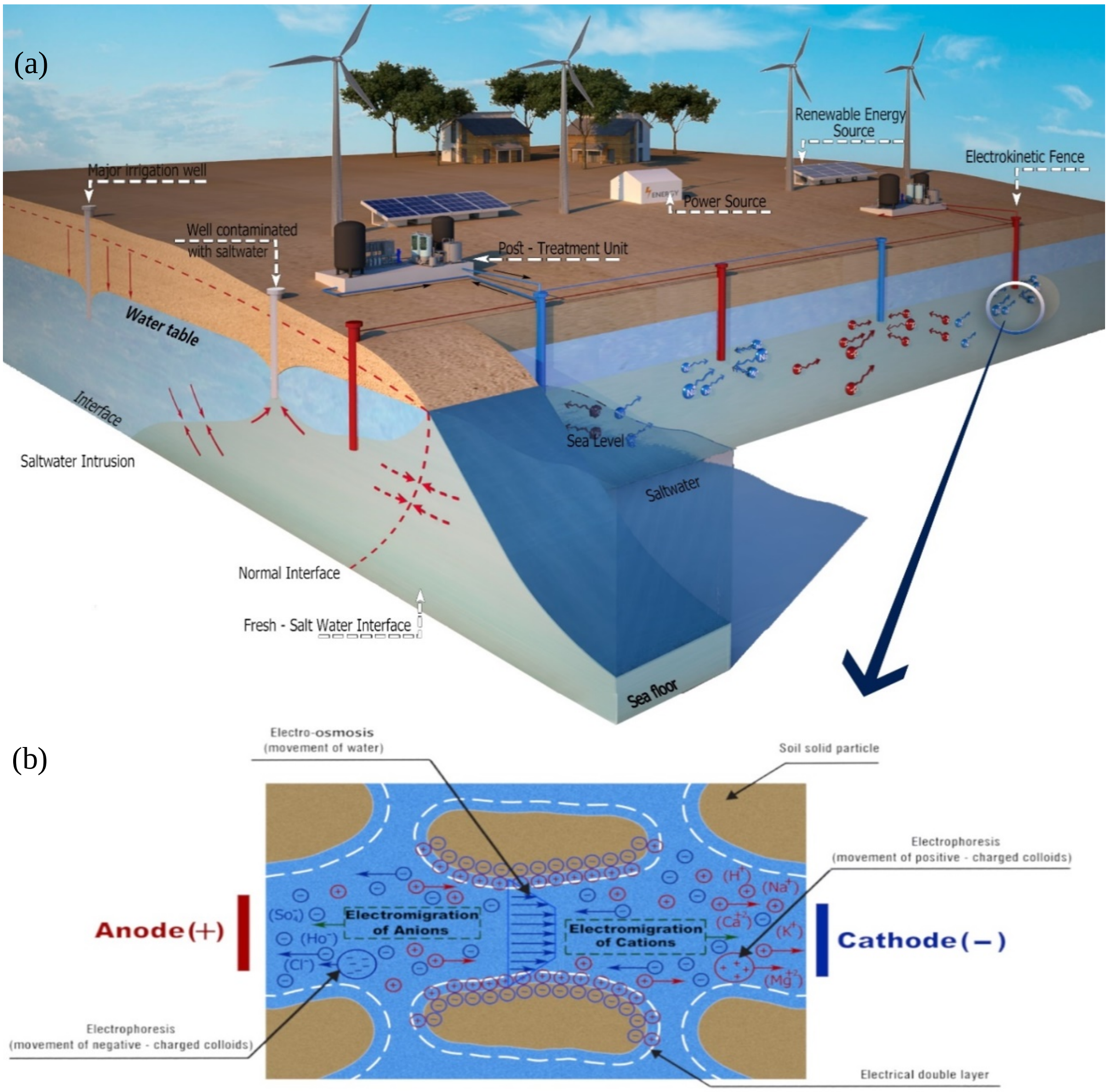


Figure 2.1: (a) Schematic of the implementation of a typical proposed *in-situ* electrokinetic fence against sea water intrusion and (b) representation of electrokinetic transport phenomena with the soil matrix (Adapted from Reddy [23]).

2.2.2 Predominant contaminant transport mechanisms

The predominant contaminant transport mechanisms that occur during electrokinetic remediation are electromigration, electroosmosis [18] and electrophoresis [24]. The main influencing factors on their migration velocity and direction are soil pH and electrode reactions [15]. Under the condition of sub-acidity and neutrality, pollutants mainly migrate towards the cathode with electroosmotic flows; however, when the pH is relatively high, the main migration mode is electromigration and the pollutants will move towards the anode [15]. The change in soil pH can change the chemical states of contaminants, rendering them immobile. Furthermore, it can also change the magnitude and direction of electroosmotic flow, affecting the advective transport of contaminants in soil pore fluid by electroosmosis [24]. The direction of electroosmotic flow may reverse during a prolonged application of a DC electric field across fine grained soils [25-27]. The zeta potential of most soils, except for quartz, is negative, because soil surfaces carry a negative charge that causes the electroosmotic generally from anode to cathode. The pH and ionic strength of the pore fluid may affect the value of zeta potential and zeta potential is reported to decrease linearly with logarithm of the pH of the porous medium [28]. High acidic solution causes the zeta potential to become less negative and even to attain positive values at low pH. As a result flow rates have been reported to decrease if the pH of the electrolyze is depressed below neutral and to increase at alkaline pH values [29]. The effect of zeta potential on electroosmotic permeability has further been investigated by Shang [30]. The phenomenon of reverse electroosmotic flow is not well understood. Therefore, controlling soil pH is very important for the success of electrochemical remediation [24]. Moreover, these ions can polarize the electrodes and reduce the effectiveness of the imposed dc electric field.

Electromigration

Electromigration, also known as ionic migration, is the movement of the dissolved ionic species present in the pore fluid toward the electrode of opposite charge. Anions move toward the anode and cations move toward the cathode. Electromigration is the major transport process for ionic metals, polar organic molecules, ionic micelles, and colloidal electrolytes [23]. Basically, electromigration will occur with any species that forms ions in aqueous environments [31]. The transport of H^+ and OH^- ions generated by electrolysis reactions is also attributed to electromigration [18, 23]. The process of electromigration can therefore be applied to contaminants such as [31]:

- Inorganic anions and cations.
- Organic carboxylic acids and phenols.
- Sulfonated aliphatic and aromatic compounds like some dyestuffs.
- Detergents and some pesticides.

The degree of electromigration depends on the mobility of ionic species, conductivity of the soil, soil porosity, pH gradient, applied electric potential, initial concentration of the specific ion and the presence of competitive ions [23]. Furthermore, the mobility of the ions depends on the strength of the applied electric field, the size of the pores (or porosity), and the tortuosity, which allows for the fact that the particles have to weave their way around the soil particles [32].

Ion velocity due to electromigration can be calculated [32, 33]:

$$v_{eo} = u_i \frac{dv}{dl} n\tau \tag{2.3}$$

where τ is tortuosity, n is porosity, and $\frac{dv}{dl}$ is the strength of the electric field, volts (v) across the length of soil (l), u_i is the ion mobility, which is given in equation (2.4)

Ionic mobility (u_i) is defined as the velocity of the ionic species under the effect of unit electric field and is estimated using the Nernst- Einstein -Townsend relation:

$$u_i = \frac{D_i |z_i| F}{RT} \tag{2.4}$$

where D_i is the molecular diffusion coefficient, R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$), and T is the absolute temperature (K).

The effective ion mobility u_i^* is defined by equation (2.5). And it is considered the movement of a given ion in a porous matrix with a tortuous path. The effective ionic mobility of a specification is a function of its molecular diffusion coefficient, soil porosity, tortuosity factor, and charge.

$$u_i^* = n\tau u_i \tag{2.5}$$

Typical approximate values for ion mobilities in a free solution at 25°C are Na:5, K:8, H:36, OH:21 ($10^{-8}\, m^2\, V^{-1}\, s^{-1}$) [32, 34]. Notably, hydrogen ions move almost twice as fast as OH^- ions. Thus, in a field of 1 $V\, cm^{-1}$, the electromigration velocity of a sodium ion in a free solution is about 1.8 $cm\, h^{-1}$. In soil, tortuosity must be considered, so it will be somewhat less than this. Acar and Alshawabkeh reported that the electromigration velocity in soil is typically about 4.7 times less than that in a free solution, so this will reduce the velocity in the above example to about 0.38 $cm\, h^{-1}$ [8, 32].

Electroosmosis

Electroosmosis, on the other hand, is a field-induced convection of water through a porous medium with a surface charge. It depends on the electric current through the soil, the flow resistance of soil, and the frictional drag exerted by the migrating ions in the water molecule and this flow originates at the electric double layer of the soil pores [10]. Moreover, electroosmotic flow is produced because the locally existing excess ions migrate in a plane parallel to the particle surface towards the oppositely charged electrode, and, as they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces [18, 35]. Because of the isomorphous substitution and the presence of broken bonds in the soil structures, excess mobile cations are required to balance the negative fixed charges on the soil particle surfaces [10]. Therefore, mobile cations exert more momentum to the pore fluid than do mobile anions. As a result, there is a net movement of fluid relative to soil particles under the influence of electroosmosis [10]. Under an electric potential, the locally excess ions migrate in a plane parallel to the particle surface toward the oppositely charged electrode. As they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces, producing electroosmotic flow [36]. In many instances, electroosmotic flow plays the most important role in the removal of contaminants within the system.

Advective flow occurs due to hydraulic gradient and electrical gradient. The hydraulic flow (q_h) due to hydraulic gradient (i_h) is defined by Darcy's law:

$$q_h = k_i i_h \tag{2.6}$$

where k_h is the hydraulic conductivity. This flow is significant for permeable soils such as sand, which has a hydraulic conductivity greater than 10^{-3} $cm\ s^{-1}$; however, this flow in clayey soils is negligible due to very low hydraulic conductivity (10^{-6} - 10^{-9} $cm\ s^{-1}$).

In 1879, Helmholtz introduced one of the first theories concerning electroosmosis, and Smoluchowski modified it in 1914 [36]. According to the Helmholtz-Smoluchowski theory, the electroosmotic flow velocity (v_{eo}) is directly proportional to the applied voltage gradient (E_z), zeta potential (ζ), and dielectric constant (D) of the fluid, and it is inversely proportional to the fluid viscosity (η) [36]:

$$v_e = -\frac{D\zeta}{\eta} E_z \tag{2.7}$$

The Helmholtz-Smoluchowski equation can also be expressed in terms of the volumetric flow rate q_{eo}:

$$q_{eo} = nA\frac{D\zeta}{\eta} E_z \tag{2.8}$$

where n is the porosity and A represents the cross sectional part of the soil. Additionally, the use of the effective porosity (n_e) or the porosity (n) divided by the tortuosity squared (n/τ) may be more accurate than using the porosity (n) [36]. The electro-osmotic permeability coefficient (k_{eo}) is computed as follows:

$$k_{eo} = n\frac{D\zeta}{\eta} \tag{2.9}$$

Electroosmosis is determined by the following factors [31]:

- The mobility of the ions and charged particles present in the pore fluid, including those ions and particles entering into the pore fluid via ion exchange.
- The hydration of ions and charged particles present in the pore fluid.
- The electrical charge and direction of movement of ions and particles, resulting in net water transport.
- The ionic strength or ion concentration.
- The viscosity of the pore fluid.
- The temperature.
- The soil porosity.

The volume of water removed per unit of time is directly proportional to the electrical power used per unit of volume of removed water. Thus, the faster the water transport, the more power is necessary to remove the same volume of water [31]. Electroosmosis can be used as an *in-situ* flushing technique for the mobilization of the non-charged hydrocarbon or chloroethene contaminants from the subsurface. Once accessible, contaminants may be degraded *in-situ* or could be moved further through the soil into an accessible area and then treated *ex-situ* by physical or biological treatment processes without the requirement to excavate subsurface soils. For electroosmosis to be the driving force for the removal of contaminants, the hydraulic conductivity of the soil should be less than $10^{-5}\ mm\ s^{-1}$ [37]. If the opposing hydraulic gradient is above $10^{-5}\ mm\ s^{-1}$ the movement of contaminants toward the cathode of the circuit would be negated by water movement in the opposite direction. It is reported that electroosmotic conductivity is generally between 1 and $10^{-8}\ m^2\ V^{-1}\ s^{-1}$ for a variety of soil types [38, 39].

Electrophoresis

Electrophoresis (also known as cataphoresis) is the transport of charged particles (e.g., colloidal size, clay, and organic matter particles suspended in the pore fluid) and bound contaminants toward the electrode of the opposite polarity due to the application of a low DC or voltage gradient relative to the stationary pores fluid. The movement of these particles is similar to the movement of ions. In the pore fluid of clay soils, the particles participate in the transfer of electrical charges and influence the electrical conductivity and the electroosmotic flow [36]. Compared with ionic migration and electroosmosis, mass transport by electrophoresis is negligible in low permeability soil systems. However, mass transport by electrophoresis may become significant in soil suspension systems, and it may also be a dominant transport mechanism for biocolloids (i.e., bacteria) and micelles [36].

2.2.3 Application of electrokinetic remediation

Numerous laboratory studies and a very few field applications have been conducted to investigate the electrokinetic processes to date [10]. Electrokinetic remediation can be applied to treat polluted soils, sediments, and groundwater with inorganic species such as lead, cadmium, chromium, mercury, zinc, iron, magnesium, and other soluble salts [40-48], organic species such as phenol [49-58], and radionuclides [59-61]. The direction and quantity of contaminant movement are influenced by the contaminant concentration, solubility, speciation, degree of hydrophobicity, soil type and structure, and the mobility of contaminant ions, as well as the interfacial chemistry and the conductivity of the soil pore fluid [13, 19]. The remedial efficiency generally depends on the nature of the contaminants and soil properties, such as pH, permeability, adsorption capacity, buffering capacity, and geochemical processes (such as acid/base reactions and migration, dissolution/precipitation, redox reactions, complexation, and speciation) [6, 13, 62].

The areas in which electrokinetic have been applied successfully to some extent include increasing pile strength, stability of soil during excavation and embankments, increasing flow rate of petroleum production, removal of salts from agricultural soils, removal of metallic objects from the ocean bottom, injection of grouts, microorganisms and nutrients into the subsoil strata of low permeability, barriers and leak detection systems in clay liners, dewatering of clayey formations during excavation, control and decontamination of hazardous wastes, removal of chemical species from saturated and unsaturated porous medium, removal of gasoline hydrocarbons and trichloroethylene from clay and removal or separation of inorganic and organic contaminants and radionuclides [10].

The first application of electrokinetic was made by Casagrande in 1939 for consolidation and stabilization of soft fine grained soils [10]. Yeung has reported different potential applications of electrokinetic in hazardous waste site remediation. He stated that these applications can be applied individually or combined with others

[63]. Some researchers observed that electrokinetic remediation is often applied at the laboratory scale and that it is rarely applied to the real field [64]. However, given that this technology was introduced for soil remediation in the late 1930s [65], it has only been drawing interest over the last decade [63, 66-70], and hence, much focus is on laboratory scale trials [44, 69, 70]. Lately, there has been slow progress to the pilot scale. For instance, in Korea, the electrokinetic remediation technique became known in the mid-1990s [70]. Various studies, which included enhanced electrokinetic remediation techniques, modification of electrokinetic remediation reactors/systems, hybrid electrokinetic remediation technology, and monitoring/modelling of electrokinetic remediation processes, pilot-scaled and field application of electrokinetic remediation have been conducted in different cases to provide higher performance and understanding of the processes used to remove contaminants [70] by using this technology. Among these studies, a pH conditioning electrokinetic remediation field study at a shooting area was conducted to remove heavy metals (e.g., lead and copper) from soil. In 2011, Kim et al. controlled catholyte pH by using nitric acid to enhance the mobility of heavy metals, and they implemented two types of electrokinetic remediation configuration (i.e., rectangular and hexagonal). It was intended to be scaled up in the future [70], which thus suggests that the project could have yielded positive results.

Another interesting *ex-situ* project was performed in Korea to investigate the electrokinetic removal of salts from saline soil. One of the objectives of the project was to ensure reduced electrical energy consumption while using a pulsed current that periodically repeated on/off settings by using a DC power supply [71]. The results of this project showed that the pulse powered electrokinetic remediation system reduced the electrical energy consumption to more than one half of that of conventional power and that the system effectively prevented pH changes in the soil and electrode corrosion. A smaller amount of cations was removed in the pulse power system; however; this was beneficial for the growth of plants [71].

2.2.4 Configuration of electrokinetic remediation

Approaches and classification

Many articles have written extensively about the configuration and application of electrokinetic remediation. Therefore, the focus in this section is directed towards two important approaches based on the different electrokinetic phenomena. Furthermore, the conditions under which electrokinetic remediation is applied and the environment in which it is performed are also explained. The first approach is the removal of electrically charged ions by electromigration in which ions move under an applied electric direct current (DC) field. Lageman, Pool, and Seffinga of Geokinetics developed this approach commercially for practical applications in the late 1980s [72-76]. The concept of this approach relies on circulating electrolytes by inducing an electrical DC into the soil through arrays of anodes and cathodes placed across a plume. The electrodes are not in direct contact with the soil but hang in ion-permeable wells in which the contaminants are removed as they approach the fence. This approach functions as a soil remediation and a barrier technology [3, 31, 72]. The second approach can act as a barrier, and it relies on the movement of pore water through the electrical double layer created on porous media by creating a counter-gradient flow to stop the migration of contaminant under the hydraulic flow [72, 77, 78].

These approaches are based on the three main contaminants transport mechanisms, which have been described in detail in section 2.2.2.

Electrokinetic remediation technology can be applied in separate ways, which have given rise to different classifications. For instance, Lageman et al. classified the application of electrokinetic remediation into four groups, namely: *in-situ* and *ex-situ*, batch *ex-situ*, electrokinetic fence, and electrokinetic biofence [72]. *In-situ* and *ex-situ* applications of electrokinetic remediation have been demonstrated. For instance, in the Netherlands, four rows of electrodes have been installed at a galvanizing plant in an in situ reclamation project of soil contaminated with nickel and zinc [79]. During in situ application of electrokinetic remediation for which electrodes were placed directly in the ground, contamination was recovered with minimal disturbance to the site. The batch *ex-situ* configuration was applied on a contaminated medium that was treated *ex-situ* after it was transported to a mobile batch facility [79]. Another configuration, the electrokinetic fence, was introduced by Lageman, Pool, and Seffinga in 1989 [21]. This configuration consists of a row of DC electrodes installed in the ground to halt the migration of contaminated groundwater from a point source [21, 79]. Yeung and Mitchel investigated the potential of electrokinetic fencing as an effective measure to stop migration of contaminants under a hydraulic gradient [1]. Figure 2.2 shows a scheme for different electrokinetic barrier approaches. They applied it on clay with experiments aimed at mobilizing sodium chloride [1, 2]. Furthermore, in 2005, Lynch et al. evaluated the application of electrokinetic fence in one and two-dimensional (1D and 2D) configurations. Their results showed that such an application can significantly reduce heavy-metal contamination spreading against a hydraulic gradient [3]. Electrokinetic fences have been successfully applied in a coupled configuration, in which an electric field is applied perpendicular to the main direction of groundwater flow and contaminants can be removed at the electrodes solution [3, 4]. The electrokinetic biofence (EBF), whereby a row of filters of nutrients are placed upstream of the chain of electrodes [32], has also been tested. In this configuration, groundwater transports the dissolved nutrients towards the electrodes under the influence of the electrical field, which thus disperses the electrically charged nutrients homogeneously between the electrodes and enhances biodegradation in the process [80]. Such an electrokinetic biofence, which consisted of 3 cathodes, 2 anodes, and 24 infiltration wells, was applied as a pilot project in a chemical laundry at Wildervank in the Netherlands to enhance the biodegradation of volatile organic compounds in groundwater at the zone of the fence by dispersing dissolved nutrients upstream of the fence. The infiltration wells were filled with nutrients and electron donors. These compounds dissolved in the groundwater and were homogeneously dispersed through the soil under the influence of the induced electrical field [4, 32].

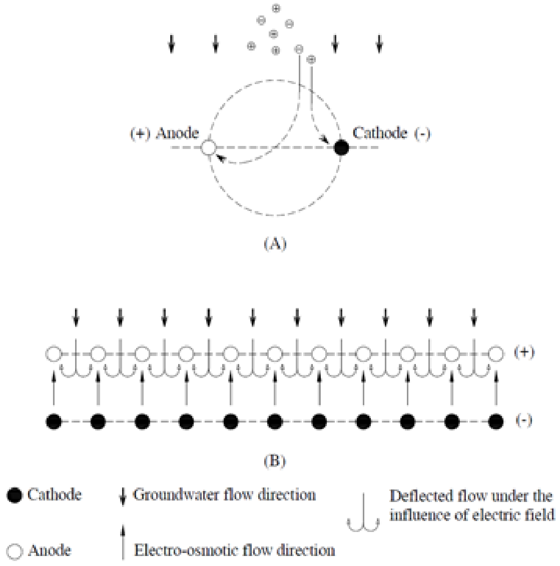


Figure 2.2: Scheme of The electrokinetic barrier: (A) one row of Anodes-Cathodes approach, contaminant ions deflected towards the oppositely charged electrode (Adapted from Lageman & Pool [80]) (B) two rows of electrodes approach to prevent the contaminant migration (Adapted from Narasimhan & Sri Ranjan [22]).

Closed and open electrokinetic systems

Eid et al. have performed experimental laboratory tests to study the nitrate gradient developed under the influence of an electrical potential in two systems [81]. The first had no flow (closed system) and different electrode materials were used (i.e., carbon, copper, and stainless steel) [81], and the second had flow opposite to the direction of the electrical current and carbon electrodes were used [82]. In the closed system, results show that the electrokinetic process effectively concentrates and retains nitrate close to the anode by using either carbon or copper electrodes. However, less movement of NO_3^- is reported if stainless steel electrodes are used [81]. The results also indicate that the rate of nitrate migration is higher with closer electrode spacing and with a lower initial nitrate concentration. Additionally, significant clean-up of Na^+ is observed after application of an electrical current for 12 *h* in 70% of the soil sample close to the cathode[81]. In an open system, the results reveal that electromigration can be an effective measure for concentrating and retaining nitrate close to the anode in saturated sandy soil even under a hydraulic gradient [81, 82]. Moreover, in both systems the results show that the movement of NO_3^- through a soil column is influenced by the pH gradient developed during the electrokinetic process [81]. However, these experiments are conducted on the basis of an uncontrolled acid/base front that is generated during the experiments, and this results in increased energy costs, especially if the current density is constant [81]. In this regard, certain conditioning precautions are usually taken to control the large developed pH to enable practical and economical applications [81].

Electrode materials and configuration

An important aspect of electrokinetic remediation is the electrode configuration. Electrode configurations influence the active area of the electric field, which is the major driving force to remove metal contaminants toward oppositely charged electrodes [25, 64, 83]. Additionally, the spacing between same polarity electrodes has a significant role in cost calculations and process efficiency [25, 83]. Alshawabkeh et al. reported that the spacing between same-polarity electrodes is as significant in cost calculations and in process effectiveness as it is between anodes and cathodes for 1D applications [83]. Kim et al. investigated the influence of electrode configurations on the efficiency of electrokinetic remediation by applying four different setups of electrode in a rice field near a zinc refinery plant located in Janghang, South Korea [64]. They found that there was a correlation between the electrical energy consumption and both the area covered by the electrodes and the current density under a constant voltage gradient. They also advised that the groundwater flow and soil temperature should be monitored during the remediation process and that the configuration should be considered to minimize unnecessary transport of contaminants. On the basis of theoretical modelling, Alshawabkeh et al. suggested that a 2D electrode configuration has a smaller inactive electric field area than a 1D electrode configuration, as shown in Figure 2.3 [83]. Other research groups investigated 2D configurations such as rectangular or hexagonal [84, 85].

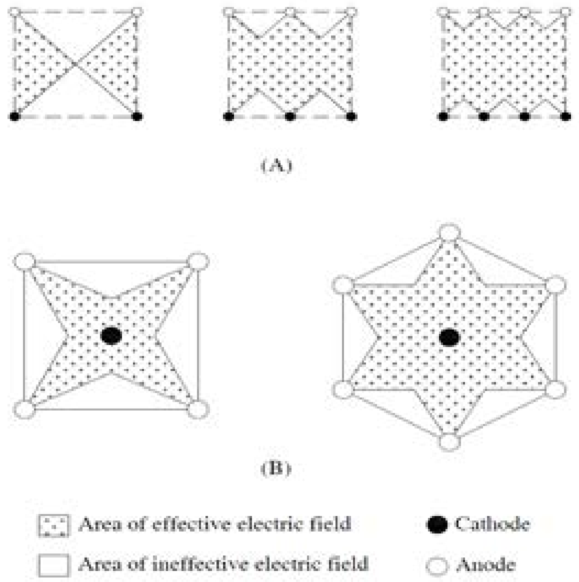


Figure 2.3: Estimation of the area of ineffective electric field for different electrode configurations: a) 1D parallel electrodes configuration and b) 2D centralized cathode with surrounding anodes (Adapted from Alshawabkeh [83]).

Zhang et al. applied both a horizontal and a vertical electrical field in four operation modes in a bench-scale experiment for remediation of chromium-contaminated soil. In their findings, the 2D crossed electrical field appeared to be a promising and practical method for the remediation of soils contaminated with heavy metals [85]. Kim et al. conducted a study to improve salt removal from saline soil on pilot scale by an electrokinetic remediation system with electrodes in a hexagonal configuration [84]. This configuration shows that the removal efficiency is enhanced because the inactive area of the electric field is significantly minimized, which is not the case with a 1D configuration.

However, the 2D configuration may require a longer operation time, which would unfortunately lead to a higher energy consumption and unexpected geochemical changes related to changes in pH, and this could negatively affect crop production [84]. They therefore recommend further development of an optimal electrokinetic remediation for higher removal efficiencies while reducing electric energy consumption and promoting crop production by using pH-control mechanisms [84].

Another aspect of interest is the type of electrode materials used in electrokinetic remediation. There has been much discussion about the importance of the choice of materials and the strength and limitations of certain materials if used in electrokinetic remediation. However, the proper selection of electrode materials and their role in soil remediation has been overlooked [86]. Aspects such as mechanical, thermal, economic, and corrosion resistance require more research for optimal selection and removal efficiency [87]. It has been generally accepted that cost effective and inert materials should be used such as carbon, graphite, and platinum [16, 19]. In basic electrochemistry, metallic anodes made of iron, for example, could be oxidized and dissolved due to electrolysis, and this results in the introduction of corrosive products into soil mass, which can cause contamination of unwanted metals in treated soil [71]. However, for economic reasons it is more appropriate to use much cheaper and reliable electrodes such as titanium, stainless steel, and even plastic electrodes [19]. Electrodes named dimensionally stable anodes (DSAs) have been widely used in the wastewater treatment industry. A major advantage of these electrodes is their long lifetime under conditions of oxygen evolution and organic electro-oxidation [88, 89]. $RuO_2|Ti$ is one type of DSA electrode that has been successfully used in the electrokinetic remediation process of soils contaminated with hydrocarbons, whereby the removal efficiency was over 90% in the anodic section and over 75% in the middle and cathodic section after 48 h treatment [89]. Pérez-Corona et al. evaluated $IrO_2^{-}Ta_2O_5|Ti$ electrodes in the electro-remediation of hydrocarbon- contaminated soil. They developed polarization curves in three ways to obtain the density corrosion current to the standard. Their results were high compared to other publications [89]. Based on this information, it is important for the user of these electrodes to consider all these competing aspects and make a choice that would ensure value for money in terms of removal efficiency.

2.2.5 Enhancement of electrokinetic remediation

Every technology is expected to perform to its optimum level. However, sometimes technologies perform below their optimum level, and electrokinetic remediation technology is no exception; in many cases, application of electrochemical remediation alone is not adequate to remediate the contaminated soil to the required acceptance level. Therefore, the technology is enhanced by coupling with other remediation technologies as part of a remediation train of processes [90]. As a remediation technology, electrokinetic remediation is expected to ensure complete removal of contaminants that are being removed; however, some inefficiency in the removal of contaminants by electrokinetic remediation has been reported [91-95]. Notably, the success of electrokinetic remediation is highly dependent on the ability of the contaminants to migrate. In that regard, it is essential that the contaminant species are desorbed from the soil and converted into a soluble or dissolved state [90, 96]. Fundamentally, soil is composed of three phases (air, water, and soil solid particles) [6] and if soil is contaminated, it becomes a multiphase material with different chemical states [6]. Generally, these coexisting phases and chemical states of contaminants are contaminant specific, dynamic, and reversible, and they depend on environmental conditions, particularly the pH of the environment. Thus, they are interrelated with the geochemical processes associated with the electrochemical remediation processes, which require proper control to enhance the remediation process [6, 96]. If a DC electric field is applied across the soil through electrodes inserted in the soil profile, it results in electrokinetic flow processes, electrochemical reactions, and, more importantly, geochemical processes [6]. The geochemical processes include the generation of a pH gradient; change in the zeta potential of soil particle surfaces; change in direction of electroosmotic flow, sorption, and desorption of contaminants onto/from soil particle surfaces; buffer capacity of soil; complexation; redox reactions; and interactions of these processes [6]. Geochemical processes may enhance or retard electrokinetic remediation processes [6]. The synergy can achieve results that are better than the sum of technologies applied individually. Many techniques to enhance solubility of contaminants and extraction efficiency of electrochemical remediation of contaminated soil have been developed throughout the years [90].

There are three primary objectives of using enhancement techniques for electrokinetic remediation in order to improve the removal efficiency and guarantee an optimal performance [90]. They are to (1) to solubilize contaminants in soil and to keep them in mobile states; (2) control the soil pH within a range of values favoring the application of electrochemical remediation; and (3) destruct, breakdown, or transform the contaminants simultaneously or sequentially. The enhancement techniques that have been developed and applied are classified into three inter-related principal groups: (a) techniques that solubilize contaminants and keep them in mobile states; (b) techniques that control soil pH; and (c) remediation techniques that can be coupled with electrochemical remediation synergistically (hybridization) to destruct, breakdown, or transform the contaminants simultaneously or sequentially [90]. The three enhancement techniques are briefly discussed here under.

Contaminant-solubilizing methods

This methodology has been developed to solubilize contaminants during electrokinetic remediation. It includes lowering the soil pH and introducing enhancement agents [90]. It is known that metals are more soluble in a low pH environment [90, 97, 98]. During electrokinetic remediation, H^+ and OH^- ions are generated due to the electrolysis process, and they can migrate through the soil profile, which thus leads to the creation of an acid/base front in the soil profile. However, the mobility of H^+ ions is higher than that of OH^- ions, which causes the acid front to migrate faster than the base front [8, 69, 99-101]. Thus, creating a low pH environment specifically in low acid/base buffer capacity leads to a successful degree of metal extractability from soil [90]. For natural soils of high acid/base buffer capacity, strong acids and weak acids have been used as enhancement agents to neutralize the excess amount of OH^- ions generated at the cathode and to lower of the soil pH. However, the level of pH should be maintained to a level that favours removal efficiency [90]. If the soil pH is below the point of zero charge, the direction of electro-osmotic flow is reserved, which thus diminishes cation removal by electro-migration [6, 102, 103]. Moreover, a very low pH condition may adversely impact the environment [90, 104-107]. When the acid/base buffer capacity of soil is high (i.e., the resistance of soil to pH change is high), it is very difficult to lower the soil pH by the H^+ ions generated by electrolysis or introduction of acid to the soil. This would trigger the need to utilize enhancement agents to desorb contaminants sorbed on soil particle surfaces and to keep them in the dissolved phase. Those enhancement agents include: (1) chelants or chelating agents; (2) complexing agents; (3) surfactants and co-solvents; (4) oxidizing/reducing agents; and (5) cation solutions [90]. The choice of enhancing agent depends on the type of contaminant present and the soil conditions [108] and is thus crucial in achieving successful contaminant removal efficiency.

In general, enhancement agents should have these important characteristics [63, 96]: (1) they should not form insoluble salts with the contaminant within the range of variation of pH values during the process; (2) they should form soluble complexes with the contaminant that can be efficiently migrated by a direct-current electric field; (3) they and their contaminant complexes should be chemically stable over a wide range of pH values; (4) they should have a higher affinity for the contaminant than soil particle surfaces; (5) they and their contaminant complexes should not have a strong affinity for soil particle surfaces; (6) they should not generate toxic residues in the treated soil; (7) they should not generate an excessive quantity of wastewater, and the end products of the treatment process should be amenable to concentration, precipitation, recovery, treatment, and/or recycling; (8) they should be cost-effective including reagent costs, handling costs, and treatment costs for the resulting waste collected and/or wastewater generated; (9) they should not induce excessive solubilization of soil minerals or increase the concentrations of any harmful species in the soil pore fluid; and (10) if possible, they should complex selectively with target contaminant species.

Chelation is the formation or presence of two or more separate bonds between a bidentate or multidentate ligand (i.e., the chelant and a single metal central atom or ion) [90]. Chelating agents desorb toxic metals from soil particle surfaces by forming strong water-soluble complexes that can be removed by chelant-enhanced electrochemical remediation. Ethylenediaminetetraacetic acid (EDTA), (diethylenetriamine) pentaacetic acid (DTPA), and citric acid are the most frequently used chelating agents in electrochemical remediation [90]. A detailed review of the use of chelants in electrochemical remediation is given by Yeung and Gu [109]. Citric acid was reported as one of the most effective chelating agents for enhancement of electro-osmotic flow [110-112]. The use of chelating agents still presents a challenge for treatment and disposal of the toxic used extraction fluid, as it is rich in metal-chelant complexes. The current recycling methods are also not efficient and there is a call for more robust recycling methods for chelants that would also increase the economic value of chelant-enhanced electrochemical remediation [90]. Complexing agents are chemicals that form coordination complexes with metal ions [90]. Complexing agents such as I^-, Cl^-, NH_3^- and OH^- are introduced into soil as conditioning acids or bases during electrochemical remediation process. Acetic acid is a complexing agent that is frequently utilized to enhance electrochemical remediation [90, 113-115], and although it is not as effective as HNO_3, for instance, it is preferred [90]. It can neutralize the electrolysis product at the cathode to reduce energy consumption, and it can keep the electrolyte pH within a certain range by its acid/base buffering capacity. Moreover, it is relatively cheap, biodegradable, and environmentally safe [90]. Other complexing agents include ammonium acetate and cyclodextrins, which are nontoxic and biodegradable [90].

There are synthetic and natural surfactants or co-solvents that may act as adhesives, flocculating agents, wetting agents, foaming agents, detergents, de-emulsifiers, penetrants, and dispersants [90]. Surfactants can lower the surface tension of a liquid to allow easier spreading, and the interfacial tension between two liquids, or between a liquid and a solid [90]. They have been observed by many researchers as feasible in enhancing heavy-metal extraction from soil and sludge [90, 116]. Factors that need to be considered in the selection of surfactants in electrochemical remediation include: 1) efficiency and effectiveness of the surfactant in remediating the contamination; 2) biodegradability of the surfactant and degradation products; 3) toxicity of the surfactant and its degradation products to humans, animals, plants, and the ecology; 4) its ability to be recovered, recycled, and reused; 5) public perception and regulatory restrictions; 6) functionality of the surfactant at different pH values; 7) electrical charges, if any, carried by the surfactant; and 8) cost [90]. A co-solvent is a second solvent added in small quantity to the primary solvent to form a mixture that may greatly enhance the solvent power of the primary solvent due to synergism. Co-solvents such as ethanol [90, 117, 118], n-butylamine [90, 119, 120], n-propanol [90, 121], acetone, and tetrahydrofuran [90, 119] have been examined for their ability to enhance the solubilization of organic compounds such as polycyclic aromatic hydrocarbons and diesel oil in soil during the electrochemical remediation process [90].

Oxidizing or reducing agents can be injected into contaminated soil to manipulate the in situ chemistry and microbiology, to enhance extraction of contaminants, or to reduce their toxicity through oxidation or reduction reactions [90]. Oxidizing agents may include air or oxygen or chemical oxidants, such as hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$) or sodium permanganate ($NaMnO_4$), ozone, chlorine, and oxygen-releasing compounds. Contaminants are chemically or microbially oxidized. Similarly, reducing agents such as Fe^{2+}, Fe^0, calcium polysulfide, and sodium dithionite can be used to reduce contaminants in soil [90].

An increase in ionic strength (electrolyte concentration) of the soil pore fluid increases the electrical conductivity of the soil and energy consumption of the process. Conversely, a decrease in ionic strength (electrolyte concentration) increases the thickness of the diffuse double layer, and this leads to a decrease in the coefficient of electro-osmotic conductivity and a reduction in the electroosmotic flow rate and electromigration of the ions. However, the electric current flowing through the soil is reduced, and this leads to lower energy consumption [90].

Control methods for soil pH and reservoir conditioning techniques

This methodology is applied to eliminate the adverse impact of electrode reactions and the result of electrolytic decomposition [90]. The splitting of water near the anode generates H^+ ions and causes the pH to decrease near the anode, which aids heavy-metal desorption from the surface of the soil particles. Conversely, water splitting at the cathode generates OH^- and causes the pH to increase near the cathode, which causes heavy metals to precipitate and makes them very difficult to remove with an electric field [17, 104]. Electrode reservoir solution conditioning is important to maintain the pH of the anolyte and catholyte within appropriate ranges specific to the contaminants being remediated [122, 123]. This methodology is the most important in soils of low acid/base buffer capacity for which the resistance to pH change of these soils is low. Thus, the aim of this enhancement technique is to hinder the generation and transport of alkaline media into the soil [124]. Two main techniques are mainly applied in this methodology, and they involve applying conditioning agents at the electrode reservoirs [122, 125] and using ion-exchange membranes [126, 127].

2.2.6 Coupled or integrated electrochemical remediation techniques

The potential of coupling electrokinetic remediation with other remediation techniques may provide further improvement for contaminant removal and enhance their individual remediation efficiencies [90, 128]. Despite a high removal of enhancement techniques, the feasibility of such techniques is limited due to high costs, longer treatment time, and/or constraints on injecting the selected enhancement solutions into the subsurface [128]. Therefore, hybridization processes are proposed to overcome these limitations [90, 108, 128]. There are numerous opportunities for hybridization processes, and they include, but not are limited to, electrokinetic bio-barriers [4], electrokinetic (permeable) reactive barriers [129-131], electrokinetic oxidation/reduction [50, 132, 133], electrokinetic bioremediation [134-136], electrokinetic phytoremediation [137-139], electrokinetic thermal treatment [140], and electrokinetic ultra-sonication [141, 142]. Page and Page outlined other techniques that have been combined with electro remediation for further improvement of contaminant removal [108]. It should be noted, however, that these possibilities have yet to be investigated.

2.3 Electrokinetic removal of soluble salts

Since the first application in 1936, there have been some other applications of electrokinetic remediation in the removal of salts (Table 2.1).

Cho et al. effectively removed salts such as nitrate, chloride, potassium, and sodium salts from saline greenhouse soil by using electrokinetic remediation [143]. Kim et al. applied electrokinetic remediation for the removal of sodium and chloride in tidelands soil material [144]. Their observations were that as the operation period increased, the salinity of the tideland material decreased gradually and that the electrical current increased gradually with the operation time; this resulted in an increase in the total energy consumption. The results also showed complete removal of sodium and significant reduction in electrical conductivity of the tideland material to 65.5% of the initial value, but the removal efficiency of chloride was 58.5% after 10 days. Jia et al. successfully transported nitrate through soil by an electrokinetic process against the hydraulic gradient. Furthermore, they concluded that coupling electrokinetic remediation with the sludge layer brings beneficial effects of desalination (e.g., 72.2% saline removal) in a period of about 36-48 *h* experiments [145]. Cho et al. achieved significant nitrate removal efficiency (81.86 %) after 48 *h*. However, even though the electrical conductivity (EC) was above the 2.5 $dS\ m^{-1}$ benchmark suitable for cultivating crops, approximately 40% of the saline soil was restored. This was confirmed by a significant decrease in the EC with increases in operation time (i.e., 24-48 *h*) [46]. Similarly, Choi et al. could not reduce the EC to the recommended value for crop growth after 60 days though the efficiency was 80 and 60% for top and bottom, respectively. However, salt ions were removed significantly [146]. In their *in situ* experiments, they achieved 90% reduction of nitrate, sodium, and chloride [146]. Cho et al. also achieved excellent results in their attempt to remove nitrates from agricultural lands. They used voltage gradients of 1, 2, and 3 $V\ cm^{-1}$ applied for 48 and 96 *h*. The highest nitrate removal efficiencies were 80% at 48 *h* and 99% at 96 *h* [144]. Jia et al. concluded that electrokinetic remediation can effectively retain nitrates near the anode and against gravity in sandy column [147]. Lageman and Pool concluded that electrokinetic remediation can be used to remove sodium and chloride from saline water, which thus allows water to meet the water-quality standards for irrigation and drinking purposes [80]. This conclusion was drawn after they used computer simulations to deploy an electric fence as a means to intercept sodium and chloride ions at the front edge of an advancing fresh-saline water interface.

The use of electrokinetic remediation to remove salts in contaminated soils does have challenges. For instance, Kim et al. reported that during their study in which they were removing sodium and chloride, they experienced the formation of complexes with magnesium and calcium such as $[MgCl]^+$ or $[CaCl]^+$ that was associated with a lower removal of chloride [144]. These complexes had positive charges and moved towards the cathode by electromigration in the direction opposite to that of chloride migration. In addition, some chlorides form a complex with sodium as dissolved NaCl. The problem is that this complex is a non-charged species, and it cannot be migrated by an electric field, which explains why the amount of chloride removed is smaller than the amount of sodium removed. In addition, a high concentration of chloride in the anolyte solution may inhibit the removal of chloride from the tideland material because of back diffusion into the soil section from the anolyte solution [144]. Moreover, sodium is normally removed by electromigration and electroosmosis mechanisms, which act in the same direction [46, 144]. However, in the case of chloride, the major removal mechanism is electro-migration, which can be inhibited by electroosmotic flow [144]. Cho et al. experienced a problem with sulfate removal, whereby it was retarded because of precipitation with calcium and more interaction with soil particles, even though nitrate and chloride were removed completely [148]. The electrokinetic remediation method still presents evident shortcomings and some limitations. As explained in the previous section, the development of an acidic medium at the anode lowers the pH to below 2 and an alkaline medium at the cathode increases the pH to above 10; this results from the electrolysis process, which is a main feature in electrokinetic remediation [149-151], and it represents one of these shortcomings. Xu et al. introduced a sludge layer on electrokinetic remediation as an enhancing technique of saline soil remediation by using electrokinetic remediation. Through the analysis of testing results, this enhanced technology can make up the shortcoming of the late effect on anode dehydration baking (i.e., the use of a sludge layer in an electrokinetic system provides a longer term of electroosmotic flow) which moderately increases the initial current density. However, a significant increase will lead to premature cracking of the soil beside the anode, which accelerates the corrosion process and produces too much heat at the electrode) and polarity movements of water, which thereby provides current density and results in 72.2% saline removal, which is 28.4% or even higher than the desalination efficiency of other enhanced electrokinetic systems under similar testing conditions [152].

Table 2.1: Studies demonstrated the efficiency and feasibility of the EK technique for restoring salt-accumulated soils

Description	Target contaminants	Model scale	Current/Voltage applied	Electrodes material		Duration	Achieved results	Ref.
				Anode	Cathode			
Enhanced EK remediation of saline soil by sludge layer	Na^+, Cl^-, Ca^{2+}, Mg^{2+}	Lab scale	1.5-3.0 *mA/cm²* 2.0-3.3 *V/cm*	-	-	120 *h*	72% saline removal percentage	[1]
In situ pulse power EK remediation: Direct current EK regime, Pulse power EK regime	Na^+, Cl^-, Ca^{2+}, SO_4^-	Pilot scale	30 *V*	High-cast silicon iron & Fe	Fe	1 *Month*	56% EC reduction in DC-EK, 72% EC reduction in Pulse-EK, 55% EC reduction in enhanced Pulse-EK. Na^+ (32-81%), Ca^{2+} (-8%-47%)^{1}, Cl^- (66-7%). SO_4^{2-} ions was quite different depending on the test zone and conditions.	[2]
Modification of salt affected properties using EK treatments	ESP (Exchangeable Sodium Percentage) & SAR (Sodium Absorption Ratio)	Lab scale	0.5 *V/cm*	Mild Steel	Mild Steel	10-14 *days*	ESP and SAR decreased by 90%, Compressive strength increased by 100% and 200% in unenhanced and lime enhanced EK respectively	[3]
Removal of salts in greenhouse soil using Electrokinetic Process	Na^+, Cl^-, Ca^{2+}, K^+, SO_4^-, NO_3^-	Lab scale	1 *V/cm*	Platinum-coated titanium	Graphite	6, 12, 24, and 48 *h*	63.41%-81.86% NO_3^- removal efficiency for 6h and 48h respectively, 50% removal for Cl^- and SO_4^-, 40% EC reduction	[4]
Electrokinetic restoration of saline agricultural lands	Na^+, Cl^-, Ca^{2+}, K^+, $SO4^-$, NO^{3-}	Lab scale	1, 2, and 3 *V/cm*	Platinum-coated titanium	Graphite	48 and 96 *h*	EC decrements: at 48h, 40.4%, 46.1%, and 59.3% for 1, 2, and 3 *V/cm* respectively. At 96 *h*, 48.7%, 53.5% & 51.4% for 1, 2 and 3 *V/cm* respectively. NO^{3-} removal: >80% at 48 *h* and >99% at 96 *h*. Cl^- removal after 96 *h* was substantially higher than that after 48 *h*. $SO4^-$, and Ca^{2+} did not change significantly between 48 and 96 *h*	[5]
Combined electro-bio kinetics technology on nitrate removal	NO^{3-}	Lab scale	20 *V*	Titanium	Graphite	7 *days*	The concentration of NO^{3-} at anodic area of soil was higher when compared to cathode in electrokinetic system, while adding bacteria in EK (EK+bio) system; the NO^{3-} concentration was almost zero (100% removal efficiency) in all the area of soil.	[6]
In situ electrokinetic removal of nitrate from greenhouse soil: pilot test 1 (pair of electrodes were installed horizontally in the furrows), pilot test 2 (two anodes and one cathode)	NO^{3-}	Pilot scale	Test 1 : constant current ranged from (1-5 *A*) applied in 3 steps Test2: constant current 1 *A*	Iron (Fe) pipe electrode	Iron (Fe) pipe electrode	64 *days*	The NO^{3-} removal was >90% in both tests. EC reduced up to 87%. The energy consumed for the EK pilot test 1 operation was much lower than that used in the EK pilot test 2.	[7]
Hexagonal 2D Electrokinetic system	Cl^-, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^-	Pilot scale	1 *V/cm*	Stainless steel	Stainless steel	14 *days*	NO^{3-} removal was higher than chloride removal. SO_4^- removal was uniform across all layers. Mg^{2+} was higher after treatment 30% removal efficiency for K^+ & Ca^{2+}. 19% average reduction in EC. The overall removal efficiency was not sufficiently high because of the relatively short operating time.	[8]
Electrode Configuration for Electrokinetic Restoration of Greenhouse Saline Soil (one anode in the center of the cell and two cathodes at the end of the cell)	Cl^-, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^-	Lab scale	1 and 2 *V/cm*	Graphite	Pt-coated titanium	6 *days*	NO_3^- and Cl^- removal (100%). The removal of anions under 2 *V/cm* was slightly higher than those under 1 *V/cm*. SO_4^- removal was very low. K^+ (50%), Ca^{2+} and Mg^{2+} showed similar patterns. 1 *V/cm* is more efficient when taking into account both removal and energy. The higher-voltage gradient showed removal efficiency similar to that of the lower voltage gradient	[9]

Effect of Electrode Materials on Electrokinetic Reduction of Soil Salinity	Na^+, Cl^-, SO_4^-	Lab scale	4 *V/cm*	(Ti/(IrO2 + RuO2)) , Pt, Si/BDD (boron-doped diamond) , and Fe	Graphite	14 *days*	In all tests Na^+ and Cl^- removal (>97%). EC was reduced 64-74% in the tests with DSA, Pt, and Si/BDD anodes. Fe Anode tests showed higher reduction of SO_4^- concentration and resulted in higher EC reduction (≈90%) than the other anode tests. Fe anode is more suitable for restoration of SO_4^- rich saline soil than other insoluble anodes.	[10]
Ex situ pilot scale electrokinetic restoration of saline soil using pulsed current	Cl^-, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^-	Pilot scale	1 *V/cm* The system with pulsed current was on/off periodically every 15 *min*	Stainless steel	Stainless steel	9 *weeks*	Slightly less removal efficiency in the pulse power system compared with conventional DC power system. The pulse power system lowered the electrical energy consumption to 64% and effectively prevented pH changes and electrode corrosion compared with conventional DC power system.	[11]
Electrokinetic salts removal of greenhouse in field test	Na^+, Cl^-, K^+, NO_3^-, Ca_2^+, Mg^{2+}, SO_4^-	Field test	0.8 *V/cm*	High Silicon Cast Iron (HSCI) rod	Fe plate	2 *months*	90% removal effectively for (Na^+, Cl^-, NO_3^-). Ca^{2+}, Mg^{2+}, SO_4^- were not removed from the soil effectively. 73-83%. EC reduction efficiency in top soil on the average. The energy consumption was about 980 *kWh/m*^{3}, which was higher than lab scale experiment.	[12]
Pulse-enhanced electrokinetic restoration of sulfate-containing saline greenhouse soil	Na^+, Cl^-, K^+, NO_3^-, Ca_2^+, Mg^{2+}, SO_4^-	Lab scale	1 *V/cm*	Pt-coated Ti	Pt-coated Ti	28 *days*, 14 *days* for the pulse power tests	62% EC reduction efficiency in pulsed-power tests and normal power tests. The pulsed process lowered the electrical energy consumption to 50% of that of the conventional process. The frequency of on/off switching did not influence the total reduction in salinity, but the amounts of SO_4^- and Ca_2^+ removed were correlated with the on/off frequency positively and negatively, respectively.	[13]
Nitrate control by Electrokinetic in different soils	NO_3^-	Lab scale	0.5 *mA/cm*^{2}	Stainless steel	Stainless steel	9 *h*	In clayey soil, the EK effect on ion movement decreased. The loamy soil showed a slight increase in nitrate concentration near the anode. But the clayey soil showed no change. The sandy soil required the highest electrical potential difference to obtain the desired current level; loamy and clayey soils required less.	[14]
Electromigration of nitrate in sandy soil	Na^+, NO_3^-	Lab scale	(1.5, 3, 5, 10 *mA*) 30-90 *V*	Carbon, Copper, and Stainless steel	Carbon, Copper, and Stainless steel	5-24 *h* in the closed system, 12 *h* in the open system	In closed system: 60% nitrate removal is achieved at the cathode, while only 20% removal is achieved within the middle potion. Significant clean-up of Na+. The electro-kinetic process effectively concentrated and retained nitrate close to the anode.	[15]

[1] The minus sign means a final content is over its initial value.

In their experiments, an intermittent current is regarded as a way to improve energy efficiency and to decrease project costs of treatment [152]. However, it was concluded that further research on the thickness, the forms of the sludge layer, and other buffer materials instead of sludge is needed to obtain a better desalination percentage and lower costs of saline amelioration [152]. Jo et al. investigated a process of reducing the electric energy consumption in electrokinetic restoration of saline soil by applying on/off power pulsing regime. The results stated that pulse-enhanced electrokinetic restoration of saline soil can decrease energy consumption to 50% of that of the conventional process, while producing a similar decrease in salinity [153].

2.3.1 Significance and limitations of electrokinetic remediation

Advantages of electrokinetic remediation

The major advantages of the electrokinetic remediation are that (a) it can be implemented *ex-situ* [24, 128] and *in-situ* with minimal disruption [10], thereby eliminating excavation costs [154] and thus decreasing the potential onsite pollution [15], (b) it is well suited for fine grained, heterogeneous media, where other processes can be ineffective, (c) accelerated rates of contaminant extraction and transport may be achieved [10], (d) it proves to be a feasible remediation process, because of the simplicity of the procedure especially if a high degree of removal can be achieved [154], (e) it can be used for remediation of soils with low permeability (the application of traditional technologies is restricted due to the hydraulic conductivity), (f) it can reduce remediation time and lower the treatment cost (i.e., the cost is much lower compared to when using other traditional remediation technologies for treatment of per ton or cubic meter of contaminated soil), (g) its efficiency can be easily improved through hybridization with other remediation technologies [15] such as bioremediation, Fenton processes, reactive barriers, phytoextraction, etc. [24, 128], (h) can be used to extract several types of pollutants including their mixture (such as heavy metals, radionuclides, organic contaminants), it can be easily applied in both saturated or unsaturated conditions (yet in presence of water) [24, 128]. Korolev et al. observed the following advantages when using electrokinetic remediation technique over other methods for the treatment of oil contaminated soils: (a) a possibility of cleaning soils and underlying grounds directly in the rock mass down to a considerable depth; (b) high remediation degree and efficiency; (c) wide range of petroleum products that can be removed from soils by using this technique; (d) comparatively low cost of this remediation technique (compared to bioremediation and other methods); (e) relatively high rate of the remediation process [73].

Disadvantages of electrokinetic remediation

As the soil chemical fluid system is an electrochemical system [90, 155], many electrochemical reactions are occurring simultaneously during electrochemical remediation of contaminated soil [6, 90], thus rendering the remediation process more complex [63]. Moreover, the large specific area of the fine grained soil provides numerous sites for soil contaminant interactions. These interactions are soil specific, contaminant specific, dynamic, reversible, and pH dependent. The coupling of electrochemical reactions with the soil contaminant interactions makes the electrochemical remediation process extremely complex [90].

Similar to most remediation technologies, electrochemical remediation can only extract mobile contaminants from soil [6, 90, 96]. Contaminants can occur as sorbed species on soil particle surfaces, sorbed species on colloidal particulates suspended in soil pore fluid, dissolved species in soil pore fluid, or solid species as precipitates [90]. Only contaminants that occur as dissolved species in the soil pore fluid or sorbed species on colloidal particulates suspended in soil pore fluid can be extracted by most remediation technologies, and electrochemical remediation is no exception [90, 96].

Although enhanced electrokinetic remediation technique has great potential, the effectiveness of the process can be highly dependent on soil solution contaminant chemistry [18]. Changes in the surface charge of the soil particles (zeta potential) and changes in the pore fluid properties (such as dielectric constant and viscosity) influence the electroosmotic flow. In addition, the electrical gradient may not be uniform through the soil, so the electroosmotic flow is generally not uniform spatially (i.e., the electroosmosis permeability coefficient (k_{eo}) through the soil commonly varies with time), and as a result of these physicochemical changes, the electroosmotic flow may cease or even reverse in direction [18]. Furthermore, soils may be extremely variable and complex substances, both structurally and compositionally [18, 156], and contaminant chemistry, desorption, and solubilization reactions, as well as the mass transport mechanisms that occur during electrokinetic treatment may significantly complicate the process [18].

The electrolysis reactions greatly affect the remediation process because the ionic products (H^+ and OH^-) may electro-migrate and/or they may be transported by electroosmotic advection toward the oppositely charged electrode location [18]. Thus, an acidic (H^+) front of the solution may move from the anode toward the cathode, and/or an alkaline (OH^-) front of the solution may move from the cathode toward the anode. The rate of electromigration may also be affected by ionic mobility and, since hydrogen ions are smaller and have a greater mobility than hydroxide ions, the acidic front generally but not always moves faster through the soil. The reaction kinetics, or the rate of electrolysis reactions at the electrodes, may also affect the generation and movement of the hydrogen and/or hydroxide ions [18]. Incidentally, for low acid buffering clayey soils such as kaolin, the inflow of H^+ ions has the effect of causing the mineral surface charge to become more positive which by Helmholz-Smoluchowski theory, decreases the electroosmotic flow toward the cathode [18].

A study by Korolev et al. revealed that the electrokinetic remediation technique is not efficient in treating soils which have been contaminated with oil for more than six months [73]. Additionally, the very low pH environment developed during the remediation process may impact the environment adversely and render the remediated soil not readily arable afterwards [90].

Specific application limitations of electrokinetic remediation include: (a) poor solubility, (b) weak desorption capacity, as well as (c) lower removal efficiency of pollutants and longer remediation time, in the case of single EK technique [15]. Additionally, (d) in many cases reagent addition is needed in order to enhance and speed up remediation, (e) treatment efficiency strongly depends upon the characteristics of the porous medium, such as buffering capacity, mineralogy, organic matter content, saturation, salinity, type of contaminants and their speciation, (f) design and operation can be cumbersome due to complex dynamics of the electrochemical transport and chemical processes, (g) detailed laboratory investigations are needed in order to predict material behavior, optimize the operating parameters and predict the removal rates and overall cost of remediation, (h) specially developed tools for field-scale implementation, design, and testing are still lacking [24, 128].

2.3.2 Electrochemical seawater fencing approach as *in-situ* method versus *ex-situ* desalinization approach

The purpose of this research work is to find/test new solution to lessen the impact of seawater intrusion, i.e., increased salinity into fresh water coastal aquifers which are providing fresh water to people. A variety of methodologies and measures are commonly used to control the sweater intrusion. The selection and suitability of each method depends on site specific conditions. However, the key factor in any aquifer restoration measure is to maintain the freshwater level above the equivalent seawater level. Notably, the lack of a substantial surplus of freshwater source may cause any seawater control method ineffective and infeasible. Thus, mitigating seawater intrusion continues to be a challenge and a search for new solutions is still continuing. One possible solution to prevent salinization of aquifers is the use of electrokinetic barrier. The application of electrokinetic barriers along the coast to fence off the migration of sodium chloride ions is proposed in this work as a new measure to lessen the impact of salinity problem caused by seawater intrusion into aquifer. The gains may comprise water conservation and salts removal. Usually, fresh water required in the conventional seawater control measure is obtained from different sources such as but not limited to, harvesting rainfall, treatment of sewage or desalinization of saltwater. In case of desalination, there are three types of desalination solutions: Multiple Effect Distillation (MED), Reverse Osmosis (RO), and Hybrid Desalination, which couples multiple effect distillation and reverse osmosis technology [157]. Desalination technology has been around for centuries. In the Middle East for instance, people have long evaporated brackish groundwater or seawater, then condensed the vapor to produce salt free water for drinking or, in some cases, for agricultural irrigation. Worldwide about 300 million people get some freshwater from more than 17,000 desalination plants in 150 countries. Middle east countries have dominated that market out of necessity and energy availability, but with threats of freshwater shortages spreading around the world, others are rapidly joining their ranks [158]. This is confirmation of the pressure exerted on governments across the globe to ensure they provide sufficient drinking water to their citizens, which is a human right matter. It is with noting that the human right to safe drinking water was first recognized by the United Nation General Assembly and the Human Rights Council as part of binding international law in 2010 [159]. The right to water entitles everyone to have access to sufficient, safe, acceptable, physically accessible and affordable water for personal and domestic use [160]. In 2015, 844 million people still lacked even a basic drinking water service most of whom are in developing countries [161] and that number is expected to reach 1,8 billion by 2025 [162]. For instance, water availability per capita in Egypt has fallen by more than 60 percent since 1970. Egypt is more than 30 percent below the threshold for scarcity and is considered “water poor,” a condition that is expected to worsen in the years ahead. One of the proposed solutions to Egypt’s water challenges is desalination [162]. However, desalination could be a challenge for many countries that have challenges of finance, technical capabilities, and human resource to first develop the plant and also sustain its operation and maintenance. Hence the continued research for feasible alternative solutions is crucial, especially for the control of seawater intrusion without using fresh water, which is so desperately needed for human consumption, as part of the solution to control seawater intrusion. However, this requires investigating whether the control of seawater intrusion is in the end not more expensive than the production of extra freshwater using other methods that would be required to prevent seawater intrusion.

Tom Pankratz, a desalination consultant and editor of the weekly trade publication "*Water Desalination Report*" was quoted as saying that *"It seems simple enough: Take the salt out of water so it's drinkable. But it is far more complex than it appears at first glance*". It is also increasingly crucial in a world where freshwater resources are progressively strained by population growth, development, droughts, climate change and more [158]. Desalination is expensive an most modern desalination facilities use reverse osmosis, in which water is pumped at high pressure through semipermeable membranes that remove salt and other minerals [24]. It consumes a lot of electricity [162] and requires expensive infrastructure [163]. For instance, after years of struggling with drought, Australia brought six reverse osmosis plants online from 2006 to 2012, investing more than $10 billion [158]. Additionally, the new Gaza seawater desalination plant with a minimum production capacity of 150,000 $m^3 d^{-1}$ is expected to cost $694 million. The project has already received 80% of the funding from fourteen countries and various institutions, including the Islamic Development Bank and the European Union [164]. This shows how challenging it can be to secure funding for the development of a desalination plant, particularly in developing and least developed countries. Hence, electrokinetic technique was investigated to assess its feasibility as an alternative method to control seawater intrusion for many coastal regions, especially in developing countries, which are known to be faced with finance in most cases.

A potential drawback of reverse osmosis is that membranes foul with time, resulting in an increase in pressure drop and/or a decrease of permeate flux and/or increase in salt passage [165, 166]. Moreover, reverse osmosis plants release large quantities of highly concentrated salt water and other pollutants back into the seas and oceans as part of the desalination process, creating problems for marine environments[163]. A lot of desalination facilities use open ocean intakes; these are often screened, but the desalination process can still kill organisms during intake or inside the plant's treatment phases. It is therefore very critical that plans to use seawater must consider the implications for marine species [158].

Additionally, it has been reported that the energy costs of desalination plant around the world are estimated 55% of plants' total operation and maintenance costs. Furthermore, it takes most reverse osmosis plants about three to $10 kW\ h$ of energy to produce one cubic meter of freshwater from seawater [24]. Another limiting factor of using reverse osmosis is that feed water should be cleaner in order to enhance the performance of reverse osmosis. Plants in Bahrain, Japan, Saudi Arabia and China are using pre-treatment for a smoother reverse osmosis process [158]. However, this adds more cost to the operating cost of the reverse osmosis systems.

Apart from the issue of energy consumption, those using desalination are faced with the challenge of how to get rid of a lot of concentrated brine after desalination. Every two gallons a facility takes it means one gallon of drinkable water and one gallon of water that is about twice as salty as when it came in. Most plants discharge this back into the same body of water that serves as the intake source [158]. Moreover, the establishment of desalination plant and laying of associated pipelines are subjected to a process of environmental impact assessment, the decision of which takes some time to be made, thus presenting potential delay of the project long [167]. For example, the development process for the Carlsbad desalination plant in San Diego County in the USA began in 1998 and the plant came into operation in 2015. The process of obtaining all of the necessary permits and negotiating water purchase agreements with potential off takers proved to be significantly more difficult than expected. In total the plant faced 13 legal challenges, the last of which was cleared in June 2011. The majority of these lawsuits were environmentally related challenges and they resulted in lengthy administrative delays. In order to mitigate the environmental impacts of the plant's seawater intake, the developer, Poseidon agreed to establish 66 *acres* of wetlands in the San Diego Bay and to purchase carbon emission offsets [157].

A study of seawater barriers along the West Coast Basin in California concludes that injection wells have been successfully used to battle seawater intrusion in the over-drafted aquifers since the early 1950s [80, 168]. With a total length of the barriers of 27.6 *km* and an average barrier depth of 130 *m*, the barrier surface area amounts to 3,588,000 m^2. Annual costs of water injection (37.8×106 m^3) and maintenance amount to US$ 19 million. This leads to a cost of US$ 5.3 per m^2 of barrier surface area. Cost calculations of an electrokinetic fence assuming similar conditions arrive at about US$ 4 per m^2 of fence area, or a total of US$ 14.3 million, a difference of US$ 4.7 million. Moreover, in this particular case about 2/3 of the annual running costs pertain to depreciation cost of the electrokinetic fence over a period of 25 *years*, while the remaining 1/3 are electricity and maintenance costs, assuming US$ 0.10 per *kW h*. Coastal areas in general, have good wind conditions and a large part of the annual energy demand could be obtained from wind energy. Together with solar energy, which more often than not is also abundantly available, energy could for a major part be generated by sustainable sources such as wind energy and solar power [80, 169].

The unit costs of reverse osmosis processes have declined from \$5.0/m^3 in 1970 to less than \$1.0/m^3 today, however, the unit costs for seawater desalination are still above \$1.0/m^3, especially for smaller plants. However, for large capacity reverse osmosis plant the unit costs have declined to about \$0.55/m^3 [170, 171]. Moreover, the cost of brine removal still needs to be factored in. The cost of brine disposal is estimated to be 4-5% of the capital cost for a seawater reverse osmosis plant [172]. In the case of inland brine disposal, brine removal costs can be a more significant portion of desalination costs (10-25%) depending on the circumstances. Therefore, when considering options for massive implementation of desalination, environmental impacts will have to be internalized and to be minimized by proper planning [173]. Apart from the cost of process equipment and removal of brine, there is another important element to consider, transportation of water, there is a need to transport water from desalination plants to where water is needed, Zahou and Tol in their study conducted a literature review on the costs of water transport with a view to estimate the total cost of desalination and the transport of desalinated water to selected water stress cities. Transport costs range from a few cents per cubic meter to over a dollar. A 100 *m* vertical lift is about as costly as a 100 *km* horizontal transport (\$0.05–0.06/m^3). They suggest that transport makes desalinated water prohibitively expensive in highlands and continental interiors [173].

The analysis presented here provides a general trend of costs for desalination as an attempt to relate it to the cost of EK. However, it is accepted that the selection of most appropriate technology as it is the case with this research, whereby electrokinetic technique is proposed as the possible alternative method for seawater intrusion, should be based on careful in-depth study of the technology under various site specific conditions and economics, as well as local needs. As a result, further research work is needed to be conducted to gather more information that will fill the existing knowledge gap in this initial research work. The analysis of the comparisons between *ex-situ* desalination and electrokinetic remediation technique highlights the crucial aspects which should be considered when intending to use desalination to provide high quality water for controlling seawater intrusion. These aspects could be enormous and would require a lot of investment (i.e., financial and human resources) as opposed to electrokinetic technology. Additionally, electrokinetic could be effective in addressing seawater intrusion, however, full scale field application of electric fence should be implemented in order to determine the real cost at that level.

2.4 Seawater intrusion

2.4.1 Context of seawater intrusion

It is known that the global demand for freshwater is rising while the challenges for the supply of fresh water are increasing by the day. One of the threats to the availability of freshwater today is soil salinity. Soil salinity refers to the state of accumulation of soluble salts in the soil [174]. The most common soluble salts in soils are cations (e.g., sodium, potassium, and calcium) and anions (e.g., chloride, sulfate, and nitrate) [175]. Soil salinity is categorized into primary and secondary salinities. Primary salinity is mainly caused by natural processes, owing to a high salt content of the parent material or in groundwater, whereas secondary salinity occurs as a result of anthropogenic activities such as irrigation practices [176, 177], which account for about 20% of the world’s irrigated areas [178], and over extraction of groundwater, especially from coastal aquifers [179, 180]. One of the main causes of salinity in coastal areas is seawater intrusion, which is the landward incursion of seawater through subsurface movement [181].

Seawater intrusion can degrade water quality to levels that exceed acceptable drinking and irrigation water standards and endanger future water exploitation in coastal aquifers. This problem is intensified by large population growth, notably because 70% of the world population occupies coastal areas [182]. Secondary salinity seems to be taking the upper hand. Szabolcs reiterated that about 100,000 km^2 of irrigated land are abandoned each year, mainly owing to the adverse effects of secondary salinization and alkalinization [183]. However, Gupta and Abrol warned that the availability of accurate data concerning salt affected lands around the world are rather scarce [184], which thus suggests that the information should be read or used with some degree of caution. They argued that there is a lack of systematic surveys; there is a continuous change in the extent of salinization, owing to secondary salinization or seawater intrusion and the differences between countries’ approaches for detecting and classifying salt affected soils [185]. However, some valuable information regarding global salinity is available. Statistics relating to the extent of salt affected areas vary according to authors, though generally, estimates are close to 10,000,000 km^2, which represent about 7% of the earth's continental surface area or approximately 10 times the size of a country such as Venezuela or 20 times the size of France [40, 178]. In addition to these naturally salt-affected areas, about 770,000 km^2 have been salinized as a consequence of human activities, with 58% of these areas concentrated in irrigated lands [178]. On average, 20% of the world's irrigated lands are affected by salts, but in countries such as Egypt, Iran, and Argentina, this figure increases to more than 30% [178].

Various intervention measures to address the problem of salinity have been developed and implemented. Among these, electrokinetic remediation is worth special attention. This technology has been explored for many decades to understand the various aspects of soil remediation [63]. The first electrokinetic remediation configuration was used in a field trial by Puri and Anand in 1936 for the removal of sodium hydroxide from soil [65].

Following the work of Puri and Anand in 1936, many applications of electrokinetic remediation have been introduced, and they have been focused mainly on the removal of heavy metals (e.g., lead, chromium, arsenic, zinc, cadmium, copper, and mercury) [186, 187], particularly in low permeability soils and also on the remediation of groundwater at waste disposal and spill sites for which conventional methods such as pump-and-treat fail [8, 11, 21, 41, 42, 77, 187-194]. However, this shift has resulted in biased attention for research in the field of salt removal. For instance, the removal of excess amounts of soluble salts, especially in sandy soils, has not received the necessary attention. The real reason for this shift (i.e., from salt recovery to treatment of heavy metals contaminated soils) is not known to the authors, however, it can be presumed that in those early years, the issue of salt removal and recovery did not make good economic sense. The issue of salt contamination was not as serious as it is today; the issue of heavy metal contamination was considered more serious, and given that their effects were already better known, they needed immediate attention. Heavy metals in larger quantities can be dangerous [195, 196], and their accumulation in soil and plants has potential human health risks [197]. Nowadays, the problem of salinity is huge; it has never been more serious, particularly the issue of seawater intrusion with its complexity [181]. The question is, does electrokinetic remediation have a role to play in addressing the problem of salinity with respect to seawater intrusion?

2.4.2 Seawater intrusion phenomena

An aquifer is a geological formation that can store and transmit water. Usually it is connected hydraulically to other inland aquifers; a costal aquifer in particular is hydraulically connected to the sea and it is the final discharge area of the continental water system. Thus, it is considered the final stage in the natural water cycle [198, 199].

Under natural conditions in a coastal aquifer, the fresh water flows towards the sea and the saline water presses inland towards the aquifer. In the contact zone a salt-freshwater interface is shaped at the bottom of the aquifer between the fresh water and the greater dense, underlying seawater [200]. The saltwater wedge penetrates inland against the natural gradient of the freshwater table, this inland move depends on the aquifer's geometry and hydraulics properties, and, the distance of the interface penetration inland varies inversely with magnitude of the freshwater discharged into the sea. Consequently even a reduction of fresh water storage in the aquifer causes intrusion of seawater inland [200]. Thus the increase in the groundwater exploitation results in moving the interface to more inland position. Therefore, for the sweater intrusion successful management it is necessary to take into account the spatial condition and the shape of the salt-freshwater interface. Ghyben-Herzberg principle describes the position of an interface between fresh and saline water in an aquifer (Figure 2.4), they assumed that a static equilibrium exists under steady state conditions, motionless seawater and a hydrostatic pressure distribution exists between the freshwater and seawater with different densities. The hydrostatic balance can be illustrated by the U-tube shown in Figure 2.4, the pressure on each side must be equal; therefore,

$$\rho_s g h_s = \rho_f g (h_s + h_f) \tag{2.10}$$

where $\rho_s$is the saline water density, which equals to 1.025 $g\ cm^{-3}$ (2.5% heavier than freshwater), ρ_f is the fresh water density, which equals to 1.000 $g\ cm^{-3}$, g is the acceleration of gravity, h_s is the distance from the saltwater surface (mean sea level) to the interface between the fresh and saline waters h_f, is the fresh water head above the saltwater. The result is, at any distance from the sea, the depth of a stationary interface below sea level is 40 times the height of the freshwater table above sea level:

$$h_s = 40 h_f \tag{2.11}$$

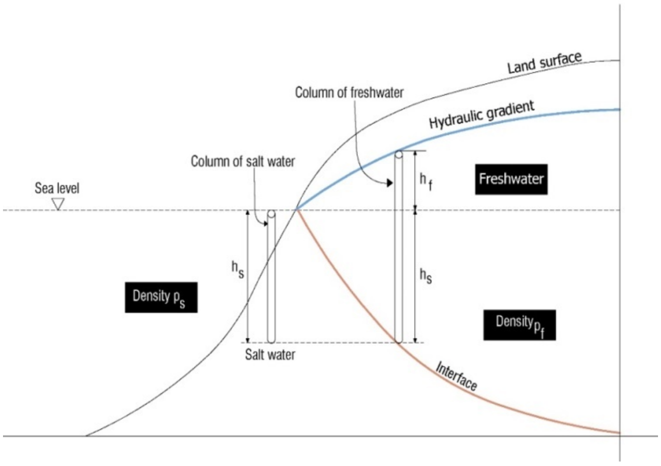


Figure 2.4: The Ghyben-Herzberg interface model [200].

A simplified model based on Dupuit assumptions [200] and Ghyben-Herzbeg approximation expresses a relationship between the total fresh water discharge to the sea and the length of seawater intrusion (interface toe, L):

For confined aquifer:

$$Q_f = \frac{B^2 k_f}{2\delta L} \tag{2.12}$$

And for unconfined aquifer:

$$Q_f = \frac{B^2 k_f}{2L}\left(\frac{1+\delta}{\delta^2}\right) - \frac{RL}{2} \tag{2.13}$$

where Q_f is the discharge of fresh water to the sea, k_f is the hydraulic conductivity, B is the saturated thickness of the aquifer, $\delta = \frac{\rho_f}{\rho_s - \rho_f}$, R is recharge coefficient (precipitation rate) onto the surface, and L is the distance of the base of the interface inland from the coast.

The equations above show clearly that as the freshwater discharge increases the extent of the seawater intrusion decreases. Thus, within a framework of coastal aquifer management, the interface toe (L) is a decision variable that is controlled by the freshwater recharge and/or pumping in coastal aquifers [200-203].

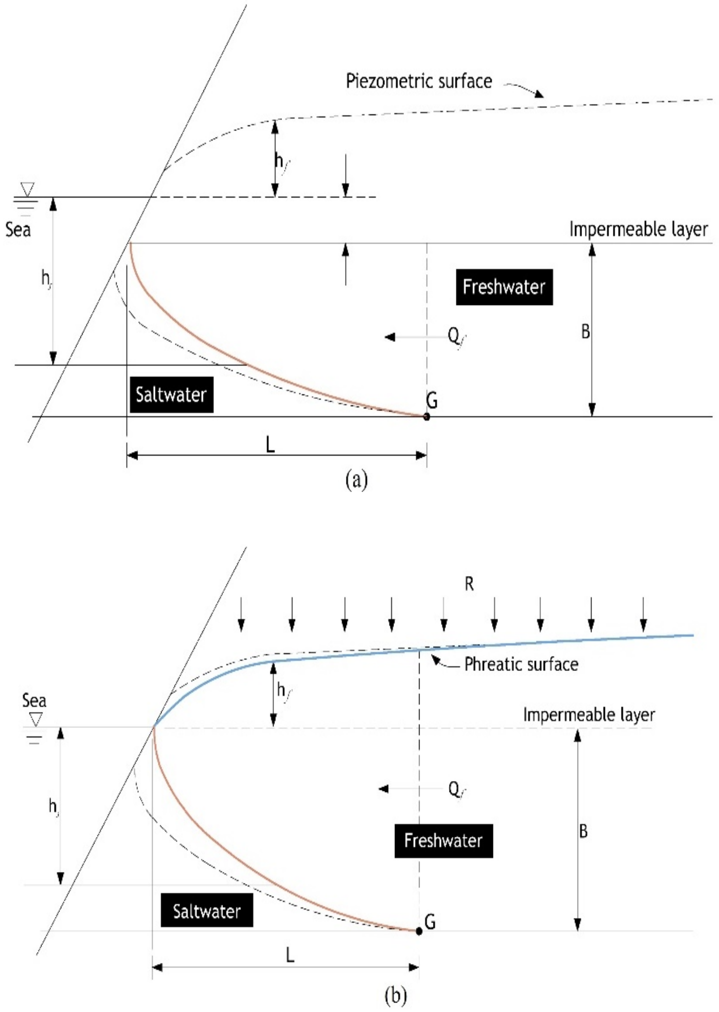


Figure 2.5: Stationary interface derived by the Dupuit (Ghyben-Herzberg) approximation, (a): confined aquifer, (b): unconfined aquifer [200].

2.4.3 Seawater intrusion management and control

Todd [202] listed various measures that are commonly used to control seawater intrusion with different principles that may include: (1) rising groundwater level by reducing groundwater extraction or altering pumping patterns; (2) maintaining the freshwater ridge along the coast above the sea level by artificial recharge; and (3) Development of barriers against seawater intrusion, different types of barriers can be considered: Positive barrier by introducing a source of water into the aquifer, negative barrier by pumping close to the coastline, thus intercepting the saltwater, and low permeability subsurface barriers. In some cases, combinations of some of these measures may be applied [202, 204, 205]. However, the overriding principle of most is to increase the volume of fresh groundwater water and / or reducing the volume of saltwater[206]. Some major classical methods are discussed in the following paragraphs.

Controlling pumping draft

This measure requires reduction in extraction or rearranging of areal pumping patterns sufficiently so that groundwater level will rise to or above sea level. Changing the location of pumping wells, typically by dispersing them in land areas, can aid in re-establishing a stronger seaward hydraulic gradient [201].

Yii-Soong Tsao built up a finite element model for the management of groundwater in the Yun-Lin basin in southern Taiwan. He concluded that in some cases modifying the distributing of well fields even without significantly reducing the extraction of groundwater could mitigate seawater intrusion. In other hand, authorities has sometimes to impose new rules to forbidding new well drilling and a large cut in groundwater extraction is urgently needed in addition to further steps and methodologies such as increasing surface water supply, and conjunctive use of groundwater and surface water however all these are easy to suggest but hard to apply [207]. An important step in any program for altering pumping patterns such as well relocation or reduction in pumping draft must be the determination of the basic water rights of the individual water users of groundwater in the basin. Because of reduction in total draft of groundwater as an expected consequence of altering the pumping pattern, it is necessary as prerequisite to initiation of this method of control is to provide a source of supplemental water supply at reasonable cost, sufficient in quantity and with suitable quality to equal reduction in ground water draft [207]. Therefore, well-prepared strategies for a sustainable exploitation of groundwater should layout a long term plan that provides direction for governmental authorities and private institutions to work in tandem to combat seawater intrusion.

Artificial recharge

Natural replenishment of aquifers is a very slow phenomenon and often is unable to maintain the groundwater reservoir with excessive exploitation of groundwater resources. Thus, artificial recharge efforts are basically aimed at augmentation of the natural movement of surface water into the groundwater reservoir through suitable civil construction techniques [208, 209].

Todd has defined artificial recharge as a process that augments the natural movement of surface water into an aquifer by several techniques [202]. A broad range of technologies and methods, have been developed and applied in various parts of the world for artificial recharge [201, 208, 210-213]. Several factors play a role in selecting the recharge method, such as, topography, geologic, soil conditions, and the availability of water to be recharged. In other circumstances, water quality and climate may be an important factor. The artificial recharge systems include water spreading; recharge wells and pumping to induce recharge from surface water bodies [201]. With reclaimed municipal wastewater, surface spreading or percolation, and direct aquifer injection are commonly used [208]. Water spreading is suitable only in unconfined aquifers and it works more effectively if there is no impervious layer between the water table and the flooded areas, recharge wells and pumping to induce recharge from surface water bodies [201]. Well injection does not retain contaminants through soil filtration. Thus, this technique is often used where aquifers are deep or where the topography or the existing land use makes surface application infusible or too expensive [208].

Artificial recharge assists in overcoming problems associated with overdrafts [214]. In coastal aquifers one of the primary goals for using artificial recharge is to control seawater intrusion. Injection fresh water through a battery of recharge wells parallel to the coastline attempt to raise the piezometric head of the fresh water aquifer. The injection wells create a pressure ridge adjacent and parallel to the coastline that is above sea level and push the saline interface down and back towards the coast [215]. A particular case of artificial recharge is the injection barrier; it aims to ensure that the piezometric level remains higher than the potential energy level of fresh water required to counter the flow from seawater into the aquifer [198].

Artificial recharge requires a reliable and sufficient source of water. For injection wells barrier, harvested rainwater and treated wastewater are commonly used. Water for recharging specially by using injection wells has to be properly treated for avoiding aquifer contamination and to ensure the effectiveness of the artificial recharge system and might be necessary to minimize the clogging effects [216, 217]. An extensive treatment for reclaimed municipal wastewater has been performed for direct injection consisting of microfiltration and reverse osmosis and ultraviolet disinfection in several California groundwater recharge projects [208, 211, 218].

Extraction barriers

The lack of surface water especially in arid and semiarid regions makes such measures inapplicable. Therefore, pumping of brackish water from the dispersion zone can mitigate the seawater intrusion. Sherif and Hamza applied a two dimensional finite element model to verify this technique, the results of the tested runs showed a reduction in the dispersion zone due to brackish water pumping [219]. Another consisting finding by Kacimov et al. Using an analytical model developed for a shallow alluvial coastal aquifer in the Batinah area of Oman [220], it has been shown that by pumping of saltwater from the intruded part of the aquifer would mitigate the seawater intrusion and can pull the dispersion zone back to the shoreline. Brackish groundwater requires carefully designed abstraction wells and a maintained balance between the recharge and discharge to guarantee a stagnant interface [219]. The location of pumping wells affects the quality of the pumped brackish water from dispersion zones, which can be used to develop green lands or to irrigate certain crops or can be used by desalination plants to reduce the production cost of water; this has been applied in desalination plants in Oman and Spain. Otherwise, if no water is needed the pumped water can be spilled back to the sea [219-221]. The main drawback of this practice is that wells may end up with pumping much more freshwater than saltwater and contaminate freshwater resources [204, 222]. Jorreto et al. recorded a fall in electrical conductivity of the water intake from the delta aquifer to the desalination plant and a partial extraction of continental freshwater, concluding that withdrawing saltwater may have important consequences on the freshwater availability upstream [223].

Impermeable subsurface barrier

A subsurface barrier can be defined as a semi-impervious or impervious wall constructed underground in coastal aquifers across the groundwater flow and parallel to the coast, generally located between the production wells and the shoreline [206]. It is used to prevent the infiltration of seawater inland and augmenting the groundwater storage capacity simultaneously. A subsurface barrier is likely more effective only in shallow formation and it should be rest on an impervious layer, and impervious barrier is normally more effective. However, some investigators including Sugio et al. address the weakness of an impervious subsurface barrier: the accumulation of pollutants upstream of the barrier creates a problem for the production wells and difficult to bleed seaward through this barrier and for this reason semi-impervious barriers should be constructed instead [224]. The construction of subsurface barrier is done by excavation of a trench backfilled usually with bentonite clay [225], or by constructing underground steel or sheet piles, the construction for such barrier being characterized by a high cost, and in the past this method was not readily available [202, 226, 227]. The cost is highly dependent on the depth of cut-off wall, length of wall and specific material availability [206]. Basri developed implicit and explicit simulation-optimization models for design of a subsurface barrier that controls seawater intrusion in order to reduce barrier construction costs, making the development of the barrier economically viable, and attractive [225].

2.5 References

1. Yeung, A.T. and J.K. Mitchell, *Coupled fluid, electrical and chemical flows in soil.* Géotechnique, 1993. **43**(1): p. 121-134.

2. Mitchell, J.K. and A.T. Yeung, *Electro-kinetic flow barriers in compacted clay.* Transportation Research Record, 1990(1288).

3. Lynch, R.J., et al., *Preliminary tests of an electrokinetic barrier to prevent heavy metal pollution of soils.* Electrochimica Acta, 2007. **52**(10): p. 3432-3440.

4. Godschalk, M.S. and R. Lageman, *Electrokinetic Biofence, remediation of VOCs with solar energy and bacteria.* Engineering Geology, 2005. **77**(3-4): p. 225-231.

5. Khodadoust, A.P., K.R. Reddy, and O. Narla, *Cyclodextrin-enhanced electrokinetic remediation of soils contaminated with 2,4-dinitrotoluene.* Journal of Environmental Engineering-Asce, 2006. **132**(9): p. 1043-1050.

6. Yeung, A.T., *Geochemical processes affecting electrochemical remediation*, in *Electrochemical remediation technologies for polluted soils, sediments and groundwater*. 2009. p. 65-94.

7. Ibanez, J.G., et al., *Laboratory experiments on electrochemical remediation of the environment - Part 3: Microscale electrokinetic processing of soils.* Journal of Chemical Education, 1998. **75**(5): p. 634-635.

8. Acar, Y.B. and A.N. Alshawabkeh, *Principles of electrokinetic remediation.* Environmental Science & Technology, 2002. **27**(13): p. 2638-2647.

9. Yeung, A.T. and S. Datla, *Fundamental formulation of electrokinetic extraction of contaminants from soil.* Canadian Geotechnical Journal, 1995. **32**(4): p. 569-583.

10. Karim, M.A., *Electrokinetics and soil decontamination: concepts and overview.* Journal of Electrochemical Science and Engineering, 2014. **4**(4): p. 297-313.

11. Probstein, R.F. and R.E. Hicks, *Removal of contaminants from soils by electric fields.* Science, 1993. **260**(5107): p. 498-503.

12. Acar, Y.B., et al., *Electrochemical processing of soils: Theory of pH gradient development by diffusion, migration, and linear convection.* Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology, 1990. **25**(6): p. 687-714.

13. Lukman, S., et al., *Geochemical modeling of trivalent chromium migration in saline-sodic soil during Lasagna process: impact on soil physicochemical properties.* ScientificWorldJournal, 2014. **2014**: p. 272794.

14. Ravina, I. and D. Zaslavsky, *Non-linear electrokinetic phenomena I: Review of literatur.* Soil Science, 1968. **106**(1): p. 60-66.

15. Huang, D.Q., et al., *Electrokinetic Remediation and Its Combined Technologies for Removal of Organic Pollutants from Contaminated Soils.* International Journal of Electrochemical Science, 2012. **7**(5): p. 4528-4544.

16. Yeung, A.T., C.-n. Hsu, and R.M. Menon, *Physicochemical soil-contaminant interactions during electrokinetic extraction.* Journal of Hazardous Materials, 1997. **55**(1-3): p. 221-237.

17. Hicks, R.E. and S. Tondorf, *Electrorestoration of metal contaminated soils.* Environ Sci Technol, 1994. **28**(12): p. 2203-10.

18. Khodadoust Amid, P., R. Reddy Krishna, and O. Narla, *Cyclodextrin-Enhanced Electrokinetic Remediation of Soils Contaminated with 2,4-Dinitrotoluene.* Journal of Environmental Engineering, 2006. **132**(9): p. 1043-1050.

19. Virkutyte, J., M. Sillanpää, and P. Latostenmaa, *Electrokinetic soil remediation — critical overview.* Science of The Total Environment, 2002. **289**(1-3): p. 97-121.

20. Giannis, A., et al., *Chelating agent-assisted electrokinetic removal of cadmium, lead and copper from contaminated soils.* Environ Pollut, 2009. **157**(12): p. 3379-86.

21. Lageman, R., W. Pool, and G. Seffinga, *Electro-reclamation in theory and practice. Forum on Innovative Hazardous Waste Treatment Technologies*. 1989, EPA/540/2-89/056.

22. Narasimhan, B. and R. Sri Ranjan, *Electrokinetic barrier to prevent subsurface contaminant migration: theoretical model development and validation.* Journal of Contaminant Hydrology, 2000. **42**(1): p. 1-17.

23. Reddy, K.R. and C. Cameselle, *Electrochemical remediation technologies for polluted soils, sediments and groundwater*. 2009: John Wiley & Sons.

24. MASI, M., *Electrokinetic remediation of heavy metal-contaminated marine sediments: experiments and modelling*. 2017, University of Pisa.

25. Alshawabkeh, A.N., A.T. Yeung, and M.R. Bricka, *Practical Aspects of In-Situ Electrokinetic Extraction.* Journal of Environmental Engineering, 1999. **125**(1): p. 27-35.

26. Yeung, A.T., C.-n. Hsu, and R.M. Menon, *EDTA-Enhanced Electrokinetic Extraction of Lead.* Journal of Geotechnical Engineering, 1996. **122**(8): p. 666-673.

27. Eykholt, G.R. and D.E. Daniel, *Impact of System Chemistry on Electroosmosis in Contaminated Soil.* Journal of Geotechnical Engineering, 1994. **120**(5): p. 797-815.

28. Hunter, R.J., *Zeta potential in colloid science: principles and applications*. Vol. 2. 2013: Academic press.

29. Shapiro, A.P. and R.F. Probstein, *Removal of contaminants from saturated clay by electroosmosis.* Environmental Science & Technology, 1993. **27**(2): p. 283-291.

30. Shang, J.Q., *Zeta potential and electroosmotic permeability of clay soils.* Canadian Geotechnical Journal, 1997. **34**(4): p. 627-631.

31. Lageman, R. and W. Pool, *Experiences With Field Applications of Electrokinetic Remediation*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater* 2009, John Wiley & Sons, Inc.

32. Lynch, R.J., *Electrokinetic Barriers for Preventing Groundwater Pollution*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*. 2009.

33. Narasimhan, B. and R.S. Ranjan, *Electrokinetic barrier to prevent subsurface contaminant migration: theoretical model development and validation.* Journal of Contaminant Hydrology, 2000. **42**(1): p. 1-17.

34. Atkins, P. and J. De Paula, *Elements of physical chemistry*. 2013: Oxford University Press, USA.

35. Eykholt, G.R., *Driving and complicating features of the electrokinetic treatment of contaminated soils*. 1992, University of Texas at Austin.

36. Reddy Krishna, R. and C. Cameselle, *Overview of Electrochemical Remediation Technologies*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*. 2009, John Wiley & Sons, Inc.

37. Bruell Clifford, J., A. Segall Burton, and T. Walsh Matthew, *Electroosomotic Removal of Gasoline Hydrocarbons and TCE From Clay*. Journal of Environmental Engineering, 1992. **118**(1): p. 68-83.

38. Casagrande, L., *Stabilization of soils by means of electro-osmosis: State of the art*. Journal of the Boston Society of Civil Engineers, 1983. **69**(2): p. 255-302.

39. Lohner Svenja, T., et al., *Coupled Electrokinetic–Bioremediation: Applied Aspects*. 2009.

40. Metternicht, G.I. and J.A. Zinck, *Remote sensing of soil salinity: potentials and constraints*. Remote Sensing of Environment, 2003. **85**(1): p. 1-20.

41. Suzuki, T., et al., *A mechanistic study of arsenate removal from artificially contaminated clay soils by electrokinetic remediation*. J Hazard Mater, 2013. **254-255**: p. 310-7.

42. Hamed, J., Y.B. Acar, and R.J. Gale, *Pb(Ii) Removal from Kaolinite by Electrokinetics*. Journal of Geotechnical Engineering-Asce, 1991. **117**(2): p. 241-271.

43. Lestan, D., C.L. Luo, and X.D. Li, *The use of chelating agents in the remediation of metal-contaminated soils: a review*. Environ Pollut, 2008. **153**(1): p. 3-13.

44. Kim, D.H., J.M. Cho, and K. Baek, *Pilot-scale ex situ electrokinetic restoration of saline greenhouse soil*. Journal of Soils and Sediments, 2011. **11**(6): p. 947-958.

45. Willis, M. and J. Haley, *Market Research Report Electrokinetic Demonstration at Naval Air Weapons Station, Point Mugu, California*. 1997, LB AND M ASSOCIATES INC LAWTON OK.

46. Cho, J.-M., et al., *Restoration of Saline Soil in Cultivated Land Using Electrokinetic Process*. Separation Science and Technology, 2009. **44**(10): p. 2371-2384.

47. Wang, J., et al., *Remediation of mercury contaminated sites - A review*. J Hazard Mater, 2012. **221-222**: p. 1-18.

48. Anderson, R., *Resource guide for electrokinetics laboratory and field processes applicable to radioactive and hazardous mixed wastes in soil and groundwater from 1992 to 1997*. 1997.

49. Acar, Y.B., H. Li, and R.J. Gale, *Phenol Removal from Kaolinite by Electrokinetics*. Journal of Geotechnical Engineering, 1992. **118**(11): p. 1837-1852.

50. Yang, G.C. and Y. Long, *Removal and degradation of phenol in a saturated flow by in-situ electrokinetic remediation and Fenton-like process*. J Hazard Mater, 1999. **69**(3): p. 259-71.

51. Thepsithar, P. and E.P.L. Roberts, *Removal of Phenol from Contaminated Kaolin Using Electrokinetically Enhanced In Situ Chemical Oxidation.* Environmental Science & Technology, 2006. **40**(19): p. 6098-6103.

52. Lima, A.T., et al., *Assessing PAH removal from clayey soil by means of electro-osmosis and electrodialysis.* Sci Total Environ, 2012. **435-436**: p. 1-6.

53. Gomes, H.I., C. Dias-Ferreira, and A.B. Ribeiro, *Electrokinetic remediation of organochlorines in soil: enhancement techniques and integration with other remediation technologies.* Chemosphere, 2012. **87**(10): p. 1077-90.

54. Polcaro, A.M., et al., *Electrokinetic removal of 2,6-dichlorophenol and diuron from kaolinite and humic acid-clay system.* J Hazard Mater, 2007. **148**(3): p. 505-12.

55. Lopez-Vizcaino, R., et al., *Electroremediation of a natural soil polluted with phenanthrene in a pilot plant.* J Hazard Mater, 2014. **265**: p. 142-50.

56. Ribeiro, A.B., et al., *Removal of organic contaminants from soils by an electrokinetic process: the case of atrazine. Experimental and modeling.* Chemosphere, 2005. **59**(9): p. 1229-39.

57. Ribeiro, A.B., E.P. Mateus, and J.-M. Rodríguez-Maroto, *Removal of organic contaminants from soils by an electrokinetic process: The case of molinate and bentazone. Experimental and modeling.* Separation and Purification Technology, 2011. **79**(2): p. 193-203.

58. Lopez-Vizcaino, R., et al., *The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment.* Separation and Purification Technology, 2012. **88**: p. 46-51.

59. Kim, G.N., et al., *Development of pilot-scale electrokinetic remediation technology for uranium removal.* Separation and Purification Technology, 2011. **80**(1): p. 67-72.

60. Agnew, K., et al., *Electrokinetic remediation of plutonium-contaminated nuclear site wastes: results from a pilot-scale on-site trial.* J Hazard Mater, 2011. **186**(2-3): p. 1405-14.

61. Kim, K.H., et al., *Electrokinetic processing for the removal of radionuclides in soils.* Separation Science and Technology, 2003. **38**(10): p. 2137-2163.

62. Kim, S.-S., S.-J. Han, and Y.-S. Cho, *Electrokinetic remediation strategy considering ground strate: A review.* Geosciences Journal, 2002. **6**(1): p. 57-75.

63. Yeung, A.T., *Milestone developments, myths, and future directions of electrokinetic remediation.* Separation and Purification Technology, 2011. **79**(2): p. 124-132.

64. Kim, W.S., et al., *In situ field scale electrokinetic remediation of multi-metals contaminated paddy soil: Influence of electrode configuration.* Electrochimica Acta, 2012. **86**: p. 89-95.

65. PURI, A.N. and B. ANAND, *Reclamation of Alkali Soils by Electrodialysis.* Soil Science, 1936. **42**(1): p. 23-28.

66. Shen, Z., et al., *Relations between sorption behavior and electrokinetic remediation effect in soils contaminated with heavy metals.* Soil Research, 2008. **46**(5): p. 485-491.

67. Reynolds, D.A., et al., *Electrokinetic migration of permanganate through low-permeability media.* Ground Water, 2008. **46**(4): p. 629-37.

68. Weng, C.-H., et al., *Laboratory-Scale Evaluation of Cr(VI) Removal from Clay by Electrokinetics Incorporated with Fe(O) Barrier.* Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 2006. **10**(3): p. 171-178.

69. Weng, C.-H. and H.-W. Tsai, *A pilot-scale test of electrokinetic remediation of Cr (VI) contaminated kaolinite incorporated with zero-valent iron.* J. Environ. Eng. Manage, 2009. **19**(6): p. 379-387.

70. Kim, B.K., et al., *Research and field experiences on electrokinetic remediation in South Korea.* Separation and Purification Technology, 2011. **79**(2): p. 116-123.

71. Kim, D.H., et al., *Ex situ pilot scale electrokinetic restoration of saline soil using pulsed current.* Separation and Purification Technology, 2013. **120**: p. 282-288.

72. Lageman, R., R.L. Clarke, and W. Pool, *Electro-reclamation, a versatile soil remediation solution.* Engineering Geology, 2005. **77**(3-4): p. 191-201.

73. Korolev, V.A., *Electrochemical soil remediation from environmental toxicants: Results and prospects.* Moscow University Geology Bulletin, 2008. **63**(1): p. 11-18.

74. Slater, J.E., D.R. Lankard, and P.J. Moreland, *Electrochemical Removal of Chlorides from Concrete Bridge Decks.* Materials Performance, 1976. **15**(11): p. 21-26.

75. Hamnett, R., *A study of the processes involved in the electro-reclamation of contaminated soils.* 1980: University of Manchester.

76. Pool, W., *A process for electroreclamation of soil material, an electric current system for application of the process, and an electrode housing for use in the electric current system*. 1989.

77. Acar, Y.B. and R.J. Gale, *Electrochemical decontamination of soils or slurries*. 1992, Google Patents.

78. Shapiro, A.P., P.C. Renaud, and R.F. Probstein, *Preliminary Studies on the Removal of Chemical-Species from Saturated Porous-Media by Electroosmosis.* Physicochemical Hydrodynamics, 1989. **11**(5-6): p. 785-802.

79. Lageman, R., *Electroreclamation. Applications in the Netherlands.* Environmental Science & Technology, 2002. **27**(13): p. 2648-2650.

80. Lageman, R. and W. Pool, *Elektrokinetische schermen tegen intrusie zout water.* H 2 O, 2011. **44**(21): p. 45.

81. Eid, N., et al., *Electro-migration of nitrate in sandy soil.* J Hazard Mater, 2000. **79**(1-2): p. 133-49.

82. Eid, N., et al., *Nitrate Electromigration in Sandy Soil in the Presence of Hydraulic Flow.* Journal of Irrigation and Drainage Engineering, 1999. **125**(1): p. 7-11.

83. Alshawabkeh, A.N., et al., *Optimization of 2-D Electrode Configuration for Electrokinetic Remediation.* Journal of Soil Contamination, 2010. **8**(6): p. 617-635.

84. Kim, D.H., et al., *Hexagonal two dimensional electrokinetic systems for restoration of saline agricultural lands: A pilot study.* Chemical Engineering Journal, 2012. **198**: p. 110-121.

85. Zhang, P., et al., *2D crossed electric field for electrokinetic remediation of chromium contaminated soil.* J Hazard Mater, 2010. **177**(1-3): p. 1126-33.

86. Méndez, E., et al., *Electrode materials a key factor to improve soil electroremediation*, in *Electrochemical Cells-New Advances in Fundamental Researches and Applications*. 2012, InTech.

87. Mendez, E., et al., *Effects of electrode material on the efficiency of hydrocarbon removal by an electrokinetic remediation process.* Electrochimica Acta, 2012. **86**: p. 148-156.

88. Ouattara, L., et al., *Electrochemical comparison of IrO2 prepared by anodic oxidation of pure iridium and IrO2 prepared by thermal decomposition of H2IrCl6 precursor solution.* Journal of Applied Electrochemistry, 2009. **39**(8): p. 1361-1367.

89. Pérez-Corona, M., et al., *Evaluation of IrO2-Ta2O5| Ti electrodes employed during the electroremediation of hydrocarbon-contaminated soil.* Sustain. Environ. Res., 2013. **23**(4): p. 279.

90. Yeung, A.T. and Y.Y. Gu, *A review on techniques to enhance electrochemical remediation of contaminated soils.* J Hazard Mater, 2011. **195**: p. 11-29.

91. Karagunduz, A., *Electrokinetic transport of chlorinated organic pesticides.* Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater, 2009: p. 235-248.

92. Mukhopadhyay, B., J. Sundquist, and R.J. Schmitz, *Removal of Cr(VI) from Cr-contaminated groundwater through electrochemical addition of Fe(II).* J Environ Manage, 2007. **82**(1): p. 66-76.

93. De Gioannis, G., et al., *Enhanced electrokinetic treatment of different marine sediments contaminated by heavy metals.* J Environ Sci Health A Tox Hazard Subst Environ Eng, 2008. **43**(8): p. 852-65.

94. Reddy, K.R. and S. Chinthamreddy, *Enhanced electrokinetic remediation of heavy metals in glacial till soils using different electrolyte solutions.* Journal of Environmental Engineering-Asce, 2004. **130**(4): p. 442-455.

95. Colacicco, A., et al., *Enhanced electrokinetic treatment of marine sediments contaminated by heavy metals and PAHs.* Chemosphere, 2010. **81**(1): p. 46-56.

96. Yeung, A.T., *Contaminant Extractability by Electrokinetics.* Environmental Engineering Science, 2006. **23**(1): p. 202-224.

97. Chuan, M.C., G.Y. Shu, and J.C. Liu, *Solubility of heavy metals in a contaminated soil: Effects of redox potential and pH.* Water, Air, and Soil Pollution, 1996. **90**(3-4): p. 543-556.

98. Reddy, K.J., L. Wang, and S.P. Gloss, *Solubility and mobility of copper, zinc and lead in acidic environments.* Plant and Soil, 1995. **171**(1): p. 53-58.

99. Acar, Y.B. and A.N. Alshawabkeh, *Electrokinetic Remediation. I: Pilot-Scale Tests with Lead-Spiked Kaolinite.* Journal of Geotechnical Engineering, 1996. **122**(3): p. 173-185.

100. Manassero, M., et al., *Coupled phenomena in environmental geotechnics*. 2013: CRC Press.

101. Al-Hamdan, A.Z. and K.R. Reddy, *Transient behavior of heavy metals in soils during electrokinetic remediation.* Chemosphere, 2008. **71**(5): p. 860-71.

102. Afshin, A., et al., *Electroosmotic phenomena in organic soils.* American Journal of Environmental Sciences, 2009. **5**(3): p. 310-314.

103. Ahmad, K., K.A. Kassim, and M.R. Taha, *Electroosmotic flows and electromigrations during electrokinetic processing of tropical residual soil.* Malaysian Journal of Civil Engineering, 2006. **18**(2): p. 74-88.

104. Almeira O, J., C.-S. Peng, and A. Abou-Shady, *Simultaneous removal of cadmium from kaolin and catholyte during soil electrokinetic remediation.* Desalination, 2012. **300**: p. 1-11.

105. Wang, H.F., N. Takematsu, and S. Ambe, *Effects of soil acidity on the uptake of trace elements in soybean and tomato plants.* Appl Radiat Isot, 2000. **52**(4): p. 803-11.

106. Marschner, B. and A.D. Noble, *Chemical and biological processes leading to the neutralisation of acidity in soil incubated with litter materials.* Soil Biology & Biochemistry, 2000. **32**(6): p. 805-813.

107. Sahoo, P.K., et al., *Influence of different forms of acidities on soil microbiological properties and enzyme activities at an acid mine drainage contaminated site.* J Hazard Mater, 2010. **179**(1-3): p. 966-75.

108. Page, M.M. and C.L. Page, *Electroremediation of contaminated soils.* Journal of Environmental Engineering-Asce, 2002. **128**(3): p. 208-219.

109. Yeung Albert, T. and Y.-Y. Gu, *Use of Chelating Agents in Electrochemical Remediation of Contaminated Soil.* 2012.

110. Li, G., et al., *Comparison of approaching and fixed anodes for avoiding the 'focusing' effect during electrokinetic remediation of chromium-contaminated soil.* Chemical Engineering Journal, 2012. **203**: p. 231-238.

111. Pazos, M., et al., *The impact of electrokinetic treatment on a loamy-sand soil properties.* Chemical Engineering Journal, 2012. **183**: p. 231-237.

112. Bassi, R., S.O. Prasher, and B.K. Simpson, *Extraction of metals from a contaminated sandy soil using citric acid.* Environmental Progress, 2000. **19**(4): p. 275-282.

113. Hanay, O., et al., *Removal of Pb from sewage sludge by electrokinetics: effect of pH and washing solution type.* Environ Technol, 2009. **30**(11): p. 1177-85.

114. Kim, G.N., et al., *An analysis of a flushing effect on the electrokinetic-flushing removal of cobalt and cesium from a soil around decommissioning site.* Separation and Purification Technology, 2008. **63**(1): p. 116-121.

115. Rajic, L.M., et al., *Behavior of zinc, nickel, copper and cadmium during the electrokinetic remediation of sediment from the Great Backa Canal (Serbia).* J Environ Sci Health A Tox Hazard Subst Environ Eng, 2010. **45**(9): p. 1134-43.

116. Doong, R.A., Y.W. Wu, and W.G. Lei, *Surfactant enhanced remediation of cadmium contaminated soils.* Water Science and Technology, 1998. **37**(8): p. 65-71.

117. Saichek, R.E. and K.R. Reddy, *Effects of system variables on surfactant enhanced electrokinetic removal of polycyclic aromatic hydrocarbons from clayey soils.* Environ Technol, 2003. **24**(4): p. 503-15.

118. Wan, J., et al., *Solubility-enhanced electrokinetic movement of hexachlorobenzene in sediments: a comparison of cosolvent and cyclodextrin.* J Hazard Mater, 2009. **166**(1): p. 221-6.

119. Li, A., K.A. Cheung, and K.R. Reddy, *Cosolvent-enhanced electrokinetic remediation of soils contaminated with phenanthrene.* Journal of Environmental Engineering-Asce, 2000. **126**(6): p. 527-533.

120. Coletta, T.F., et al., *Cation-Enhanced Removal of Lead from Kaolinite by Electrokinetics.* Journal of Environmental Engineering, 1997. **123**(12): p. 1227-1233.

121. Han, H., et al., *Electrokinetic Remediation of Soil Contaminated with Diesel Oil Using EDTA–Cosolvent Solutions.* Separation Science and Technology, 2009. **44**(10): p. 2437-2454.

122. Zhou, D.M., et al., *Electrokinetic remediation of a Cu-Zn contaminated red soil by controlling the voltage and conditioning catholyte pH.* Chemosphere, 2005. **61**(4): p. 519-27.

123. Kim, D.H., et al., *Electrokinetic remediation of fluorine-contaminated soil: conditioning of anolyte.* J Hazard Mater, 2009. **161**(1): p. 565-9.

124. Puppala, S.K., et al., *Enhanced electrokinetic remediation of high sorption capacity soil.* Journal of Hazardous Materials, 1997. **55**(1-3): p. 203-220.

125. Gidarakos, E. and A. Giannis, *Chelate Agents Enhanced Electrokinetic Remediation for Removal Cadmium and Zinc by Conditioning Catholyte pH.* Water, Air, and Soil Pollution, 2006. **172**(1-4): p. 295-312.

126. Kim, W.S., S.O. Kim, and K.W. Kim, *Enhanced electrokinetic extraction of heavy metals from soils assisted by ion exchange membranes.* J Hazard Mater, 2005. **118**(1-3): p. 93-102.

127. Shen, Z., et al., *Comparison of electrokinetic soil remediation methods using one fixed anode and approaching anodes.* Environ Pollut, 2007. **150**(2): p. 193-9.

128. Reddy Krishna, R. and C. Cameselle, *Overview of Electrochemical Remediation Technologies*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater* 2009, John Wiley & Sons, Inc.

129. Chung, H.I. and M. Lee, *A new method for remedial treatment of contaminated clayey soils by electrokinetics coupled with permeable reactive barriers.* Electrochimica Acta, 2007. **52**(10): p. 3427-3431.

130. Athmer, C.J. and S.V. Ho, *Field Studies: Organic-Contaminated Soil Remediation with Lasagna Technology*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*. 2009.

131. Weng, C.H., *Coupled electrokinetic–permeable reactive barriers.* Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater, 2009: p. 483-503.

132. Pazos, M., et al., *Remediation of contaminated marine sediment using electrokinetic–Fenton technology.* Journal of Industrial and Engineering Chemistry, 2013. **19**(3): p. 932-937.

133. Kim, S.S., J.H. Kim, and S.J. Han, *Application of the electrokinetic-Fenton process for the remediation of kaolinite contaminated with phenanthrene.* J Hazard Mater, 2005. **118**(1-3): p. 121-31.

134. Kim, S.J., et al., *Application of a new electrolyte circulation method for the ex situ electrokinetic bioremediation of a laboratory-prepared pentadecane contaminated kaolinite.* J Hazard Mater, 2005. **118**(1-3): p. 171-6.

135. Choi, J.H., et al., *Nitrate removal by electro-bioremediation technology in Korean soil.* J Hazard Mater, 2009. **168**(2-3): p. 1208-16.

136. Xu, W., et al., *A laboratory feasibility study on a new electrokinetic nutrient injection pattern and bioremediation of phenanthrene in a clayey soil.* J Hazard Mater, 2010. **184**(1-3): p. 798-804.

137. Cang, L., et al., *Effects of electrokinetic-assisted phytoremediation of a multiple-metal contaminated soil on soil metal bioavailability and uptake by Indian mustard.* Separation and Purification Technology, 2011. **79**(2): p. 246-253.

138. Cang, L., et al., *Impact of electrokinetic-assisted phytoremediation of heavy metal contaminated soil on its physicochemical properties, enzymatic and microbial activities.* Electrochimica Acta, 2012. **86**: p. 41-48.

139. Cameselle, C., R.A. Chirakkara, and K.R. Reddy, *Electrokinetic-enhanced phytoremediation of soils: status and opportunities.* Chemosphere, 2013. **93**(4): p. 626-36.

140. Smith, G.J., *Coupled Electrokinetic–Thermal Desorption.* Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater, 2009: p. 505-535.

141. Pham, T.D., et al., *Combined ultrasonication and electrokinetic remediation for persistent organic removal from contaminated kaolin.* Electrochimica Acta, 2009. **54**(5): p. 1403-1407.

142. Pham, T.D., R.A. Shrestha, and M. Sillanpaa, *Electrokinetic and Ultrasonic Treatment of Kaolin Contaminated by POPs.* Separation Science and Technology, 2009. **44**(10): p. 2410-2420.

143. Cho, J.-M., S.-Y. Park, and K. Baek, *Electrokinetic restoration of saline agricultural lands.* Journal of Applied Electrochemistry, 2010. **40**(6): p. 1085-1093.

144. Kim, K.J., et al., *Electrokinetic removal of chloride and sodium from tidelands.* Journal of Applied Electrochemistry, 2010. **40**(6): p. 1139-1144.

145. Jia, X.H., et al., *Electrokinetic control of nitrate movement in soil.* Engineering Geology, 2005. **77**(3-4): p. 273-283.

146. Choi, J.-H., et al., *Removal characteristics of salts of greenhouse in field test by in situ electrokinetic process.* Electrochimica Acta, 2012. **86**: p. 63-71.

147. Jia, X., et al., *Nitrate pollution control in different soils by electrokinetic technology.* Transactions of the Asae, 2005. **48**(4): p. 1343-1352.

148. Cho, J.-M., et al., *Electrode Configuration for Electrokinetic Restoration of Greenhouse Saline Soil.* Separation Science and Technology, 2012. **47**(11): p. 1677-1681.

149. Kornilovich, B., et al., *Enhanced electrokinetic remediation of metals-contaminated clay.* Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2005. **265**(1-3): p. 114-123.

150. Qadir, M., A. Ghafoor, and G. Murtaza, *Amelioration strategies for saline soils: a review.* Land Degradation & Development, 2000. **11**(6): p. 501-521.

151. Lee, Y.J., et al., *Electrokinetic Remediation of Saline Soil Using Pulse Power.* Environmental Engineering Science, 2013. **30**(3): p. 133-141.

152. Xu, H., et al., *An enhanced electrokinetic remediation of saline lands by sludge layer.* Journal of Food Agriculture & Environment, 2012. **10**(1): p. 709-713.

153. Jo, S.U., et al., *Pulse-enhanced electrokinetic restoration of sulfate-containing saline greenhouse soil.* Electrochimica Acta, 2012. **86**: p. 57-62.

154. Apatoczky, J.E., *The chemical enhancement of electrokinetic soil decontamination.* 1992.

155. Yeung, A.T., *Fundamental aspects of prolonged electrokinetic flows in kaolinites.* Geomechanics and Geoengineering, 2006. **1**(1): p. 13-25.

156. Mitchell, J., *Fundamentals of Soil Behavior, John Wiley and Sons, Inc., New York.* 1993.

157. Wangnick, K., *International Desalination Association IDA.* 2016, Worldwide Desalting Plants Inventory Report.

158. Bienkowski, B., *can saltwater quench our growing thirst?* 2015.

159. Nations, U. *The human right to water and sanitation. Resolution adopted by the General Assembly on 28 July 2010: A/RES/64/292. Geneva.* 2010 [cited 2018 August 18]; Available from: http://www.un.org/en/ga/search/view_doc.asp?symbol=A/RES/64/292.

160. Water, U. *Human Rights to Water and Sanitation.* 2018 [cited 2018 25 September]; Available from: http://www.unwater.org/water-facts/human-rights/.

161. (UNICEF), W.H.O.W.a.t.U.N.C.s.F. *Progress on drinking water, sanitation and hygiene.* 2017 [cited 2018 22 September]; Available from: http://www.who.int/mediacentre/news/releases/2017/launch-version-report-jmp-water-sanitation-hygiene.pdf.

162. Barron, R. *Meet the Egyptian team that may revolutionize water desalination.* 2016 [cited 2018 25 August]; Available from:

https://madamasr.com/en/2016/03/11/feature/society/meet-the-egyptian-team-that-may-revolutionize-water-desalination/.

163. Delacey, L. *Cheap, simple technique turns seawater into drinking water*. 2015 [cited 2018 20 August]; Available from: https://newatlas.com/new-desalination-method-egypt/39941/.

164. Intelligence, M.A.G.W., *Water Desalination Report*. 2018.

165. Vrouwenvelder, J.S., et al., *Biofouling of spiral-wound nanofiltration and reverse osmosis membranes: A feed spacer problem.* Water Research, 2009. **43**(3): p. 583-594.

166. Farhat, N.M., et al., *Effect of water temperature on biofouling development in reverse osmosis membrane systems.* Water Res, 2016. **103**: p. 149-159.

167. Intelligence, M.A.G.W., *Water Desalination Report*. 2009.

168. Johnson, T., *Battling seawater intrusion in the central & west coast basins.* WRD Technical Bulletin, 2007. **13**.

169. Lageman, R., *Preliminary assessment of the application of an electrokinetic ring fence for the removal of radionuclides from groundwater at fukushima daiichi nuclear power plant*. 2015.

170. Ettouney, H.M., et al., *Evaluating the economics of desalination.* Chemical Engineering Progress, 2002. **98**(12): p. 32-39.

171. Busch, M. and B. Mickols, *Economics of desalination–reducing costs by lowering energy use.* Water Wastewater Int, 2004. **19**(4): p. 18-20.

172. Hafez, A. and S. El-Manharawy, *Economics of seawater RO desalination in the Red Sea region, Egypt. Part 1. A case study.* Desalination, 2003. **153**(1): p. 335-347.

173. Zhou, Y. and R.S.J. Tol, *Evaluating the costs of desalination and water transport.* Water Resources Research, 2005. **41**(3).

174. Rengasamy, P., *World salinization with emphasis on Australia.* J Exp Bot, 2006. **57**(5): p. 1017-23.

175. Sonon, L.S., U. Saha, and D. Kissel, *Soil salinity testing, data interpretation and recommendations.* C. o. A. a. ES The University of Georgia Cooperative Extension, College of Family and Consumer Sciences, editor. University of Georgia. UG, Atlanta, Georgia, USA, 2012: p. 1-6.

176. Podmore, C., *Irrigation salinity–causes and impacts.* Primefact, 2009. **937**(1): p. 1-4.

177. CSIRO. *Salinity fact sheet*. 2010 [cited 2017; Available from: http://www.watersciencelab.com.au/assets/teacher_ref/SalinityFactsheet_CSIRO.pdf.

178. Ghassemi, F., A.J. Jakeman, and H.A. Nix, *Salinisation of land and water resources: human causes, extent, management and case studies*. 1995: CAB international.

179. Moujabber, M.E., et al., *Comparison of Different Indicators for Groundwater Contamination by Seawater Intrusion on the Lebanese Coast.* Water Resources Management, 2006. **20**(2): p. 161-180.

180. Kathijotes, N. and C. Panayiotou, *Wastewater reuse for irrigation and seawater intrusion: evaluation of salinity effects on soils in Cyprus*. Journal of Water Reuse and Desalination, 2013. **3**(4): p. 392-401.

181. Werner, A.D., et al., *Seawater intrusion processes, investigation and management: Recent advances and future challenges*. Advances in Water Resources, 2013. **51**: p. 3-26.

182. Vengosh, A., *Salinization and Saline Environments A2 - Holland, Heinrich D*, in *Treatise on Geochemistry (Second Edition)*, K.K. Turekian, Editor. 2014, Elsevier: Oxford. p. 325-378.

183. Szabolcs, I., *global problems of salt-affected soils*. Acta Agronomica Hungarica, 1987.

184. Gupta, R.K. and I.P. Abrol, *Salt-Affected Soils: Their Reclamation and Management for Crop Production*, in *Advances in Soil Science: Soil Degradation*, R. Lal and B.A. Stewart, Editors. 1990, Springer New York: New York, NY. p. 223-288.

185. Nations, F.a.A.O.o.t.U., *Advances in the assessment and monitoring of salinization and status of biosaline agriculture : report of an expert consultation held in Dubai, United Arab Emirates, 26-29 November 2007 / Food and Agriculture Organization of the United Nations*. World soil resources reports, 0532-0488 ; 104., ed. Food, et al. 2009, Rome: Food and Agriculture Organization for the United Nations.

186. Reddy, K.R., C.Y. Xu, and S. Chinthamreddy, *Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis*. J Hazard Mater, 2001. **84**(2-3): p. 279-96.

187. Mulligan, C.N., R.N. Yong, and B.F. Gibbs, *Remediation technologies for metal-contaminated soils and groundwater: an evaluation*. Engineering Geology, 2001. **60**(1-4): p. 193-207.

188. Reddy, K.R. and S. Chinthamreddy, *Effects of initial form of chromium on electrokinetic remediation in clays*. Advances in Environmental Research, 2003. **7**(2): p. 353-365.

189. Wittle, J.K. and S. Pamukcu, *Electrokinetic treatment of contaminated soils, sludges, and lagoons. Final report*. 1993, Electro-Petroleum, Inc., Wayne, PA (United States); Lehigh Univ., Bethlehem, PA (United States). Dept. of Civil Engineering.

190. Reddy, K.R., K. Maturi, and C. Cameselle, *Sequential Electrokinetic Remediation of Mixed Contaminants in Low Permeability Soils*. Journal of Environmental Engineering, 2009. **135**(10): p. 989-998.

191. Suzuki, T., et al., *EDDS-enhanced electrokinetic remediation of heavy metal-contaminated clay soils under neutral pH conditions*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014. **440**: p. 145-150.

192. Acar, Y.B., et al., *Removal of cadmium (II) from saturated kaolinite by the application of electrical current*. Géotechnique, 1994. **44**(2): p. 239-254.

193. Bruell, C.J., B.A. Segall, and M.T. Walsh, *Electroosomotic Removal of Gasoline Hydrocarbons and TCE From Clay*. Journal of Environmental Engineering, 1992. **118**(1): p. 68-83.

194. Pamukcu, S. and J.K. Wittle, *Electrokinetic Removal of Selected Heavy-Metals from Soil*. Environmental Progress, 1992. **11**(3): p. 241-250.

195. Jarup, L., *Hazards of heavy metal contamination.* Br Med Bull, 2003. **68**: p. 167-82.

196. Martin, S. and W. Griswold, *Human health effects of heavy metals.* Environmental Science and Technology briefs for citizens, 2009. **15**: p. 1-6.

197. Khan, S., et al., *Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China.* Environ Pollut, 2008. **152**(3): p. 686-92.

198. López-Geta, J.A. and J.d.D. Gómez-Gómez, *The problem of saltwater intrusion into coastal aquifers, their protection and remediation.* 2006.

199. Custodio, E., *Myths about seawater intrusion in coastal aquifers.* Groundwater and saline intrusion, 2004. **18**: p. 599-608.

200. Bear, J. and A.H.-D. Cheng, *Modeling groundwater flow and contaminant transport.* Vol. 23. 2010: Springer Science & Business Media.

201. Todd, D.K. and L.W. Mays, *Groundwater Hydrology*. 2005: Wiley.

202. Todd, D.K., *Salt-Water Intrusion and Its Control.* American Water Works Association, 1974. **66**(3): p. 180-187.

203. Scholze, O., G. Hillmer, and W. Schneider. *Protection of the groundwater resources of Metropolis CEBU (Philippines) in consideration of saltwater intrusion into the coastal aquifer*. in *17th Salt water intrusion meeting, Delft, the Netherlands*. 2002.

204. Pool, M. and J. Carrera, *Dynamics of negative hydraulic barriers to prevent seawater intrusion.* Hydrogeology Journal, 2009. **18**(1): p. 95-105.

205. Tsanis, I.K. and L.-F. Song, *Remediation of Sea Water Intrusion: A Case Study.* Groundwater Monitoring & Remediation, 2001. **21**(3): p. 152-161.

206. Allow, K.A., *The use of injection wells and a subsurface barrier in the prevention of seawater intrusion: a modelling approach.* Arabian Journal of Geosciences, 2011. **5**(5): p. 1151-1161.

207. Tsao, Y., *Simulation model for the management of groundwater in the Yun-Lin basin.* Improvements of Methods of Long Term Prediction of Variations in Groundwater Resources and Regimes Due to Human Activity, 1982: p. 333-343.

208. Asano, T. and J.A. Cotruvo, *Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations.* Water Res, 2004. **38**(8): p. 1941-51.

209. Raju, T. and R. Agashe, *Manual on artificial recharge of ground water*. 1994: Central Ground Water Board.

210. Huisman, L. and T.N. Olsthoorn, *Artificial groundwater recharge*. 1983: Pitman Advanced Publishing Program.

211. Asano, T., *Artificial recharge of groundwater*. 2016: Elsevier.

212. Dillon, P., *Management of Aquifer Recharge for Sustainability: Proceedings of the 4th International Symposium on Artificial Recharge of Groundwater, ISAR-4: Adelaide, South Australia 22-26 September 2002*. 2002: AA Balkema.

213. Aertgeerts, R. and A. Angelakis, *State of the art report: Health risks in aquifer recharge using reclaimed water.* WH Organization. Copenhagen, 2003.

214. Brown, R.F. and D.C. Signor, *Artificial Recharge - State of the Arta.* Ground Water, 1974. **12**(3): p. 152-160.

215. Luyun, R., Jr., K. Momii, and K. Nakagawa, *Effects of recharge wells and flow barriers on seawater intrusion.* Ground Water, 2011. **49**(2): p. 239-49.

216. Bouwer, H., *Artificial recharge of groundwater: hydrogeology and engineering.* Hydrogeology Journal, 2002. **10**(1): p. 121-142.

217. Baveye, P., et al., *Environmental Impact and Mechanisms of the Biological Clogging of Saturated Soils and Aquifer Materials.* Critical Reviews in Environmental Science and Technology, 1998. **28**(2): p. 123-191.

218. Asano, T. and K.L. Wassermann, *Groundwater Recharge Operations in California.* Journal - American Water Works Association, 1980. **72**(7): p. 380-385.

219. Sherif, M.M. and K.I. Hamza, *Mitigation of Seawater Intrusion by Pumping Brackish Water.* Transport in Porous Media, 2001. **43**(1): p. 29-44.

220. Kacimov, A.R., et al., *Control of sea-water intrusion by salt-water pumping: Coast of Oman.* Hydrogeology Journal, 2009. **17**(3): p. 541-558.

221. Guhl, F., et al., *Geometry and dynamics of the freshwater—seawater interface in a coastal aquifer in southeastern Spain.* Hydrological Sciences Journal, 2006. **51**(3): p. 543-555.

222. Bear, J., et al., *Seawater intrusion in coastal aquifers: concepts, methods and practices*. Vol. 14. 1999: Springer Science & Business Media.

223. Jorreto, S., et al., *The fresh water-seawater contact in coastal aquifers supporting intensive pumped seawater extractions: A case study.* Comptes Rendus Geoscience, 2009. **341**(12): p. 993-1002.

224. Sugio, S., K. Nakada, and D.W. Urish, *Subsurface Seawater Intrusion Barrier Analysis.* Journal of Hydraulic Engineering, 1987. **113**(6): p. 767-779.

225. Hasan Basri, M., *Two new methods for optimal design of subsurface barrier to control seawater intrusion.* 2001.

226. Rogoshewski, P., *Remedial action technology for waste disposal sites*. 1983, United States: Noyes Data Corp.,Park Ridge, NJ.

227. Hanson, G. and A. Nilsson, *Ground-Water Dams for Rural-Water Supplies in Developing Countries.* Ground Water, 1986. **24**(4): p. 497-506.

3 CHLORINE ELECTROCATALYSIS AND ELECTROKINETIC REMEDIATION

3.1 Introduction

Intensive research work has been carried out by many researchers across the globe in the last two decades on the feasibility of the application of electrokinetic remediation as an alternative remediation technology. However, the applications of electrokinetic remediation are still confined to laboratory scale models. Moreover, few pilot scale and field applications have been tested and/or applied despite the interesting remediation efficiency and promising results reported in literature. Literatures also reveal that most of the studies focused on the transport phenomena which occur across the soil matrix and also the physicochemical reactions as well as changes in the soil matrix which are driven by the created electrical field. As a result, no attention was paid on the reactions around the electrodes surface with a view to establish better knowledge that would enable improvement of selectivity of electrodes and thus improve the efficiency of this technology.

On the other hand, many other electrochemical industrial applications which fall within the same concept such as chlor-alkali process has been substantially improved by the enhancing and improving the selectivity of electrodes kinetics and hence the power expenditure has been also reduced. This could be also utilized also in the field of electrokinetic remediation and would play an important factor in enhancing the efficacy in terms of contaminants removal or saving energy.

It is very well known that during electrolysis of sodium chloride brine chlorine gas and sodium chlorate form two base chemicals that are being produced, which find uses in many areas of industrial chemistry [1]. Although the industrial production of these chemicals started over a century ago, there are still factors that limit the energy efficiencies of the processes. Attention has been paid to the unwanted production of oxygen gas, which decreases the charge yield by up to 5% [1]. Understanding the factors that control the rate of oxygen production requires understanding of both chemical reactions occurring in the electrolyte, as well as surface reactions occurring on the anodes [1].

The oxygen evolution side reaction (OER) which occurs in chlor-alkali and sodium chlorate production as well as during the application of electrokinetic remediation in saline media is connected to catalytic processes in the electrolyte and on the anode surface, whereby oxygen might be evolved both electrochemically and chemically through water or hypochlorite decomposition [1]. Thus, it is essential, to get a complete picture of the selectivity issue in these industrial processes, it is important to understand the compositions of both the electrolyte and the anode and the influence of other process conditions, such as current density and temperature, which affect reactions both in the bulk electrolyte and on the anode surface [1]. Thus much more focus is required to study the influence of electrode composition (more specifically anode composition) on the efficacy of electrokinetic applications in saline media.

Chlorine gas is the main chemical produced predominantly through electrolysis of sodium chloride brine at electrodes (anode). Chlorine is also the main product released when applying electrokinetic in saline media or electrolytes. Chlorine gas is used in a wide variety of applications in industry and in water treatment. During chlor-alkali production, the main side reaction in industrial electrolytic cells is the production of oxygen; which is also a typical side reaction when electrokinetic technology is applied to treat saline soil. The unwanted oxygen production could results in reducing the removal efficacy of chloride ions across the electric fence or in the application of electrokinetic in saline soil remediation. Therefore, further studies of the factors that could influence the selectivity between chlorine and oxygen production during electrokinetic application in saline soil is warranted.

The selectivity between chlorine evolution and oxygen evolution on the anode surface is related to the intrinsic selectivity potential of the material of the anode used. Here, the properties (surface structure and composition) of the anode are the determining factors [1].

Electrochemical cells using, for example, steel or activated Ni cathodes and dimensionally stable anodes (DSA, dimensionally stable anode [1-3]. DSA are mixed ruthenium-titanium oxide (RTO) coatings of rutile RuO_2 and TiO_2 deposited on Ti. Commercial DSA electrodes most often contain one or more other additional dopant materials with coatings containing varying amounts of RuO_2 and TiO_2 [1]. In these coatings, the RuO_2 and TiO_2 components form solid solutions, where Ru^{IV} and Ti^{IV} are part of the same rutile lattice [1, 4, 5]. While rutile RuO_2 has a high electronic conductivity [6], pure rutile TiO_2 is a semiconductor with a band gap of 3 *eV* [7]. Nevertheless, the mixed oxide has a high electronic conductivity, enabling its use as an electrode, as the doping with Ru^{IV} introduces new electronic states in the region of the TiO_2 band gap [8, 9]. The preparation and usage of dimensionally stable anodes was patented by Beer in a series of patents in the 1960s (Britain) and 1970s (United States) [1, 10]. The discovery of DSA has been called “one of the greatest technological breakthroughs of the past 50 *years* of electrochemistry” [11], Since then, the usage of DSAs in these processes has led to significant energy savings due to their lower potentials at industrial current densities [11, 12].

However, as the name implies, their most important advantage over previous graphite electrodes is their stability, with modern DSAs being able to operate at industrial current densities for more than 10 years [10]. The literatures state that the selectivity in the chlor-alkali and chlorate processes is not a simple concept, as it involves both direct formation of oxygen on the anode as well as oxygen resulting from bulk reactions. However, secondary reactions in the bulk and reactions involving decomposition of hypochlorous acid species on the anode are another part of the overall selectivity and are of key importance. Therefore, the study of the selectivity in these processes thus requires methods that can account for both anode reactions and bulk reactions and reaction products in both liquid and gas phase [1]. For both processes, modern experimental and theoretical methods should be used to gain a deeper understanding of the interplay between anode activity and selectivity, composition and structure. The combination of theoretical modelling and modern characterization methods is well-suited to exploring the details of heterogeneous and homogeneous (electro) catalytic reactions. These tools now allow for detailed understanding of the electronic structure of practical catalysts. The knowledge gained from studies combining theory and experiments could then be used to improve the selectivity and activity of electrodes used in chlor-alkali and sodium chlorate production. They could also be used to start exploring the details of the relatively poorly understood bulk-phase reactions, where catalytic processes are involved both in unwanted oxygen evolution reactions as well as in the formation of sodium chlorate [1]. The latter aspect is especially interesting, as an understanding of the catalysis of sodium chlorate formation could result in new ways of accelerating the reaction, with important consequences for sodium chlorate process design[7].

Karlsson et al. have published a comprehensive review on the selectivity between oxygen and chlorine evolution [1]. It was clear that the issue of selectivity between the main reactions in chlor-alkali or chlorate process and the oxygen evolving side reactions requires further study. Although the effect of several factors such as the current density are relatively well known, yet the details of the effects of process parameters, electrolyte composition, and electrode characteristics on the selectivity issue, as well as the mechanisms and relative importance of the suggested oxygen forming reactions, are still not well researched [1].

Before explaining the chlorine evolution reaction and oxygen evolution reaction, as well as the surface chemistry of the electrodes, it is important to touch on the fundamental water splitting process, the water electrolysis [13].

3.2 Water electrolysis

By applying a voltage to two electrodes immersed in an aqueous electrolyte, water can be electrochemically decomposed, evolving hydrogen at the negative pole, the cathode, and oxygen at the positive pole, the anode. During this process, protons or hydroxide ions must pass through the electrolyte to enable the electrochemical reactions at the electrodes. In order to achieve low extents of charge transport losses in electrolyzers, electrolytes with high conductivities are typically used. Such highly conductive electrolytes provide large quantities of ionic charge carriers (protons or hydroxide ions) and are thus either strong bases or acids [14]. The reaction equations in acidic and alkaline aqueous regimes are shown hereunder:

Anode reaction $$2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^- \qquad (3.1)$$

Cathode reaction $$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \qquad (3.2)$$

This is an easy or simple reaction as it involves water splitting into two chemical elements, H_2 and O_2. However, in the case where other elements are involved in the system, the system will become thermodynamically unstable and be kinetically favourable. This is the case with the electrochemical reaction of NaCl solutions at high concentrations, which mimics seawater, particularly during electrokinetic remediation, whereby three gases evolve ($H_2/Cl_2/O_2$). This process is addressed in detail in subsequent sections.

3.3 Electrochemical reactions and gas evolution of the Cl_2/O_2 systems during electrokinetic remediation

Central to the process of electrokinetic remediation is the efficient migration of anions and cations in separate directions to anodes and cathodes [15]. Hence, research studies on this topic (electrokinetic remediation) have focused mainly on the transport behavior of targeted ions in the electrolyte across the soil media towards the anodes and cathodes. These studies have however, ignored one of the significant aspects of electrokinetic technology, electrocatalytic reactions at the electrodes (anodes and cathodes). Moreover, it is important to understand different electrocatalytic reactions involved in the systems, especially whereby chlorine reaction is involved [16].

Understanding the factors that control oxygen evolution requires an understanding of the chemical reactions occurring in the electrolyte, as well as the surface reactions occurring on the anodes [1]. Moreover, the knowledge about gas-evolving electrochemical reactions is critical on the general understanding of surface science and at the same time, in being applicable for addressing real industrial problems [15]. The most important factor affecting the electrochemical reaction rate and mechanism is the adsorption interaction between reactants/reaction products and the electrode (catalyst). Additionally, the composition, structure, and dimension parameters that determine electron structure of the catalyst's active sites, adsorption conditions and the reaction kinetic characteristics are important [17].

This study focuses on the assessment of the migration of ions in the electrolyte and on the chlorine evolution reaction in the anode, solely because chlorine is the target element which should be more oxidized. This is mainly due to the fact that there is a tendency for chlorine and oxygen to compete, whenever they are in the same reaction system.

3.3.1 Chemistry of chlorine evolution reaction (CER)

The solubility of chlorine in pure water is complicated by two factors: it reacts chemically with water hydrolysing to form chloride ions (Cl^-) and hypochlorous acid (HOCl); and at relatively low pressures (near atmospheric) chlorine is an oxidant gas that is moderately soluble in water forms a hydrate ($Cl_2.8H_2O$) which separates out [18]. The chlorine evolution reaction is a two-electron transfer reaction [15]. Chlorine is produced during the electrode process via the anodic oxidation of Cl^- given by Equation (3.3). The produced molecular chlorine is according to Henry's law dissolved following the equilibrium given by Equation (3.4). The amount of dissolved chlorine responds to the partial pressure of chlorine gas above the electrolyte. Dissolved chlorine is further dis-proportionated according to Reaction (3.5). One critical aspect during the anodic Cl_2 evolution is the control of the pH value (see Equation (3.1)). The optimal pH value should be between 1 and 3 in order to avoid side reactions [15], particularly oxygen evolution [19].

$$2Cl^- \rightleftharpoons Cl_2 + 2e^- \tag{3.3}$$

$$2Cl_{2(g)} \rightleftharpoons Cl_{2(aq)} \tag{3.4}$$

$$Cl_{2(aq)} + H_2O \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)} + HOCl_{(aq)} \tag{3.5}$$

An additional importance of the control of the pH value is reflected by the intensity of oxygen evolution as a side reaction [15]. The reason for parasitic oxygen evolution as a side reaction, especially at high current densities, is because the equilibrium potential for Cl_2 evolution is 1.36 *V* at room temperature and standard conditions, which is slightly larger than the equilibrium potential for oxygen evolution, which is 1.23 *V* under the same conditions [20]. Three reaction paths have been proposed:

1- The Volmer-Heyrovsky (or Volmer-Tafel) reaction path starts with electrochemical discharging of Cl^- ions under the formation of adsorbed species on the surface and continues with electrochemical recombination. This reaction path, although accepted by many authors, may not respond to reality because of the significant impact of the pH value on the kinetics (in aqueous solution), that cannot be explained by the shown reactions (Reactions (3.6) to (3.8))[21].

$$Cl^- \rightleftharpoons Cl_{(ads)} + 2e^- \tag{3.6}$$

$$Cl_{(ads)} + Cl^- \rightarrow Cl_2 + e^- \tag{3.7}$$

$$Cl_{(ads)} + Cl_{(ads)} \rightarrow Cl_2 \tag{3.8}$$

2- A reaction path starts with Volmer's elementary step, but then continues with a reaction between the adsorbed chlorine species $Cl_{(ads)}$ and water yielding hypochloric acid that subsequently disproportionate. This reaction path includes the existence of an adsorbed species on the surface but additionally includes the influence of water and can be considered more realistic than the Volmer-Heyrovsky pathway (Equations (3.9) to (3.11)) [15].

$$Cl^- \rightleftharpoons Cl_{(ads)} + 2e^- \tag{3.9}$$

$$Cl_{(ads)} + H_2O \rightarrow HOCl + H^+ + e^- \tag{3.10}$$

$$HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O \tag{3.11}$$

3- A third reaction path starts with the anodic discharge of water, continues with reaction between Cl^- ions and the formed $OH_{(ads)}$ species, producing hypochloric acid. This reaction also includes an adsorbed species and the influence of the pH value (Equations (3.12) to (3.14)) [15].

$$H_2O \rightleftharpoons OH_{(ads)} + H^+ + e^- \tag{3.12}$$

$$Cl^- + OH_{(ads)} \rightarrow HOCl + e^- \tag{3.13}$$

$$HOCl + H^+ + Cl^- \rightleftharpoons Cl_2 + H_2O \tag{3.14}$$

3.3.2 Chemistry of oxygen evolution reaction (OER)

The oxygen evolution reaction chemistry is presented by showing the water splitting process, whereby molecular hydrogen and oxygen are generated individually at the cathode and anode, respectively. In general, the overall water splitting process can be represented as follows [22]:

$$2H_2O + Energy \rightarrow 2H_2 + O_2 \tag{3.15}$$

The oxygen evolution reaction and hydrogen evolution reaction can be described by the following two electrochemical reactions:

In alkaline solution $4OH^- \rightarrow O_2 + 2H_2O + 4e^- (V_{Anode} = 1.23V\ vs. RHE)$ (3.16)

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \quad (V_{Cathode} = 0.0V\ vs. RHE) \quad (3.17)$$

In acid solution $2H_2O \rightarrow O_2 + 4H^+ + 4e^- (V_{Anode} = 1.23V\ vs. RHE)$ (3.18)

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (V_{Cathode} = 0.0V\ vs. RHE) \quad (3.19)$$

where V_{Anode} and $V_{Cathode}$ are the equilibrium potentials for the oxygen evolution reaction and hydrogen evolution reaction, respectively.

In terms of a mechanistic analysis of the oxygen evolution reaction, a major difficulty lies in the fact that the oxygen evolution reaction is a complex process involving the transfer of four electrons [15, 22]. Since electrons are transferred one at a time the process will, by necessity, be multistep in which distinct intermediates are generated on the electrode surface. Consequently, the oxygen evolution reaction may follow any of a number of different pathways [22].

3.4 Toxicity of chlorine on soil, plants, and humans

Chlorine is one of the major products formed when applying Electrochemical fencing in media with high concentration of chloride ions. Chloride ions are converted into chlorine during electrokinetic remediation process and because of the toxicity of chlorine, it is important to highlight this aspect that will necessitate precautionary control measures when applying electrokinetic fencing which will ensure that when electrokinetic remediation is applied it does not become a dangerous method that would give rise to more serious problem than salinity itself. Moreover, chlorine is used for disinfection purposes and by highlighting its production during electrokinetic remediation processes could lead to development of measures for its recovery from the system.

Chlorine (Cl_2) occurs predominantly as Cl^- in soil and plants. It is an essential micronutrient of higher plants and participates in several physiological metabolism processes. Its functions in plant growth and development include osmotic and stomatal regulation, evolution of oxygen in photosynthesis, and disease resistance and tolerance. At adequate levels of supply, chlorine improves the yields and quality of many crops such as onions and cotton if the soils are deficient in this nutrient. When excessive, chlorine can be as a major component of salinity in soil, as well as stress and toxic to plants [23]. Natural inputs of chlorine to soils come mainly from rainwater, sea spray, dust, and air pollution. In addition, human practices, such as irrigation and fertilization, contribute significantly to chlorine deposition. The rates of chlorine deposition to soils range from 1 to >1000 $kg\ ha^{-1}$, depending on location and cultural practices [23, 24]. The negative effects could be observed in some crops when the applied dose increased to 200-400 $mg\ kg^{-1}$; for most crops the negative effects are obvious when the applied dose increases to 400-600 $mg\ kg^{-1}$; and the yields of most crops decreases rapidly when the applied chlorine exceeded 800 $mg\ kg^{-1}$ [23].

Chlorination is most widely used inexpensive and effective chemical process for multiple applications, such as the deactivation of pathogens such as *Escherichia coli*, *Rotavirus*, *Salmonella*, and *Shigella*, *adenoviruses* and *Pseudomonas aeruginosa* species in drinking water, swimming pool water and wastewater [25]. Water plays an important role in the maintenance of human health; therefore, its consumption should be safe, easily accessible, adequate in quantity, and free from contamination [26, 27]. The disinfecting property of chlorine in the water is based on the oxidizing power of the free oxygen atoms and on chlorine substitution reactions [28]. However, chlorination is the only active technique used all over the world for disinfection in which chlorine byproducts generates trihalomethanes (THM’s; mainly chloroform) and halo acetic acids (HAA’s), with smaller amounts of haloaldehydes, haloacetonitriles (HAN’s) and haloketones (HK’s) and these often cannot be identified and degraded [27]. Long-term risks of consuming chlorinated water include excessive free radical formation, which accelerates aging, increases vulnerability to genetic mutation and cancer development, hinders cholesterol metabolism, and promotes hardening of arteries. Furthermore, excess free radicals created by chlorinated water also generate dangerous toxins in the body which have been directly linked to liver malfunction, and weakening of the immune system [29]. Chlorine also destroys antioxidant vitamin E, which is needed to counteract excess oxysterols/free radicals for cardiac and anti-cancer protection [29].

3.5 Influence of electrode selectivity on oxygen evolution reaction and chlorine evolution reaction, and its relevance to electrokinetic seawater fencing.

Selectivity of electrode material is one of the significant aspects of electrochemical analysis and surface chemistry, particularly during chlorine evolution. The field of surface functionalization is a multi-faceted one. Researchers want to modify surfaces for rather opposite purposes: either they want to make a surface more reactive (and often selectively reactive towards a particular molecule or class of molecules) or they want to render it completely unreactive [30].

When subjecting a sodium chloride solution (which mimics sea water) to electrochemical processes, as in the electrokinetic technique, sodium ions and hydroxyl ions form sodium hydroxide at the cathode and create the alkaline electrolyzed oxidized water [31, 32]. Simultaneously, acidic electrolyzed oxidized water is generated at the anode to form chlorine (Cl_2), hypochlorite ions (OCl^-), hypochlorous acid (HOCl) and hydrochloric acid (HCl) and gaseous oxygen (O_2) [31, 32]. During electrochemical reactions, cations do not contribute to the established potential difference because according to a general assumption, cations (e.g., Na^+ ions) have a stable solvation sphere which can be removed only by polarization at the cathode [15].

The equilibrium potential for Cl_2 evolution is 1.36 *V* at room temperature and standard conditions, which is slightly larger than the equilibrium potential for oxygen evolution, which is 1.23 *V* under the same conditions [13]. This means that under chlorine evolution the simultaneous evolution of oxygen tends to occur as a parasitic side reaction, especially at high current densities. However, depending on the employed catalyst, oxygen evolution usually requires a somewhat larger over potential than chlorine evolution[13]. So a higher oxygen evolution potential and a lower chlorine evolution potential of the electrode are needed in order to acquire a higher chlorine evolution efficiency [33].

There is a variety of abundant, cheap and non-noble metals which are suitable as catalyst materials [34]. Anodic reactions on the other hand receive more attention, simply due to the fact that these reactions proceed at oxidized and reconstructed surfaces, which differ substantially from the open circuit conditions both in the case of chlorine evolution reaction and oxygen evolution reaction [15]. The most active anode catalysts in chlorine production industry are usually based on RuO_2, however, RuO_2 is barely stable at the high potentials. Resultantly, RuO_2 is mixed with IrO_2 and additives such as TiO_2 and SnO_2, in order to improve the stability [13]. Unfortunately, RuO_2 is known to be a good catalyst for oxygen evolution as well as for chlorine evolution. This suggests an overlap of the activity volcanoes for the two reactions, and it has in fact been suggested that high catalytic activity for chlorine evolution is fundamentally linked with high oxygen evolution activity[13, 35]. These aspects would be directly related to the behavior of anodic reaction under the application of electrochemical treatment to control seawater intrusion, or when applying electrokinetic remediation in saline groundwater aquifers, whereby oxygen is produced and competes with chlorine for dominance in the saline water.

In the case of oxygen evolution reaction, platinum group transition metals are being preferred because they are the only moderately stable and active catalysts for oxygen evolution. Moreover, they are scarce and costly [36]. This then limits the amount of the precious metal catalysts that can be technically used. As a result, some nanostructured catalysts have been used to increase the surface area [37]. However, in the case of chlorine evolution, the dominant anode material used is the dimensionally stable anode (DSA), Ti coated by a mixed oxide of RuO_2 and TiO_2 [1].

The oxygen evolution current efficiencies behavior by [1] is illustrated in Figure 3.1.

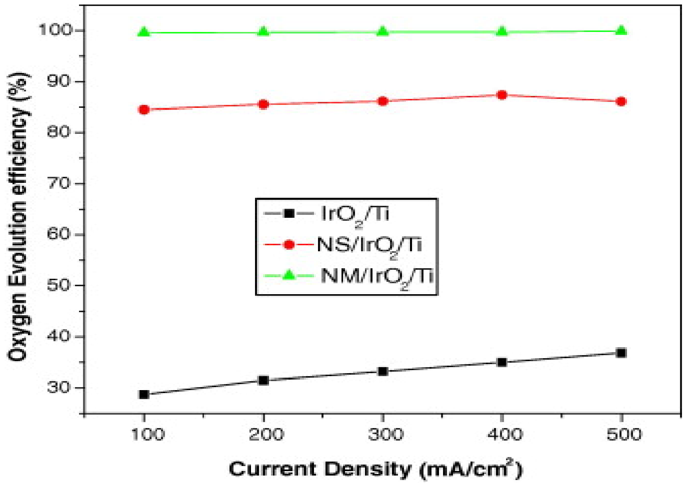


Figure 3.1: Oxygen evolution current efficiency of various electrodes as a function of current density in 0.5 *M* NaCl and pH 8.3, at 30 ℃. Three different electrodes were utilized: Iridium oxide-coated titanium electrodes (IrO_2/Ti); Nafion solution coated IrO_2/Ti electrode ($NS/IrO_2/Ti$); and Nafion membrane coated IrO_2/Ti electrode ($NM/IrO_2/Ti$) [1].

The general overview of the oxygen evolution efficiency behavior in Figure 3.1 basically shows the synergistic effects of multi-component catalyst systems in enhancing oxygen evolution reaction catalytic activity. The analysis of Figure 3.1 points out that oxygen evolution current efficiency for the IrO_2/Ti electrode increases marginally to just below 40% with increase in current density. However, a different behavior was reflected when NS/IrO_2/Ti electrode and the NM/IrO_2/Ti electrode were utilized. Their oxygen evolution current efficiency was about 85% and 100%, respectively. Moreover, current density did not play any significant role in the achievement of these respective efficiencies.

The electrokinetically enhanced remediation process is fairly simple to implement and operate, but the fundamental reactions that govern the remediation method are complex. An adequate knowledge of the contaminant transport mechanisms and the physical, chemical, and electrochemical processes is essential in order to optimize system performance [38]. Furthermore, the fundamental knowledge of the electrocatalytic reaction (e.g., the impact of the electrode material on the rate of the electrode reaction) is of utmost importance for improving the reaction efficiency [39] as well as electrokinetic remediation. In particular, controlling selectivity, while reducing the energy consumption of economically important reaction processes for the purpose of chemical energy conversion or industrial synthesis of chemicals, is of high importance, particularly in electrochemical technologies such as brine electrolysis where the chemical reaction is driven by electricity [11, 39].

Furthermore, the understanding of electrocatalytic gas evolving reactions, especially a delicate situation whereby during chlorine evolution reaction, oxygen evolution reaction is a side reaction which needs to be minimized or even completely eliminated [40] would have a significant influence in high salinity removal by the electrokinetic process, especially energy efficiency. In this instance, selectivity is a major concern due to the fact that activation of water is a source of an additional oxidation of the transition metal oxides used as catalysts and the main pathway for degradation of the catalyst layer [39, 41]. The influence of the structure and reaction of electrodes, especially the dimensionally stable anodes (DSA) in either binary or ternary oxides, and their related synergistic effects in enhancing chlorine evolution reaction and/or oxygen evolution reaction catalytic activity have a direct bearing on the choice of electrode materials for the improvement of stability, activity or selectivity during chlorine evolution reaction and/or oxygen evolution reaction. This is very much important since both oxygen evolution reaction and chlorine evolution reaction can occur during anodic polarization (at potentials above 1.05 V) in a concentrated aqueous solution of NaCl [40]. This is significant considering the fact that an important factor in the removal of contaminants during electrokinetic remediation is the transport of the acid front developed by the anode reaction. Moreover, contaminant transport and removal by electrokinetic are dependent on several factors including electrode reactions, pH and surface chemistry of the soil, equilibrium chemistry of the aqueous system, electrochemical properties of the contaminants and hydrological properties of the soil medium [42].

More importantly, understanding electrocatalytic reactions would assist in the identification of conditions that are favorable for electrokinetic remediation. For instance, conditions that would ensure the enhancement of bioremediation, which is favorable for remediation of hot spots or source areas, and the development of reactive electrochemical barriers, particularly for the treatment of contaminated groundwater plumes [43], which includes saline water due to seawater intrusion.

Notably, catalytic reactions have a direct link with some of the fundamental parameters being evaluated during electrokinetic remediation, which include electrode requirements, effectiveness of electric field distribution, remediation time, energy expenditure, pH, and electrical conductivity [44, 45]. Understanding the chemistry of chlorine evolution reaction and oxygen in general and the electrodes performance in particular could contribute towards an improved understanding of the behavior of metal ions during electrokinetic treatment, which would resultantly be useful in predicting and enhancing the efficacy of the electrokinetic process. Therefore enhancing the selectivity of the electrodes instead of the electrolyte (or soil matrix) could be a new enhancement methodology that would not only influence the removal efficiency and make electrokinetic a more feasible remediation technique but also make it a dual process, whereby chlorine that is produced as a by-product at the surface of the electrodes is put to a good economic use. However, the economic feasibility would have to be conducted first, but it could be considered.

3.6 References

1. Karlsson, R.K.B. and A. Cornell, *Selectivity between Oxygen and Chlorine Evolution in the Chlor-Alkali and Chlorate Processes*. Chemical Reviews, 2016. **116**(5): p. 2982-3028.

2. Vogt, H., et al., *Chlorine Oxides and Chlorine Oxygen Acids*. 2010.

3. Ullmann, F., et al., *Ullmann's encyclopedia of industrial chemistry*. 5th, completely rev. ed. ed. 1985, Weinheim, Federal Republic of Germany ;: VCH.

4. Hine, F., M. Yasuda, and T. Yoshida, *Studies on the Oxide-Coated Metal Anodes for Chlor-Alkali Cells*. Journal of The Electrochemical Society, 1977. **124**(4): p. 500-505.

5. Gerrard, W.A. and B.C.H. Steele, *Microstructural investigations on mixed RuO2-TiO2 coatings*. Journal of Applied Electrochemistry, 1978. **8**(5): p. 417-425.

6. Over, H., *Surface Chemistry of Ruthenium Dioxide in Heterogeneous Catalysis and Electrocatalysis: From Fundamental to Applied Research*. Chemical Reviews, 2012. **112**(6): p. 3356-3426.

7. Kavan, L., et al., *Electrochemical and Photoelectrochemical Investigation of Single-Crystal Anatase*. Journal of the American Chemical Society, 1996. **118**(28): p. 6716-6723.

8. Glassford, K.M. and J.R. Chelikowsky, *Electronic structure ofTiO2:Ru*. Physical Review B, 1993. **47**(19): p. 12550-12553.

9. García-Mota, M., et al., *Electronic Origin of the Surface Reactivity of Transition-Metal-Doped TiO2(110)*. The Journal of Physical Chemistry C, 2012. **117**(1): p. 460-465.

10. Hayfield, P., *Development of the noble metal/oxide coated titanium electrode*. Platinum metals review, 1998. **42**(2): p. 46-55.

11. Trasatti, S., *Electrocatalysis: understanding the success of DSA®*. Electrochimica Acta, 2000. **45**(15): p. 2377-2385.

12. Duby, P., *The history of progress in dimensionally stable anodes*. Jom, 1993. **45**(3): p. 41-43.

13. Hansen, H.A., et al., *Electrochemical chlorine evolution at rutile oxide (110) surfaces*. Physical Chemistry Chemical Physics, 2010. **12**(1): p. 283-290.

14. Schalenbach, M., et al., *Acidic or alkaline? Towards a new perspective on the efficiency of water electrolysis*. Journal of The Electrochemical Society, 2016. **163**(11): p. F3197-F3208.

15. Zeradjanin Aleksandar, R., et al., *Role of Water in the Chlorine Evolution Reaction at RuO2-Based Electrodes—Understanding Electrocatalysis as a Resonance Phenomenon*. ChemSusChem, 2012. **5**(10): p. 1897-1904.

16. Bockeris, J.M. and A.S. Huq, *The mechanism of the electrolytic evolution of oxygen on platinum*. Proc. R. Soc. Lond. A, 1956. **237**(1209): p. 277-296.

17. Tarasevich, M.R. and O.V. Korchagin, *Electrocatalysis and pH (a review)*. Russian Journal of Electrochemistry, 2013. **49**(7): p. 600-618.

18. Gevantman, L., *Solubility of selected gases in water.* Nitric oxide (NO), 2000. **308**(3.348): p. 10-4.

19. Tahir, M., et al., *Electrocatalytic oxygen evolution reaction for energy conversion and storage: A comprehensive review.* Nano Energy, 2017. **37**: p. 136-157.

20. Hansen, H.A., et al., *Electrochemical chlorine evolution at rutile oxide (110) surfaces.* Phys Chem Chem Phys, 2010. **12**(1): p. 283-290.

21. Zeradjanin, A.R., *Efficiency of electrocatalytic gas evolution on transition metal-oxides.* 2012.

22. Doyle, R.L. and M.E.G. Lyons, *The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design*, in *Photoelectrochemical Solar Fuel Production: From Basic Principles to Advanced Devices*, S. Giménez and J. Bisquert, Editors. 2016, Springer International Publishing: Cham. p. 41-104.

23. Chen, W., et al., *Chlorine Nutrition of Higher Plants: Progress and Perspectives.* Journal of Plant Nutrition, 2010. **33**(7): p. 943-952.

24. White, P.J. and M.R. Broadley, *Chloride in Soils and its Uptake and Movement within the Plant: A Review.* Annals of Botany, 2001. **88**(6): p. 967-988.

25. Kitajima, M., et al., *Chlorine inactivation of human norovirus, murine norovirus and poliovirus in drinking water.* Letters in Applied Microbiology, 2010. **51**(1): p. 119-121.

26. Barot, J. *Water security: Life-giving, Life-saving.* in *Regional Health Forum*. 2007.

27. Botlagunta, M., B. Js, and P. Mathi, *Water chlorination and its relevance to human health.* Asian J Pharm Clin Res, 2015. **8**(1): p. 20-24.

28. Ge, F., L. Zhu, and H. Chen, *Effects of pH on the chlorination process of phenols in drinking water.* J Hazard Mater, 2006. **133**(1-3): p. 99-105.

29. Hattersley, J.G., *The negative health effects of chlorine.* Journal of Orthomolecular medicine, 2000. **15**(2): p. 89-95.

30. Bardini, L., *Oxygen: problems and solutions in electrochemistry*. 2013, alma.

31. Hsu, S.-Y., *Effects of flow rate, temperature and salt concentration on chemical and physical properties of electrolyzed oxidizing water.* Journal of Food Engineering, 2005. **66**(2): p. 171-176.

32. Hsu, G.-S.W., C.-W. Hsia, and S.-Y. Hsu, *Effects of electrode settings on chlorine generation efficiency of electrolyzing seawater.* Journal of Food and Drug Analysis, 2015. **23**(4): p. 729-734.

33. Shao, D., et al., *High-performance Ti/Sb–SnO2/Pb3O4 electrodes for chlorine evolution: Preparation and characteristics.* Journal of Hazardous Materials, 2014. **267**: p. 238-244.

34. Gerken, J.B., et al., *Electrochemical water oxidation with cobalt-based electrocatalysts from pH 0-14: the thermodynamic basis for catalyst structure, stability, and activity.* J Am Chem Soc, 2011. **133**(36): p. 14431-42.

35. Trasatti, S., *Electrocatalysis in the anodic evolution of oxygen and chlorine.* Electrochimica Acta, 1984. **29**(11): p. 1503-1512.

36. McCrory, C.C., et al., *Benchmarking hydrogen evolving reaction and oxygen evolving reaction electrocatalysts for solar water splitting devices.* Journal of the American Chemical Society, 2015. **137**(13): p. 4347-4357.

37. Baldizzone, C., et al., *Stability of Dealloyed Porous Pt/Ni Nanoparticles.* ACS Catalysis, 2015. **5**(9): p. 5000-5007.

38. Saichek, R.E. and K.R. Reddy, *Surfactant-enhanced electrokinetic remediation of polycyclic aromatic hydrocarbons in heterogeneous subsurface environments.* Journal of Environmental Engineering and Science, 2005. **4**(5): p. 327-339.

39. Zeradjanin, A.R., et al., *Rational design of the electrode morphology for oxygen evolution - enhancing the performance for catalytic water oxidation.* RSC Advances, 2014. **4**(19): p. 9579-9587.

40. Zeradjanin, A.R., et al., *On the faradaic selectivity and the role of surface inhomogeneity during the chlorine evolution reaction on ternary Ti-Ru-Ir mixed metal oxide electrocatalysts.* Physical Chemistry Chemical Physics, 2014. **16**(27): p. 13741-13747.

41. Martelli, G.N., R. Ornelas, and G. Faita, *Deactivation mechanisms of oxygen evolving anodes at high current densities.* Electrochimica Acta, 1994. **39**(11): p. 1551-1558.

42. Alshawabkeh, A.N. and Y.B. Acar, *Removal of contaminants from soils by electrokinetics: A theoretical treatise.* Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology, 1992. **27**(7): p. 1835-1861.

43. Alshawabkeh, A.N., *Electrokinetic Soil Remediation: Challenges and Opportunities.* Separation Science and Technology, 2009. **44**(10): p. 2171-2187.

44. Alshawabkeh, A.N., et al., *Optimization of 2-D Electrode Configuration for Electrokinetic Remediation.* Journal of Soil Contamination, 1999. **8**(6): p. 617-635.

45. Chen, X.J., et al., *Enhancing electrokinetic remediation of cadmium- contaminated soils with stepwise moving anode method.* J Environ Sci Health A Tox Hazard Subst Environ Eng, 2006. **41**(11): p. 2517-30.

4 EXPERIMENTAL SETUP AND METHODS

4.1 Introduction

Laboratory experiments were carried out in order to determine the feasibility of using the electrokinetic technology to control seawater intrusion and reduce salinity in soil and groundwater. To achieve this goal, the experimental work was divided into two parts: (1) batch experiments; and (2) bench scale electrokinetic extraction experiments.

The batch experiments provided a basic understanding on properties of soil particles and on the interactions between sand and the spiked salts ions under different conditions. The scope of the batch experiments included: (1) salts recovery tests, which were performed using different extracts at variable soil to water ratios and evaluated the recovery rate; (2) conducting acid/base buffer capacity to examine the resistance of the specimen to various pH values under strong acid and strong base conditions.

The bench scale experiments were done by applying a constant DC voltage in a constant mode to remove high concentrations of soluble salts in sandy soil. The objectives of the electrokinetic extraction experiments were: (1) to assess the physicochemical reactions that occur simultaneously during the electrokinetic fencing process, with a view to develop an understanding of the phenomena that occur during the process; (2) to evaluate the performance of electrokinetic or electromigration fencing in reducing soluble salts in sandy soil pore fluid with the purpose of gathering knowledge of how the technology can best remove salts in high concentration solutions from the system,

(3) to identify parameters that would enhance the removal efficiency of the process in high conductive media caused by high salts contents.

In this chapter, the procedures of each test performed in this study are presented. Furthermore, the properties of the sand soil used and the details of the apparatus used to perform electrokinetic extraction experiments are also presented.

4.2 Material and methods

4.2.1 Electrokinetic experimental apparatus

Several apparatuses of various shapes, sizes, and materials have been developed by individual researchers to study the electrokinetic remediation process and as such, different parameters are being used for different purposes. More importantly, these apparatuses have been developed to satisfy particular research goals [1-7]. Therefore, no standard apparatus exists to investigate effects of various parameters on the efficiency of electrokinetic extraction of contaminants from soils [4]. Some apparatuses allow extraction of pore fluid from the specimen and reservoir fluid during the experiment to determine the distribution of contaminant in the specimen as a function of time. However, insertion of sampling probes may disturb the fluid and contaminant flow pattern, and may also cause the removal of a significantly large volume of pore fluid to generate an unnecessary hydraulic gradient in the specimen. Unwanted ions introduced by the sampling probe may also affect the electrical conductivity of the specimen and, subsequently, the voltage distribution in the specimen. Preferential sorption of selected chemicals by the filter at the tip of the sampling probe may adversely affect the quality of the sampled pore fluid. Despite these challenges, electrokinetic remediation has proven successful in soil remediation.

A major difference in the configuration of laboratory electrokinetic columns is the electrodes configuration and arrangement. Most of the existing columns use a four electrode arrays arrangement as one configuration or a two electrodes arrays arrangement as another configuration [4].

In this Ph.D. thesis, the four electrodes arrays arrangement configuration was followed. Two outer electrodes (i.e., active electrodes) were used as used as current electrodes (feeder). In addition, two inner electrodes (i.e., passive electrodes) were used as voltage measurements electrodes. The active and passive electrodes were separated by the electrolyte solution. The passive electrodes were located in direct contact with the specimen edges. These passive electrodes regulate the voltage applied at the active electrodes and hold it constant across the specimen during the experiment, thus, they provide proper monitoring for the potential distribution across the specimen [4, 8]. More importantly, this configuration allows accurate measurements independently for the energy consumed in the reservoir and in the specimen during the electrokinetic treatment process [4]. Moreover, it monitors the transition resistance which may occur between the soil as well as within the anode and cathode reservoirs [8]. However, this configuration fails to represent field conditions adequately [4].

On the other hand, using the two electrode configuration does not provide a proper monitoring of the potential distribution across the specimen and hence fails to explain the effect of the reservoir conditioning on the efficiency of the electrokinetic extraction [4]. Additionally, this configuration can consume excessive electrical power in the electrolyte reservoirs depending on the chemistry of the electrolytes, thus rendering the voltage gradient across the specimen too small to be effective [4].

Some researchers have performed constant current experiments in the past. Their common observation was that, as the resistance of the specimen increases as a function of time, due to the removal of conductive contaminants and possibly a decrease in the degree of saturation, the power consumption also increases, provided that the current passing through the specimen is maintained constant. In some cases, the experiments had to be terminated prematurely as the power demand exceeded the capacity of the power supply. In some instances, excessive heat was generated, which could cause adverse effects such as desiccation or cracking in the specimen. Moreover, it is difficult to interpret results obtained from constant current experiments quantitatively because the driving force for fluid and the migration of the contaminant is the voltage gradient.

In addition to the different electrodes configurations in developing the electrokinetic column, researchers applied two different approaches in carrying the electrokinetic experiments, whether performing constant current experiments [9-14] or constant voltage experiments [15-18].

A constant current condition is used to keep the net rate of the electrolysis reaction constant during the experiments and to minimize complications arising from boundary conditions [19]. However, the application of a constant voltage gradient helps to interpret the results from the experiments quantitatively as it is the driving force for the migration mechanisms [4].

Electrokinetic cell

The electrokinetic extraction column consists of three major parts, namely the cylindrical soil cell and two sided flanges (Figure 4.1).

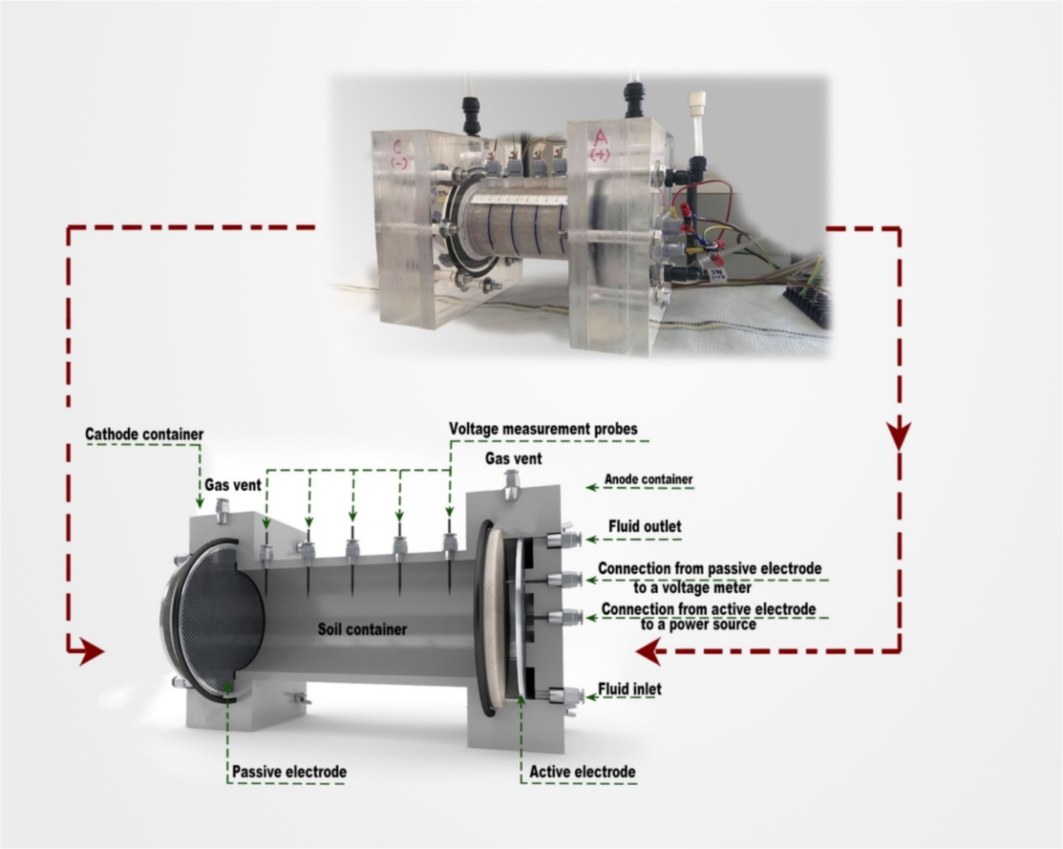


Figure 4.1: Electrokinetic extraction column.

The cylindrical soil cell accommodates the sand sample. It is made of a transparent plexiglas and has an inside diameter of 7.5 *cm* and a length of 15.3 *cm*. The cell has five ports installed along the longitudinal axis of the cell in order to provide access for the installation of stainless steel voltage measurement probes during the electrokinetic extraction experiment. This cell is connected to two flanges, the anode compartments on one end, and the cathode compartment on the opposite end. Additionally, the cell is designed to be positioned horizontally in order to eliminate the effects of gravity induced hydraulic flow. Each compartment houses two electrodes (i.e., active and passive) and the electrolyte solutions. This is in addition to a filter paper and a perforated plate at the soil sample end face. This configuration would prevent soil particles from migrating into the electrolyte reservoirs. The electrolyte reservoir is equipped with a gas vent, which is located at the highest point of the reservoirs. The electrodes are made of an iridium oxide coated titanium grid. These electrodes are inert; therefore, they did not react or participate in the chemical reactions during the electrokinetic remediation process.

The electrical circuit was designed to maintain a constant voltage across the soil specimen during experimentation. The distribution of voltage across the specimen as well as along the length of the specimen at the measurements probes were measured as a function of time. The measurement probes were made of the same material of the electrodes. The flow rate of electric charges (i.e., electrical current), which was passing through the specimen, was determined by *Ohm's* Law and measured as a function of time. The external resistance was connected through the electrical circuit. All the measurements of voltage and current were recorded continuously by a computerized data acquisition unit from National Instrument supported with graphical programming software (LabVIEW). The HP 6645A Agilent programmable 200W Power Supply (120V/1.5A) was used to supply the desired constant voltage gradient across the sample. A schematic monograph of the electrokinetic test setup used in this study is shown in Figure 4.2.

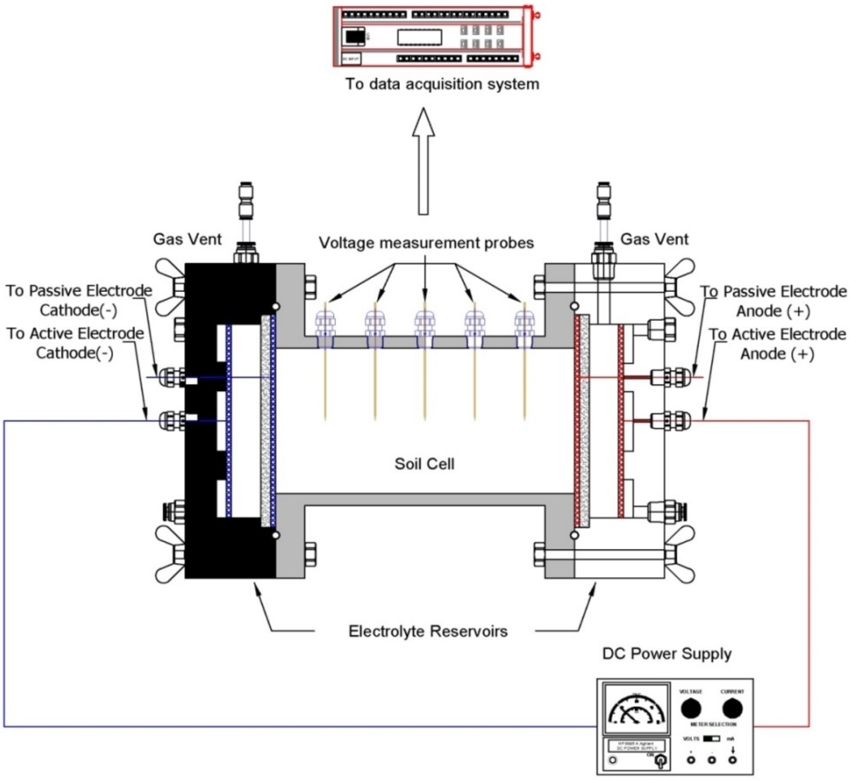


Figure 4.2: Electrokinetic experimental setup scheme.

Soil media (Silica sand)

The sand used to conduct the experiments was purchased from US Silica. This model soil is a naturally rounded silica sand of nearly pure quartz (Silica content > 98%), which is being mined around Ottawa, Illinois area. In order to avoid additional and difficult controllable geochemical reactions such as adsorption/desorption processes, and to create known basic conditions, all experiments were conducted with this model soil. Furthermore, the sand was relatively free from impurities and was having water content lower than 0.1%. The constituent grains of this sand are uncrushed and therefore rounded. Chemical and physical characteristics of the sand are presented below in Table 4.1 and the granulometric data are shown in Table 4.2.

Table 4.1: Characteristics of US Silica Sand.

Property	Unit	Value
Chemical Analysis		
Silica (SiO_2)	%	98.2
Iron Oxide (Fe_2O_3)	%	0.14
Aluminium Oxide (Al_2O_3)	%	0.49
Titanium Dioxide (TiO_2)	%	0.02
Potassium Oxide (K_2O) content	%	0.21
Calcium Oxide (CaO)	%	0.02
Sodium Oxide (Na_2O)	%	0.06
Magnesium Oxide (MgO)	%	0.01
Physical Characteristics		
Particles density	g/cm^3	2.65
Bulk density	g/cm^3	1.6 -1.8
pH		6.5-7.2

Table 4.2: Granulometric data of US Silica Sand Graded.

US SIEVE	Percent retained (%)	Percent passing (%)	ASTM Specification (%)
#16	0.0	100	100
#30	0.3	99.7	96 to 100
#40	30.3	69.4	65 to 75
#50	44.8	24.6	20 to30
#100	24.6	0	0 to 4
PAN	0.0	-	-
Total	100.0	-	-

Model solution (Salinized water)

Seawater is not uniformly saline throughout the world, however, the vast majority of seawater has a salinity of between 3.1% to 4%, with an average of 3.5%. In real values, this means that every *kilogram* (roughly one *litter* by volume) of seawater has approximately 35 *grams* of dissolved salts, and the average density of seawater at the surface is 1.025 *kg* l^{-1}. Sodium (Na^+) and chloride (Cl^-) ions make approximately 86% of the total dissolved salts in seawater, becoming the dominating salts.

The other most abundant ions are sulfate (SO_4^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and potassium (K^+). By weight these ions represent about 99 % of all sea salts.

Two salinized water models were used in the electrokinetic extractions experiments. In the first model only sodium chloride (NaCl) with 3.5% concentration was used to represent the salinity concentration of seawater. The solution was prepared by dissolving 35 *grams* of crystalline/certified ACS reagent grade sodium chloride (NaCl) supplied by Fisher Chemical in one liter of Milli-Q deionized water.

The second model solution was prepared by using a simulated sea salt mix containing elements found in natural seawater in quantities greater than 0.0004%. The salt mix was provided by Lake Product Company LLC. The salt meets the updated standard ASTM D 1141-98 (2013) [20]. The compositions of the salt mix are presented in Table 4.3. The second model solution was prepared by dissolving 41.953 *grams* of sea salts in 1 *liter* of Milli-Q deionized water.

Table 4.3: The compositions of the sea salt mix.

Composition	Of Sea Salt mix (%)	Of Substitute Ocean Water solution	(*g/l*)
NaCl	58.490	NaCl	24.53
$MgCl_2.6H_2O$	26.460	$MgCl_2$	5.2
Na_2S0_4	9.750	Na_2S0_4	4.09
$CaCl_2$	2.765	$CaCl_2$	1.16
KCl	1.645	KCl	0.695
$NaHCO_3$	0.477	$NaHCO_3$	0.201
KBr	0.238	KBr	0.101
H_3BO_3	0.071	H_3BO_3	0.027
$SrCl_2.6H_2O$	0.095	$SrCl_2$	0.025
NaF	0.007	NaF	0.003
		Total	36.032

4.3 Batch experiments

4.3.1 Assessment of different soil to water ratios (SP, 1:2, 1:5) in saline soil.

It is essential for this study to determine the soil salinity with a reliable and yet relatively easy method. This batch experiment was carried out to assess the possibilities of measuring electrical conductivity as well as ion concentrations in the extracts of different soil to water ratios, (SP, 1:2, 1:5), and to compare them with those measured in saturated paste extract.

Unlike the saturated paste extract method, the extraction methods of different soil to water ratios do not attempt to simulate natural soil conditions. Due to the consistency in the amount of water used and objective nature of the method, the extraction methods of different soil water ratios can reduce the difficulties in sample preparation and reproducibility often encountered in the saturated paste extract method [21]. Ion concentrations and electrical conductivities of the extracts of different soil water ratios are typically lower than those of saturated paste extracts as a result of the increased dilution effect. Despite the differences in the results among these methods, analyzing soil salinity samples using extraction methods of different soil to water ratios shows simplicity and reduced time investments, and they are mainly useful when the objectives are to evaluate the relative changes rather than the absolute solute content. The results showed that a correlation exists between values measured in saturated paste extracts and in extracts of different soil to water ratios for electrical conductivity and ion concentrations. Based on the results, it was concluded that extracts of (1:2) or (1:5) soil to water ratios can be used to estimate saturated paste electrical conductivity and ion concentrations of soils. Therefore, (1:5) soil to water ratio was selected in this study.

Preparation and analysis of extracts

The procedures followed in this study to prepare the extracts (SP, 1:2 and 1:5) were similar to the procedures done by Sonmez et al. [22], and the results were compared with the results from Ozcan at al. [23], which are reported by Sonmez et al. However, the main difference was in the used soil samples, in Sonmez et al. they used natural soil collected from the field which contains 88% sand, 4.36% Silt, and 6.92% clay, while the sand used in this study was silica sand of nearly pure quartz (Silica content > 98%) mined by US Silica. Thus, soil texture is different and geochemical reactions such as adsorption/desorption were assumed not have a pronounce influence in the sand used in this study. Moreover, a difference was also in preparing the main sample for further analysis with different soil to water extracts, in their study the samples have different mass and saturated with different salinity levels chosen according to the range of salinity level given by Soil Survey Staff (1951). The saline water was prepared using by adding the various amounts of NaCl, KCl, and $CaCl_2$. Each level of artificially salinized soil was replicated three times. Having saturated the soils for one month, the soils are air dried, ground and sieved (2 *mm* sieve). In this study, the sand was artificially salinized with only NaCl and salinity levels were (0.01, 0.1, 0.3, 0.6, and 1 *M*), the sand sample was saturated for one week.

Saline water was prepared by adding different amounts of NaCl into Milli-Q deionized water to obtain concentrations for different levels of salinity. The salinity levels ranged from 0.01 *M* to 1 *M*. Each level of artificially salinized soil was replicated three times.

Saturated paste extracts were prepared by adding salinized water to approximately 120 *g* sand sample and the pastes were stirred until it reached a condition of complete saturation. The saturated pastes were allowed to reach equilibrium over 24 *h*. The extracts obtained by vacuum were filtered using a Whatman #42 filter and analysed for Na^+, Cl^-, electrical conductivity, and pH.

Suspensions of (1:2) soil to water ratio were prepared by adding 40 *ml* of salinized water to 20 *g* of sand soil sample. These suspensions were shaken for 24 *hours* inside plastic bottles. The extracts obtained from the suspensions were filtered using a Whatman #42 filter and then analyzed using the same methods applied on the saturated paste extracts.

Suspensions of (1:5) soil to water ratio were prepared by adding 100 *ml* of salinized water to 20 *g* of sand soil sample. These suspensions were shaken for 24 *hours* inside the bottles. The extracts obtained from the suspensions were filtered using a Whatman #42 filter and then analyzed using the same methods applied on the saturated paste extracts.

pH measurements

There are various techniques for soil pH measurement, which vary according to the solution used and the soil-to-solution ratio. Soil pH is commonly measured in a salt solution either 0.01 *M* $CaC1_2$ or 1 *M* KCl concentration because it is less affected by soil electrolyte concentration and moreover, it provides a more consistent measurement [24]. Alternatively, soil pH could also be measured in water, the pH difference between measurements in water and $CaCl_2$ is related to the soil solution electrolyte concentration. The soil pH in this study was measured in water using a (1:5) soil to water mixture after shaking for 2 *hours*. The measurement was conducted using the pH electrode InLab Expert Pro-ISM (Mettler Toledo SevenCompact S-220). Before the pH was measured, the instrument was calibrated at various pH values, ranging from 4.01- 7.01- 10.01, which were based on a standard solution.

Measurement of electrical conductivity

The electrical conductivity of the specimen was measured the conductivity of the soil pores fluid, using the Thermo-Scientific Orion Star A212 Benchtop Conductivity Meter and Orion DuraProbe 4-Electrode Conductivity Cells. The same procedures that were followed when assessing the samples extract regarding the pH measurements or ion concentration were also followed in the preparation for the electrical conductivity measurements. Thus the conductivity of the soil pores solution was measured in 1:5 soils to water extracts after shaking for 2 *hours*. A three point calibration was performed using Thermo Scientific Orion: 100 $\mu S\ cm^{-1}$, 1413 $\mu S\ cm^{-1}$, and/or 12.9 $\mu S\ cm^{-1}$ conductivity standards.

Acid/Base buffer capacity test

An acid/base buffer capacity test is important to understand how the soil pH would vary in an electrokinetic extraction experiment. It measures the resistance of the system to pH change upon addition of an acid and/or base. The components of the soil that contribute to the buffer capacity are weak acids such as carbonic acid, silicic acid and organic matter; some hydrolyzable cations such as aluminum and iron; and clay minerals, which have sorption sites available for sorption of H^+/OH^- in the solution phase [25]. The amount of acid /base added to the soil sample is plotted against the pH to generate a titration curve. The slope of the curve at each specific pH gives the buffer capacity of the system at that pH. In this study, a strong acid (1 *M* NHO_3 and a strong base 1 *M* NaOH were used for the titration of the soil samples. The 1 *M* HNO_3 was prepared by diluting a concentrated HNO_3 solution, whereas 1 *M* NaOH was prepared from dissolving NaOH salt in Milli-Q deionized water.

Twenty soil suspension samples of (1:5) soil to water ratio were prepared by adding 100 *ml* of deionized water to 20 g of sand soil. Different quantities of acid or base were added to each tube. The samples were then shaken for 24 *hours*. The final pH values of the samples ranged between 2 to 12. When the target pH values had not been reached, an additional acid or base was added to the samples. The measurements were conducted using the pH electrode InLab Expert Pro-ISM (Mettler Toledo SevenCompact S-220), after calibration based on standard solutions with a pH range of 4.01-7.01- 10.01.

4.4 Bench scale electrokinetic experiments

4.4.1 Specimen preparation and experimental protocol

In preparation for the bench scale experiments, a predetermined procedure was followed to prepare a homogeneous and saturated specimen of equally distributed initial salt concentration for the electrokinetic extraction experiment. The sand sample was weighed before being loaded into the soil cell. The cell, which was placed vertically, was first filled with a known predetermined volume and concentrations of salt solution, the selected volume of the spiking solution guaranteed a fully saturated sand column with an initial gravimetric water content ranging between 0.18 to 0.20 and a porosity of around 0.3. Then the sand sample was slowly poured into the tube to displace the solution. In this way, the air in the soil was removed, avoiding spurious electrical resistance that could be triggered by air bubbles inside the tube. Then the glass filter papers (Whatman Grade GF/C) were placed on the soil and the electrolytes flanges were assembled. Furthermore, the cell was placed horizontally and the electrolyte reservoirs were filled with deionized water in a very low and at similar flow rate simultaneously in both sides of the electrolytes reservoirs. This procedure was necessary in order to avoid unintentionally created convection pressure, which may lead to the movement of the dissolved ions to only one side of the column. The deionized water used as electrolyte solution will cause a dilution of the initial salt concentration in the sand column because the readily dissolved ions will diffuse due to the concentration difference towards the electrolytes reservoirs. However, this dilution will bring the concentration to a more reliable value such that it would be measured inland at the saltwater interface between the fresh groundwater and seawater.

The glass filter paper was selected for its chemical resistivity to chlorine reactions at the anode compartment. Another type of filter paper would be damaged or dissolved during the chlorine evolution process causing the sand to pour out of the column when running the experiment. It was noticed that after several test trials, and in order to guarantee a homogeneous distribution of the salts constituents in the column, it was important to allow the column to equilibrate over a period of at least 48 *hours*.

Three main series of experiments were carried out. The first experiment was a control test experiment. This was essential to evaluate the initial conditions of the column, and to use this information as a baseline for comparison between the results of the experiments before and after applying the electrical potential. In the second series of experiments, a salinized solution containing only sodium chloride ions as a model solution was assessed. The idea here was to eliminate the complexity of the system as much as possible in order to better understand the process. Another reason is that these two elements make up the majority of the ions composition in seawater as mentioned previously. The last sets of experiments were carried out using the salinized solution model, which contained the actual sea salts and other elements in addition to sodium and chloride ions. The second and third sets of experiments were carried out under different operation conditions such as running time and applied voltages. Table 4.4 gives an overview of the different experimental series carried out in the bench scale electrokinetic cells. Notably, in these experiments, sand is used and the ions are artificially spiked into the sand, for which it is expected that soil removal is probably not as difficult as it would be in real contaminated soils. Natural soils usually contain fine particles such as clay particles, which have a high surface area, causing a larger retention time for dissolved species. The chemical and physical characterizations of the soils and solutions used in the experiments have been described in the previous sections (Sec. 3.2.2 and 3.2.3). Moreover, all the tests were carried out in triplets in order to obtain reproducible data.

Table 4.4: Experimental operation conditions and initial parameters' values.

	Model solution Concentration *gram/liter*	**Applied voltage** **(*V/cm*)**	**Duration** **(*h*)**	**Electrolyte**
Control experiments series	35.065	-	48	DI-water
NaCl experiments series	35.065	0.5	24	DI-water
	35.065	0.5	72	DI-water
	35.065	0.5	168	DI-water
	-	0.5	24	DI-water
Sea salts experiments series	36.032	0.5	24	DI-water
	36.032	0.5	72	DI-water

At the end of the experiments, the sand was extruded from the soil cell and divided into 5 equal segments. Each segment was sectioned into several parts, which were used to carry out the measurements of different parameters. The following parameters were determined: water content distribution, pH distribution, electrical conductivity distribution, as well as anions and cations concentration distribution. The electrical conductivity and pH were determined following the protocols mentioned previously. Samples for elements analysis were also done following the 1:5 soils to water suspension ratio. In the sodium chloride experiments series, deionized water was used as extraction solution and additionally, ions were measured using a Mettler- Toledo seven compact pH/Ion bench meter SC S200-K with Ion combination ISE probes for both chloride and sodium concentrations. In the case of sea salts experiments, Ion chromatography was used, and so were anions such as chloride and sulphate, using a Dionex ICS-5000 system. The separation is achieved using a Thermo Scientific™ Dionex™ IonPac™ AS20 analytical column and Dionex IonPac AG20 and a hydroxide eluent, which can be electrolytically generated using a Thermo Scientific Dionex EGC Potassium Hydroxide (KOH) Eluent Generator Cartridge. Before the analyses were done, several measurements attempts were carried out for a known concentration of chloride and sulfate in order to optimize the operating conditions and to ensure peak separations for the two elements, chloride, and sulfate. Cations in the sea salts experiments were extracted with 1 *N* Ammonium acetate extraction solution at pH 7.0 and analyzed using an Agilent 240 AA Atomic Absorption Spectrometer from Agilent Technologies.

4.5 References

1. J., H., A. Y., and G. R., *Pb(II) Removal from Kaolinite by Electrokinetics.* Journal of Geotechnical Engineering, 1991. **117**(2): p. 241-271.

2. Mitchell, J.K. and A.T. Yeung, *Electro-kinetic flow barriers in compacted clay.* Transportation Research Record, 1990(1288).

3. Eykholt, G.a.D., D., *Impact of System Chemistry on Electroosmosis in Contaminated Soil.* Journal of Geotechnical Engineering, 1994. **120**(5): p. 797-815.

4. Yeung, A., et al., *Design, fabrication, and assembly of an apparatus for electrokinetic remediation studies.* ASTM geotechnical testing journal, 1997. **20**(2): p. 199-210.

5. Yeung, A.T., S.M. Sadek, and J.K. Mitchell, *New apparatus for the evaluation of electro-kinetic processes in hazardous waste management.* Geotechnical Testing Journal, 1992. **15**(3): p. 207-216.

6. Pamukcu, S., L.I. Khan, and H.-Y. Fang, *Zinc detoxification of soils by electro-osmosis.* Transportation Research Record, 1990(1288).

7. Pamukcu, S. and J.K. Wittle, *Electrokinetic removal of selected heavy metals from soil.* Environmental Progress, 1992. **11**(3): p. 241-250.

8. Gregolec, G., *Fundamental Aspects of Using Electric Fences for Groundwater Remediation.* 2008, Verlag nicht ermittelbar.

9. Villen-Guzman, M., et al., *Acid Enhanced Electrokinetic Remediation of a Contaminated Soil using Constant Current Density: Strong vs. Weak Acid.* Separation Science and Technology, 2014. **49**(10): p. 1461-1468.

10. Lindgren, E.R., E.D. Mattson, and M.W. Kozak, *Electrokinetic Remediation of Unsaturated Soils*, in *Emerging Technologies in Hazardous Waste Management IV.* 1994, American Chemical Society. p. 33-50.

11. Sruthy, O. and S. Jayalekshmi, *Electrokinetic remediation of heavy metal contaminated soil.* Int J Struct & Civil Engg, 2014. **3**.

12. Hamed, J., Acar, Y., and Gale, R., *Pb(II) Removal from Kaolinite by Electrokinetics.* Journal of Geotechnical Engineering, 1991. **117**(2): p. 241-271.

13. Villen-Guzman, M., et al., *Scaling-up the acid-enhanced electrokinetic remediation of a real contaminated soil.* Electrochimica Acta, 2015. **181**: p. 139-145.

14. Iannelli, R., et al., *Electrokinetic remediation of metal-polluted marine sediments: experimental investigation for plant design.* Electrochimica Acta, 2015. **181**: p. 146-159.

15. Suzuki, T., et al., *EDDS-enhanced electrokinetic remediation of heavy metal-contaminated clay soils under neutral pH conditions.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014. **440**: p. 145-150.

16. Almeira O, J., C.-S. Peng, and A. Abou-Shady, *Simultaneous removal of cadmium from kaolin and catholyte during soil electrokinetic remediation.* Desalination, 2012. **300**: p. 1-11.

17. Altaee, A., R. Smith, and S. Mikhalovsky, *The feasibility of decontamination of reduced saline sediments from copper using the electrokinetic process.* Journal of Environmental Management, 2008. **88**(4): p. 1611-1618.

18. Peng, G. and G. Tian, *Using electrode electrolytes to enhance electrokinetic removal of heavy metals from electroplating sludge.* Chemical Engineering Journal, 2010. **165**(2): p. 388-394.

19. Acar, Y.B. and R.J. Gale, *Electrochemical decontamination of soils or slurries*. 1992, Google Patents.

20. ASTM (D1141-98), *Standard Practice for the Preparation of Substitute Ocean Water*, in *American Society for Testing and Materials, USA*. 2013, ASTM International, West Conshohocken, PA.

21. RICHARDS, L.A., *Diagnosis and Improvement of Saline and Alkali Soils.* Soil Science, 1954. **78**(2): p. 154.

22. Sonmez, S., et al., *Assessment of different soil to water ratios (1:1, 1:2.5, 1:5) in soil salinity studies.* Geoderma, 2008. **144**(1): p. 361-369.

23. Ozcan, H., et al. *Comparison of four soil salinity extraction methods*. in *Proc. 18th International Soil Meeting on Soil Sustaining Life on Earth, Managing Soil and Technology, Sanlıurfa, TR*. 2006.

24. Minasny, B., et al., *Models relating soil pH measurements in water and calcium chloride that incorporate electrolyte concentration.* European Journal of Soil Science, 2011. **62**(5): p. 728-732.

25. Cang, D., J. Wang, and X. Zhang, *"Acidity."Physical chemistry of paddy soils.* 1985: p. 131 -156.

5 RESULTS AND DISCUSSION

5.1 Batch experiments

5.1.1 Introduction

This section presents the results of the batch experiments and these results are also being discussed. These experiments include: (1) salts (NaCl) recovery test performed to evaluate the efficiencies of different extracts at different soil to water ratios; and (2) Examining acid/base buffer capacity to determine the resistance conducting acid/base buffer capacity to examine the resistance of the specimen to pH variation when these specimen were brought into contact with a strong acid or a strong base.

5.1.2 Assessment of ion concentrations at saturation paste, (1:2) and (1:5) ratios

The ion concentrations of saturated paste versus different soil to water ratios for sandy soil are presented in Figure 5.1. From the figure it is observed that, the relationship of the ions concentrations extracted from the saturated paste and from different soil to water ratios was significantly correlated. Additionally, when the soil water extract ratio was 1:2, the coefficient of determination (r^2) was 0.9984 for sodium and 0.9998 for chloride. Moreover, when the soil water extract ratio was 1:5, the coefficient of determination (r^2) was 0.9992 for sodium and 0.9991 for chloride. In this study, the results showed that highly significant correlation exists between values measured in saturated paste extracts and in extracts of different soil to water ratios for electrical conductivity and ion concentrations. Similar to Ozcan et al. and Sonmez et al., the slopes of the regression lines are increasing, depending on soil to water ratios and the influence of dilution effect. An increasing slope for the regression equations of electrical conductivity and ion concentrations was observed when soil to water ratio is increased from (1:2) to (1:5), indicating that additional water causes dilution. In a sense, the slopes of the regression equations can be considered as a dilution ratio. The slopes of the regression lines for (1:2) and (1:5) soil to water ratios including the intercept found in this study are higher than those given by Ozcan et al. The differences in results can be attributed to soil clay content, clay type as well as artificially salinized soils used in this study.

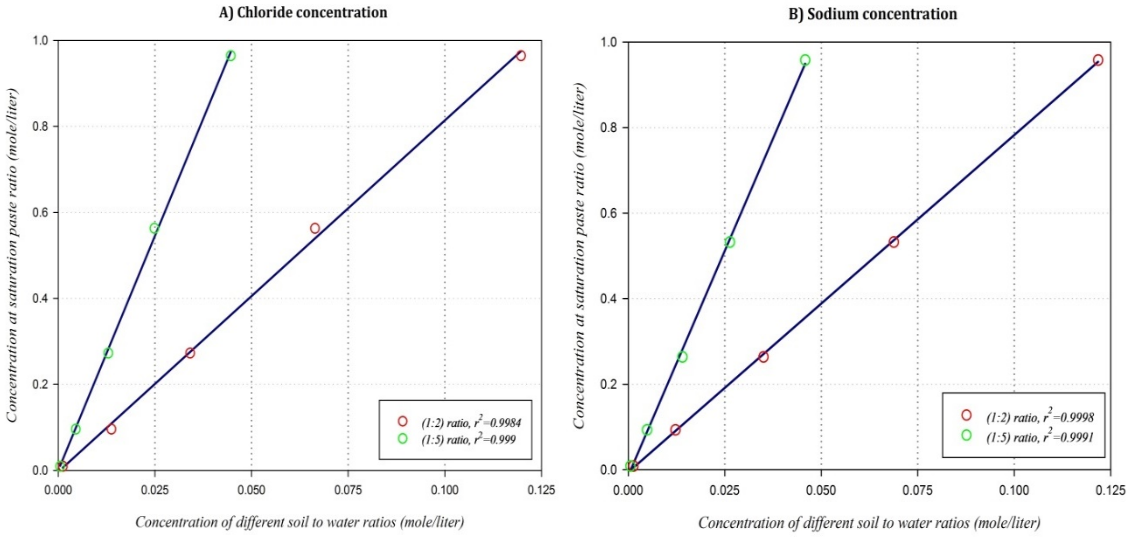


Figure 5.1: Relationships of saturated paste ion concentrations with different soil to water ratios: A) Chloride concentration, B) Sodium concentration.

5.1.3 Assessment of electrical conductivity and pH at saturation paste, (1:2), (1:5) ratios.

The electrical conductivity of soil to water is commonly used to assess soil salinity because it is an easier method than the standard saturated paste extract. Essentially, the electrical conductivity of soil to water extracts is converted into electrical conductivity at saturation paste because plant response and salinity remediation are mainly based on electrical conductivity at saturation paste values. In this batch experiment, the electrical conductivity was assessed at different soil to water ratios by following the procedures which are explained in section 4.3.1. Linear regression models were established for the electrical conductivity at (1:2) and (1:5) soil to water ratios. The results showed that the electrical conductivity at saturation paste correlated significantly with coefficients of determination of 0.9985 at (1:2) soil to water extracts ratio and 0.9983 at (1:5) soil to water extracts as depicted in Figure 5.2. A higher slope for the regression equations of electrical conductivity was observed when the soil to water ratio increased from (1:2) to (1:5), indicating that additional water causes dilution.

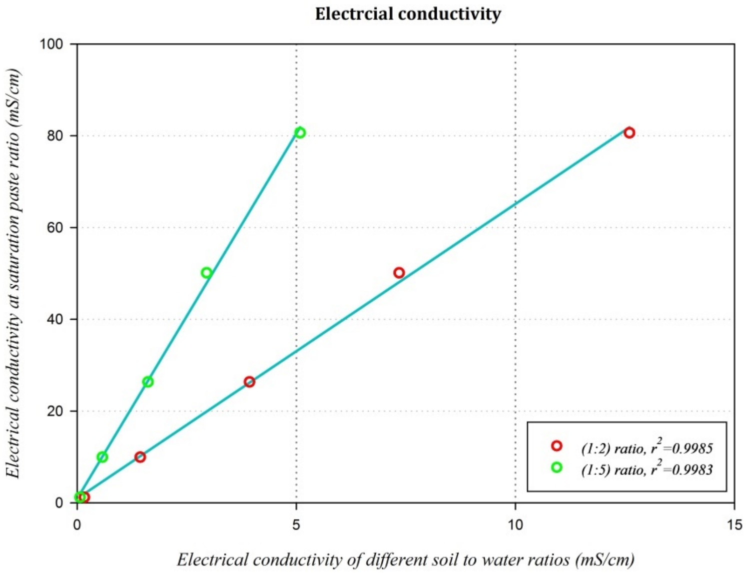


Figure 5.2: Relationships of saturated paste electrical conductivity with different soil to water ratios.

The influence of the soil to water ratio and salinity on pH is illustrated in Figure 5.3. There was no significant variation, although the pH values at (1:2) or (1:5) soil to water ratio show a slight change (less than 0.05). However, higher changes were expected as dilution and salinity increase. This is because of the ions exchange with absorbed cations on the soil surface. However, this was not the case in this study, which could be attributed to the fact of carrying out the tests in sandy and artificially salinized soil using only sodium chloride solution. Therefore, in this study only a 1:5 soil to water ratio was used in all measurements to maintain consistency in the pH measurements when comparing pH values of one experiment with that of another experiment. Moreover, it was observed that the pH difference between the two methods became smaller with increasing soil electrical conductivity (EC).

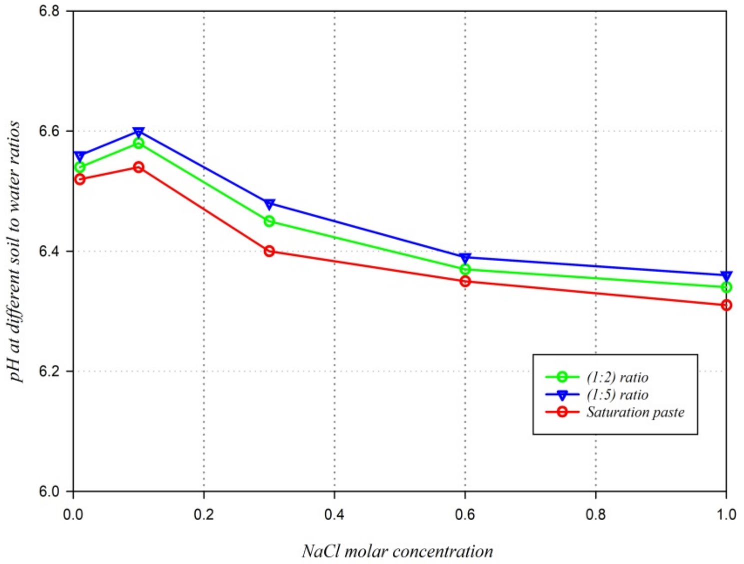


Figure 5.3: Relationships of saturated paste pH with different soil to water ratios.

5.1.4 Soil acid/base buffer capacity test

The Buffer capacity of a soil-solution system is defined as the quantity of a strong base/acid needed to induce one pH unit increase/decrease to the system [1]. In this test, a titration curve of the behavior of silica sand upon addition of an acid or base was created. A detailed description is presented in section 4.3.1. The acid/base buffer capacity of silica sand as a function of pH is shown in Figure 5.4. The slope of the curve at each pH gives the buffer capacity of the system at that specific pH under the condition of the test. It can be observed that the titration curve has a steeper slope at both pH extremes. This implies that the silica sand has higher buffer capacities at these extremes pH values. Furthermore, a closer analysis of Figure 5.4 shows that it doesn't take much acid or base to induce a pH change in the sand. For instance it takes about 100 μl of 1 M HNO_3 to lower the pH from 5.63 to 3.3 while for the same amount of base the pH rises up from 5.63 to 11.4. The inferences that can be drawn hereof is that it is much easier to induce a high pH environment in the sandy soil used in this study.

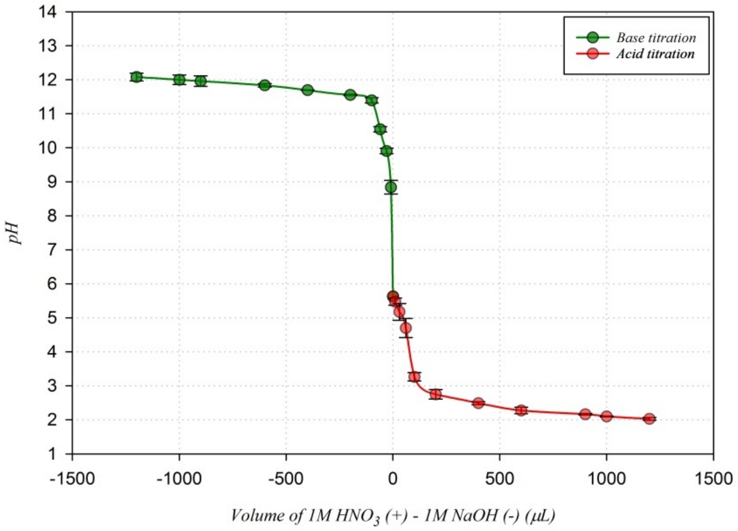


Figure 5.4: Acid/Base titration curve of silica sand.

5.2 Bench scale electrokinetic experiments

Application of electrokinetic technology for extraction or as a barrier in the removal or interception of high concentration of soluble salts from silica sand soil has been investigated. In this chapter, laboratory experiments were carried out to investigate the fundamental electromigration behavior of ions under the influence of an electrical gradient when using coarse grained soil. Experimental evidence obtained in this study is provided to explain electrokinetic phenomena and to better understand the physics and chemistry associated with the electrokinetic extraction process. Initial experiments were conducted by using a sodium chloride model solution only (presented first). They were then followed by experiments carried out using sea salts model solution.

5.2.1 Model solution sodium chloride (NaCl)

Variation of current and voltage

Characterization of the soil used is presented in chapter 4 (Table 4.1), and the model solution used was a NaCl solution. An overview of the test conditions for the experiments with electrical gradient is given in Table 5.1. Applying an electrical field only, several groups of tests were carried out with the same operation conditions (i.e., model solution concentration and applied voltage drop). However, the duration of the experiments was changed. The duration of the first group was 24 *hours*, 72 *hours* for the second group and for 168 *hours* for the third group. The development of potential gradients and current of the three group experiments was in agreement within the first

24 *h* or 72 *h*, indicating a good experimental reproducibility. Hence, mainly the results and conclusions of the 72 *hours* and 168 *hours* test are presented hereafter.

Table 5.1: Overview of the electromigration experiment series.

Test group	Sodium Chloride Spiking solution (*mole/l*)	pH	Average Soil EC $_{1:5}$ ($\mu S/cm$)	Applied Voltage (*V/cm*)	Duration (*h*)	Electrolyte
1	0.6	6.5	1450- 1500	0.5	24	DI-water
2	0.6	6.5	1450-1500	0.5	72	DI-water
3	0.6	6.7	1450-1500	0.5	168	DI-water

The current trace shows an increase within the first 24 *hour*s (Figure 5.6) after reaching a maximum value of approximately 180 *mA*. The initial rise in current in the three test groups represents an increased electrical conductivity in the soil, which was influenced by the results of additional ions produced by electrolysis of water, where hydrogen H^+ and hydroxide OH^- ions produced at the electrodes move faster into the soil than other dissolved salts ions move out of the soils towards the electrodes. The subsequent steep decrease in current (group 2 and 3) arises from the formation of a low electrical conductivity zone within the soil, which could be attributed to the formation of H_2O when the oppositely charged protons and hydroxide ions meet. Under certain conditions the movement of solutes in the pore solution can cease completely [2], these situations have been identified as a result of electrolysis products. Thus, during electro-migration and without anolyte and catholyte chemical control, quasi-steady conditions could be established. In this case ions produced at each electrode meet within the soil at a reaction plane. This phenomenon has been reported by Dzenitis [3]. By using inert electrodes, the electrolysis of water leads to production of H^+ at the anode and OH^- at the cathode. This results in developments of a low-pH front migrating from anode to cathode and a high pH the cathode to the anode. And when these fronts meet, it is expected to react and form water. This region is characterized by low electric conductivity and high electric field strength. As a consequence the electrolyte of the system is separated by this reaction plane into two binary zones: the anode zone on one side, dominated by chloride and hydrogen ions, and the cathode zone on the other side, dominated by sodium and hydroxide ions (Figure 5.5).

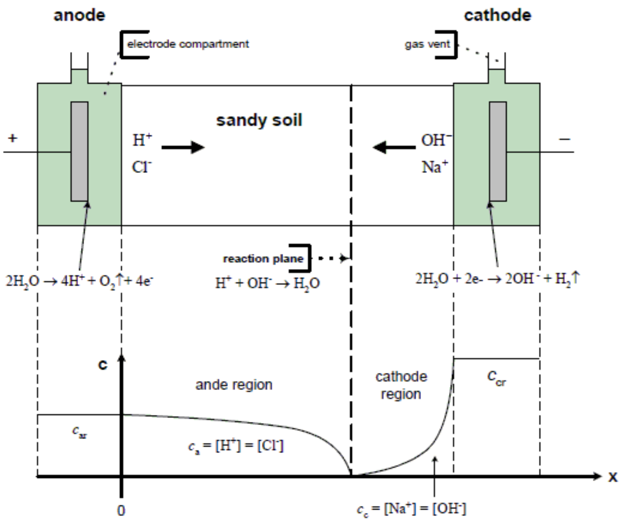


Figure 5.5: Schematic diagram of electro-migration and binary electrolyte regions (NaCl is the initial electrolyte and H^+ and OH^- are the primary electrode products), adapted from Dzenitis [3].

This phenomenon has to be considered in aquifers where the groundwater velocity is slow or where the soil system chemistry is very simple and pore solution chemistry is the dominant parameter, e.g. in sandy aquifers. Alternatively, it could also be caused by precipitation of impurities in this zone as the pH rises. The current dropped to 40 *mA* after 48 *hours* and continued to decrease to a steady state at around 20 *mA* (Figure 5.6) after 72 *hours*, which is an evidence of the removal of dissolved ions from the specimen.

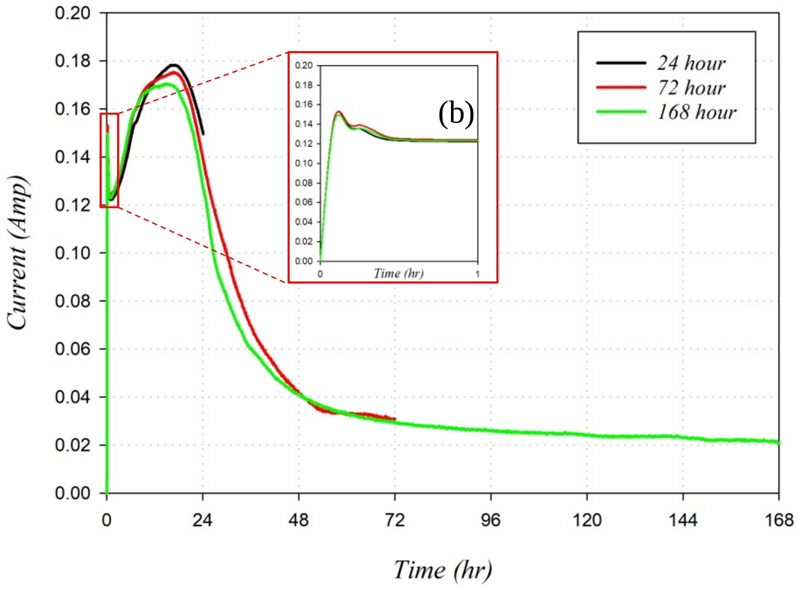
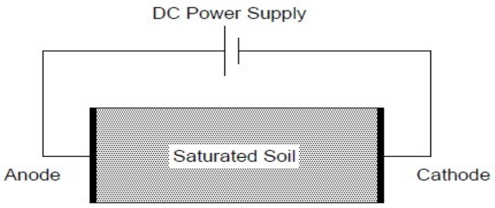
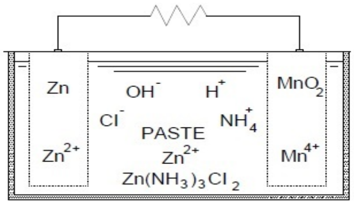


Figure 5.6: Variation of electrical current passing through the specimen with time.

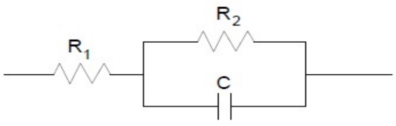
On the other side, this trend of current development during the tests could be due to the polarization occurring in the diffusion layer; this assumption is related to the electrochemical behavior in the diffusion layer in vicinity of electrodes surfaces. However, this is believed to occur on the early stage of the process (Figure 5.6 (b)), where the current reaches a limited current value before it decays, a trend of current similar to that occurring in a battery. Apparently the soil specimen behaves similarly to a battery. In a battery the electric current flowing through it decays during the charging process [4]. In fact, the structures of an electrokinetic extraction cell housing a soil specimen and a battery cell are very similar. An electrokinetic extraction cell is basically consisted of an anode, cathode, and a conductive medium which is a mixture of soil particles and electrolyte. A Leclanche’ type battery contains two electrodes and a conductive medium that can be a liquid or paste [5]. Figure 5.7 compares the structure of an electrokinetic cell and a Leclanche’ cell and showing the equivalent electrical circuit (i.e., RC circuit) representing this system. In the equivalent electrical circuit, the impedance between the electrodes and the conductive medium in the interface region is represented as R2, while R1 represents the impedance of the electrode-electrolyte interfaces that include the impedances of the conductive medium (i.e., conductive electrolyte in the soil) and the electrodes, C is the capacitance of the double layers formed at the electrode surfaces [4, 6, 7]. The circuit presented in Figure 5.7(c) is widely accepted and provides sufficient accuracy for most purposes [7].



(a) Electrokinetic cell



(b) Leclanche cell



(c) Equivalent circuit of a Leclanche cell

Figure 5.7: Schematic layout of (a) an electrokinetic cell, (b) a Leclanche cell, and (c) the equivalent circuit of a Leclance cell (Adapted from Hsu [4]).

Moreover, There are three possible mechanisms which can transport ions to electrode surface: (a) diffusion in a concentration gradient, (b) migration of ions in a potential gradient, and (c) convection[8]. In this study, there was no hydraulic gradient or stirring in electrolyte solution, thus no convection is expected to occur. Diffusion is expected to occur within the diffusion layer near the electrode surface, and migration will be the main process under the influence of applied electric gradient across the cell. Initially, for instance, when looking into the anode surface, the concentrations of ions in the diffusion layer is equal to the concentration in the bulk solution, two ions are contributing in the reaction at the electrode surface within the diffusion layer, chloride ions Cl^- is being oxidized and thus decreases by time within the diffusion layer, and hydrogen ions H^+ is being produced until a saturation level, causing the pH in the electrolyte to decrease to a value of 1.6. These two electrochemical processes will cause the current to increase initially until chloride ions are used up, and hydrogen ion production reach to a saturation limit within the diffusion layer. At this stage, current reached to a limited current value (Figure 5.8) before decay in the current occurred. This decay in the current would be caused by the limitation of reduction or oxidation due to limitation imposed by ion transports in the diffusion layer and limitation in electrochemical reactions occurred at the electrode surface.

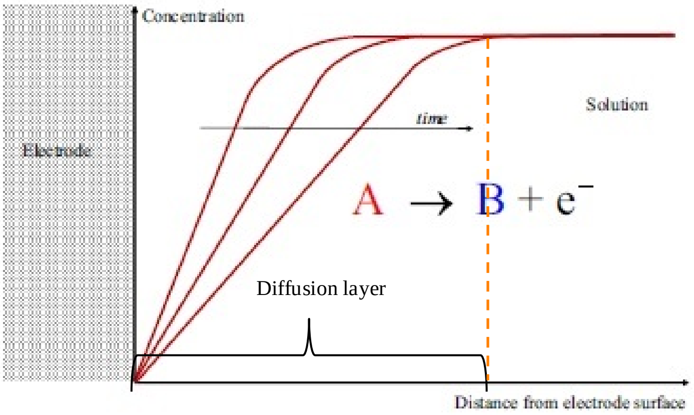


Figure 5.8: Diffusion layer which forms when the compound A is oxidized to form B on an electrode surface (Adapted from Scholz [8]).

After the initial stage of current decay, variation of current through the system is no longer controlled by the RC properties of the system, but instead influenced by the properties of the electrolyte solution in the soil. The current increases to reach a maximum value of 180 *mA* due to the ions migration towards the electrodes and then decay in the current occurs again to reach a steady state value due to depletion of ions in the cell.

The development of steady state conditions with time and space is also documented by developing the voltage gradients between the probes. The distribution of electric potential along the specimen is closely related to the conductivity of the specimen, and the development of the interfaces potential between the electrodes and the soil mass. At the very beginning of the experiments, the electrical potential was linearly distributed Figure 5.9. In this instance, the constituents in the specimen were uniformly distributed and the conductivity in each section was almost identical, as shown also in Figure 5.10. As time progressed, the development of interface potential, polarization of electrodes, and movement of ions caused by electro-migration process changed as a function of time as indicated by the different electric potential profile shown in Figure 5.9. Similar phenomena have been reported by Gabriele, 2008 [9].

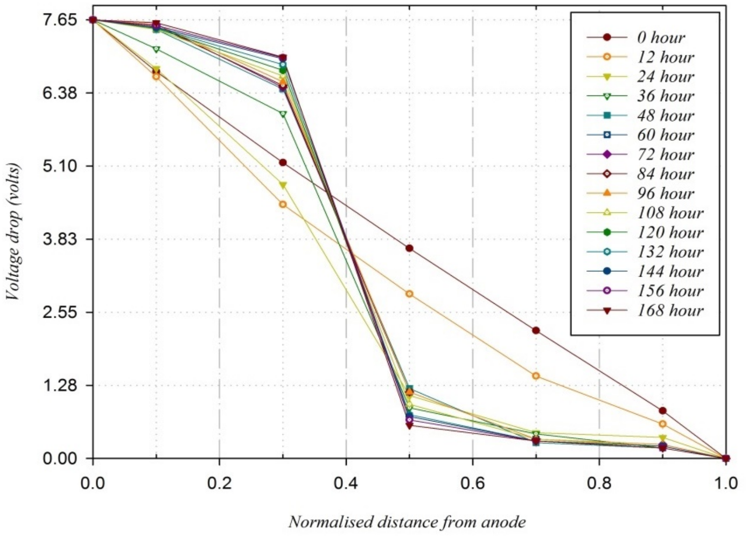


Figure 5.9: Variation of voltage with time and distance.

A large voltage drop has developed within a small zone while across the rest of the soil core voltage gradients were smaller, this region could be because of the reaction plane where the electrolysis products H^+ and OH^- meet and form water, as explained by Deznitis [3], which separates the electrolytes into two binary zones. A steep electrical conductivity gradient has also been developed in consistent with the potential gradient, reflecting a sudden drop of electrical conductivity within this section (Figure 5.10). The electromigration of ions can lead to local changes of ion concentration, which in turn result into local changes of the electric field. As the electromigration velocity of a species is proportional to the electrical field, the velocity is high where steep voltage gradients exist and vice versa. Thus, it would be expected that ions entering the region with high electrical field strength will migrate out readily whereas migration ceases in the nearby region with low voltage gradients.

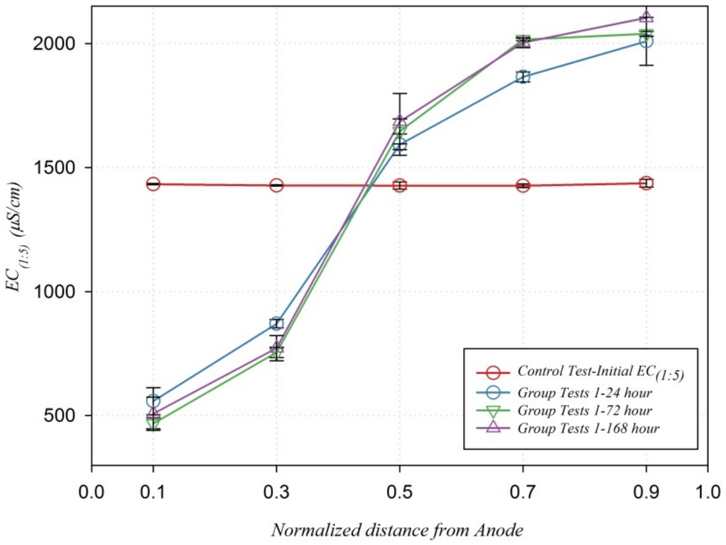


Figure 5.10: Variation of soil electric conductivity across the specimen with time and distance.

The formation of a reaction plane within the soil, a zone with a lower conductivity reflected by the development of the potential gradient within the soil core, is documented by the traces of the five potential probes (Figure 5.11). Probe 1 is located next to the cathode, probe 5 next to the anode. Voltages of probes 4 and probe 5 increase whereas voltages of probes 1 to probe 3 decrease before they reach constant values after approximately 48 *hours*. Moreover, it is evident from Figure 5.11 that the voltage drop between probe 3 and probe 4 increases with time as a result of formation of the zone of low conductivity, which is attributed to the formation of the reaction plane between the two binary zones formed in in the cell, or a possible precipitation of metal contaminants (metal impurities) within this zone, thus rendering this region relatively less conductive. Based on the traces of the current and the voltages, it can be concluded that within approximately 72 *hours* steady state conditions were reached.

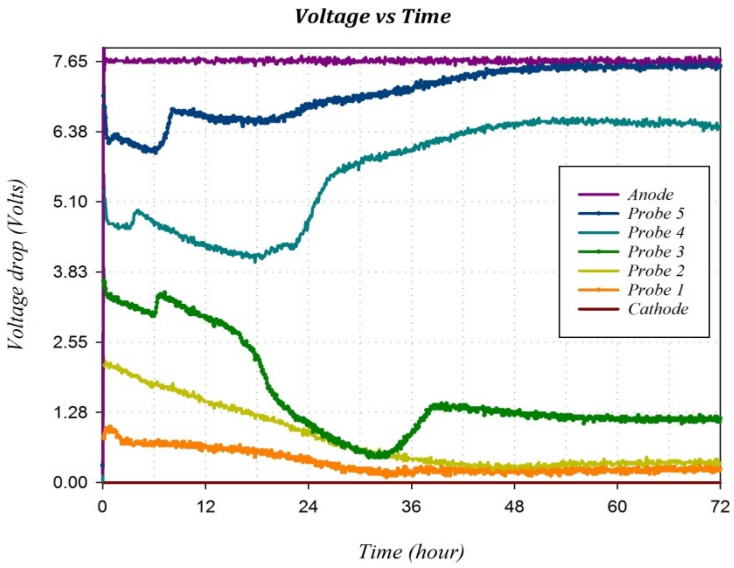


Figure 5.11: Temporal developing potential at the different probes.

Electrical conductivity assessment in cell

Figure 5.10 shows the initial distribution of electrical conductivity across the soil, it also shows the changes in the soil conductivity across the soil after the experiments. The lower conductivity near the anode with respect to the initial value reflects the removal of the ionic species near the anode. A higher conductivity was observed closer to the cathode as sodium ions were migrating and accumulating in those sections. A steep electrical conductivity gradient has also been developed in consistent with the potential gradient, reflecting a sudden drop of electrical conductivity between the two binary zones. When an electric field is applied to a wet soil mass, an electric current is induced. In contrast to metals, the electric current in fluids does not result from moving electrons but from the motion of charged particles or ions, respectively [9]. The electrical conductivity or electrical resistance would change due to variations in pores sizes (i.e., porosity), tortuosity in the porous medium, variation in pore fluid concentration, and double layer electrolyte concentration [10].

In electrokinetic soil processing, conductivity can either be estimated from electrical potential drop across the supplied electrodes and the current across the electrodes (apparent conductivity), or it could be directly measured by probes in the soil (*in-situ*) or the pore fluid (*ex-situ*) with a conductivity meter, in this study the electrical conductivity was assessed after the experiments by measuring the pore fluid conductivity *ex-situ* (as explained in the methodology chapter). In addition, it was also estimated from the voltage drop and current recorded during the experiments.

Applying *Ohm's* law for electrolytes:

$$V_{(volts)} = R_{f(\Omega)} \times I_{(amp)} \tag{5.1}$$

where V is the voltage, R is the electric resistance, and I is the current. The electric resistance R of an electrolyte measured between two electrodes areas A (cm^2) with a distance l cm is described by:

$$R = \rho \frac{l}{A} \tag{5.2}$$

where ρ is the specific resistance (Ωcm). The reciprocal of the specific resistance is the electric conductivity. Thus, the apparent electrical conductivity of soil (EC) calculated from the electrical potential drop across the electrodes, is defined as[10]:

$$EC_{app(\frac{S}{cm})} = \frac{I_{(amp)} \times L_{(cm)}}{V_{(volts)} \times A'_{(cm^2)}} \tag{5.3}$$

Where I is the current, V is the voltage difference between the current generating electrodes, L is the specimen length, and A' is the effective cross-sectional area of the specimen which is considering the porosity of the specimen.

Hamed, has reported that in a relatively simple electrolyte system (i.e., low ionic strength), conductivity values are sensitive indicators of H^+ and OH^- concentrations if the they exceed the pore fluid ionic concentrations [10]. However, it is not necessarily to reflect the same condition in this study as the electrolyte salts concentrations is relatively high, and it is more an indicator of the salts ions migrating towards the oppositely charged electrode. The calculated apparent conductivity is a good approximation of the actual soil conductivity of only during the early stage of electromigration, before a significant polarization takes place and when the background electrolyte condition is relatively constant across the cell [4, 10], which is evident by the linear voltage distribution across the sample at the beginning of the experiments, i.e., at initial time = 0 (Figure 5.9). Therefore, the initial apparent conductivity value of approximately 22000 $\mu S\ cm^{-1}$ calculated across the electrodes compares favorably with the initial conductivity at saturation paste of 23,500 $\mu S\ cm^{-1}$ measured in the pores fluids in segments across the cell (Figure 5.12). The measured conductivity $EC_{1:5}$ was approximately 1,450 $\mu S\ cm^{-1}$, while the electrical conductivity value at saturation paste which is compared with the calculated apparent conductivity was estimated using the relationship of the saturated paste electrical conductivity with the electrical conductivity at soil to water ratio 1:5 (section 5.1.2).

However, at longer time of processing, the apparent conductivity EC_{app} values calculated by the potential difference across the cell and current supplied may significantly differs across the cell due to the electrochemical overpotentials required to derive the electrode reactions may contribute to the measured voltage. And hence return different apparent conductivity values, or because of the significant variation in the electrolyte concentrations across the cell [10]. Moreover, when an ordinary diffusion is present and there are concentrations gradients, *Ohm's* law does not hold because there is a contribution to the current from diffusion [11]. Because of the above mentioned reasons, and in order to develop a better understanding of the electrochemistry associated with electro-migration, it is necessary to evaluate the conductivity across the cell. At the end of each test, conductivity measurements were done across each segment in the pore fluid (Figure 5.10). Conductivity is directly related to the mobility and concentration of the ions carrying the charge; it is evident from the comparison of Figure 5.10 and the ion distribution across the cell segments that the measured electrical conductivity was more affected by the distribution of sodium ions across the cell.

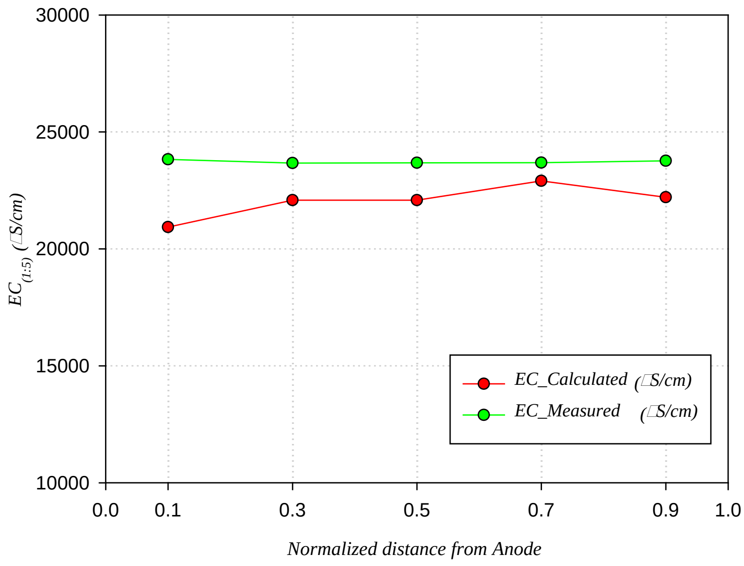


Figure 5.12: calculated and measured electrical conductivity across the cell

pH distribution

The change in pH is directly related to the background electrolysis reaction that occurs in the electrolyte solution at both sides of the soil column. Protons (H^+) are produced in the anodic compartment, and hydroxyl (OH^-) ions are produced in the cathodic compartment. In all experiments, the pH dropped to a very low value, around 2-1.6 in the anodic compartment, while it rises up to 13.6 in the cathodic compartment, as shown in Figure 5.15.

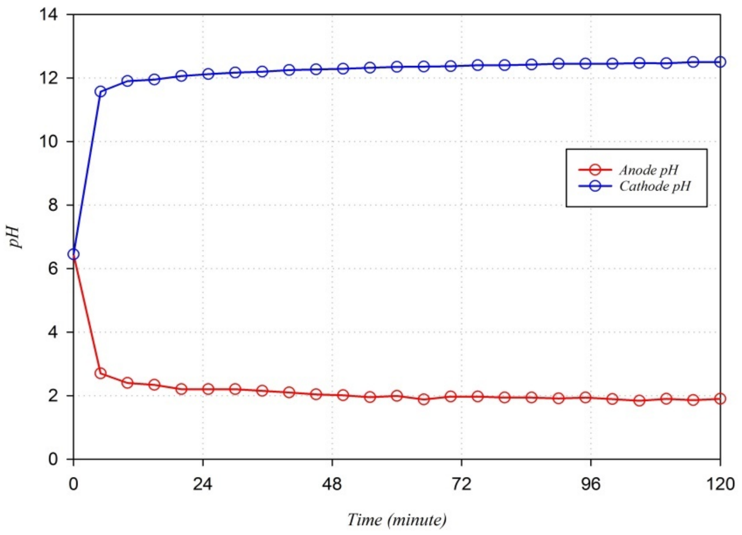


Figure 5.13: Variation of pH with time in anolyte and catholyte.

Hydrogen ions generated by electrolysis at the anode are expected to migrate towards the cathode and contribute to the low pH around the anode, therefore creating an acidic front that will advance across the soil specimen. Conversely, a basic front due to the migration of the hydroxyl ions which have been generated at the catholyte solution will migrate through the soil towards the anode. In this study, since there is no any externally applied hydraulic potential at either side of the soil specimen, the main transport mechanism for both protons and hydroxyl is ionic migration caused by the electrical gradient, another transport mechanism is attributed to the diffusion caused by generated chemical gradient. It has been reported that the advance of the basic front towards the anode will be much slower than the advance of the acid front towards the cathode because of the counteracting electroosmotic flow and also because the H^+ ions have a high mobility of about twice the ionic mobility of the OH^- ion. As a consequence, the acid front dominates the chemistry across the specimen [2, 12, 13]. In this study, the alkaline advanced more a across the soil cell specimen and it is in contrary to previously reported findings. Eventually the acidic front was retarded and not advancing significantly across the specimen. The laboratory observation of the advancing pH front is shown in Figure 5.14. From the observation, it is evident that the alkaline pH front advanced with time and dominated across the soil cell. The figure shows the advancing of the base front, it also shows the reaction plane near the forth probe closer to the anode. As discussed previously, this reaction plane represents the reaction plane where the two fronts (i.e., the acidic and basic front) meet and divides the cell into two binary zones.

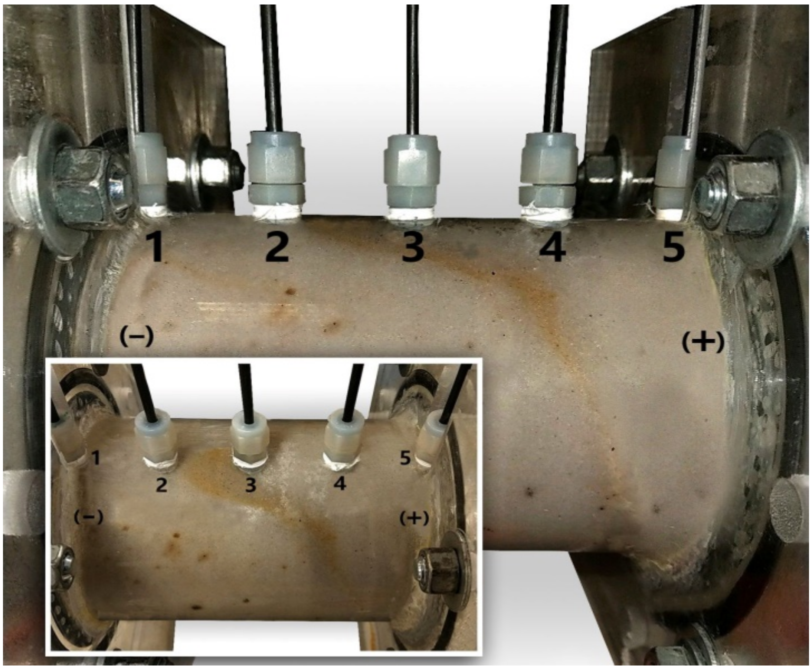


Figure 5.14: The advancement of the pH front across the soil.

Figure 5.15 demonstrates the results of the pH measurements showing that a higher pH value than the initial pH dominates across the soil cell.

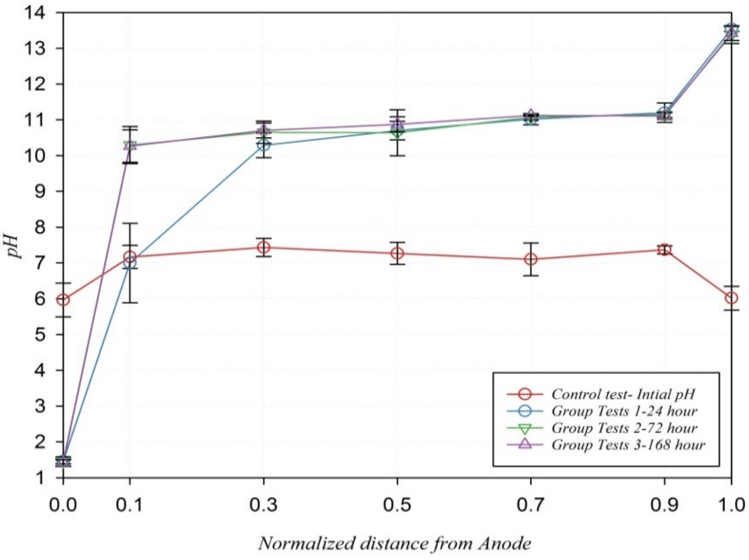


Figure 5.15: Variation of pH with time across the soil specimen.

These results show that the soil media and the chemistry of the soil pores play a major rule in defining the pH profile across the soil under the influence of an electrical potential, and that it is not necessarily the case that a low pH value will dominate across the sample as a result of the electrolysis process occurring in the electrolyte solutions.

However, a study by Cho et al. on the application of electrokinetic restoration of saline agriculture lands has reported that the soil pH was decreased mostly in the sections very near to the anode and increased in the sections closer to the cathode, while in the middle of the soil no pH change was noted and remained near the initial pH value (around 7). These results are more similar to the results observed in this study [14]

In this study, one possible reason could be a reversed advection flow (i.e., reversed electroosmotic flow) moving towards the anode (Figure 5.16). However, there was no notable flow collected from the anodic compartment or a rise in the electrolyte solution as a possible result of any electroosmotic flow. Figure 5.16 shows some impurities, possibly, iron oxide diffused to the direction of the anode. The reversed electroosmotic flow is contrary to the known direction of electroosmotic flow in the application of electrokinetic remediation (i.e., flowing towards the cathode), which could be influenced by the surface charge of the solid matrix, represented by the zeta potential, which could be attributed to the charge properties of sandy soil. This observation requires more attention to study the characteristics of the zeta potential (ζ) and the zeta potential distribution of silica particles; this was not investigated in this study. However, in order to better asses the changes in the pH changes within the soil matrix it would be highly recommended that a study to be conducted regarding the influence of the zeta potential of silica sand on transport mechanisms under an electrical potential in silica sand media.

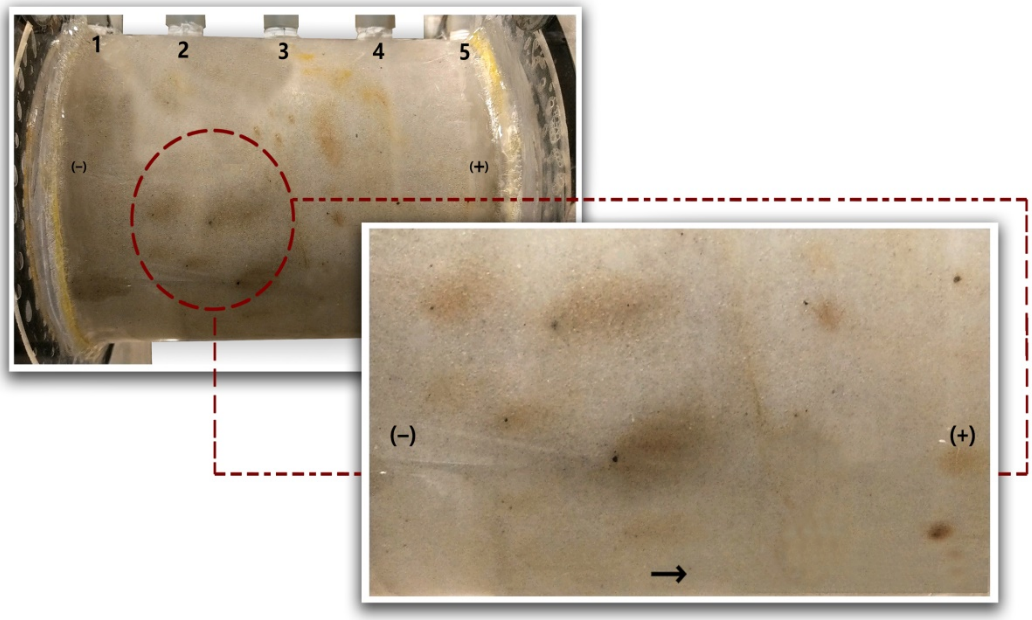


Figure 5.16: Observed impurities diffusing to the direction of the positive electrode.

The effect of the zeta potential distribution and its influence on the direction of the electroosmotic flow has been studied more intensively on clay soil and the focus was mainly on its effect on the removal of cationic species. Several enhancement methodologies have been reported in order to keep the electroosmotic flow in one direction i.e. towards the cathode and thus in favor of cationic species removal. However, in contrary and when the interested species to be removed from a soil matrix comprises both positively and negatively charged species, then dealing with a changeable dynamic process such as the electroosmotic flow becomes a very challenging problem, Since the direction of ionic migration of species is dictated by the polarity of the charges carried by the contaminant species, electroosmotic flow may enhance or diminish the removal of some of the contaminant species in the soil. When electroosmotic flow is driven from the anode toward the cathode, the removal of cationic species is enhanced as cationic migration is accelerated by electroosmotic flow. The removal of anionic species is diminished as anionic migration is retarded by electroosmotic flow. More importantly, a forward electroosmotic flow, i.e. from the anode toward the, cathode, promotes the development of a low pH environment in the soil. On the other hand, a reverse electroosmotic flow may enhance the removal of anionic species. However, it may raise the pH in the soil and cause precipitation in the soil and thus limits their removal.

Moreover, most experimental studies available in the literature are based on an observed average zeta potential of particles. Thus, analyses of data using the average zeta potential alone can lead to misleading and erroneous conclusions. Kim and Lawler reported in their study on characteristics of the zeta potential distribution in silica particles that in contrary to most researchers' assumptions, most of zeta potential distributions for silica particles were broad [15]. Parks reported that the pH_{PZC} (with pH_{PZC} indicating pH at the *point of zero charge*, where the net charge of a solid particle is zero) of silica is between pH 2.0 and 3.5 [16], while Findlay et al noticed that the pH_{PZC} of Min-U-Sil is below 2.0 [17]. This variability of reported data regarding the zeta potential distribution, particularly silica sand, requires more attention to this issue and more specific studies about its influence on electrokinetic applications and its efficiency in sandy soil.

On the other side, most soil particle surfaces are negatively charged as a result of isomorphous substitution and presence of broken bonds [18]. The zeta potential at the soil particle/pore fluid is thus negative. When a dc electric field is imposed on the system, the mobile positive ions exert more momentum than the fixed negative ions on the pore fluid. Thus, the pour fluid is driven from the anode towards the cathode by electroosmosis. Therefore, electroosmosis is conventionally taken to be the hydraulic flow induced flow by an externally applied electrical gradient from the anode towards the cathode [19]. However, when the chemistry of soil-fluid system is changed by a prolonged application of an electric field or the existence of contaminants in the pore fluid, the direction of electroosmotic flow may be reversed, i.e., from cathode to anode. This reversal of flow happens when the initially negative surface becomes less negative, approach zero or may become positive at a pH around the point of zero charge, which could have happened during the experiments in this study and created a reverse electroosmotic flow. Moreover, silica is a solid with uncharged silanol groups ($\equiv Si–OH$) and charged silicic acid groups ($\equiv Si–O^{-}$) *on* its surface [20]. In milled silica particles, the SiO_4^{4-} coordination tetrahedron is imperfect leaving silicon and oxygen unsatisfied bonds at each particle surface [21]. In aqueous suspensions of silica particles, these free bonds are neutralized by OH^{-} and H^{+} species. Therefore, partial or total particle surface hydroxylation can result in the formation of silanol groups [$Si(OH)_n$] which in pure water dissociate through the following reactions:

$$\equiv SiOH + OH^{-} \rightleftharpoons Si{-}O^{-} + H_2O \tag{5.4}$$

$$\equiv SiOH + H^{+} \rightleftharpoons Si{-}OH_2^{+} + H_2O \tag{5.5}$$

Thus, silica particles may end up being negatively charged in water suspension in basic pH and positively charged under acidic pH [22, 23]. However, this still does not prove a reveres electroosmotic flow occurred in the cell, neither explains why the acidic front was retarded through the soil cell; nonetheless a back flow of electroosmotic flow towards the anode still could be a reason to slow up the migration of H^{+} in the soil specimen.

Several factors can affect the magnitude and the charge of zeta potential in silica particles; however, the pH and ionic strength of the electrolyte solution play a major role in determining the zeta potential distribution. The zeta potential of the soil particle surface increases (becomes less negative) with increase in the ionic strength of the background solution. Yeung reported, the increase in ionic strength of the background solution reduces the Zeta Potential of Cadmium-Contaminated Natural Clay thickness of the diffuse double layer [24], resulting in an increase in zeta potential following the principle of electrostatics [25, 26].

Because of the temporal and spatial dynamic changes in the behavior of the electrokinetic phenomena in soil and its influence in the dynamic changes in soil pH and ion concentration in soil media, controlling the zeta potential distribution and mainly in favoring the removal efficiencies of the targeted elements, or on the other side, maintaining a favorite soil pH value (i.e., a pH value that enhances the removal process or a pH value that does not negatively affect the soil eco-system), which could be the most critical and challenging phenomenon to cope with.

Another reason that could possibly contribute to the retardation of the movement of the H^+ across the cell could be the charge conservation and neutralization effect within the soil specimen. As mentioned above, during electromigration and without anolyte and catholyte chemical control, quasi-steady conditions could be established. As a consequence, the electrolyte of the system is separated by a reaction plane into two binary zones. The negatively charged species (chloride) migrate towards the anode surface where it undergoes an oxidation process converting the ionic species (Cl^-) into molecular chlorine gas (Cl_2) which in turn vents out of the system, resulting in a lower negative charge within the system. On the other hand, Sodium ions migrate towards the cathode and accumulate near the cathodic zones, but it doesn’t leave the system because of the configuration of the used experimental set up. As a result of both processes, accumulation of more positive charge in the system occurs. Therefore, the interrupted charge balance somehow enhances the movement of the negatively charged hydroxyl species to migrate across the soil specimen, or this would suppress the migration of the positively charged hydrogen species from moving across the soil specimen. In order to test which reason is more influential on suppression of the acidic front migration, three tests were carried out with only deionized water as a model solution. The results are shown in Figure 5.17. The tests were carried out for 48 *hours* and 72 *hours* under a potential gradient of 0*.5* $V\ cm^{-1}$ the third test was carried out for 72 *hours* and under a potential gradient of 1 $V\ cm^{-1}$. A very similar trend in pH profile was observed in all the three tests. However, in the first test a slight acidic condition was observed in the first section near the anode, but with time the pH kept rising to a higher value. In addition, the rise in pH values was less significant than when sodium chloride was used as a model solution. These results support the argument that a possible reversed electroosmotic flow, even in a very week magnitude, it could have enhanced the migration of the alkaline front across the soil specimen and retarded the advancing of the acidic front.

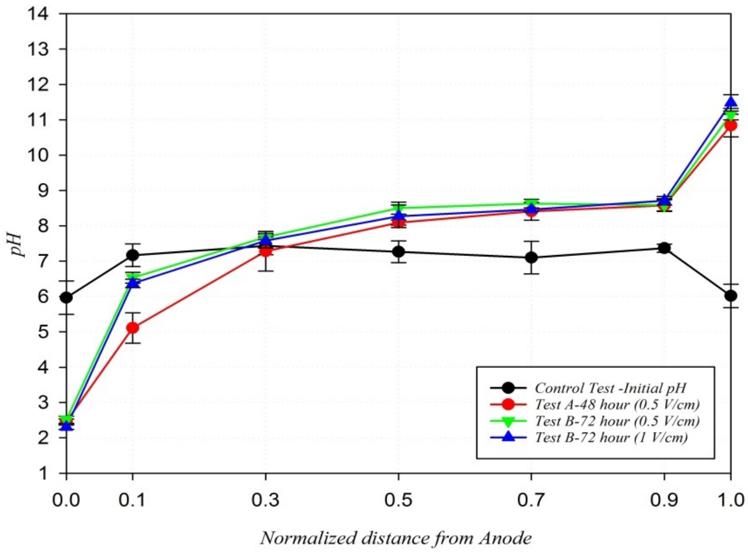


Figure 5.17: Variation of pH with time across the soil specimen using deionized water as a solution model.

Salt residuals in soil compartment

In this study, the charged dissolved ions were transported in the soil specimen under the action of an applied voltage gradient, which influenced the dissolved sodium Na^+ and chloride Cl^- ions and deflected them towards the oppositely polarized electrodes accordingly. The distribution of normalized residuals (C/C_0) of Na^+ and Cl^- which remained in the soil profile after the experiments are shown in Figure 5.18. In fact, the figures represent the respective movement of Na^+ and Cl^- ions, as well as their removal efficiency. Chloride and sodium ions were transported towards the anode and cathode, respectively, mainly through the electromigration transport process. However, as mentioned above the observed reversed electroosmotic flow may also have contributed to the chloride removal because the flow direction was towards the anode. The chloride was removed from the soil to a much higher extent than sodium. Moreover, more chloride ions were removed and more sodium ions migrated towards the cathode when the experiments were carried out for a longer time (168 *hours*), however, the difference was not significant when comparing the results of experiments carried out for 72 *hours* with experiments carried out for 168 *hours*. An average of 73% of chloride was removed during experiment group 1, which was carried out for only 24 *hours*. Most of the sodium from the sections near the anode and from the anodic electrolyte solution was removed and migrated towards the cathode: more than 85-90% of dissolved sodium from those sections was migrated to the sections near the cathode, the migrated sodium accumulated gradually from the third section (in the middle of the soil specimen) and started to build up near the cathode and in the cathodic electrolyte. Experimental group

2 and 3 were running for 72 *hours* and 168 *hours*, respectively. They show better removal efficiencies under the same condition. In those cases, more than 85% of chloride was removed from the system, and more sodium migrated toward the cathode.

The higher removal of chloride can be attributed to the formation of chlorine gas at the anode surface. A chlorine smell was evident during the experiment. A mixture of chlorine gas and oxygen gas due to H_2O electrolysis are formed at the anode surface where it eventually vented out of the cell. However, no further processing for the vented gases or collection was carried out, which is an important aspect to consider during a field application.

The cathode attracts sodium ions Na^+, positive hydrogen ions pulled from the water molecules and reduced to hydrogen gas and releasing hydroxide ions into the electrolyte solution. Only the hydrogen ions are discharged at the cathode, it should be noted that, the more reactive a metal is, the less readily its ion is reduced on the electrode surface. Therefore, H^+ ions have a greater tendency to be discharged than Na^+ ions because they are relatively less stable than the Na^+ ions, hence the H^+ ions are selectively discharged over Na^+ ions despite the high concentration of Na^+ ions. Thus, The H^+ ions are then reduced by electron gain to form hydrogen gas at the cathode, and the Na+ ions remain in the electrolyte solution.

Sodium is inert and does not undergo any reduction process; it only migrates and accumulates near the cathode regions or in the cathodic electrolyte and exists in the form of dissolved sodium hydroxide. Eventually, sodium removal would be easily enhanced by just using a circulating system. The removed cathode and anode electrolytes can be combined as brine and disposed/injected or beneficially reused. For example, when a sodium hydroxide solution brought to contact the chlorine gas a portion or all of the chlorine gas is converted into sodium chloride and bleach.

In this study, experiments were carried out without applying a hydraulic gradient. Thus, changes in ion concentration within the model soil (sand) are solely due to electromigration. However, the detectable reversed advection flow was observed during the experiments (Figure 5.16), and it contributed to the chloride removal, as the direction of the flow was towards the anode. In other words, it suppressed the migration of sodium ions towards the cathode. Other studies reported the opposite trends in the removal of both sodium and chloride, and that it was due to the contribution of the electroosmotic flow in different direction (i.e., towards the cathode) [14].

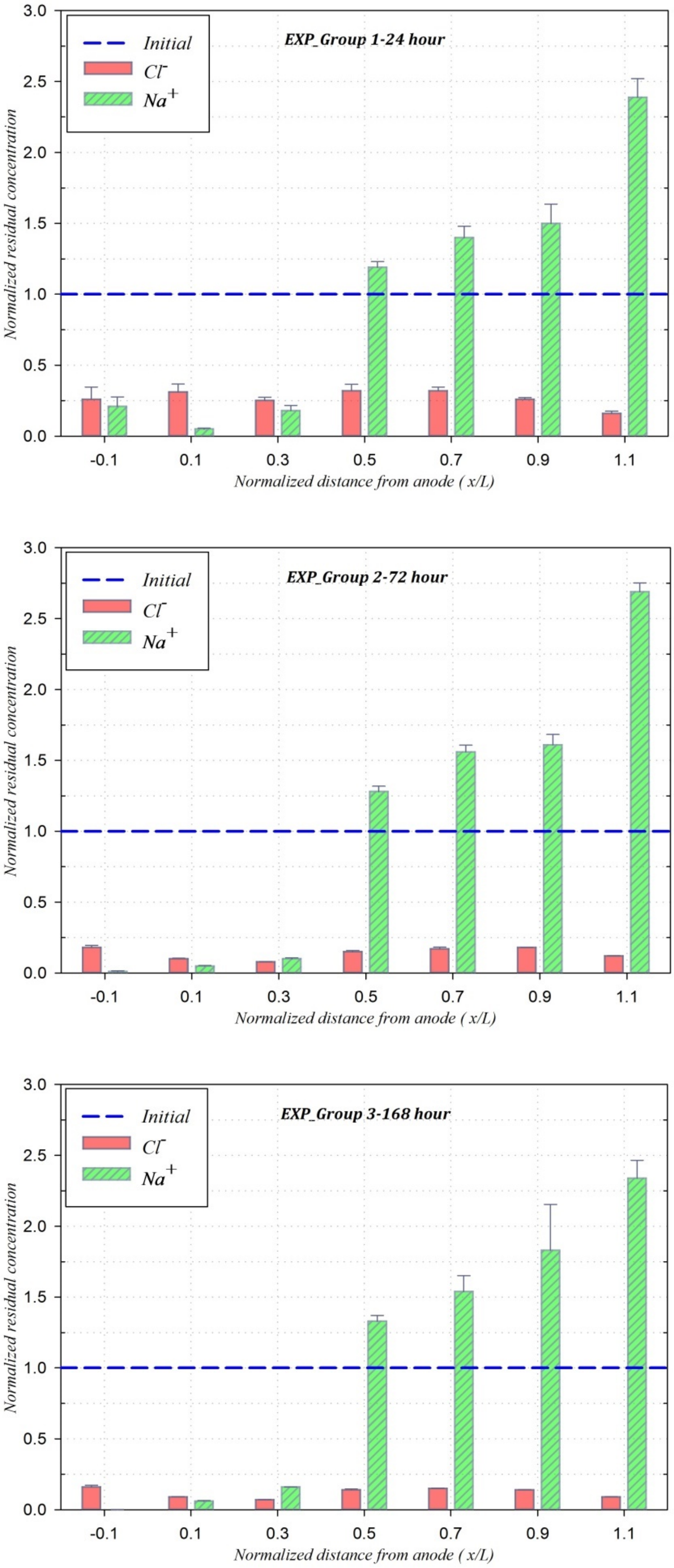


Figure 5.18: Normalized ions residual concentration

The chloride ions undergo an oxidation process when reaching the anode surface; chloride converts to molecular chlorine (Cl_2), which in turn undergoes a hydrolysis process (Equation (5.6)), forming a dissolved hypochlorous acid (HOCl). The HOCl is a weak acid and pH dependent according to Equation (5.7). The hypochlorous acid would also go onto deprotonation and forming a hypochlorite ion (OCl^-), this could cause some drawback to the process as some of those species would react with sodium and might diffuse back in the soil, beside the toxicity influence of those species in the soil.

$$Cl_{2(g)} + H_2O \rightleftharpoons HOCl + H^+ + Cl^-, \qquad K_1 = \frac{[HOCl][H^+][Cl^-]}{Cl_2} \tag{5.6}$$

$$HOCl \rightleftharpoons H^+ + OCl^-, \qquad K_2 = \frac{[H^+][OCl^-]}{[HOCl]} \tag{5.7}$$

As shown in Figure 5.19, chlorine hydrolysis is a pH dependent, and chlorine in the molecular form will be dominant at pH 2 (which is the measured pH value in the anodic electrolyte). When the pH increases or is more alkaline, other species such as HOCl and OCl^- become more dominant. This information presents an opportunity for a feasible method/scheme to control the pH. Keeping the pH under 2 (very low) will help to keep most of the chlorine species formed during the oxidation process, are in the form of molecular chlorine.

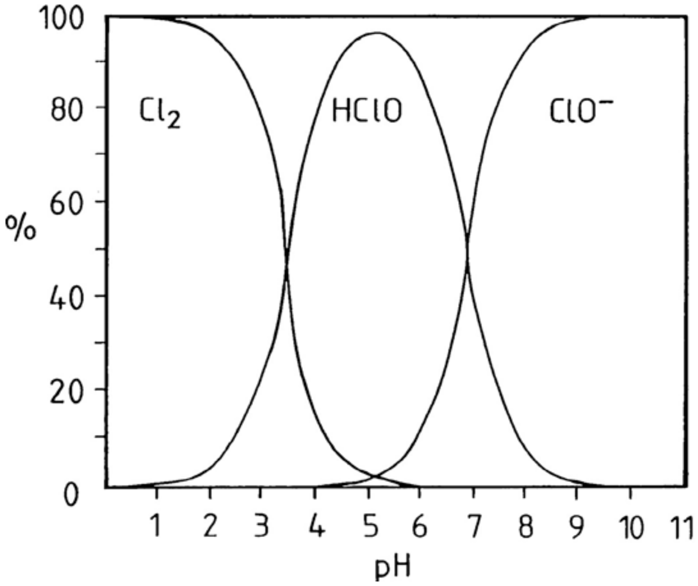


Figure 5.19: Percentages of active chlorine species Cl_2, HOCl, and ClO^- as a function of anolyte pH at 90°C and 200g NaCl dm^{-3} . The percentages are calculated using equilibrium constants for Cl_2 hydrolysis and HOCl deprotonation [27].

After reaching a saturation level, chlorine gas starts to form and vent out of the system. This phenomenon was observed in this study. The collected anodic electrolytes from the anodic compartment always contain chlorine species, as shown in Figure 5.20 (left), but because the pH was always in the range under 1.6, it would be assumed that most of the chlorine that is present is only in the form of molecular chlorine (Cl_2), which volatiles after some time, Figure 5.20 (right) , this is evident as by time chlorine detected in the samples was vented out and almost no trace of chlorine remains in the container.

Figure 5.20: Chlorine evidence collected from the anodic electrolyte: (left) after the experiment, (right) the same solution after few weeks.

5.2.2 Model solution sea salts

The same procedures and protocols of electrokinetic extraction using a sodium chloride model solution have been followed in the second part of the experiments when using a sea salt solution as the model solution. Two series of tests were carried out under the same experimental condition; however, the tests were carried out under different applied voltages. In the first series an applied voltage of 0.5 $V\ cm^{-1}$ was used, while an applied voltage of 1 $V\ cm^{-1}$ was used in the second series. Moreover, the tests were carried out for 72 *hours*. The results regarding the development of current, potential gradients change in ions concentration and pH absolutely coincided with the NaCl experiment.

Variation of current and voltage

The general trend of the electrical current variation with time was observed under a constant voltage condition. Figure 5.21 shows the variation of current with time in two series of experiments using sea salt. Under the applied voltage of 0.5 $V\ cm^{-1}$, a peak value was observed with the same range of the experiments using NaCl. This shows that even with different dissolved ions, the soil matrix gains similar electrical criteria. This also supports the fact that the major constituents of ions in the solution were sodium and chloride in both model solutions, which contribute to the major charge carrier in the solution. In the second series, and under a higher voltage gradient, a higher peak (Figure 5.21) was observed as current and voltage are related directly according to *Ohm's* Law. As stated before, the increase in the current at the beginning of the experiments is in fact due to the electrolysis process and the production of H^+ and OH^-, which move into the soil matrix and contribute to a higher electrical conductivity of the soil specimen as a charge carrier, before the dissolved ions start getting depleted and the resistance of the soil matrix increases and current starts to drop. However, the difference in time between the peaks is an indication of the faster electrolysis process; or, in other words, the production rate of protons and hydroxides in the second series. Steady state was also reached faster in the second series of experiments, which could be an indication of a faster removal rate of dissolved ions from the specimen.

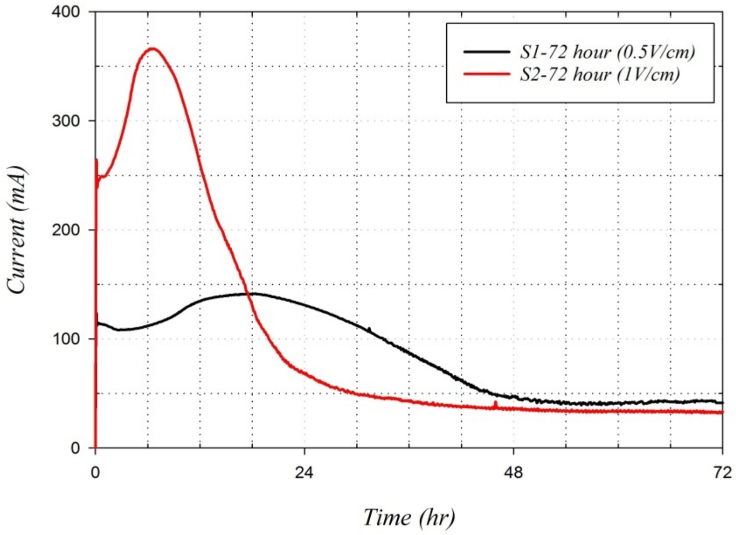


Figure 5.21: Variation of electrical current passing through the specimen with time.

The temporal changes of voltage with time at different probes along the soil cell are shown in Figure 5.22. Furthermore, the development of steady state conditions as a function of time is also documented by the development of the voltage gradients between the probes.

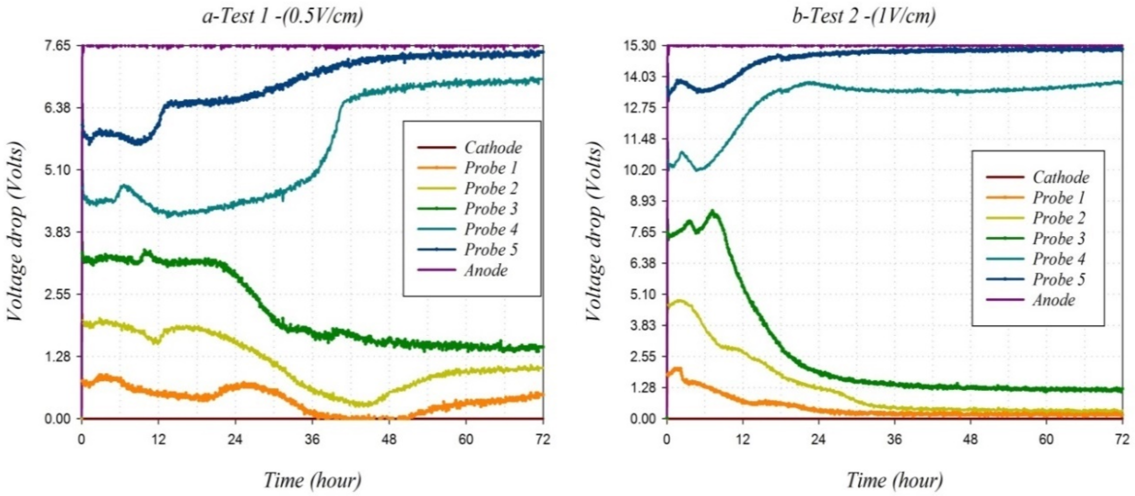


Figure 5.22: Temporal development of voltage at different probes.

Similar to the NaCl experiment, Figure 5.21 shows the current trace at the beginning of the experiments reflects the processes of electrolysis of water at the electrodes and the production of hydrogen and hydroxides ions at both the anode and the cathode respectively, which causes the increase in the current at the beginning. The subsequent decrease of the current after, reflects the formation of the reaction plane as explained in section 5.2.1 (i.e., this zone is characterized by a steep voltage gradient) which in turn is an indication factor for the separation of ions in the soil cell and forming two binary zones (Figure 5.22), where the two pH fronts meet within the soil. The two binary zones: the anode zone on one side would be dominated by species such as HCl, H_2SO_4, H_2CO_3, and the cathode zone on the other side, dominated by the NaOH, $Ca(OH)_2$, or other formed species with cations. Moreover, the steady state conditions started to develop after 48 *hours* for both the experiment as shown in Figure 5.21.

Based on the traces of the current and the voltages, it can be concluded that within approximately 36 *hours* steady state conditions were reached in the tests under an applied voltage of 1 $V\ cm^{-1}$, while in the first series of experiments (under an applied voltage 0.5 $V\ cm^{-1}$) a steady state began to develop after 60 *hours*. The development of steady state conditions as a function of time and space is also documented by developing the voltage gradients between the probes along the soil cell (Figure 5.23). The electrical conductivity for the soil pores was measured. Generally, it was following the same trend as when only NaCl solution was used as a solution model. However, the measurement shows lower values or a better reduction in the soil electrical conductivity.

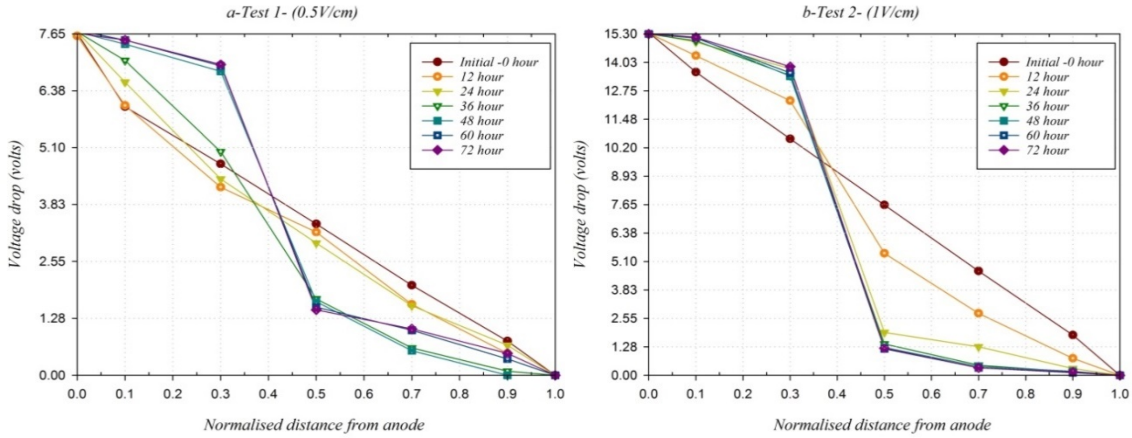


Figure 5.23: Variation of voltage with time and distance: (a) 0.5 *V cm*$^{-1}$, (b) 1 *V cm*$^{-1}$.

This could be attributed to the fact that in those experiments precipitation occurs, and thus those elements did not contribute significantly in the soil electrical conductivity measurement. The electrical conductivity distribution of the soil before and after experiments is shown in Figure 5.24. It was observed also from the figure that a higher applied voltage across the soil cell does not necessarily lead to more reduction, or differently stated, a better removal efficiency of dissolved salts. The process would be accelerated and the ion migration was enhanced under a higher voltage gradient, which is also shown by achieving the steady state condition in the second experiments, which is faster than when a lower voltage gradient was applied. This implies that applying a higher voltage gradient or higher current would just lead to a more energy expenditure but not necessarily achieve a more enhanced ion removal or reduction in electrical conductivities.

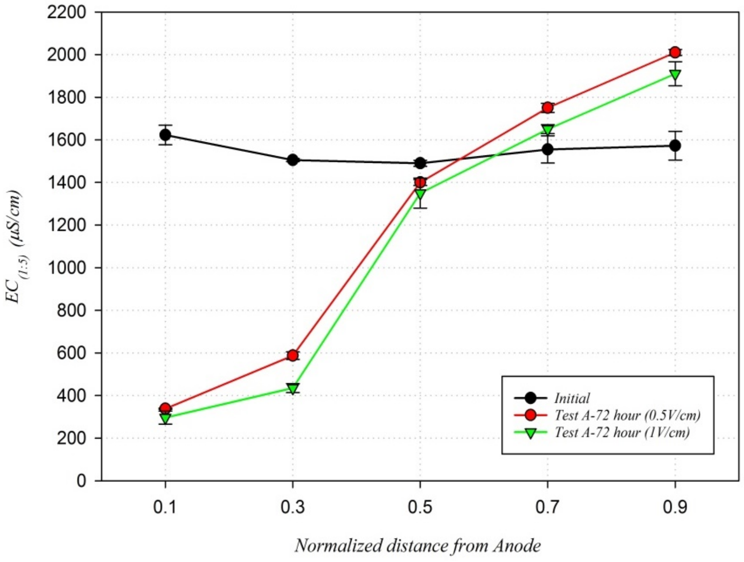


Figure 5.24: Variation of soil electrical conductivity across the specimen with time and distance.

pH distribution

Among all the geochemical processes, the generation of a pH gradient in contaminated soil has the most profound impact on the electrochemical remediation process, as the change of pore fluid pH has a significant influence on the mechanism and degree of sorption and desorption of contaminants onto and from soil particle surfaces, complex formation and precipitation of chemical species, and so on, thus affecting the feasibility and efficiency of electrochemical remediation of contaminated soils. As a result of generation of hydrogen and hydroxide ions at the anode and the cathode, an acidic environment is developed in the vicinity of the anode and an alkaline environment in the vicinity of the cathode, respectively. Although the mechanism of the migration of the acid front is not fully understood, most researchers observe a propagation of an acid front from the anode toward the cathode. Similarly to the pH results of the NaCl solution model, the alkaline profile dominated across the soil cell as depicted in Figure 5.25.

Some researchers describe the acid front propagation process by applying the advection-dispersion equation to the transport of hydrogen and hydroxide ions using the measured ionic mobilities and diffusivities of hydrogen and hydroxide ions [28, 29]. However, it is well known in physical chemistry that the measured ionic mobilities of hydrogen and hydroxide ions are exceptionally high in comparison with those of other ions. In fact, these ions are transferred along a series of hydrogen-bonded water molecules by the rearrangement of hydrogen bonds, as shown in Figure 5.26. Water molecules are oriented under the influence of the imposed DC electrical field.

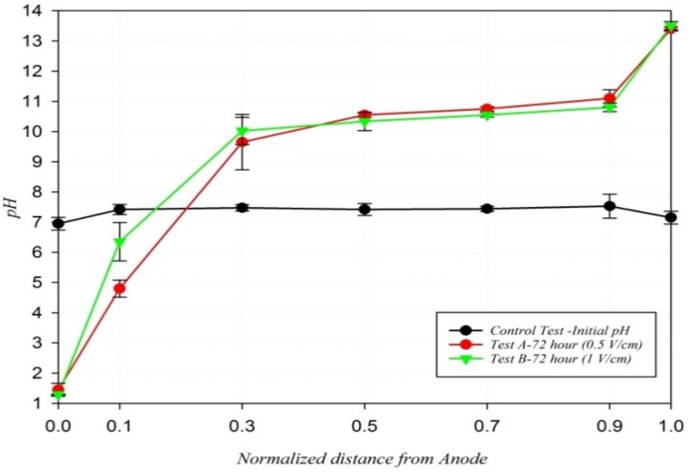


Figure 5.25: Variation of pH with time across the soil cell.

The initial bonding between a hydrated hydrogen ion and a group of oriented water molecules is shown in Figure 5.26(a), and the final rearranged bonding is shown in Figure 5.26(b), resulting in the apparent migration of the hydrogen ion. Similarly, the hydrated hydroxide ion migrates in the opposite direction. Therefore, the measured ionic mobilities of these ions are not related to their actual ionic migration velocities. The phenomena cast serious doubt on the validity of applying the advection-dispersion equation to describe the migration of hydrogen and hydroxide ions in contaminated soil and to compute the resulting pH distribution in the soil.

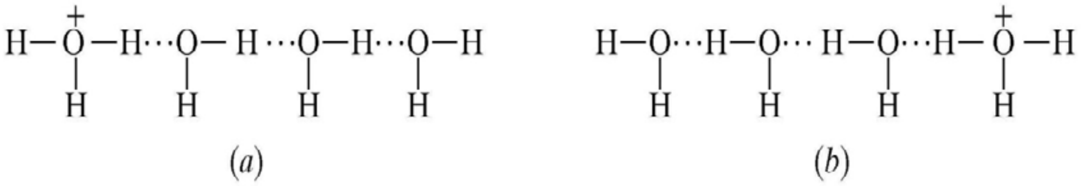


Figure 5.26: Transfer mechanisms of hydrogen ions in water: (a) The initial bonding in a group of oriented water molecules, (b) The final bonding in a group of oriented water molecules [30].

Moreover, As soil fluid chemical systems must be electrically neutral, charges cannot be added to, formed in, or removed from a system without the simultaneous addition, formation, or removal of an equal number of the opposite charge [31]. Yeung and Datla proposed an electrokinetic transport model through which the electrical neutrality of the system is restored, primarily by the immediate availability of hydrogen and hydroxide ions [32]. Their model explains the phenomena observed in this study, whereby the acid front has never been observed flushing through the specimen to develop a uniform acidic pore fluid environment. Therefore, as a result of the depletion of the negative charged ions in the soil cell, the movement of the negative charged hydroxide ions was enhanced and alkaline front movement was more dominant than the acidic front within the soil cell. However, the spatial and temporal changes in the soil pH induced by an electrochemical remediation process are evident as depicted in Figure 5.25 and Figure 5.27.

In order to better evaluate the pH changes across the soil cell more accurately, samples were taken from each soil section and measured *in-situ* using a pH liquid indicator. The results are shown in Figure 5.27.

A closer look at the soil pH analysis, at cross section 3 in the middle of the soil cell (Figure 5.28), shows that acid and alkaline fronts were moving or distributed uniformly. An acidic pH value was measured on the top part, and a higher basic pH value on the lower part of the cross section, while as a result of mixing the soil section, the pH after mixing will indicate a basic pH value of around 10, as shown in Figure 5.25.

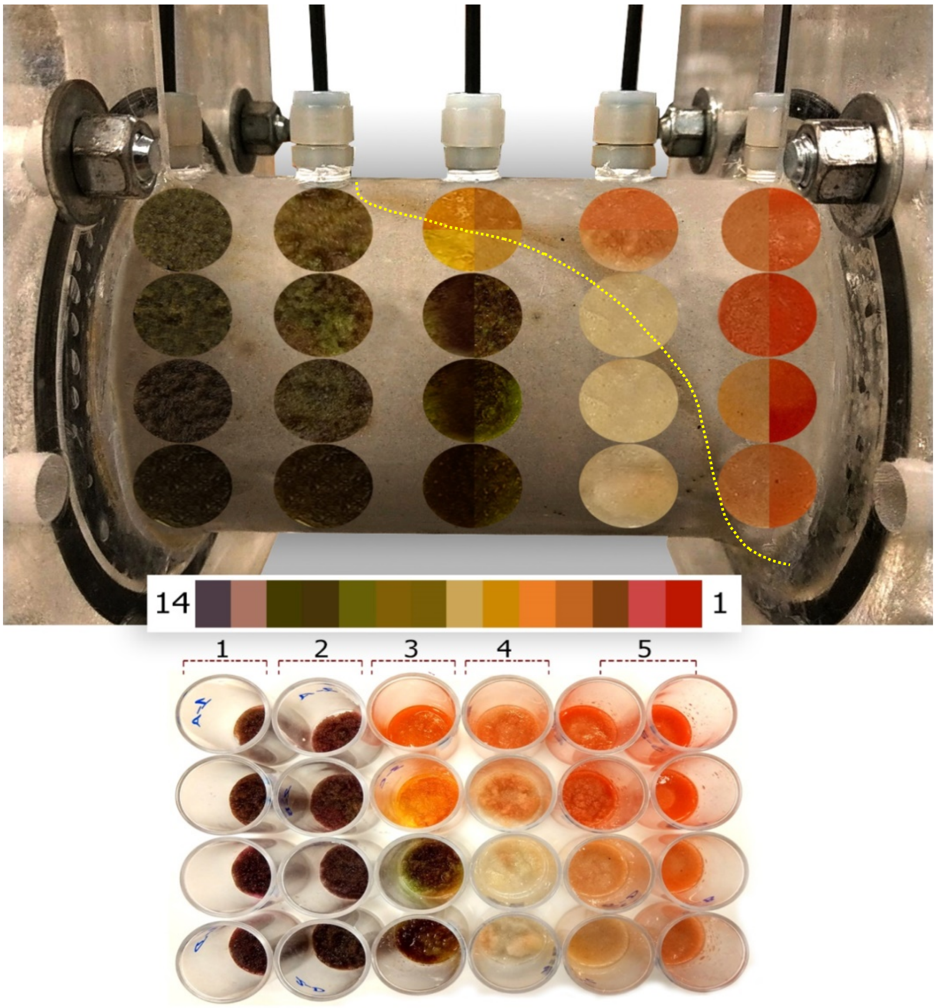


Figure 5.27: The spatial changes in soil pH induced by the electrochemical remediation process.

A closer look at the soil pH analysis, at cross section 3 in the middle of the soil cell (Figure 5.28), shows that acid and alkaline fronts were moving or distributed uniformly. An acidic pH value was measured on the top part, and a higher basic pH value on the lower part of the cross section, while as a result of mixing the soil section, the pH after mixing will indicate a basic pH value of around 10, as shown in Figure 5.25. As a conclusion, physical and chemical changes of the soil and the contaminants associated with the change in soil pH have to be carefully taken into account to in order to maximize the efficiency of electrochemical remediation of contaminated soil.

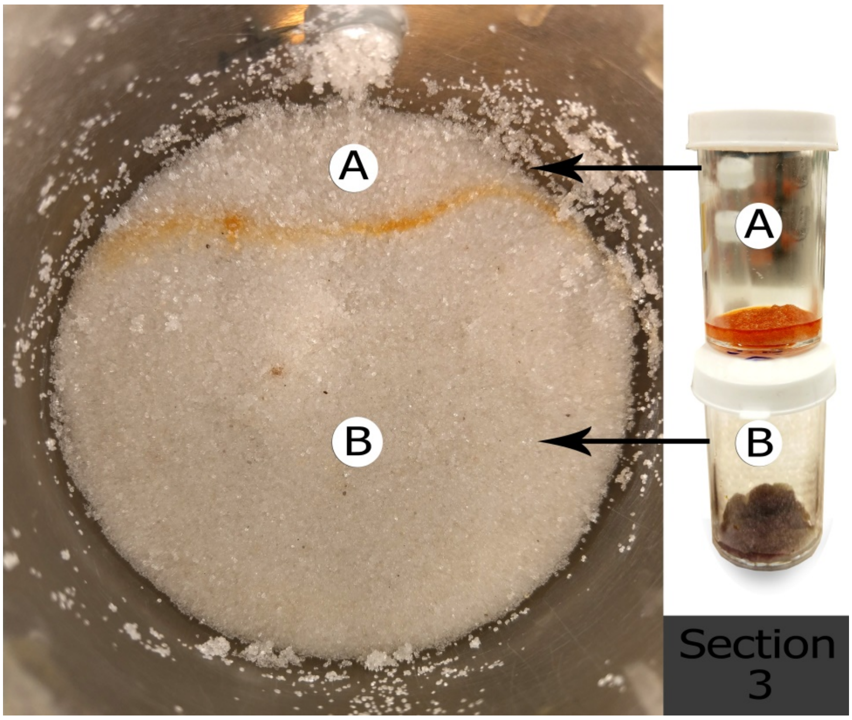


Figure 5.28: pH value measured in the middle of soil at section 3.

Salt residuals in soil compartment

The distribution of normalized residuals (C/C_0) of Na^+, K^+, Ca^{2+} and Cl^- remaining in the soil profile after the experiments are shown in Figure 5.29. Those elements form the main constituents of the sea salts, other main elements such as Mg^{2+} and SO_4^{2-} could not be analyzed due to the laboratory limitations.

Cations such as potassium, calcium, and sodium were transported toward the cathode as shown in Figure 5.29. Consequently, the concentration of cations decreased near the anodic regions and increased or accumulated near the cathodic region. The electrical conductivity profile in the soil cell and sodium and potassium distribution profiles virtually followed the same trend, which indicates that the soil electrical conductivity was influenced significantly by the residual concentration of water soluble sodium and potassium. This was also an indication of precipitation of calcium ions, because of its low solubility at a pH above 8. The removal efficiency was slightly enhanced by increasing the voltage gradient. For example, in the first two sections of the soil near the anode, about 75% of the sodium migrated towards the cathode under a voltage gradient of 0.5 $V\ cm^{-1}$, while only 10% increase was shown for the same section in the second experiments under a voltage gradient of 1 $V\ cm^{-1}$.

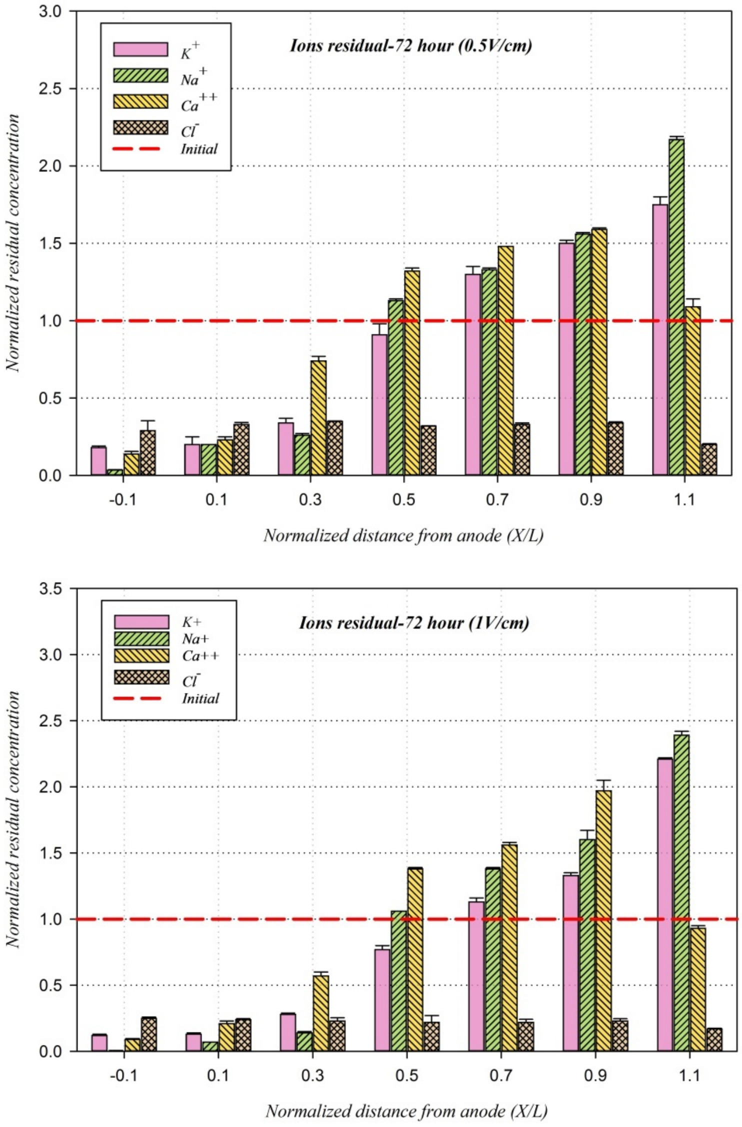


Figure 5.29: Ions residuals in soil cell under applied voltage (0.5 $V\ cm^{-1}$) above, and under applied voltage (1 $V\ cm^{-1}$) under.

Similar to the previous experiments with NaCl as model solution, chloride was easily removed from the soil cell, and the same reactions of chlorine hydrolysis would be expected at the anode surface. The mass balance analysis yielded an error in the range of 5% for both potassium and sodium ions. However, it yielded an error around 15% for calcium ions. It is hypothesized that the lower solubility of such metals in the alkaline regions may have led to precipitation of insoluble forms that were not separated from the soil, the cell wall and on the cathode surface. However, this was very evident at the cathode surface, as shown in the Figure 5.30.

Figure 5.30: Ions precipitation at the cathode surface at high pH value.

5.3 Energy expenditure and economical assessment

In the field of remediation of contaminated sites, difficulties are invariably encountered in obtaining reliable information on treatment costs from laboratory scale studies, in view of the large range of site specific conditions. However, energy consumption data obtained in laboratory scale studies are useful to provide general insights into the energy cost related to a technology. Some remediation methods may be considered expensive, but its application may be believed to be feasible in conditions when other processes have been proven ineffective, i.e. in low permeability soil and significant presence of clay require some degree of reclamation) [33]. The cost associated with electrokinetic application is usually compared with the cost of excavation and disposal of contaminated soil as hazardous waste [34]. Similarly, conventional control measures against seawater intrusion, intended to increase the volume of available fresh groundwater water and/or to reduce the volume of saltwater diffusing into an aquifer [29], are in most instances inefficient, time consuming, cost prohibitive and sometimes not feasible. Thus, the application of electrochemical fencing to counter seawater intrusion problem could provide a feasible and a more cost effective solution.

The main economic aspects in electrokinetic systems are presented by the energy consumption, fabrication, and installation of electrodes, and chemicals for an enhanced process and eventually for post treatment of electrolytes [33, 35, 36]. In electrokinetic fencing as well as any electrokinetic application, many factors including soil characteristics, contamination conditions, and electrode configuration or spacing significantly influence the energy consumption during the process [36].

In this study, the electric power consumption per cubic meter of treated soil is used to calculate the total electrical energy consumption. The energy consumption per unit volume of treated soil is calculated using the following equation [37, 38]:

$$E = \frac{1}{V_s}\int VIdt = \frac{1}{V_s}\int \frac{V^2}{R}dt \tag{5.8}$$

where E is the energy consumption ($W\ h\ m^{-3}$); V_s is the volume of the soil sample (m^3); V is the applied voltage (*V*); I is the current intensity (*Amp*). In tests with constant voltage conditions, the energy expenditure is directly related to the time integral of the inverse of the resistance across the cell or directly related to the apparent conductivity.

Table 5.2: The electric energy consumption and chloride removal (%) (NaCl model).

Test number	Test 1	Test 2	Test 3
Voltage applied ($V\ cm^{-1}$)	0.5	0.5	0.5
Operation time (*h*)	24	72	168
Chloride reduction (%)	73	86	88
Energy ($kW\ h\ m^{-3}$)	43.20	85.87	96.38

The calculated results are tabulated in Table 5.2. In the three test groups the same constant voltage was applied across the cell. However, the tests differ in duration only. It can be seen that at the tests operated for 24, 72, and 168 *hours* the chloride removal and energy expenditure are 73%, 86%, 88% and 43.2, 85.87, 96.36 $kW\ h\ m^{-3}$, respectively. With the time increase, the chloride removal and energy consumption both increase. When the time increases from 24 *h* to 72 *h*, the differences of energy consumption are more significant than those of the chloride removal. Although the chloride removal was higher at longer operation time, the operation for 24 *hours* seems to be more economical. On the other side, the energy consumption associated with sodium removal was not assessed here, despite the high removal efficiency up to 99% on the soil sections near the anodic part, sodium ions accumulated in the soil sections near the cathodic part and thus not removed entirely from the system due to the lab configurations used in this study. For this reason, a calculation of the energy consumption associated with sodium removal from soil would lead to misinterpretations. The calculated energy consumption data for the sea salts tests groups are presented in Table 5.3. In these tests the applied voltage was different. Voltage potentials of 0.5 and 1 $V\ cm^{-1}$ were applied for group 1 and group 2, respectively.

Table 5.3: The electric energy consumption and chloride removal (%) (Sea salts model).

Test number	**Test 1**	**Test 2**
Voltage applied ($V\,cm^{-1}$)	0.5	1
Operation time (h)	72	72
Chloride reduction (%)	63	74
Energy ($kW\,h\,m^{-3}$)	69.8	166.4

When the applied voltage drop increased from 0.5 $V\,cm^{-1}$ to 1 $V\,cm^{-1}$, the differences of energy consumption are more significant than those of the chloride removal. This leads to the conclusion that, despite the fact that an increasing applied voltage accelerates the removal efficiency, more energy will be wasted when experiments are operated for the same time. Thus, operating under a higher voltage drop would be more efficient when operating for a shorter time before shutting down the process. However, from the test data presented, it is not possible to discern the optimal energy needed to reduce salinity from the cell.

It is difficult to compare electrical energy consumption for each chemical element or unwanted elements in contaminated soil. Thus it would be important to develop a method to predict the electrical energy consumption for the removal of each ion, and it is helpful to understand the influence of the removal of each element on the total energy consumption. Moreover, other energy losses to be considered are the energy consumption used in *Ohmic* heating and electrolysis reactions in the electrode surface, which is also a part of the energy consumption for the removal of each element from the soil or along the electric fence. Additionally, during the electrokinetic process where the ions/metals are removed by electromigration, the electrical energy consumption is proportional to the number of removed ions and the electric charge of the ions. Ion complexation such as ions complexed with chloride (Cl^-) will affect the electric charge of the ion and hence the interaction between each ion may affect the energy consumption, where these influences are not considered.

On the other side, utilizing renewable energy would reduce environmental impact. Some studied focused on how to reduce the energy consumption needed using a pulsed electric field i.e., periodic power instead of a constant application of voltage [39, 40]. This approach may lead to a significant reduction of the total energy consumption in electrokinetic treatment[40].

5.3.1 Practical aspects for field application and scale up the technology

Several factors are also influencing the total cost of scaling up for field implementation and scaling up the technique [41]. Factors affecting full scale field implementation and electrode configuration include: (1) location and size of any inactive electric field spots that can be developed; (2) number and costs of electrodes per unit area to be treated; and (3) time requirements of the designed remediation process. Moreover, Factors affecting the selection of electrode spacing include: (1) costs; and (2) processing time required. Larger electrode spacing will reduce the number of boreholes and installation costs, but will increase the processing time required and operation costs. The costs of each electrode depend on the material used, complexity of installation, and dimensions. The number of electrodes per unit volume of soil to be treated depends on electrode configuration and spacing. The installation costs depend on the method of installation, depth of the electrodes to be installed, and number of electrodes to be installed. The total costs of electrodes per unit volume of soil to be treated include the material and fabrication costs of the electrodes and their installation costs in the field.

On the other side, if the effluent from the process required posttreatment or a small portion of the treated soil needs to be removed due to accumulation of a high concentration of contaminant that cannot be extracted, there will be posttreatment costs. These costs are highly site and contaminant specific. They are also dependent on the enhancement agent used in the process. Therefore, they have to be quantified on a case-by-case basis. These factors must be carefully considered before the technology can be successfully implemented in the field, these aspects are explained in detail by Alshawabkeh et al. [41, 42].

In addition to the above factors regarding the electrode system, some other aspects are practically important to consider:

- Power distribution system: Electric power is applied to the electrode system by a power supply. Several units can be connected either in series or in parallel to give the desired power output. The power units can be operated under constant voltage or current conditions in pulsed or in continuous mode [43].
- Circulation system: This is necessary for salts recovered from the electrode solutions and also for chemicals to enhance the separation and transportation of salts to the electrode solutions. Therefore, a circulation system is important for the management of the electrode solution and to maintain the parameters like temperature and pH of the anolyte as well as the catholyte. A proper circulation

control system enables complete mixing of electrode solutions and sample withdrawal also if necessary. It might also include a process piping to distribute any chemical amendments to electrode wells and to extract the contaminants from the electrode solutions, e.g., precipitation and ionic exchange [43].

- Salts recovery and disposal: The salts recovery and disposal system forms an integral part of the whole electrochemical setup. Generally, the salts that are concentrated in the electrode wells are recovered by processing the electrolyte. After regeneration, the electrolytes can be reused, thereby improving the economic balance of the process and reducing the amount of wastes. Salts can be recovered by other methods also, such as the use of ion exchange resins, and so on [44].

Major limitations and challenges for the filed application include:

- Soil heterogeneities: Heterogeneities of soil in the form of rocks can cause a discontinuity in the current flow path, which results in poorly remediated zones. Moreover, the presence of conducting materials in the soil would also adversely affect the technology performance by acting as preferential flow paths for the current, leaving the surrounding soil unaffected by the treatment, or even the dissolution of metallic objects into the soil acts as a new source of ions that generates more pollution and more electric power consumption [43].
- Remediation time: In the laboratory test, electroosmotic flow and electromigration are defined by the placement of the electrodes and the shape and configuration of the experimental setup, but this may not always give a true indication of the time required. Moreover, the soil sample is lab scale is normally homogenized before testing. In the open field, the expected electroosmotic flow and electromigration is affected by soil heterogeneity, and flow of groundwater [43].
- By-products formation: this is one of the most critical aspect when applying electrokinetic technique in highly saline medium, chlorine gas produced at the anode and different chlorine ionic species formed during the process, would dramatically affect ecosystem in the soil or in the atmosphere because of the toxicity of chlorine. Thus, the circulation system and post treatment is very important to consider carefully in such application.

5.4 References

1. Singh, U. and G. Uehara, *Electrochemistry of the double layer: principles and applications to soils.* Soil physical chemistry, 1998. **2**: p. 1-46.

2. Acar, Y.B., et al., *Electrokinetic remediation: Basics and technology status.* Journal of Hazardous Materials, 1995. **40**(2): p. 117-137.

3. Dzenitis, J.M., *Soil Chemistry Effects and Flow Prediction in Electroremediation of Soil.* Environmental Science & Technology, 1997. **31**(4): p. 1191-1197.

4. Hsu, C.-n., *Electrokinetic remediation of heavy metal contaminated soils.* 1998.

5. Crompton, T.R., *Leclanché Carbon — Zinc and Zinc Chloride Batteries*, in *Small Batteries: Volume 2 Primary Cells*, T.R. Crompton, Editor. 1982, Macmillan Education UK: London. p. 17-41.

6. Kordesch, K., *Primary Batteries—Alkaline Manganese Dioxide-Zinc Batteries*, in *Comprehensive Treatise of Electrochemistry: Volume 3: Electrochemical Energy Conversion and Storage*, J.O.M. Bockris, et al., Editors. 1981, Springer US: Boston, MA. p. 219-232.

7. Huber, R., *Leclanché batteries.* Batteries, KV Kordesch (ed.), 1974. **1**: p. 1-239.

8. Scholz, F., *Voltammetric techniques of analysis: the essentials.* ChemTexts, 2015. **1**(4): p. 17.

9. Gregolec, G., *Fundamental Aspects of Using Electric Fences for Groundwater Remediation*. 2008, Verlag nicht ermittelbar.

10. Hamed, J.T., *Decontamination of Soil Using Electro-Osmosis*. 1990.

11. Probstein, R.F., *Transport in Fluids*, in *Physicochemical Hydrodynamics*. 2005.

12. Acar, Y.B., et al., *Removal of cadmium (II) from saturated kaolinite by the application of electrical current.* Géotechnique, 1994. **44**(2): p. 239-254.

13. Acar, Y.B. and A.N. Alshawabkeh, *Principles of electrokinetic remediation.* Environmental Science & Technology, 1993. **27**(13): p. 2638-2647.

14. Cho, J.-M., S.-Y. Park, and K. Baek, *Electrokinetic restoration of saline agricultural lands.* Journal of Applied Electrochemistry, 2010. **40**(6): p. 1085-1093.

15. Kim, J.-K. and D.F. Lawler, *Characteristics of zeta potential distribution in silica particles.* Bulletin of the Korean Chemical Society, 2005. **26**(7): p. 1083-1089.

16. Parks, G.A., *The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems.* Chemical Reviews, 1965. **65**(2): p. 177-198.

17. Findlay, A.D., D.W. Thompson, and E. Tipping, *The aggregation of silica and haematite particles dispersed in natural water samples.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1996. **118**(1-2): p. 97-105.

18. Alshawabkeh, A.N. and Y.B. Acar, *Removal of contaminants from soils by electrokinetics: A theoretical treatise.* Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology, 1992. **27**(7): p. 1835-1861.

19. Yeung, A.T., C.-n. Hsu, and R.M. Menon, *Physicochemical soil-contaminant interactions during electrokinetic extraction.* Journal of Hazardous Materials, 1997. **55**(1-3): p. 221-237.

20. Franks, G.V., *Zeta potentials and yield stresses of silica suspensions in concentrated monovalent electrolytes: isoelectric point shift and additional attraction.* J Colloid Interface Sci, 2002. **249**(1): p. 44-51.

21. Antonio Alves Júnior, J. and J. Baldo, *The Behavior of Zeta Potential of Silica Suspensions*. Vol. 04. 2014. 29-37.

22. Frenkel, D., *Colloidal systems. Playing tricks with designer "atoms".* Science, 2002. **296**(5565): p. 65-6.

23. Dove, P. and J. Rimstidt, *Silica-water interactions.* Reviews in Mineralogy and Geochemistry, 1994. **29**(1): p. 259-308.

24. Yeung Albert, T., *Diffuse Double-Layer Eqautions in SI Units.* Journal of Geotechnical Engineering, 1992. **118**(12): p. 2000-2005.

25. Chorom, M. and P. Rengasamy, *Dispersion and zeta potential of pure clays as related to net particle charge under varying pH, electrolyte concentration and cation type.* European Journal of Soil Science, 1995. **46**(4): p. 657-665.

26. Niriella, D. and R.P. Carnahan, *Comparison Study of Zeta Potential Values of Bentonite in Salt Solutions.* Journal of Dispersion Science and Technology, 2006. **27**(1): p. 123-131.

27. Bergner, D., *Reduction of by-product formation in alkali chloride membrane electrolysis.* Journal of Applied Electrochemistry, 1990. **20**(5): p. 716-722.

28. Alshawabkeh, A.N. and Y.B. Acar, *Electrokinetic Remediation. II: Theoretical Model.* Journal of Geotechnical Engineering, 1996. **122**(3): p. 186-196.

29. Eykholt, G.R. and D.E. Daniel, *Impact of System Chemistry on Electroosmosis in Contaminated Soil.* Journal of Geotechnical Engineering, 1994. **120**(5): p. 797-815.

30. Reddy, K.R. and C. Cameselle, *Electrochemical remediation technologies for polluted soils, sediments and groundwater*. 2009: John Wiley & Sons.

31. Szpyrkowicz, L., et al., *Simultaneous removal of metals and organic compounds from a heavily polluted soil.* Electrochimica Acta, 2007. **52**(10): p. 3386-3392.

32. Yeung, A.T. and S. Datla, *Fundamental formulation of electrokinetic extraction of contaminants from soil.* Canadian Geotechnical Journal, 1995. **32**(4): p. 569-583.

33. Cappai, G., et al., *Combined use of a transformed red mud reactive barrier and electrokinetics for remediation of Cr/As contaminated soil.* Chemosphere, 2012. **86**(4): p. 400-8.

34. Reddy Krishna, R. and C. Cameselle, *Overview of Electrochemical Remediation Technologies*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*. 2009, John Wiley & Sons, Inc.

35. Alshawabkeh, A.N., *Electrokinetic Soil Remediation: Challenges and Opportunities.* Separation Science and Technology, 2009. **44**(10): p. 2171-2187.

36. Alshawabkeh Akram, N., T. Yeung Albert, and R. Bricka Mark, *Practical Aspects of In-Situ Electrokinetic Extraction.* Journal of Environmental Engineering, 1999. **125**(1): p. 27-35.

37. Weng, C.-H. and H.-W. Tsai, *A pilot-scale test of electrokinetic remediation of Cr (VI) contaminated kaolinite incorporated with zero-valent iron.* J. Environ. Eng. Manage, 2009. **19**(6): p. 379-387.

38. Hamed, J., Y.B. Acar, and R.J. Gale, *Pb(II) Removal from Kaolinite by Electrokinetics.* Journal of Geotechnical Engineering, 1991. **117**(2): p. 241-271.

39. Ryu, B.-G., et al., *Pulsed Electrokinetic Decontamination of Agricultural Lands around Abandoned Mines Contaminated with Heavy Metals.* Separation Science and Technology, 2009. **44**(10): p. 2421-2436.

40. Yuan, L., et al., *The influence of macroelements on energy consumption during periodic power electrokinetic remediation of heavy metals contaminated black soil.* Electrochimica Acta, 2017. **235**: p. 604-612.

41. Alshawabkeh, A.N., A.T. Yeung, and M.R. Bricka, *Practical Aspects of In-Situ Electrokinetic Extraction.* Journal of Environmental Engineering, 1999. **125**(1): p. 27-35.

42. Alshawabkeh, A.N., et al., *Optimization of 2-D Electrode Configuration for Electrokinetic Remediation.* Journal of Soil Contamination, 1999. **8**(6): p. 617-635.

43. Lageman, R. and W. Pool, *Experiences With Field Applications of Electrokinetic Remediation*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater* 2009, John Wiley & Sons, Inc.

44. Gent, D.B., et al., *Bench- and field-scale evaluation of chromium and cadmium extraction by electrokinetics.* Journal of Hazardous Materials, 2004. **110**(1): p. 53-62.

6 GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

6.1 General conclusion

The application of electrokinetic remediation as a novel alternative technique for controlling seawater intrusion into groundwater aquifers in coastal areas is demonstrated in this dissertation. Laboratory experiments were carried out to investigate the fundamental electromigration behavior of soluble salts ions under the influence of an electrical gradient when coarse grained soil is used. The experiments were performed without applying any enhancement process. This was done in order to enable the researcher to have a better understanding of the actual physiochemical reaction occurring during electrokinetic remediation, and to identify the most contributing parameter in the removal mechanisms. Initial experiments were conducted by using a sodium chloride model solution only and then followed by experiments carried out using sea salts model solution. Since there is no any externally applied hydraulic potential at either side of the soil specimen, the main transport mechanism for soluble ions was the ionic migration caused by the electromigration transport phenomena. Experimental evidence of this study was analyzed in order to explain electrokinetic phenomena and to better understand the physics and chemistry associated with the electrokinetic extraction process. Hence, several groups of tests were carried out with the same operation conditions; however, the duration was changed. The duration of the first group was 24 *hours*, 72 *hours* for the second group and for 168 *hours* for the third group. The development of potential gradients and current of the three group experiments was in agreement within the first 24 or 72 *h*, indicating a good experimental reproducibility. The current trace shows an increase within the first 24 *hours* after reaching a maximum value of approximately 180 *mA*. The initial rise in current in the three test groups represents an increased electrical conductivity in the soil, which was influenced by the results of additional ions produced by electrolysis of water, where hydrogen H^+ and hydroxide OH^- ions produced at the electrodes move faster into the soil than other dissolved salts ions move out of the soils towards the electrodes. On the other side, this trend of current development during the tests could be due to the polarization occurring in the diffusion layer; this assumption is related to the electrochemical behavior in the diffusion layer in vicinity of electrodes surfaces.

The subsequent steep decrease in current (group 2 and 3) arises from sharp change of the electrical conductivity of soil in the cell, which could be attributed to the formation of H_2O when the oppositely charged protons and hydroxide ions meet. Alternatively, it could also be caused by precipitation of impurities in this zone as the pH rises. The current dropped to 40 *mA* after 48 *hours* and continued to decrease to a steady state at around 20 *mA* after 72 *hours*, which is an evidence of the removal of dissolved ions from the specimen. More importantly, the distribution of electric potential along the specimen is closely related to the conductivity of the specimen, and the development of the interfaces potential between the electrodes and the soil mass. The electrical conductivity or electrical resistance would change due to variations in pores sizes, i.e. porosity, tortuosity in the porous medium, variation in pore fluid concentration, and double layer electrolyte concentration. The calculated apparent conductivity is a good approximation of the actual soil conductivity of only during the early stage of electromigration, before a significant polarization takes place and when the background electrolyte condition is relatively constant across the cell. Moreover, when an ordinary diffusion is present and there are concentrations gradients, *Ohm's* law does not hold because there is a contribution to the current from diffusion [1].

At the very beginning of the experiments, the electrical potential was linearly distributed. In this instance, the constituents in the specimen were uniformly distributed and the conductivity in each section was almost identical. Lower conductivity was observed near the anode with respect to the initial value and it reflects the removal of the ionic species near the anode. Alternatively, a higher conductivity was observed closer to the cathode as sodium ions were migrating and accumulating in cathodes. A steep electrical conductivity gradient has also been developed in line with the potential gradient, reflecting a sudden drop of electrical conductivity within this section. As time progressed, a large voltage drop has developed within a small zone while across the rest of the soil core gradients, smaller voltage drop was observed.

When coming to pH, the results show that the soil media and the chemistry of the soil pores play a major rule in defining the pH profile across the soil under the influence of an electrical potential. Moreover, that it is not necessarily the case that a low pH value will dominate across the sample as a result of the electrolysis process occurring in the electrolyte solutions. Very low reversed electroosmotic flow moving towards the anode was observed. This could be attributed to the characteristics of sandy soil and the high ionic strength of the background electrolyte. Additionally, this reversed electroosmotic flow is contrary to the known direction of the electroosmotic flow i.e. flowing towards the cathode, which could be influenced by the surface charge of the solid matrix, represented by the zeta potential and the high ionic strength of the background electrolyte. This observation requires more attention to study the characteristics of the zeta potential (ζ) and the zeta potential distribution of silica particles. The charged dissolved ions were transported in the soil specimen under the action of an applied voltage gradient, which influenced the Na^+ and Cl^- ions and deflected them towards the oppositely polarized electrodes accordingly. Chloride and sodium ions were transported towards the anode and cathode, respectively, mainly through the electromigration transport process. However, as mentioned above the observed reversed electroosmotic flow also contributed to the chloride removal because the electroosmotic flow was towards the anode. The chloride was removed from the soil to a much higher extent than sodium. Moreover, more chloride ions were removed and more sodium ions migrated towards the cathode when the experiments were carried out for a longer time (168 *hours*); however, the difference was not significant when comparing the results of experiments carried out for 72 *hours* with experiments carried out for 168 *hours*. An average of 73% of chloride was removed during experiment group 1, which was carried out for only 24 *hours*. Most of the sodium from the sections near the anode and from the anodic electrolyte solution was removed and migrated towards the cathode: more than 85% of dissolved sodium from those sections was removed, the migrated sodium accumulated gradually from the third section (in the middle of the soil specimen) and started to build up near the cathode and in the cathodic electrolyte. Experimental group 2 and 3 were running for 72 *hours* and 168 *hours*, respectively. They show better removal efficiencies under the same condition. In those cases, more than 85% of chloride was removed from the system, and more sodium migrated toward the cathode. However, It can be seen that at the tests operated for 24, 72, and 168 hour the chloride removal and energy expenditure are 73%, 86%, 88% and 43.2, 85.87, 96.36 $kW\ h\ m^{-3}$, respectively. With the time increase, the chloride removal and energy consumption both increase. When the time increases from 24 to 72 *h*, the differences of energy consumption are more significant than those of the chloride removal. Although the chloride removal was higher at longer operation time, the operation for 24 *hours* seems to be more economical

When using a sea salt solution as the model solution, two series of tests were carried out under the same experimental condition; however, the tests were carried out under different applied voltages. In the first series an applied voltage of 0.5 $V\ cm^{-1}$ was used, while an applied voltage of 1 $V\ cm^{-1}$ was used in the second series. Moreover, the tests were carried out for 72 *hours*. The results regarding the development of current, potential gradients change in ions concentration and pH absolutely coincided with the NaCl experiment. The general trend of the electrical current variation with time was observed under a constant voltage condition. Under the applied voltage of 0.5 $V\ cm^{-1}$, a peak value was observed with the same range of the experiments using NaCl. This shows that even with different dissolved ions, the soil matrix gains similar electrical criteria. This also supports the fact that the major constituents of ions in the solution were sodium and chloride in both model solutions, which contribute to the major charge carrier in the solution. Considering these data, it can be concluded that the electrokinetic configuration in this study efficiently removed chloride and forced sodium to migrate towards the cathode, which could also be removed from the system by pumping out electrolytes in the cathode compartments.

6.2 Recommendations for further research

Given the obvious competing reactions between chlorine and oxygen, during water hydrolysis, it is therefore recommended that more research be conducted with the intention of harvesting the by-products. In the case of this study, it would be chlorine and oxygen harvesting. This approach could increase the interest of industrial sector in applying electrokinetic technique as a dual process, both remediation and harvesting of valuable product for industrial use. However, this aspect should be carefully thought through and be implemented with a primary objective being to remove chloride. Therefore the interest should be on how to selectively enhance the chlorine evolution process in order to remove more chloride ions from the system. Simultaneously, efforts should be put in order to suppress oxygen evolution, thus increasing the removal efficiency of chloride. For instance, maintaining low pH in the anodes compartment would limit the consequent dissociation of Cl_2 into other chlorine species and could provide better controlled removal of chlorine from the system. Moreover, it will also prevent formation of possible complexes that would otherwise form as a result of electrochemical reactions with cations such as sodium. In order to realize this objective, focus should be on enhancing selectivity of the electrodes by applying various techniques to improve the surface chemistry of the electrodes.

In order to better assess the changes in pH within the soil matrix, it is highly recommended that a study be conducted regarding the influence of the zeta potential of silica sand on transport mechanisms under an electrical potential in silica sand media.

It is also recommended that different electrodes, both unmodified and modified, be tested in relation to stability and activity to determine the feasibility and efficiency of the system in removing more chlorine and suppressing oxygen evolution. This research would help identify the best electrodes that would ensure a feasible and efficient electrocatalytic reaction under both acidic and basic conditions. The economic models should be developed so as to entice potential users and enable them to make informed decisions.

It is also important that the real seawater and soil be used to establish the efficiency, challenges, and opportunities that could emerge when this technique is applied in the real environment. This could open up the scope of applying electrokinetic technique, as well as more research niche areas.

6.3 References

1. Probstein, R.F., *Transport in Fluids*, in *Physicochemical Hydrodynamics*. 2005.

7 APPENDICES

APPENDIX (A): THEORETICAL MODEL (USING COMSOL MULTIPHYSICS)

Introduction

In this chapter, a simplified one dimensional mathematical model between two points using COMSOL Multiphysics software package is presented. A mathematical model is presented for multicomponent species transport under coupled electric and chemical potential differences. A mass balance of species and pore fluid together with the charge balance across the medium result in a set of differential equations. Sorption and precipitation reactions are not accounted in this model. Instantaneous chemical equilibrium conditions are assumed. Transport of H^+, OH^-, Na^+, Cl^-, the associated chemical reactions, electric potential are modelled. For most electrokinetic remediation cases, normally only water is reduced at the cathode, because the redox potential of alkali and alkaline earth metals is too high to be competitive with respect to the reduction of water [1, 2]:

$$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-, \qquad E^0 = -0.8277\,V \tag{7.1}$$

At the anode, water oxidation occurs:

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O, \qquad E^0 = 1.229\,V \tag{7.2}$$

However, when chloride ions are present in the anolyte, they will undergo an oxidation process and generation of Cl_2, which can be competitive to water oxidation:

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^-, \qquad E^0 = 1.356\,V \tag{7.3}$$

Theoretical development

The following assumptions are made in formalizing multicomponent species transport under an electric field:

- Diffusion and electromigration were considered as the main transport mechanisms;
- Electroosmotic flow is assumed zero as the model was implemented for a case of sandy soil;
- Electrophoretic transport was not accounted for, due to its limited relevance in electrokinetic remediation since colloid migration is hindered by the immobile phase of the porous medium [3];

- The porous medium is saturated, isotropic and isothermal (coupled heat transfer is neglected);
- The grains are non-conductive and their surface conductivity is negligible and streaming potential are negligible;
- The pore geometry characteristics, e.g., porosity, tortuosity do not change over time;
- All fluxes are linear homogeneous functions of potential gradients
- The chemical reactions precipitation/dissolution were not account;
- Aqueous phase reactions are at instantaneous equilibrium.

Under these assumptions, the ion flux density per unit cross sectional area of porous medium N_i ($mol\ m^{-2}\ s^{-1}$) of a dissolved chemical species *i* can be expressed as [4]:

$$N_i = -D_i^* \nabla c_i - U_i^* c_i \nabla \emptyset \tag{7.4}$$

where D^*_i ($m^2\ s^{-1}$) is the effective diffusion coefficient of the *i-th* species, c_i ($mol\ m^{-3}$) the concentration of the *i-th* species, U^*_i ($m^2\ s^{-1}\ V^{-1}$) the effective ion mobility, $\emptyset$ (V) the electric potential.

Due to the tortuous path followed by the ions in the porous matrix during transport, the effective diffusion and ion mobility coefficients used in Equation 7.4 take into account the effect of porosity *n* and tortuosity τ [5] and they are defined as:

$$D_i^* = n\tau D_i \tag{7.5}$$

$$U_i^* = n\tau U_i \tag{7.6}$$

where D_i ($m^2\ s^{-1}$) U_i ($m^2\ s^{-1}\ V^{-1}$) are the diffusion coefficient and ion mobility at infinite dilution, respectively. The value of tortuosity factor may span in a wide range from 0.01 to 0.84 [4] depending on specific characteristics of the porous medium.

Diffusivity and ionic mobility can be related to a single property by the Nernst-Townsend-Einstein relation [4]:

$$D_i^* = \frac{D_i^* z_i F}{RT} \tag{7.7}$$

where F (96485 $C\ mol^{-1}$) is the Faraday constant, R (8.314 $J\ mol^{-1}\ K^{-1}$) is the universal gas constant, T (K) is the absolute temperature and z_i is the charge number of the *i-th* species.

For solute chemical species (i.e., ions in a solution):

$$\frac{\partial c_i}{\partial t} + \nabla . N_i = R_i \tag{7.8}$$

where c_i (*mol* m^{-3}) is the concentration of the *i-th* species, N_i is the total flux (*mol* $m^{-2}s^{-1}$) and R_i (*mol* m^{-3} s^{-1}) represents a volumetric net source or sink of c_i due to chemical reactions. Applying continuity equation (Equation (7.8)) to Equation (7.4), the mass transport of the *i-th* specie is given by the Nernst-Planck equation:

$$n\frac{\partial c_i}{\partial t} = -\nabla . [-D_i^* \nabla c_i - U_i^* c_i \nabla \emptyset] + nR_i \tag{7.9}$$

Equation (7.9) is valid only for systems in which diffusion and electromigration are considered to be the most significant transport processes.

Electro-neutrality

In electrochemical systems, the bulk of the solution can generally be considered as electrically neutral because in any control volume of the electrolyte, the electrostatic forces between ions are capable of neutralizing the charge or cause a very low level of electrical unbalance. This is true only in the bulk, while near the electrodes and near the charged surfaces of soil minerals, the formation of an electrical double layer leads to a charge unbalance.

The charge density ρ (*C* m^{-3}) in a control volume of electrolyte is:

$$\rho = F \sum_i z_i c_i \tag{7.10}$$

From the *Gauss'* law, the relation between the electric potential and the free charge density in the electrolyte is denoted as Poisson's equation:

$$\nabla^2 \emptyset = -\frac{\rho}{\varepsilon} \tag{7.11}$$

The *Poisson's* equation can be used to couple the ionic charge balance in the electrolyte with the electric potential [1, 6]:

$$\varepsilon \nabla^2 \emptyset + F \sum_i z_i c_i = 0 \tag{7.12}$$

This equation assures the electro-neutrality condition in a macroscale global system. When local electro-neutrality condition is assumed:

$$\sum_i z_i c_i = 0 \tag{7.13}$$

the Equation 7.12 reduces to the Laplace equation [7]:

$$\nabla^2 \emptyset = 0 \tag{7.14}$$

Current density and conductivity

In the electrochemical system, the current density J $(A\ m^{-2})$ is due to the motion of all charged species:

$$J = F \sum_i z_i N_i \tag{7.15}$$

If electro-neutrality condition is assumed, the conductivity σ_w $(S\ m^{-1})$ of the pore solution is the sum of all the contributing ionic movement of different species in the solution, due only to electromigration [7]:

$$\sigma_w = F \sum_i |z_i| U_i c_i \tag{7.16}$$

In Equation 7.16, no convective term is present because the electro-neutrality condition ensures that there is always a zero net charge at any local point in a dilute solution . Therefore no charge can be transported by convection.

According to the definition of effective ion mobility coefficient U^* (Equation (7.6)), the bulk conductivity of the porous medium σ $(S\ m^{-1})$, in absence of surface conductivity, can be written as:

$$\sigma_w = F \sum_i |z_i| U_i^* c_i \tag{7.17}$$

It follows that bulk and pore fluid conductivities are related by:

$$\sigma = n \tau \sigma_w \tag{7.18}$$

From Equation (7.10) and (7.18), follows that ionic current transport is given by the macroscopic *Ohm's* law:

$$J = -\sigma \nabla \emptyset \tag{7.19}$$

A current balance gives the current and potential density in the cell:

$$\nabla . J = 0 \tag{7.20}$$

which in combination with Equation (7.19) yields:

$$\nabla.(-\sigma\nabla\emptyset) = 0 \qquad (7.21)$$

Boundary and initial conditions

Four ionic species are considered in this model: Na^+, Cl^-, H^+, and OH^-. In this model it has been assumed that the ions Na^+ and Cl^- are chemically inert except for the formation of H^+ and OH^- at the electrode, thus the production of Na^+ and Cl^- is equal to zero, the only homogenous reaction that is account for is the water formation:

$$H^+ + OH^- \rightleftharpoons H_2O \qquad (7.22)$$

Boundary conditions for the given species transport equation are evaluated based on the flux of each species at the cathode and the anode. There is one component of mass fluxes at the electrode; this is due to water electrolysis (current component). The expressions for molar fluxes at the boundary are based on the electrode reaction currents according to:

$$N_i.n = \frac{v_{ij}\mathrm{j}_j}{n_jF} \qquad (7.23)$$

where v_{ij} represents the stoichiometric coefficient for the ionic species i in reaction j. using the input value n=4 for H^+ and OH^- and, v_{H+}= -4 for H^+ and v_{OH-}= 4 for OH^-.

The boundary conditions were chosen as follows. At the anode the inward flux of H^+ was calculated with the *Faraday's* law of electrolysis:

$$N_{H^+} = -\frac{J}{F} \qquad (7.24)$$

where N_{H+} ($mol\ s^{-1}$) is the flux of H^+, J ($A\ m^{-2}$) the current density.

At the cathode,

$$N_{OH^-} = \frac{J}{F} \qquad (7.25)$$

The input data used in the model are listed below in Table 7.1:

Table 7.1:Model Input data

Parameter	Value	Unit	Description
D_{Na}	1.33×10^{-5}	$cm^2.s^{-1}$	Diffusion coefficient, Na^+
D_{Cl}	2.03×10^{-5}	$cm^2.s^{-1}$	Diffusion coefficient, Cl^-
D_H	9.31×10^{-5}	$cm^2.s^{-1}$	Diffusion coefficient, H^+
D_{OH}	5.26×10^{-5}	$cm^2.s^{-1}$	Diffusion coefficient, OH^-
$C_{0,Cl}$	0.3	M	Concentration, Cl^-
$C_{0,Na}$	0.3	M	Concentration , Na^+
$C_{0,H}$	1×10^{-7}	M	Inlet concentration, H^+
$C_{0,OH}$	1×10^{-7}	M	Inlet concentration, OH^-
L	0.153	m	Cell(domain) length
τ	0.45		Tortuosity factor
n	0.3		Porosity
$k_{w,f}$	1.5×10^{-8}	$m^3\ s^{-1}\ mol^{-1}$	Kinetic forward rate constant
$k_{w,b}$	2.7×10^{-5}	s^{-1}	Kinetic backward rate constant
V_{anode}	7.65	V	Applied voltage, anode
$V_{cathode}$	0	V	Applied voltage, cathode

Results and discussion

The model was implemented numerically by coupling two physics interfaces in COMSOL, the electric current (*ec*) module to solve for voltage applied which is then coupled with the transport of diluted species (*tds*) module to solve Nernst-Planck equations. The numerical implementation consisted of a 1D closed domain having 0.153 *m* length (equal to specimen length). The domain was discretized into 741 finite elements. At the center of the domain the mesh had a maximum element size of 1 *mm* with element size refinement at the edges where a maximum element size of 10^{-6} *mm* was set. The time interval between transport and reaction steps was set to 1 *hour*. Figure 7.1 shows the predicted electrical potential distribution for 24 *hour*s along the cell. The predicted potential results in this model is closely related to the predicted conductivity of the specimen only (Figure 7.2), where the effect of polarization within the double layer near the electrode surface is not considered, which could explain the deviation between the experimental and the modelled results. Considering the fact that chloride ions were assumed to be inert and do not undergo any transformation reaction in this model, this results in accumulation of migrated chloride ions near the anode zone

(Figure 7.3) causing increasing of the conductivity with this zone, and thus the effect of increased conductivity is highly pronounced and causing the voltage gradient to decrease in the anodic zone of the cell. In the cathodic zone, the voltage gradient also decreased following the same trend in the experimental results for 24 *hour*s, which is also attributed to the accumulation of the migrated sodium ions near the cathodic zone and resulting in increase if the electrical conductivity. Similarly, a large voltage drop has developed with cell between the anodic and cathodic zone representing a drop in electrical conductivity. However, this zone spans to a larger extend (from 0.3 to 0.7) than in the experimental result. The reason could be attributed to the simplified assumption in this model.

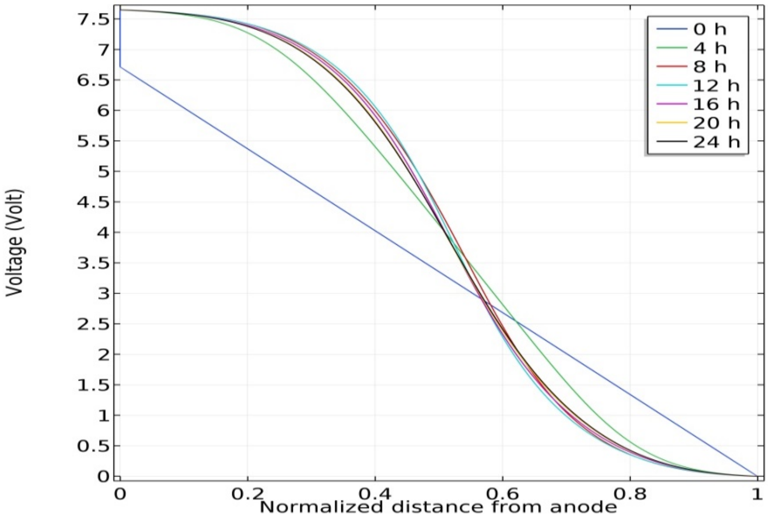


Figure 7.1: Electrical potential distribution across the cell.

The modelled electrical conductivity distribution is presented in Figure 7.2. The figure shows the low conductive zone within the cell (between 0.3 to 0.7), the electrical conductivity dropped to a very low than the initial value of electrical conductivity as the major ions contributing to the ionic strength migrated towards the oppositely charged electrode resulting in a zone of a lower electrical conductivity. Unlike the experimental results, the electrical conductivity in the anodic zone increased to a value higher than the initial value used in this model due to the accumulation of chloride ions in this zone, while in the experiments chloride ions are oxidized to form chlorine gas which was vented out of the cell causing a lower electrical conductivity near the anode.

The major sodium and chloride ions contributing in this model migrated under the influence of electrical potential towards the cathode and anode, respectively, as shown in Figure 7.3. More chloride ions migrated towards the anode and accumulated in the anodic zone in comparison with the migrated sodium ions towards the cathode; this is attributed to the higher mobility for chloride ions.

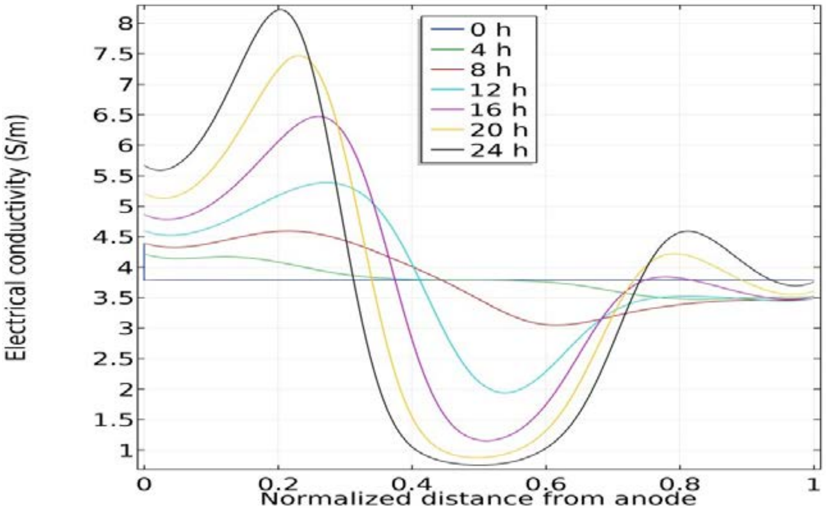


Figure 7.2: Electrical conductivity distribution across the cell.

Despite the assumption in this model where chloride ions were assumed inert and do not undergo further oxidation reaction, the ion distribution follows the observed concertation in the experiments. Moreover, the ion distribution shows that the resulted electrical conductivity is both aligned.

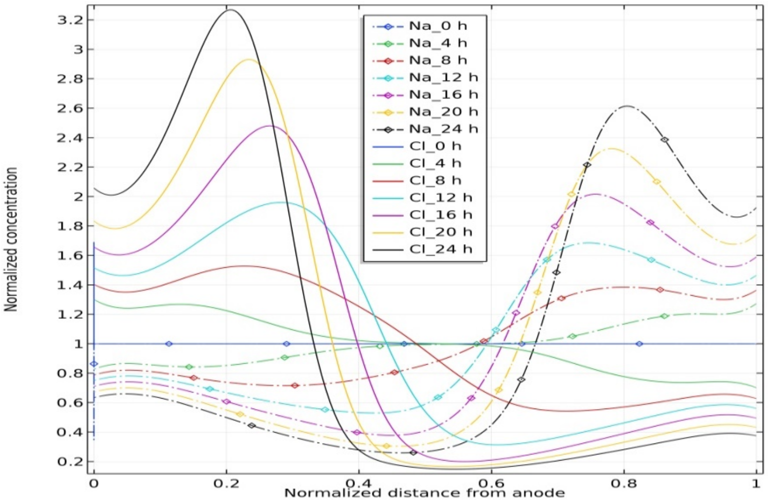


Figure 7.3: Normalized ion concentration distribution across the cell.

The comparison between the predicted and the measured concentration (normalized concentration) after 24 *hour*s for sodium ions is presented in Figure 7.4. The result shows that in both cases sodium ions migrated and accumulated in the cathodic zone. However, the predicted concertation in the middle of the cell at normalized distance of 0.5 shows a lower value than the initial value of sodium ions, while in the experimental sodium ions accumulated started from this section. The difference is possibly because the geochemical effect was not considered in the model. Generally, in both cases sodium migrated and accumulated near the cathode.

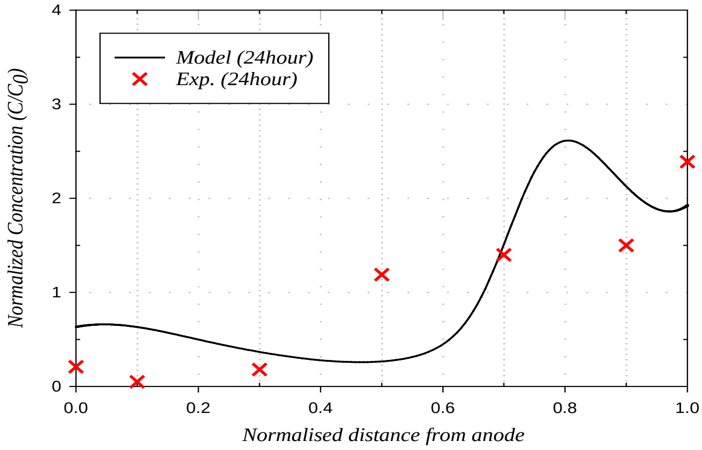


Figure 7.4: Predicted and measured normalized concentration for sodium ions for 24 *hour*.

The predicted pH profile in the cell is shown in Figure 7.5**.** Unlike the experimental results for the pH profile distribution, the pH dropped with time throughout the cell. After 24 *hours* of simulation time, the pH near the anode decreased to a value around 3.6 and in the cathodic zone decreased to a pH value of around 5.2. The difference between the predicted pH profile and the experimental pH profile is simply attributed to the simplified assumption in this model, where the revered advection flow observed during the experiment did not contribute to the migration of H^+ or OH^- in this model. However, many researchers [4, 8, 9] reported an acidic pH profile should reveal in the soil due the higher mobility of H^+.

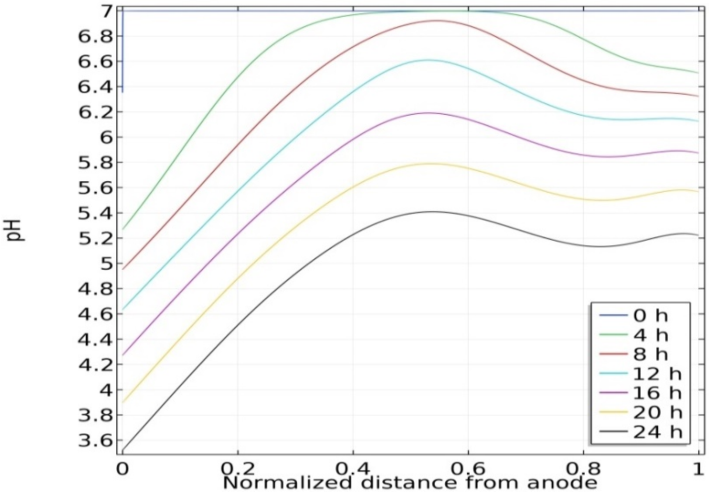


Figure 7.5: Modelled pH profile.

Conclusion

A one-dimensional transport model to simulate species transport during electro-migration of sodium chloride in porous media was numerically implemented with finite element software (COMSOL Multiphysics). The model consider the movement of aqueous "master species" only (i.e. Na^+, Cl^-) and not their complexes. The predicted results of the model were verified by comparing the predicted results with the experimental results for 24 *hours*. The model is able to reproduce the experimental data fairly accurately. The difference between model predictions and the observed data is attributed to the simplifications made. The model shows potential applicability as a tool for the design and operation of a real treatment plant. However, COMSOL alone can be used for modelling electro-migration remediation with the "Transport of diluted species" module; however it offers limited chemical reaction modelling capabilities.

APPENDIX (B): ADDITIONAL EXPERIMENTAL DATA

Introduction

Laboratory experiments were carried out in order to test the influence of the electrode arrangement on the efficiency of the electro migration removal of sodium chloride, and it is effect on pH profile across the cell. To achieve this goal, two experiments were warried out using only two electrodes configuration in the cell. In experiment A, the two active electrodes were directly attached to the soil column at the soil surface at each edge of the column. In experiment B, the electrodes were installed in the electrolyte compartment but not attached directly to the soil surface of the edges of the column which is separated by the electrolyte solution. A schematic diagram of the test columns used is shown in Figure 7.6. An overview of the test conditions for the experiments with electrical gradient only is given in Table 7.2.

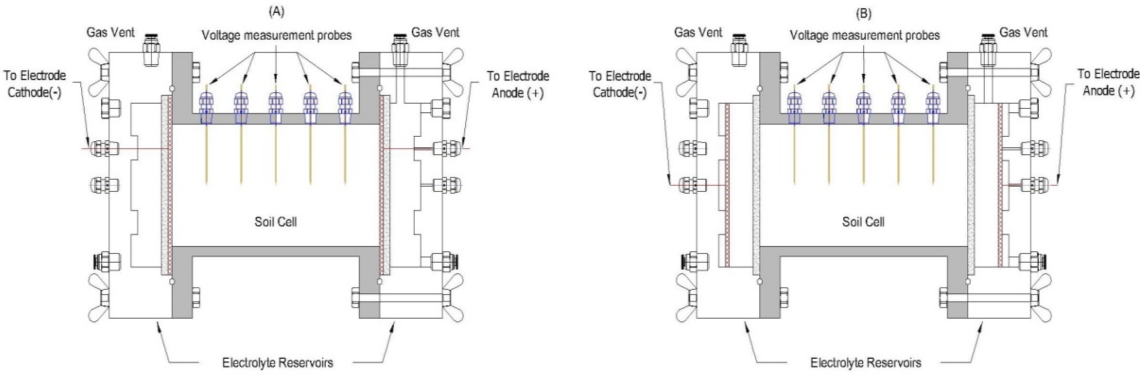


Figure 7.6: Electromigration experimental column: (A) electrodes at the soil surface, (B) electrodes in the electrolyte reservoirs.

Table 7.2: Overview of the electromigration testing experiments

Test group	**Sodium Chloride Spiking solution (*mole/l*)**	**pH**	**Average Soil EC 1:5 (*µS/cm*)**	**Applied Voltage (*V/cm*)**	**Duration (*h*)**	**Electrolyte**
A	0.6	6.5	1450-1500	0.5	72	DI-water
B	0.6	6.5	1450-1500	0.5	72	DI-water

Results

Voltage and current distribution

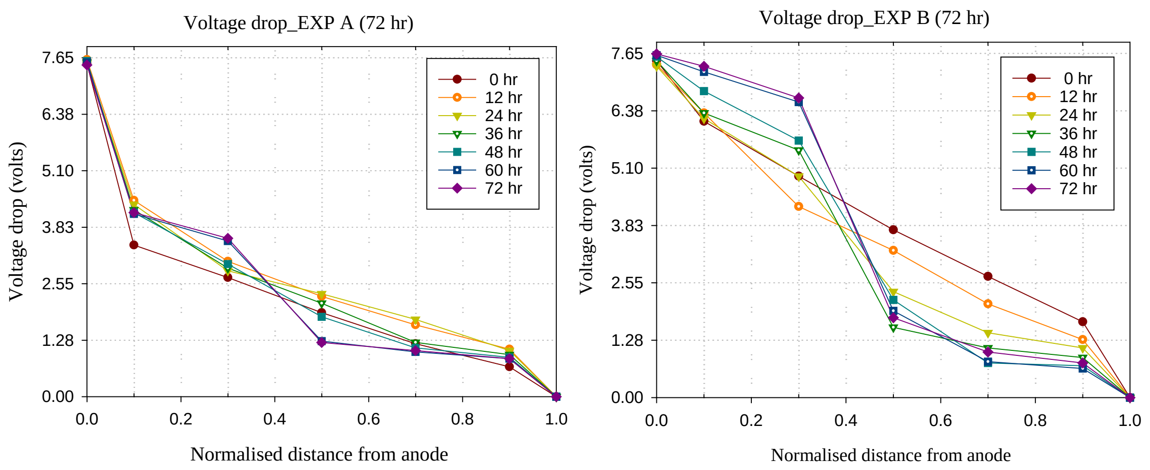


Figure 7.7: Voltage drop distribution.

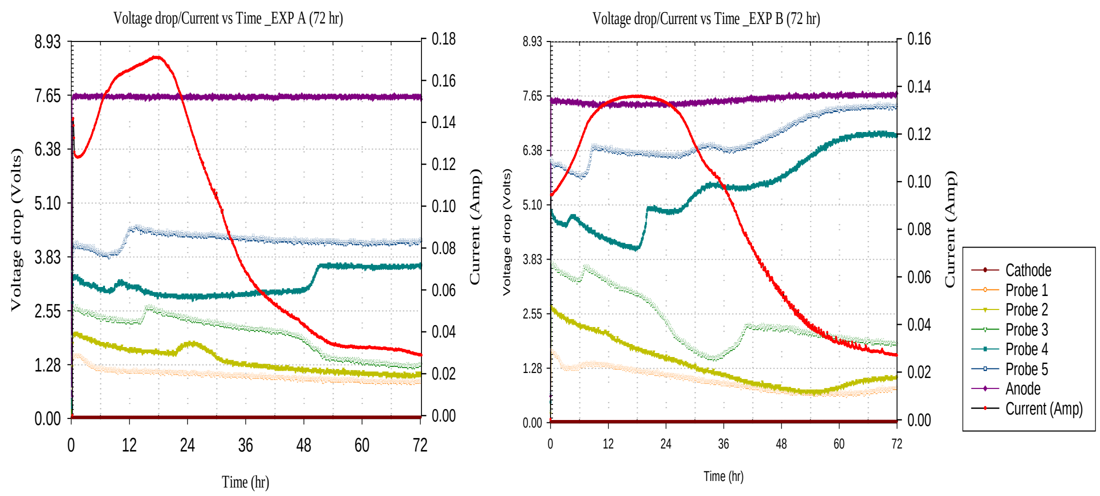


Figure 7.8: Temporal developing potential and current at the different probes.

The voltage drop across the cell is shown in Figure 7.7 for EXP A and EXP B. In EXP A, the voltage at time zero is linear showing a homogenous salt distribution within the cell. However, the steep drop between the electrodes and the soil surface is possibly attributed to an experimental error during filling the electrolyte solutions. In both experiments and similar to the experiments in Chapter 5.2.1, a large voltage drop occurred in the cell with a zone between the distance of (0.3-0.5). This large drop attributed to the development of a reaction plane where the electrolysis product H^+ and OH^- meet and form water, as explained by Deznitis [10]. A very similar voltage drop distribution as the experiments in Chapter 5.2.1 is observed during EXP B when electrodes were installed within the electrolyte compartments. Figure 7.8 confirms the observation of the creation of the reaction zone within the zone as it could be seen in the high voltage drop between probe 3 and probe 4 in both experiments (EXPA and EXPB). The current in EXPA and EXP B is also shown in Figure 7.8. An increase in the current is recorded during the first 24 *hours* of the experiments to reach a value of 0.17 and 0.14 *Amp* in EXPA and EXPB respectively. However, similar trend is observed in both experiments and in accordance to experiments in Chapter 5.2.1. The current dropped to 40 *mA* after 50 *hours* and continued to decrease to a steady state at around 30 *mA* after 72 *hours*, which is an evidence of the removal of dissolved ions from the specimen.

pH distribution

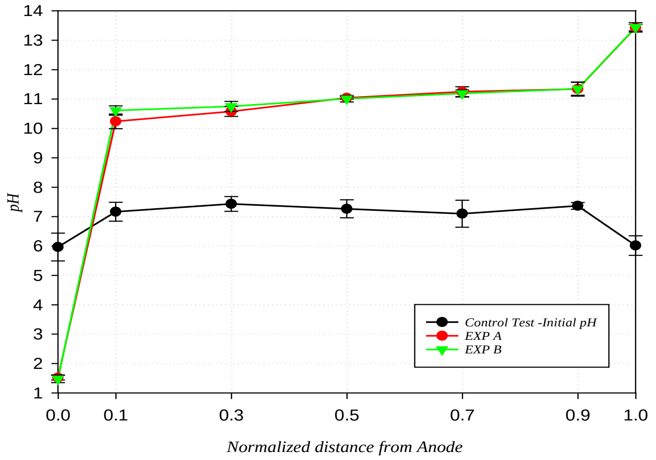


Figure 7.9: Variation of pH with time across the soil specimen.

The base front advanced more a across the soil cell specimen and it is in accordance to the results reported in Chapter 5.2.1. Similarly, the acidic front was retarded and not advancing significantly across the specimen. The laboratory observation of the advancing pH front is shown in Figure 7.9. From the observation, it is evident that the different electrode configuration (4-electrode configurations or 2 electrode configuration) doesn't have any significant influence on the pH profile development across the soil. It was suspected the cause of the un- expected retardation of the acidic front during the different experiment is because of using a 4 electrodes configuration as explained in Chapter 4.2.1. Therefore, the experiment continued using the 4 electrodes configurations.

Salts distribution

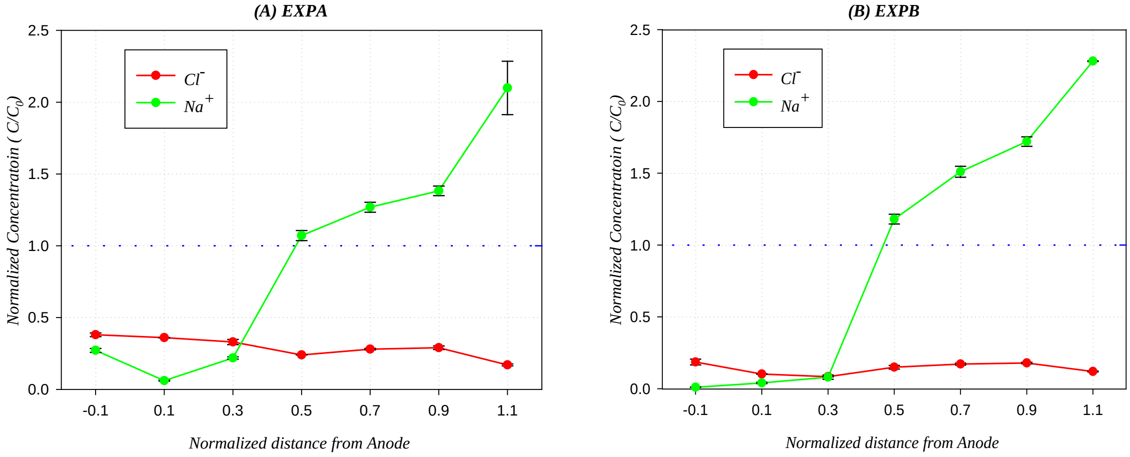


Figure 7.10: Distribution of Na+ and Cl- across the cell.

The two electrode configuration has not affect the migration of different ions in the soil. In both experiments, sodium and chloride ions migrated towards the oppositely charged electrode following the same manner in the results as shown in Figure 7.10. Given the fact voltage drop across the cell in EXPA decreased to more extend than in EXPB, this caused less ionic removal in EXPA in relative with EXPB. As a conclusion from the observed results in the 2-electrodes configuration, this dose not the electro-migration process in the cell. Thus the experiments could be equally carried out using either 4-electrodes or 2-electrodes configurations. Moreover, this also has not a significant influence on the pH profile behavior during the process. Therefore, the reasons that causing the acidic front not advancing across the cell still attributed to the explanations provided in Chapter 5.2.1.

APPENDIX (C): ADDITIONAL EXPERIMENTAL DATA

Additional experiments are presented in Appendix C. the experiments were carried out under the same configurations, conditions and procedures followed in Chapter 5.2.1. The sand used in the experiments was obtained from Sibelco group (Belgium). The sand is commercial clean silica sand of MOL-M31; the physical and chemical properties are shown in Table 9.1. Different concentrations and voltage were applied. The goal was to derive the best conditions or parameters to investigate the electro-migration phenomena to remove high sodium chloride concentrations in sandy soil.

Table 7.3: Characteristics of Silica Sand of MOL-M31 (Sibelco)

Property	Unit	Value
Chemical Analysis (XRF), (Weight %)		
Silicon (SiO_2) content	%	99.5
Fe_2O_3 content	%	0.04
Aluminum as Al_2O_3 content	%	0.20
TiO_2 content	%	0.03
K_2O content	%	0.03
Calcium oxide content	%	0.01
Physical Characteristics		
D50 (average grain size)	*µm*	370
Density	g/cm^3	2.65
Bulk density	g/cm^3	1.6
pH		7

The initial parameters of the experiments are listed in Table 7.4:

Table 7.4: Experimental conditions and initial parameters.

Test	Average Initial Cl- *mg/kg* (*dry soil*)	Average Initial Na+ *mg/kg* (*dry soil*)	pH	Average EC 1:5 (*µS/cm*)	Applied Voltage (*V/cm*)	Duration (*h*)	Electrolyte
T1	72.1	48.5	6.5	560	1	24	DI-water
T2	85.6	57.6	6.5	649	3	24	DI-water
T3	2010	1350	6.7	1300	1	24	DI-water
T4a	3770	2490	6.4	2480	1	24	DI-water
T4b	4310	2800	6.6	2630	1	24	DI-water
T5a	4200	2830	5.5	2556	0.5	24	DI-water
T5b	3920	2720	5.9	2530	0.5	24	DI-water

Electrical current of the system during the electromigration experiments was monitored. The results are shown in Figure 7.11. In all experiments, the current increased in the initial hours of the experiments and then decreased gradually over time. In T4a and T4b, for instance, the increase was more pronounced as the initial concentrations of the salt was high, thus giving a higher current to pass throughout the cell. The increase in current in the initial hours was much less pronounced in T5a and T5b because of the lower voltage applied (0.5 $V\ cm^{-1}$). In T1, the maximum current was lower than in T2, due to different constant voltages applied, 3 $V\ cm^{-1}$ and 1 $V\ cm^{-1}$, in T2 and T1, respectively. The initial increase in current showed an increase in the electrical conductivity within the soil, which could be attributed to hydrogen (H^+) and hydroxide (OH^-) ions that were generated at the electrodes by electrolysis of water.

Due to water electrolysis, OH^- and H^+ ions were generated in the catholyte and anolyte compartments, respectively. The pH of the anolyte decreased rapidly from 6.5 to less than 1.5 while the pH of the catholyte increased drastically to more than 13 (Figure 7.12). These marked changes in pH in the reservoir are realized within 24 *hours* running time. Figure 7.12 shows that after 24 *hours* of treatment in Tests 1 to 4 the soil pH profile became more alkaline across the soil cell. Furthermore, the pH increased from 6.5 to 8 near the cathodic region, and it increased to around pH 9 near the anodic region. The pH change in the electrolytes was lower under a lower voltage gradient of 0.5 $V\ cm^{-1}$ in Tests 5a and 5b (Figure 7.12 (right)), the pH decreased to 4 in the soil near the anode and increased to above 8 near the cathode. The alkaline front advanced further in the soil compared to the acid front, and an alkaline pH condition built up in the soil across the cell. These observations contrast other studies in the literature, which report that in most cases, the soil profile becomes more acidic after the electrokinetic treatment due to the advance of the acidic front at a faster rate than the alkaline front. However, a similar trend has been reported in some other cases [11, 12]. The main reason is that there is a limited reversed electroosmotic flow in our experiments, which are conducted in sand, compared to those reported in the literature using clays soil samples.

The charged dissolved ions Na^+ and Cl^- migrated in the soil under the applied voltage gradient. The distributions of normalized concentrations (C/C_0) of Na^+ and Cl^- in the soil after the experiments (4 and 5) are shown in Figure 7.13. Figure 7.13 represents the respective movement of Na^+ and Cl^- ions, as well as their removal efficiency. Chloride and sodium ions were transported toward the anode and cathode, respectively, through electromigration. A higher removal was observed for chloride than for sodium and that is because sodium is inert while chloride is transformed into chlorine gas and vented out of the cell.

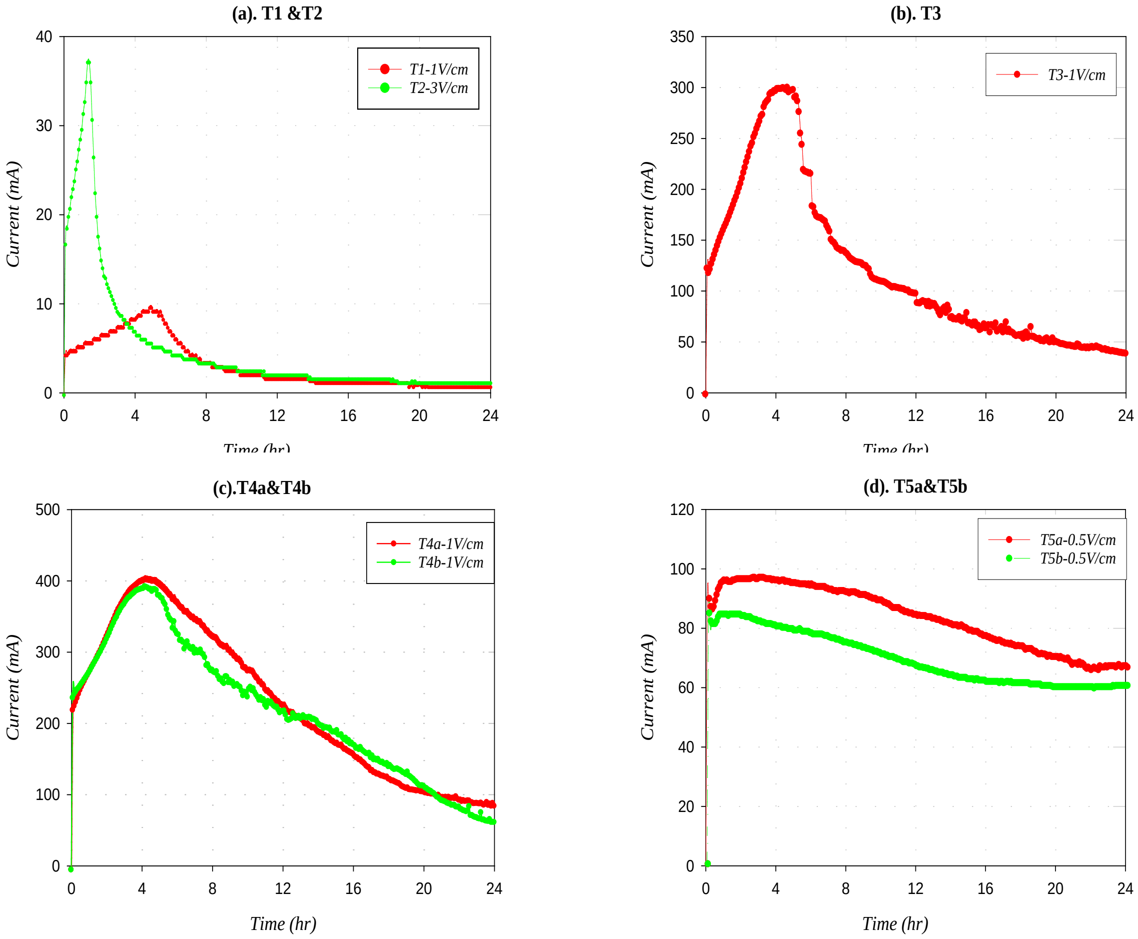


Figure 7.11: Electrical current change in time: a. Tests (1 and 2); b. Test 3; c. Tests (4a and 4b); d. Tests (5a and 5b).

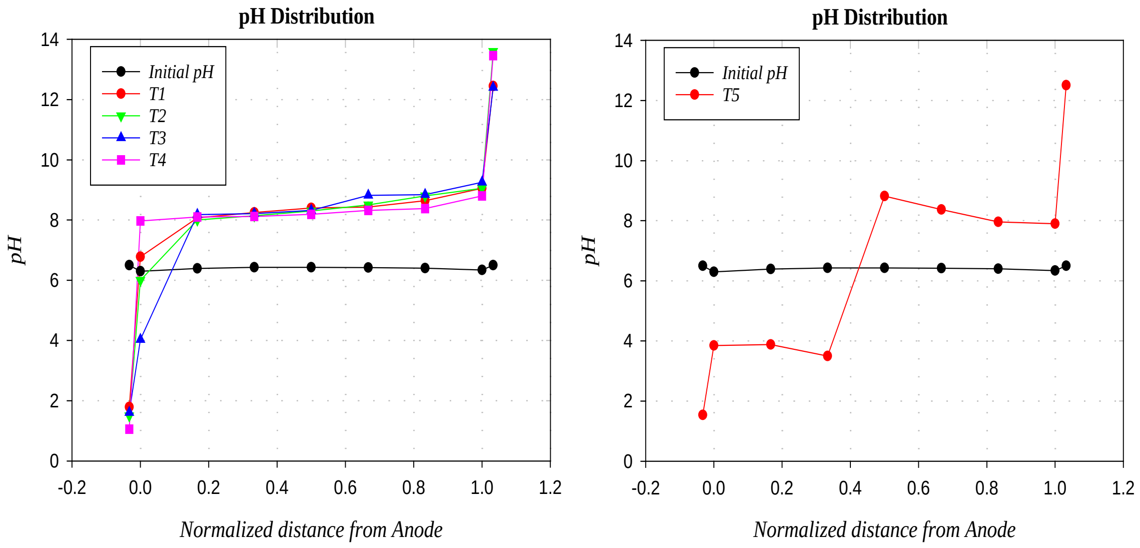


Figure 7.12: Variation of pH with time across the soil specimen.

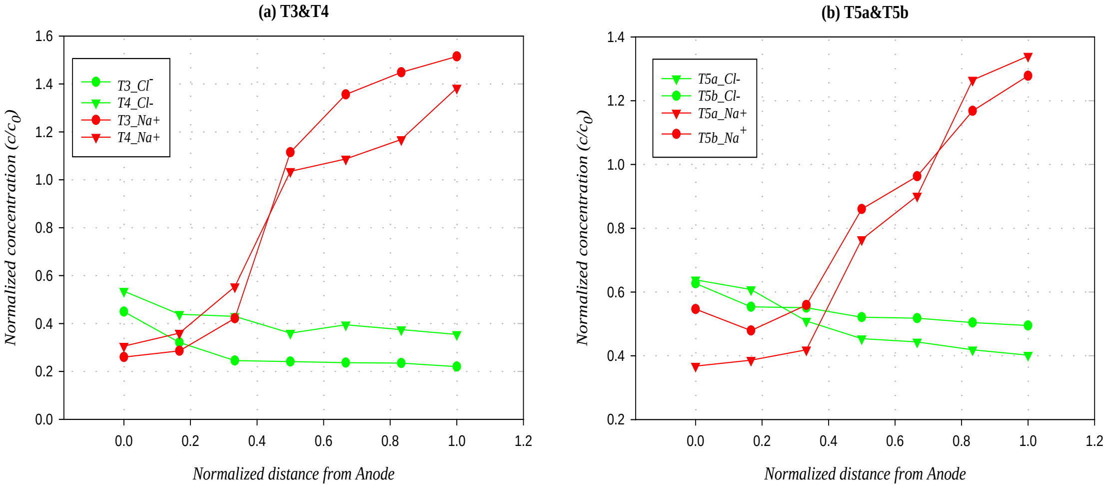


Figure 7.13: Distribution of Na^+ and Cl^- across the cell.

7.1 References

1. Paz-García, J.M., et al., *Simulation-based analysis of the differences in the removal rate of chlorides, nitrates and sulfates by electrokinetic desalination treatments.* Electrochimica Acta, 2013. **89**: p. 436-444.

2. MASI, M., *Electrokinetic remediation of heavy metal-contaminated marine sediments: experiments and modelling.* 2017.

3. Yu, J.-W. and I. Neretnieks, *Modelling of transport and reaction processes in a porous medium in an electrical field.* Chemical Engineering Science, 1996. **51**(19): p. 4355-4368.

4. Alshawabkeh, A.N. and Y.B. Acar, *Removal of contaminants from soils by electrokinetics: A theoretical treatise.* Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology, 1992. **27**(7): p. 1835-1861.

5. Shackelford Charles, D. and E. Daniel David, *Diffusion in Saturated Soil. I: Background.* Journal of Geotechnical Engineering, 1991. **117**(3): p. 467-484.

6. Johannesson, B., *Comparison between the Gauss' law method and the zero current method to calculate multi-species ionic diffusion in saturated uncharged porous materials.* Computers and Geotechnics, 2010. **37**(5): p. 667-677.

7. Pamukcu, S., *Electrochemical Transport and Transformations*, in *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater.* 2009.

8. Al-Hamdan Ashraf, Z. and R. Reddy Krishna, *Electrokinetic Remediation Modeling Incorporating Geochemical Effects.* Journal of Geotechnical and Geoenvironmental Engineering, 2008. **134**(1): p. 91-105.

9. Kim, S.-O., et al., *Numerical and Experimental Studies on Cadmium (II) Transport in Kaolinite Clay under Electrical Fields.* Water, Air, and Soil Pollution, 2003. **150**(1): p. 135-162.

10. Dzenitis, J.M., *Soil Chemistry Effects and Flow Prediction in Electroremediation of Soil.* Environmental Science & Technology, 1997. **31**(4): p. 1191-1197.

11. Eid, N., et al., *Electro-migration of nitrate in sandy soil.* Journal of Hazardous Materials, 2000. **79**(1–2): p. 133-149.

12. Altaee, A., R. Smith, and S. Mikhalovsky, *The feasibility of decontamination of reduced saline sediments from copper using the electrokinetic process.* Journal of Environmental Management, 2008. **88**(4): p. 1611-1618.

8 LIST OF PUBLICATIONS AND PRESENTATIONS ON MEETINGS/CONGRESSES

List of Publications

- **Hamdan, S. H.**, Molelekwa, G. F. and Van der Bruggen, B. (2014), Electrokinetic Remediation Technique: An Integrated Approach to Finding New Strategies for Restoration of Saline Soil and to Control Seawater Intrusion. CHEMELECTROCHEM, 1: 1104–1117.
- Jiuyang Lin, Chuyang Y. Tang, Wenyuan Ye, Shi-Peng Sun, **Shadi H. Hamdan**, Alexander Volodin, Chris Van Haesendonck, Arcadio Sotto, Patricia Luis, Bart Van der Bruggen, Unraveling flux behavior of superhydrophilic loose nanofiltration membranes during textile wastewater treatment, Journal of Membrane Science, Volume 493, 1 November 2015, Pages 690-702.

International Conferences

- Poster presentation at the 32nd Annual International Conference on Soils, Sediments, Water, and Energy, October 17-20, 2016 held in Amherst, Massachusetts.

- Poster presentation at MIT water night 2016, the potential of using an electrokinetic barrier to control saltwater intrusion, Massachusetts Institute of Technology - MIT, Boston, MA, March 11, 2016.
- Poster presentation at Symposia EREM 2017, the potential of using an electrokinetic barrier to control saltwater intrusion, held at Concordia University, in the Faculty of Engineering and Computer Science building, Canada, from August 6 to August 8 2017.

Research Mobility

- Research visit at Northeastern University, PROTECT Center, Boston, MA: (21/08/15-30/11/18).