INTERNATIONAL SYMPOSIUM ON ELECTROKINETIC REMEDIATION

Northeastern University – Boston MA USA – June 23-26, 2013

SPONSORS:

- INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY
- SUPERFUND RESEARCH PROGRAM (SRP) OF THE NATIONAL INSTITUTE OF ENVIRONMENTAL HEALTH SCIENCES
- PROTECT SRP CENTER
- NORTHEASTERN UNIVERSITY
AGENDA SUMMARY

Sunday June 23
18:00 – 19:30 Reception

Monday June 24
7:45 – 8:30 Conference Check-In and Continental Breakfast
8:30 – 9:00 Welcome and Opening Remarks
9:00 - 9:45 Keynote Lecture – Electromediation: Origins and Efficacy
9:45 – 10:00 Break
10:00 – 12:00 Session 1 – Metals Removal
12:00 – 13:00 Lunch
13:00 – 14:30 Session 2 – Lab and field testing
14:30 – 14:40 Break
14:40 - 16:40 Poster Session (440 Egan Research Center)
18:00 - 20:00 Banquet (SkyWalk Observatory, Prudential Center, 800 Boylston Street)

Tuesday June 25
7:45 – 8:30 Continental Breakfast
8:30 – 9:00 Invited Presentation – Nonlinear Electrokinetic Separations in Porous Media
9:00 – 10:30 Session 3 – Fundamentals and modeling
10:30 – 10:45 Break
10:45 – 12:30 Session 4 – Electro-water and wastewater treatment
12:30 – 13:30 Lunch
13:30 – 15:15 Session 5 - Modified Electro-processes for oil recovery and contaminant removal
15:15 – 15:30 Break
15:30 – 17:00 Session 6 – Electrokinetic-Coupled and bioprocesses
17:00 – 17:20 Poster Awards and Closing Remarks

Wednesday June 26
10:00 – 15:00 Tour – “Boston Underground”

1 All events will take place in the Egan Research Center unless otherwise noted (building #60 on the campus map at the end of this program.)
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Welcome to the 2013 International Symposium on Electrokinetic Remediation (EREM 2013). After more than a decade of successful EREM Symposia around the world, we are very excited to host the 2013 symposium in Boston, Massachusetts. EREM symposiums started in Albi, France in 1997 and since then have been held twelve times but only in Europe and Asia, specifically Lyngby, Denmark (1999); Karlsruhe, Germany (2001); Mol, Belgium (2003); Ferrara, Italy (2005); Vigo, Spain (2007); Seoul, South Korea (2008); Lisbon, Portugal (2009); Kaohsiung, Taiwan (2010); Utrecht, The Netherlands (2011) and most recently in Sapporo, Japan (2012).

Contamination of soil, water, sediments, concrete, wood, brick and other construction materials continue to be a major threat to human health globally. Although many of the contamination sources tend to be from decades of improper disposal of waste, recent extreme incidents also generate extensive contamination. Examples include the BP oil disaster in the Gulf of Mexico in 2010 and the Fukushima Daiichi nuclear disaster in 2011, which both produced widespread contamination. This is in addition to detection of emerging contaminants in water resources.

Technologies for remediation of contaminated materials have been under continuous development, validation and implementation for almost three decades. Due to difficulties in locating contamination in the subsurface – and challenges in addressing the complex and heterogeneous physical, chemical, biological and thermal subsurface conditions – only a small fraction of contaminated sites have been cleaned and contamination is still a critical issue.

Electrokinetic and electrochemical processes provide valuable and versatile tools to manage and remediate contaminated materials. Significant progress continues to be made and the annual EREM Symposium provides a venue to present and discuss recent developments in electrokinetic and electrochemical remediation to help us face the major environmental contamination challenges everywhere.

We welcome you to Boston.

Warm wishes,

Akram Alshawabkeh, PhD, PE, Fellow ASCE
Conference Chair
George A. Snell Professor of Engineering, Northeastern University
Director, Puerto Rico Testsite for Exploring Contamination Threats (PROTECT) Center
northeastern.edu/protect
CONFERENCE ORGANIZING COMMITTEE

Akram N. Alshawabkeh (Chair), Northeastern University, USA
Kitae Baek, Chonbuk National University, South Korea
Maria Elektorowicz, Concordia University, Canada
Mohammed R. Haroun, The Petroleum Institute, The United Arab Emirates
Milind K. Khire, Michigan State University, USA
J.P.G. Gustav Loch, Utrecht University, The Netherlands
Xuhui Mao, Wuhan University, China
Lisbeth M. Ottosen, Technical University of Denmark, Denmark
Sibel Pamukcu, Lehigh University, USA
Krishna R. Reddy, University of Illinois at Chicago, USA
Shunitz Tanaka, Hokkaido University, Japan
Gordon C.C. Yang, National Sun Yat-Sen University, Taiwan
Songhu Yuan, China University of Geosciences, China

Conference Coordination: Mariah Nobrega, Northeastern University
KEYNOTE LECTURE

Ronald Probstein – “Electroremediation: Origins and Efficacy”

Abstract
This paper presents the history of the development of electroremediation of contaminated soil, specifically electroosmosis and electromigration, along with its simpler applications and the critical limiting issues that arise in its use together with most recent ideas and attempts to overcome the problems limiting it effectiveness. It does not survey the vast literature that has developed in the field.

About Dr. Probstein
One of America’s foremost engineering scientists, Ronald Probstein is Ford Professor of Engineering, Emeritus at the Massachusetts Institute of Technology. His undergraduate training was at New York University’s night school and his graduate work in aeronautical engineering and physics at Princeton.

He has played a principal role in some of the most important scientific and technical achievements in the post World War II era, involving spacecraft and ballistic missile reentry physics, hypersonic flight theory, comet astrophysics, desalination, water purification, synthetic fuels, and environmental science and technology.

For these achievements, he has been honored as a member of the National Academy of Sciences, National Academy of Engineering, American Academy of Arts and Sciences, International Academy of Astronautics, and awarded an honorary doctorate from Brown University.

Author, editor, lecturer, inventor, Professor Probstein has ten critically acclaimed scientific and technical books to his credit.

Born in New York City in 1928, he lives in Brookline, Massachusetts with his wife, Irène. He has one son, Sidney, and three grandchildren.
INVITED SPEAKER

Martin Z. Bazant –
“Nonlinear Electrokinetic Separations in Porous Media”

Abstract
Salt transport in bulk water occurs by diffusion and convection, but in microfluidic devices and porous media, surface conduction and electro-osmotic flow also contribute to ionic fluxes. The classical theory of electrokinetic phenomena in porous media assumes linear response to a small voltage, where the electrolyte concentration is only weakly perturbed. When a large voltage or concentration gradient is imposed, some surprising nonlinear electrokinetic phenomena result from the competition between bulk and interfacial transport in a microstructure. At constant voltage, the microstructure can sustain an over-limiting current (exceeding diffusion limitation) without any hydrodynamic or chemical instability. At constant current, a “deionization shock” can propagate through the microstructure, leaving behind a macroscopic region depleted of ions and particles. This talk will present the mathematical theory and new experimental evidence for surface-driven over-limiting current and deionization shocks in porous glass frits, as well as applications to water purification and brine concentration by “shock electrodialysis”.

Note: This talk provides important background for the talk of Sven Schlumpberger on “Shock Electrodialysis”.

About Dr. Bazant
Martin Z. Bazant received his B.S. (Physics, Mathematics, 1992) and M.S. (Applied Mathematics, 1993) from the University of Arizona and Ph.D. (Physics, 1997) from Harvard University. He joined the faculty at MIT in Mathematics in 1998 and Chemical Engineering in 2008. His honors include an Early Career Award from the Department of Energy (2003), Brilliant Ten from Popular Science (2007), and Paris Sciences Chair (2002, 2007) and Joliot Chair (2008, 2012) from ESPCI (Paris, France). He is a leading researcher in electrokinetics and electrochemical physics.
AGENDA

Sunday June 23

18:00 – 19:30 Reception

Monday June 24

7:45 – 8:30 Conference Check-In and Continental Breakfast

8:30 – 8:45 Welcome

8:45 – 9:00 Opening Remarks

Opening Remarks: “Add Dean Aubry’s speech title here”
Nadine Aubry, Dean of Engineering, Northeastern University

9:00 - 9:45 Keynote Lecture

Electroremediation: Origins and Efficacy
Ronald Probstein, Ford Professor of Engineering, Emeritus at the Massachusetts Institute of Technology

9:45 – 10:00 Break

10:00 – 12:00 Session 1 – Metals Removal

Session Chairs:
- Sibel Pamukcu - Lehigh University, United States
- Mohammed R. Haroun - The Petroleum Institute, The United Arab Emirates

Simultaneous Removal of Pb, Cd and Zn from Heavily Contaminated Mine Tailing Soil Using Enhanced Electrochemical Process
- Reena Amatya Shrestha - The Petroleum Institute, The United Arab Emirates
- Nurcan Köleli and Aydeniz Demir - Mersin University, Turkey
- Sibel Pamukcu - Lehigh University, United States

Enhanced Electrokinetic Remediation of Cadmium-Contaminated Natural Clay by Phosphonates and EDTA
- Ying-Ying Gu - China University of Petroleum, China
- Albert Yeung - University of Hong Kong, Hong Kong

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Electrodialytic remediation of stirred and stationary soil – Direct comparison of heavy metal removal rate

- Lisbeth M. Ottosen, Pernille E. Jensen, Gunvor M. Kinkelund - Technical University of Denmark, Denmark
- Celia Dias-Ferreira - CERNAS, Agrarian School of Coimbra, Portugal
- Henrik K. Hansen - Federico Santa Maria Technical University, Chile

Remediation of subsurface mercury contamination using the iodide-assisted electrokinetic process

- Yu-Han Chiu, Gordon C. C. Yang, Chih-Lung Wang, Yen-Jung Lin - National Sun Yat-Sen University, Taiwan

Development of iron-based material for simultaneous heavy metal ions removal from water

- Liang Guo and Joseph Calo - Brown University, United States

Heavy Metal Decontamination in Abu Dhabi Offshore-Muds Generated from Refineries by Optimizing Electroremediation

- Nabeela Al Kindy, Mohammed Haroun, Nada Abou Sayed, Basma Ali, Reena Shrestha - The Petroleum Institute, The United Arab Emirates

Evaluation of the Chemical Remotion of Mercury in Presence of Different Removing Agents from Polluted Bentonite and Quartz using Anodic Stripping Voltammetry

- Erika Bustos and Irma Robles Gutiérrez - Center of Research and Technologic Development in Electrochemistry (CIDETEQ), Mexico

Arsenic species interactions with a porous carbon electrode as determined with an electrochemical quartz crystal microbalance

- Joseph Calo - Brown University, Providence, RI, USA
- Emilia Morallón, Joaquín Arias-Pardilla, D. Cazorla-Amorós - University of Alicante, Spain

12:00 – 13:00 Lunch

13:00 – 14:30 Session 2 – Lab and field testing

Session Chairs:

- Krishna R. Reddy - University of Illinois at Chicago, USA
- Gordon C.C. Yang - National Sun Yat-Sen University, Taiwan

Field Application of In-Situ Electrokinetic Remediation for Multi-Metal Contaminated Site

- Kitae Baek, Eun-Ki Jeon, Ji-Min Jung - Chonbuk National University, South Korea
- Sung-Hwan Ko and Do-Sub Shim - Ecophile Co. Ltd, South Korea

Field Scale Pilot Demonstration of Electrokinetic-Enhanced Bioremediation (EK-Bio) of a PCE Source in Low Permeability Materials

- David Gent - USACE Engineer Research Development Center, USA
- Evan Cox - Geosyntec Consultants, Canada
- James Wang - Geosyntec Consultants, USA
- Charlotte Riis and Martin Bymose - NIRAS A/S, Denmark
Sustainability evaluation of electrokinetics and other remediation alternatives for a contaminated site: A case study

- Krishna Reddy - University of Illinois at Chicago, USA

A New Two-dimensional Laboratory Apparatus for Electrokinetic Extraction

- Ying-Ying Gu - China University of Petroleum, China
- Albert Yeung - University of Hong Kong, Hong Kong

Improvement of sludge electro-dewatering process using pretreatment techniques

- Apostolos Giannis, Jeremy Tan, Jing-Yuan Wang - Nanyang Technological University (NTU), Singapore

Electrokinetic flocs formation in municipal wastewater

- Maria Elektorowicz - Concordia University, Canada

14:30 – 14:40 Break
14:40 - 16:40 Poster Session (440 Egan Research Center)
18:00 - 20:00 Banquet (SkyWalk Observatory, Prudential Center, 800 Boylston Street)

Tuesday June 25

7:45 – 8:30 Continental Breakfast
8:30 – 9:00 Invited Presentation

Nonlinear Electrokinetic Separations in Porous Media
Martin Z. Bazant, Massachusetts Institute of Technology, USA

9:00 – 10:30 Session 3 – Fundamentals and modeling

Session Chairs:
- Kitae Baek - Chonbuk National University, South Korea
- J.P.G. Gustav Loch - Utrecht University, The Netherlands

Electrochemistry and -kinetics in aqueous media containing amphoteric ions

- Maarten Biesheuvel - Wageningen University, The Netherlands

Multivariable analysis of electrodialytic remediation of contaminated harbor sediments

- Kristine Bondo Pedersen and Tore Lejon - University of Tromsoe, Norway
- Lisbeth M. Ottosen, Pernille E. Jensen, Gunvor M. Kirkelund; Technical University of Denmark, Denmark
A Generalized Model for Electrochemically-Induced Transport in Porous Media. Identification and Validation of the Fitting Parameters

- Juan Manuel Paz-García and Lisbeth M. Ottosen - Technical University of Denmark, Denmark
- Akram N. Alshawabkeh - Northeastern University, USA
- María D. Villen-Guzman and Jose M. Rodríguez Maroto - University of Málaga, Spain

Assessment of ionic strength in the direct current enhanced transport of iron nanoparticles

- Helena Gomes and Sibel Pamukcu - Lehigh University, USA
- Celia Dias-Ferreira - CERNAS, Agrarian School of Coimbra, Portugal
- Alexandra B. Ribeiro - CENSE, New University of Lisboa, Portugal

Changes of elements and mineral composition of kaolin clay by electro-osmosis

- Peng Jie - Hohai University, China

Mesoscale Modelling of the Water Adsorption and Transport Properties of Concrete

- Matthew Pinson, Hamlin M. Jennings, Martin Z. Bazant - Massachusetts Institute of Technology, USA

10:30 – 10:45 Break

10:45 – 12:30 Session 4 – Electro-water and wastewater treatment

Session Chairs:
- Maria Elektorowicz - Concordia University, Canada
- David Gent - USACE Engineer Research Development Center, USA

Optimization of Electrodialytic Separation of Heavy Metals and Phosphorous during Domestic Wastewater Treatment

- Benjamin Ebbers, L.M. Ottosen, P.E. Jensen - Technical University of Denmark, Denmark

Construction and Modification of oxides towards Formaldehyde Removal at Ambient Temperature

- Wei Xiao and Xuhui Mao - Wuhan University, China

Removal of Perchlorate from Water by Catalytic Electrochemical Processes

- C. P. Huang, D. M. Wang, Po Yen Wang - University of Delaware, USA

Electrochemical oxidation of phenolic compounds and organic acids in dilute aqueous solutions

- C. P. Huang, Chieh Sheng Chu, Yu Chi Lee, Tommy Chen - University of Delaware, USA

A hybrid electro-Pd process for groundwater remediation

- Songhu Yuan, Wei Hua, Jianguo Bao - China University of Geosciences, China
- Huayun Long - Huazhong University of Science and Technology, China
A Comparison Study on Electrokinetic Removal of Cadmium from Municipal Sewage Sludge with and without Improved Catholyte Circulation

- Jie Gao, Qishi Luo, Changbo Zhang, Bingzhi Li, Liang Meng - Shanghai Academy of Environmental Sciences, China

Cyclic electrowinning/precipitation (CEP) system for the removal of heavy metals from aqueous solution mixtures

- Joseph Calo, P. Grimshaw, G. Hradil - Brown University, USA

12:30 – 13:30  Lunch

13:30 – 15:15  Session 5 - Modified Electro-processes for oil recovery and contaminant removal

Session Chairs:

- Lisbeth M. Ottosen - Technical University of Denmark, Denmark
- Shunitz Tanaka - Hokkaido University, Japan

Electrokinetics Assisted Acidizing for Enhancing Oil Recovery in Abu Dhabi Carbonate Reservoirs

- Arsalan Ansari, Mohammed Haroun, Mohammed Motiur Rahman - The Petroleum Institute, The United Arab Emirates

Application of Electrokinetics to Achieve Smart EOR in Abu Dhabi Oil-Wet Carbonate Reservoirs

- Mohammed Haroun, Arsalan Ansari, Nada Abou Sayed, Nabeela Al Kindy, Basma Ali, Reena Shrestha, Hemanta Sarma - The Petroleum Institute, The United Arab Emirates
- J. Kenneth Wittle - Electropetroleum Inc., USA

Simulated electroremediation of drilling muds using both oxidants and surfactants

- Djamal-Eddine Akretche, Mohamed Oualid Bouakradache, Noureddine Yassaa - University of Science and Technology Houari Boumediene, Algeria
- Abdelhalim Ait-Idir - ENSP, The National Enterprise for Well Services, Algeria
- Claudio Cameselle - University of Vigo, Spain

Electrically induced hydrocarbon transport in oil bearing formations

- Ehsan Ghazanfari - Lehigh University, USA

Electroremediation of Polluted Soil with Hydrocarbon

- Erika Bustos - Center of Research and Technologic Development in Electrochemistry (CIDETEQ), Mexico

Water Purification and Brine Concentration by Shock Electrodialysis

- Sven Schlumpberger, Elaine McVay, Daosheng Deng, Martin Z. Bazant - Massachusetts Institute of Technology, USA
Electrokinetic transport mechanism of Li ions in cementitious materials by using NMR

Sofia Venglovská and Leo Pel - Eindhoven University of Technology, The Netherlands

15:15 – 15:30
Break

15:30 – 17:00
Session 6 – Electrokinetic-Coupled and bioproceses

Session Chairs:
- Songhu Yuan - China University of Geosciences, China
- Xuhui Mao - Wuhan University, China

Coupled phytoremediation-electrokientics for the remediation of brownfield sites with mixed contaminants: Preliminary results
- Claudio Cameselle - University of Vigo, Spain
- Reshma A. Chirakkara and Krishna R. Reddy - University of Illinois at Chicago, USA

Impact of DC field on Clostridium perfringens spore
- Maria Elektorowicz and Elham Safaei - Concordia University, USA

Impact of Electrical Field on Substrate Utilization Rate and Microbial Revitalization in Bio-Electrochemical Cells
- Shadi Hasan, Maria Elektorowicz, Aleksandra Kasprzyk - Concordia University, USA
- Jan Oleszkiewicz - University of Manitoba, Canada

Mobility and bioavailability of nutrients and microbial electron acceptors in bioelectroremediation processes in soils
- Esperanza Mena, José Villaseñor, Manuel. A. Rodrigo, Pablo Cañizares - University of Castilla-La Mancha, Spain

Enhancing electrokinetic remediation of molinate contaminated soil using zero valent iron nanoparticles
- Helena Gomes- CENSE, New University of Lisboa, Portugal and CERNAS, Agrarian School of Coimbra, Portugal
- Eduardo P. Mateus and Alexandra B. Ribeiro - CENSE, New University of Lisboa, Portugal
- Fan Guangping - CENSE, New University of Lisboa, Portugal and Chinese Academy of Sciences, China
- Célia Dias-Ferreira - CERNAS, Agrarian School of Coimbra, Portugal
- Zhou Dongmei - Chinese Academy of Sciences, China

Enhancement of Heavy Metals Remediation from Abu Dhabi Offshore Muds by Electrokinetics Coupled with Nano-Sized Particles and Chemicals
- Reena Amatya Shrestha, Mohamed Haroun, Nabeela Al Kindy, Nada Abou Sayed, Basma Ali- The Petroleum Institute, The United Arab Emirates
17:00 – 17:30  Poster Awards and Closing Remarks

Wednesday June 26

10:00 – 15:00  Tour – “Boston Underground”: Details provided separately
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<td>Maria Cláudia Barbosa, Leonardo Deotti, Jonathan Tenório de Lima, Márcio de Souza Soares de Almeida - COPPE, Federal University of Rio de Janeiro, Brazil</td>
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<td>Electrokinetic surfactant enhanced remediation of a tropical silty clay soil contaminated with crude oil</td>
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<td>Electrokinetic removal of heavy metals from an agricultural soil</td>
<td>Claudio Cameselle, Susana Gouveia - University of Vigo, Spain Arylein Figerora, Henrik Hansen - Federico Santa María Technical University, Chile</td>
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<td>Cesar Gomez-Lahoz, F. García-Herruzo, García-Rubio, M.D. Villen-Guzman - University of Málaga, Spain J.M. Paz- García – Technical University of Denmark, Denmark</td>
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<td>Bo-Kyong Kim, Jae-Young Lee, Tae-Soon Kwon, Woo-Hyun Chung - Korea Railroad Research Institute (KRRI), South Korea</td>
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<td>Study of the behavior of an acid-enhanced electrokinetic remediation performed with a real soil spiked with lead.</td>
<td>C. Gomez-Lahoz, C. Vereda-Alonso, F. Garcia-Herruzo, J.M. Rodriguez-Maroto, M.D. Villen-Guzman - University of Málaga, Spain</td>
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<td>M.A. Nekrasova, S. N. Sidorenko, K.A. Galkin, I.U. Pisar - Russian People’s Friendship University of Moscow, Russia</td>
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<td>Lab scale study of the influence of the acid strength over the performance of an acid-enhanced electrokinetic remediation</td>
<td>C. Gomez-Lahoz, M.D. Villen-Guzman, R.A. Garcia-Delgado, F. Garcia-Herruzo, B. Arhoun, J.M. Rodriguez-Maroto - University of Málaga, Spain</td>
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<td>J.M. Paz-Garcia - Technical University of Denmark, Denmark</td>
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<td>Precipitation-Filtering Technology for Uranium Waste Solution Generated on Washing-Electrokinetic Decontamination</td>
<td>Gye-Nam Kim, Seung-Soo Kim, Hye-Min Park, Won-Suk Kim, Uk-Rang Park, Jei-Kwon Park - Korea Atomic Energy Research Institute, South Korea</td>
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<td>Response of indigenous microorganisms to biocathodeelectrokinetics applied to remediation of soil contaminated with PAH and metals</td>
<td>Maria Elektorowicz - Concordia University, Canada</td>
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<td>Electrosorption/Electrodesorption of Arsenic on a Granular Activated Carbon in the Presence of Other Heavy Metals</td>
<td>Joseph Calo - Brown University, USA</td>
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<td>Ruben Spitz-Steinberg, Johannes Kirchner, Jenny Axén - Brown University, USA</td>
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<td>The Behavior of Metal Ion Concentrations in Solution During Co-electrodeposition</td>
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A Generalized Model for Electrochemically-Induced Transport in Porous Media. Identification and Validation of the Fitting Parameters

Juan Manuel Paz-García and Lisbeth M. Ottosen - Technical University of Denmark, Denmark
Akram N. Alshawabkeh - Northeastern University, USA
María D. Villen-Guzman and José M. Rodríguez Maroto - University of Málaga, Spain

In general, fundamental research or “modeling” has two main objectives: to increase the understanding of the physicochemical processes taking place in the modeled system, and to develop a tool for forecasting results. While, in the first approach (increasing the understanding), a sufficiently large amount of coupled theories are necessary for the scientific description of the process, in the second approach (forecasting results) simple models are preferred, with the minimum amount of the so-called fitting parameters.

In this work, a generalized physicochemical and numerical model has been developed to describe multi-species reactive transport of matter through porous media under electric fields. The model aims to be sufficiently detailed to describe the main processes, but it also aims to be a predictive tool for standard and enhanced electroremediation, electrodialytic and electrode-salination treatments.

In order to assess the prediction potential of any model, it is necessary its validation by comparison of simulations with experimental results for the estimation of the fitting parameters. Herein, these parameters defining the model are identified, for a representative case of an acid enhanced electrokinetic remediation treatment of heavy metals contaminated soil. Subsequently, experimental and simulation results are compared for the validation of the proposed model, by the estimation of the values for the aforementioned fitting parameters.

Some of the unknowns discussed here are: The competitive electrode reactions and the faradic efficiency of the corresponding electrode processes, the tortuosity-constrictivity factor determining the retarding effect on the transport coefficients due to the non-ideality of the porous media, the buffer capacity of the soil and the mineralogical speciation of the target contaminants.

For an electrokinetic treatment at a constant current, results shown that the parameters that may have a higher impact on the predictive capability are the chemical speciation of the contaminants and the solid matrix, more than those affecting the conductivity of the media. In addition to this, the chemical kinetics of the heterogeneous chemical processes seems to be one of the most important factors to be enhanced for the development of a generalized forecasting tool.

A hybrid electro-Pd process for groundwater remediation

Songhu Yuan, Wei Hua, Jianguo Bao - China University of Geosciences, China
Huayun Long - Huazhong University of Science and Technology, China
The cathode of Pd supported on Ti/TiO2 nanotubes (Pd-Ti/TiO2NTs) array is prepared by sequential anodization of Ti plate and electrodeposition of Pd(II). Characterization by field-emission scanning electron microscope (FESEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) validates the growth of TiO2 nanotubes on Ti plate and the loading of Pd particles. Significant reduction peak for 2,4-dichlorophenol (2,4-DCP) at Pd-Ti/TiO2NTs cathode is observed in the cyclic voltammetry (CV). The linear correlation of peak current with the square root of scan rate suggests that 2,4-DCP reduction is diffusion controlled. The performance of as-synthesized Pd-Ti/TiO2NTs cathode is further evaluated for the electrochemical degradation of 20 mg/L 2,4-DCP in aqueous solution in an undivided electrolytic system. The degradation efficiency is high at acidic condition, and becomes very low at alkaline condition. The maximum degradation efficiency, up to 91% within 30 min, is reached at pH 5.5. Phenol is the predominant product measured, implying that reductive dechlorination is the dominant pathway for 2,4-DCP degradation. The efficiency also increases with the increase in the cathodic potentials from 0.4 to 0.7 V (versus SCE). This study suggests that Pd-Ti/TiO2NTs cathode has a high performance in the dechlorination of 2,4-DCP in aqueous solution.

A New Two-dimensional Laboratory Apparatus for Electrokinetic Extraction

Ying-Ying Gu - China University of Petroleum, China
Albert Yeung - University of Hong Kong, Hong Kong

In this paper, the design, fabrication and assembly of a new two-dimensional (2-d) apparatus for electrokinetic extraction studies are presented in detail. The apparatus was designed to simulate the field electrokinetic soil decontamination process to better understand the various contaminant transport processes, electrochemical reactions, and physicochemical soil-contaminant interactions. The apparatus consists of an electrokinetic extraction apparatus and a consolidation apparatus. The distinct advantages of the new 2-d apparatus are: (1) it is capable of applying a non-uniform electric field across the soil specimen to better simulate the field electrokinetic extraction process; (2) it is very simple to assemble, operate, and monitor most of the important parameters controlling the extraction efficiency during the electrokinetic extraction process; (3) the electrical voltage distribution can be monitored as a function of time and space; and (4) soil samples at different locations of the specimen can be easily collected for chemical analyses after electrokinetic extraction. The results of a typical electrokinetic extraction experiment obtained by the new apparatus on a remolded natural clay specimen were reported to demonstrate the operation of the apparatus and to illustrate the various parameters measured at different spatial and temporal intervals during electrokinetic extraction.

Application of Electrokinetics to Achieve Smart EOR in Abu Dhabi Oil-Wet Carbonate Reservoirs

Mohammed Haroun, Arsalan Ansari, Nada Abou Sayed, Nabeela Al Kindy, Basma Ali, Reena Shrestha, Hemanta Sarma - The Petroleum Institute, The United Arab Emirates
J. Kenneth Wittle - Electropetroleum Inc., USA

EOR technologies such as CO2 flooding and chemical floods have been on the forefront of oil and gas R&D for the past 4 decades. While most of them are demonstrating very promising results in both lab scale and field pilots, the strive for exploring additional EOR technologies while achieving full field application has yet to be achieved. Among the emerging EOR technologies is the surfactant EOR along with the application of electrically enhanced oil recovery (EEORTM) (Arsalan, et. al, 2012), which is gaining increased popularity due to a number of reservoir-related advantages such as
reduction in fluid viscosity, water-cut and increased reservoir permeability. Nano EOR is among the new frontiers that demand more improvements, therefore, new concepts and extensive innovative experimental procedures are required to identify and address key associated uncertainties.

The procedure proposed in this study includes an understanding of the Nano-Surfactant EOR physical processes on lab-scale models of carbonate reservoir retrieved core plugs. (Ogolo et al., 2010). The main objectives include reducing the HSE concerns of handling and transporting the nano and surfactant particles as well as targeting the unswept oil.

Tests were conducted on 1.5” carbonate reservoir core-plugs from Abu Dhabi producing oilfields with porosity ranging from 10 to 24% and permeability ranging from 77 to 149 mD. Several nano particles (50 nm) including Fe3O4, CuO and NiO range were evaluated after the waterflooding stage and results compared for ultimate recovery factors against the injection of non-ionic surfactant (APG). The smart nano EOR (Haroun et al., 2012) was compared on the same cores subjected to the same conditions against smart chemical EOR by using sequential and simultaneous application of Electrically Enhanced Oil Recovery (EEORTM). The results were further compared with the oil-wet cores. A Smart Nano-Surfactant EOR process is proposed in this study that allows shifting from simultaneous to sequential Nano-Surfactant EOR alongside EK.

The experimental results at ambient conditions show that the application of waterflooding on the carbonate cores yields recovery of approximately 46-72% whereas Smart Nano EOR enhanced the recovery by 7-10%. This was further enhanced by 4-7% with the application of Smart-surfactant EOR, which could be promising for water swept reservoirs. Overall, an additional 6-11% recovery was enhanced by the application of EK as compared to chemical and nanoflooding. In addition, EK was shown to enhance the carbonate reservoir’s permeability by approximately 11-29%. Furthermore, this process can be engineered to be a greener approach as the water requirement can be reduced up to 20% in the presence of electrokinetics, enhancing economically feasibility. However, the experiments conducted on oil-wet cores have shown that the application of Smart Nano-EOR yields an additional recovery of approximately 12-13%, which is higher compared to smart surfactant-EOR that recorded an additional recovery of 8-10%. Overall, an additional net recovery of 20-32% was achieved by the application of Smart Nano-Surfactant EK EOR in oil-wet cores.

**Arsenic species interactions with a porous carbon electrode as determined with an electrochemical quartz crystal microbalance**

*Joseph Calo* - Brown University, Providence, RI, USA  
*Emilia Morallón, Joaquín Arias-Pardilla, D. Cazorla-Amorós* - University of Alicante, Spain

The interactions of arsenic species with platinum and porous carbon electrodes were investigated with an electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry in alkaline solutions. It is shown that the redox reactions in arsenic-containing solutions, due to arsenic reduction/deposition, oxidation/desorption, and electrocatalyzed oxidation by Pt can be readily distinguished with the EQCM.

This approach was used to show that the arsenic redox reactions on the carbon electrode are mechanistically similar to that on the bare Pt electrode. This could not be concluded with just classical cyclic voltammetry alone due to the obfuscation of the faradaic features by the large capacitative effects of the carbon double layer.
For the porous carbon electrode, a continual mass loss was always observed during potential cycling, with or without arsenic in the solution. This was attributed to electrogasification of the carbon. The apparent mass loss per cycle was observed to decrease with increasing arsenic concentration due to a net mass increase in adsorbed arsenic per cycle that increased with arsenic concentration, offsetting the carbon mass loss. Additional carbon adsorption sites involved in arsenic species interactions are created during electrogasification, thereby augmenting the net uptake of arsenic per cycle.

It is demonstrated that EQCM, and in particular the information given by the behavior of the time derivative of the mass vs. potential, or massogram, is very useful for distinguishing arsenic species interactions with carbon electrodes. It may also prove to be effective for investigating redox/adsorption/desorption behavior of other species in solution with carbon materials as well.

Assessment of ionic strength in the direct current enhanced transport of iron nanoparticles

Helena Gomes and Sibel Pamukcu - Lehigh University, USA
Celina Dias-Ferreira - CERNAS, Agrarian School of Coimbra, Portugal
Alexandra B. Ribeiro - CENSE, New University of Lisboa, Portugal

Zero valent iron nanoparticles (nZVI) use in soil and groundwater remediation is limited by their effective long distance transport without aggregation and reactivity loss. Electrokinetics (EK) can be used to tackle this constraint, as several studies show. Still, the effects of ionic strength that can contribute to aggregation, corrosion and low mobility of nZVI in clays were not studied. The main objective of this study was to assess these effects in a model soil (kaolin), using different electrolytes (0.001 M NaCl, 0.001 M NaOH, 0.1 M Na2SO3 and 0.05 M CaCl2), high nZVI concentrations, typical of field applications, and a constant potential of 5.0 V in a modified electrophoretic cell.

Results showed that there is an enhancement in nZVI transport under applied electric field when compared with that under diffusion (15 to 53% more). However, the nZVI electrophoretic transport appeared to be counteracted by electroosmotic advection and also by nanoparticles aggregation, due to the increased ionic strength and the formation of corrosion products with larger volumes. In the experiments using Na2SO3 and CaCl2 there was a limited enhancement in nZVI transport when compared with diffusion. The higher ionic strength of these electrolytes may have contributed to lower stability of the nanoparticles suspension, increasing their agglomeration.

Changes of elements and mineral composition of kaolin clay by electro-osmosis

Peng Jie - Hohai University, China

Electro-osmosis is a potential effective method for dewatering and consolidation of clay with low permeability. The geochemical effects of electro-osmosis in kaolin clay are studied in the laboratory. An electro-osmosis apparatus was developed. The CEC, pH, and electrical resistance of kaolin clay samples was measured, the elements and mineral compositions of different parts of soil samples were analyzed by XRD, XRF and ICP-MS tests. The results show that some significant changes of elements of kaolin clay have taken place after electro- osmosis.
Construction and Modification of oxides towards Formaldehyde Removal at Ambient Temperature

Wei Xiao and Xuhui Mao - Wuhan University, China

Indoor air purification is crucial for human health because people generally spend more than 80% of their time in houses, offices and cars. Formaldehyde (HCHO) is regarded as one of the dominating VOCs emitted from building and finishing materials including paints, wood-based panels, laminate floors and smoking fumes. High-concentration formaldehyde has far-reaching impact on human respiratory, nervous and immune systems. And long-term exposure to indoor air even containing a few ppm of HCHO may cause adverse effects on human health. Therefore, it is urgent to further develop more efficient and environmental friendly approaches for removal of formaldehyde. Herein, we report the construction and modification of oxide-based materials towards formaldehyde removal at ambient temperature. The correlation between materials microstructure (pore structure and surface area) and HCHO adsorption capability was rationalized. Furthermore, the interplay between adsorbed HCHO and oxides during treatment and regeneration processes were established and discussed. This study, we hope, will provide new insights into the design of high-performance, high-throughput, non-precious and reusable catalysts for indoor air purification at mild conditions.

Coupled phytoremediation-electrokientics for the remediation of brownfield sites with mixed contaminants: Preliminary results

Claudio Cameselle - University of Vigo, Spain
Reshma A. Chirakkara and Krishna R. Reddy - University of Illinois at Chicago, USA

Phytoremediation is the green and sustainable process in which green plants are used for the removal or elimination of contaminants in soils. Both organic and inorganic contaminants can be removed or degraded by the growing plants by several mechanisms, namely phytoextraction, rhizofiltration, phytostimulation and phytodegradation.

Phytoremediation shows several advantages. It can be applied in situ over large areas, the cost is low and the soil does not undergo significant damages during and after the remediation. However, the restoration of a contaminated site by phytoremediation requires long treatment time (several years) since the remediation depends on the growth and the biological cycles of the plant. It is only applicable for shallow depths within the depth of the roots, and the remediation efficiency largely depends of the physico-chemical properties of the soil and the bioavailability of the contaminants.

This study aims to develop a phytoremediation strategy for the remediation of three large brownfield sites polluted with mixed contaminants located in Chicago (Illinois, USA). Remediation of these sites is required to use them for recreational purposes and comply with the applicable federal and state environmental regulations that are protective of public health and on-site endangered species. According to the site investigation results, the sites were found contaminated with a mixture of organic contaminants and heavy metals.

The study first included several pot experiments to investigate the plant species suitable for phytoremediation of mixed contaminated soil. Mixed contaminated soil was prepared by spiking silty clay soil, typical of the Chicago area, with naphthalene, phenanthrene, lead, cadmium and chromium. Twelve different species of plants were grown in contaminated pots and in control pots without any contaminant. Results showed that only five species (sunflower, oat
plant, rye grass, tall fescue, green gram) were able to survive with the contaminant mixture in the soil. The maximum uptake of the contaminants was limited to 35 to 65%, mainly due to the limited bioavailability of the contaminants for the plants.

Several investigators proposed the combination of phytoremediation and electrokinetics in an attempt to avoid, in part, the limitations of phytoremediation. Basically, the coupled phytoremediation-electrokinetic technology consists in the application of a low intensity electric field to the contaminated soil in the vicinity of growing plants. The electric field may enhance the removal of the contaminants increasing the bioavailability of the contaminants by desorption and transportations of the contaminants even in short distances. Some significant variables that affect the coupled technology are as follows: the use of AC or DC current, the voltage, the mode of voltage application (continuous or periodic), the evolution of the soil pH by the electrolysis of water, and the possible addition of facilitating agent to enhance the mobility and bioavailability of the contaminants.

Though several studies have been conducted previously, the applicability of integrated phytoremediation-electrokinetics for mixed contaminants in actual field soils is still unknown. Hence, the phytoremediation investigation of the brownfields is extended to determine the potential benefits of periodically applied electric potential on the bioavailability of the contaminants and improved phytoremediation efficiency. Preliminary controlled tank experiments are conducted to evaluate the combined effects of phytoremediation and electrokinetics on the contaminant removal from the Chicago brownfield site soil. Two plant species that are shown to have promise for higher contaminant uptake are selected for this study. Experiments are conducted with electrokinetics only, phytoremediation only, and with both electrokinetics and phytoremediation. The results of these experiments allowed quantifying the benefits of integrating the two remediation technologies and also identifying the issues and challenges that have to be addressed in field applications.

Cyclic electrowinning/precipitation (CEP) system for the removal of heavy metals from aqueous solution mixtures

Joseph Calo, P. Grimshaw, G. Hradil - Brown University, USA

The description, operation, and performance of a novel cyclic electrowinning/precipitation (CEP) approach for the simultaneous removal of mixtures of heavy metals from aqueous solutions are presented. CEP combines the advantages of electrowinning in a hydrodynamic spouted particulate electrode (SPE) with that of chemical precipitation, to remove heavy metals at low concentrations as solid metal deposits on particulate cathodic particles without exporting toxic metal precipitate sludges from the process. That is, the precipitate sludge is repeatedly produced and consumed via cyclic pH swings, but is never exported from the process as waste.

The overall result of the process is a very large volume reduction of the heavy metal contaminants (e.g., on the order of $10^6$ for an initial metal ion concentration on the order of 10 ppm) as a solid metal deposit on particles that can either be safely discarded or further processed to recover particular metals. It is also demonstrated that particular metals can be concentrated on separate cathodic particle sets as a separation technique.

The performance of this approach is demonstrated with data obtained on the removal of low concentration mixtures of copper, nickel, and cadmium from aqueous solutions, as well as removal from contaminated soil leachates.
Development of iron-based material for simultaneous heavy metal ions removal from water

Liang Guo and Joseph Calo - Brown University, United States

The corrosion products of zero-valent iron (ZVI) are well known to be effective complexing agents for certain heavy metals such as arsenic. The objective of the current study was to improve the understanding of the performance of individual corrosion products (Fe3O4 and Fe2O3) for mercury and arsenic co-removal. In batch experiments at loadings of 30μg Hg(II):100mg sorbent, ZVI and Fe3O4, it was found that both are quite effective for Hg(II) removal. However, the presence of Cl- and SO42- were found to have significant effects on the removal performance with Fe2O3. About 60% of Hg(II) was removed by Fe2O3 with SO42- anion, which decreased to zero in the presence of Cl-. However, 100% removal of Hg(II) was achieved with both ZVI and Fe3O4, with no detectable influence of either anion. It was also found that mechanical mixing affected the removal performance. By comparing the behavior of two different particle sizes of the ZVI material (200 μm and 2 mm), significant improvement in performance was observed for the 2 mm particles, increasing the removal percentage from 76% to 95% with Cl- as complexation agent with mixing. It is concluded that ZVI and the iron oxides exhibit significantly different performance for mercury cation removal. Iron oxide nanoparticles, prepared electrochemically, are being developed as sorbents for the simultaneous removal of Hg(II) and As(III and V) from water. In addition, the effects of the initial concentrations of the heavy metal ions, the attendant types of cations and anions, pH, and dissolved oxygen concentration on removal performance are under investigation.

Electrically induced hydrocarbon transport in oil bearing formations

Ehsan Ghazanfari - Lehigh University, USA

Introduction

Electrically assisted transport of hydrocarbon compounds in natural porous media has generally been investigated for environmental mitigation of contaminating oils [1, 2]. Electrically enhanced oil recovery is an alternative and promising method that has gained more attention in recent decades [3, 4]. The same fundamental principle of electrically assisted transport of hydrocarbon compounds in natural porous media applies to electrically enhanced oil recovery. In water wet porous media, electroosmotic flow of mass (i.e., water, ions) is activated near the solid–liquid interfaces when a DC electrical field is applied to the formation. This interfacial movement of mass and the resulting “viscous drag” creates a driving force that transports the hydro-carbon compounds residing near the interface [5]. Also, electrophoretic transport of oil which is likely when the hydrophobic molecules are adsorbed to the surface charged colloidal particles and/or the relatively large hydrocarbon molecules form colloidal-micelles that may also be charged depending on the pH, contributes to oil production. In this study the contribution of electrochemical transformation of crude oil to the enhanced oil recovery is investigated.

Experimental Program

The surrogate formation cores were prepared using massed sand at 52%, silt at 40%, and Georgia Kaolinite clay at 8%. The formation oil used in the tests had API gravity of 17.4°; Dynamic viscosity of 2782 cP, and specific gravity of 0.95. The electrolyte solution used, had the salinity of 33,000 ppm; electrical conductivity of 45,000 μS; and pH of 7.50. The cell was 100 cm in length and 16.2 cm in diameter. Titanium electrodes, and ion exchange resin packs were used at the two ends of each cell. The tests were conducted under two different current densities (0.1 and 1 Amp/m²) for 107 days, during which the voltage gradient, current density, and oxidation reduction potential (ORP) were measured. Also,
formation samples were taken periodically for gravimetric (oil-water content), UVVA and Fourier transfer infrared (FTIR), and pH analysis.

Results and Discussion

Figure 1 shows the measured current density and total voltage across the cell during the test (for high current density cell). As it can be observed from Figure 1, the measured current density remained fairly constant during the test. Figure 2 shows the evolution of ORP measurements and the contours of pH during the test. A constant pH of about 6 was maintained within the formation for about 1 month of continuous current application using ion exchange resin packs, after which the ion-exchange resins were depleted and had to be replaced. As expected, the regions close to anode (X/L= 0 to 0.3) developed oxidation state. In the middle regions (X/L = 0.3 to 0.65) of the cores, ORP, although fluctuating somewhat, did not change appreciably, but displayed a slow transition towards reductive state in time. Near the cathode region oxidative state was dominant.

Figure 1. The current density and total voltage across the cell

Figure 2. The ORP and pH evolution in the cell during the test
References


Electrochemical oxidation of phenolic compounds and organic acids in dilute aqueous solutions

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The electrochemical oxidation of a group of phenolic compounds and organic acids of environmental importance was studied in the laboratory using cyclic voltammetric technique. A rotating ring disk (Pt) electrode was used in a three-electrode electrochemical reactor. The phenolic compounds studied were phenol, substituted phenols (i.e., nitro-, bromo- and chloro-phenols. The organic acids studied were mono-hydroxy, dihydroxy- and trihydroxy-benzoic, salicylic, protocatechuic, gallic, and pentadeca-fluoro (fluorooctanoic) acids. Results show clearly that phenolic compounds can be electrochemically oxidized as detected from the unique characteristics of voltammograms. Anodic current was proportional to the removal rate of organic compounds. Aliphatic compounds were major products of the electrolysis of phenols. There was strong evidence of aromatic ring cleavage resulted from electrochemical oxidation reaction. Among the phenolic compounds studied, phenols with the most number of hydroxyl functional group are the easiest to be oxidized; the greater the number of hydroxyl group is, the greater the anodic current results. The order of anodic current, or reaction rate, followed the increasing order of tri-hydroxy- (gallic) > dihydroxy- (protocatechuic) > monohydroxy- (salicylic)-benzoic acid. For non-carboxylic phenols compounds, the order was: pyrogallol (3 OH) > catechol (2 OH) > phenol (1 OH). Worthy of mention is the oxidation of fluoro-octanoic acid, a persistent surfactant. Results showed that fluoro-octanoic acid could be readily oxidized electrochemically as well with the production of hydrophobic dimmer, C14F30 and CO2. All phenolic compounds ultimately were decomposed to a series of simple organic acids such as fumaric, and tartaric acids. Other factor, specifically, pH played an important role on the anodic oxidation of phenols. Under alkaline condition, the hydroxy ions were oxidized readily to hydroxyl radicals, which reacted with neutral molecules and brought about ring breakage of phenols. Therefore alkaline pH favored the electrode reaction. Voltammetry technique enables the determination of standard EMF values for the organic compounds studied and the reaction mechanisms. Overall, results demonstrated that electrochemical process is feasible in treating water containing hazardous chemicals.
Electrochemistry and -kinetics in aqueous media containing amphoteric ions

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Classically, transport theory in electrokinetics and electrochemistry is based on ionic mixtures where all ions have a fixed valency (such as Na+ and Cl-). However, in water, many ions are amphoteric and co-exist in various forms, e.g. H2CO3, HCO3^- and CO3^2- co-exist, with their concentration ratio dependent on pH. pH itself depends on the concentrations of H+ and OH-, species that can be formed from the water itself, while being transported by diffusion and migration.

Here we outline theory to deal with these situations of great practical relevance, including the problems of the adsorption/desorption of NH3, H2S- or CO2 in aqueous solution. Classical theory for such problems neglects the electrical field effect, but leaving this important effect out leads to inconsistencies in the model such as non-adherence to the requirement of local electroneutrality.

We demonstrate how such a theory can be set up in case the reactions between the various forms of the amphoteric ions (e.g., NH3, NH4+) are fast, without the necessity to assume a certain kinetic rate equation. Special attention is given to the problem of the proper boundary condition at electrodes (non-zero electrical current).

We discuss how this theory can be applied to transport in porous media, where either the medium carries fixed ionic charge (such as in clays, in ion-exchange resins or membranes), or where the medium can be charged electrically (porous carbon electrodes, e.g. for water desalination). Examples are given for both situations; firstly, how upon applying high electrical currents through a membrane, the fixed membrane charge is predicted to break down because of the development of extreme pH-values in the membrane; secondly, how differential movement of H and OH may lead to measurable pH-fluctuations in the space between two porous electrodes that are charged relative to one another.

References


Electrodialytic remediation of stirred and stationary soil – Direct comparison of heavy metal removal rate

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Electrodialytic soil remediation is a method for removal of heavy metals. Good results have been obtained in laboratory scale both with treatment of stationary, water saturated soil and with remediation of soil suspended in water. The two
different setups have different uses. The first as in-situ treatment without requirement for fast remediation, as the duration is highly dependent on the distance between the electrodes and in such application the electrode spacing must have a certain distance (often meters). In the stirred setup it is possible to shorten the transport route to few mm and to have a fast and continuous process, which can be used ex-situ and if advantageous in combination with soil washing.

The present work is a direct, experimental comparison of the two options focusing on the removal rate of the heavy metals from industrially polluted soils. The electrodialytic experiments were conducted in pairs of two: one experiment with stationary soil and one with stirred soil (figure 1). The soil mass to be treated was kept the same in each pair and the volume to be treated thus varied as a result of the liquid to solid ration being much higher in the stirred system. Consequently the soil compartment was longer (10 cm vs. 1.5 - 3 cm) in the stirred system. All other parameters were kept the same within each set.

![Figure 1: Schematics of experimental cells (a) water saturated soil and (b) soil suspended in distilled water and stirred during experiments. (AN = anion exchange membrane, CAT = cation exchange membrane)](image)

The remediation of the stirred suspension was fastest for all four soils of the investigation. The acidification of the suspended soil was fastest (both in calcareous and non-calcereous soils) and following the mobilization of heavy metals for removal by electromigration. The cause for this cannot be explained by a single factor but is a combination of several. Suspending the soil means dissolution and lower overall conductivity in the central compartment, which again lowers the limiting current density for water splitting and consequently increasing the extent of acidification. In addition the exchange of H+ ions over the cation exchange membrane between catholyte and suspension is more efficient in the stirred system as this exchange is not limited by the diffusion rate for cations in the soil to an extent as in the stationary setup. Finally also the stirring itself is important as the transport route for the heavy metals is shortened.

**Electrokinetic flocs formation in municipal wastewater**

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During municipal sludge treatment, its dewatering, its decantation, and its impact on membrane fouling are strongly related to coagulation and flocculation process which result in flocs formation. Usually, chemical coagulants are applied to neutralize the sludge suspension, change zeta potential and promote flocs formation which by growing change density and undergo decantation.

This paper presents phenomena associated with formation of flocs produced during electrocoagulation of wastewater. A comparison with a chemical coagulation is also presented. Investigations of electrocoagulation processes were carried...
out in a series of: i) batch electro-reactors, ii) continuous flow lab bench electro-reactors, and iii) pilot electro-reactors. Activated sludge samples were collected from several municipal treatment plants in Quebec having the concentration of mixed liquor suspended solids (MLSS) between 3,000 to 16,000 mg/l. Voltage gradient and current densities changed adequately. In all experiments, aluminum anode was used as a sacrificial electrode; subsequently, a number of electrochemical processes took place in the MLSS shaping sludge characteristics (e.g. electrocoagulation, electrophoresis, electroosmoos, electro-migration of ions, radicals’ production and gases release on both electrodes. Daily analyses were performed on wastewater samples over the experimental period of many months.

Size of formed flocs was measured using the particle size analyser. The samples were stirred gently in the syringe before injecting into the instrument. In order to measure zeta potential of the suspension, 50 ml of sludge sample was centrifuged, the supernatant was discarded and mixed with a few drops of the activated sludge. This later mixture was placed inside the electrophoretic cell of the zeta meter for flocs zeta potential measurement. The final value was provided as an average of 10 readings. Sludge filterability was evaluated as specific resistance to filtration (SRF). Sample sludge was filtrated in a Buchner funnel under a vacuum, and during the filtration, the filtrate volume was recorded versus time.

Once the current field was activated, aluminum ions were released from anode into the sludge, which was able to neutralize the negative charge of the organic colloids and thereby reducing the repulsive forces between the colloids by reducing the magnitude of zeta potential. The results showed that magnitude of zeta potential of the colloidal system was ranging between -12 to -40 mV – much higher than in control cells. Application of lower current densities did not show substantial changes in zeta densities, while current densities between 20 to 35 A/m² exhibited outstanding changes for some pools of flocs. The magnitude of zeta potential was reduced; some flocs even had a positive zeta potential over a short time-off, probably due to a continuous rate of aluminum flocs formation. This change of zeta potential reflects the possibility of bio-flocculation and forming larger size of flocs.

Mean particle size distribution of flocs changed over the operating period and current density. Furthermore, two-stage electro-flocculation process was observed during this study. First stage consists on an electro-flocculation when colloids form larger flocs mainly due to the reducing of the repulsive forces between the colloids/flocs reflected by changing the magnitude of zeta potential. As time go by, the second stage can be observed when floc size shrinks due to the removal of bound water from the flocs. This trend of increasing followed by decreasing of floc size was observed whenever the current density was strong enough to cause electro-flocculation and electro-extraction of bound water. It was found that minimum current density is required to provide the driving forces for the bound water to move out of the flocs.

The results of this research have practical applications in electro-bioreactors.

**Electrokinetic transport mechanism of Li ions in cementitious materials by using NMR**

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Alkali Silica Reaction (ASR) is a complex mechanism based on chemical reactions between alkalis and reactive silica and transport of reaction products and water. In itself the reactants and the sources for ASR are well known: alkalis react with reactive silica in aggregate particles forming a gel. Here water is the medium for the transport of the alkalis. The gel is first mobile, but subsequently becomes immobilized. Next, water acting as a reactant is absorbed causes swelling of
the gel. This in turn produces cracking of concrete. As a result of cracking the permeability of the concrete will increase and external alkalis can penetrate the concrete more easily and hence increase ASR damage [1]. Moreover due to cracking, the material will also become more vulnerable to other deterioration mechanisms. Therefore once ASR has started, one can get a run-away of action and reaction.

It is known that the addition of lithium ions can prevent deleterious ASR by forming a non-expansive gel [2]. In case of an existing concrete structure the lithium ions have to be transported into the cementitious matrix. There are several mechanisms that can be used for ionic transportation, such as an ionic migration, diffusion, and absorption. The ionic elektrokinetic migration is probably the most effective mechanism to reach sufficient concentration in larger penetration depth to stop the ASR with in a given time.

The delivery of lithium ions into concrete materials by using electrical field was firstly proposed Page [3]. The transport mechanisms involved in the lithium migration in ASR affected concrete are not very well known. In this study we have used special approach based on Nuclear Magnetic Resonance to measure lithium transport mechanisms non-destructively in cementitious materials during the elektrokinetic process. To these end we have first look at the elektrokinetic process transport mechanism of lithium ions in less complicated materials than concrete, i.e., fired clay rick and calcium-silica brick. These measurements have been compared in which we have taken the main transport process into consideration.


**Electrokinetics Assisted Acidizing for Enhancing Oil Recovery in Abu Dhabi Carbonate Reservoirs**

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Acidizing has been remarkably useful in increasing the effective permeability in the near well-bore region as a result of removing wellbore damage and creating artificial flow channels in our tight reservoirs. However, conventional acidizing also encounters problems in limiting depth of penetration to a near well-bore effect. In addition, the high concentration of acid injected creates HSE issues, as it is a hazard to handle, transport and inject into the well. However, one of the emerging technologies is the application of electrokinetics (EK); termed as electrically enhanced oil recovery (EEOR). EK is gaining increased popularity due to a number of economical and environmental advantages such as reduced flowing viscosity, reduced water-cut, and no depth limitation. This paper presents recent research that demonstrates the impact of electrokinetics on matrix acid stimulation in Abu Dhabi carbonate reservoirs with varying acid concentrations and voltage gradients.
Core-plug samples (1 & 1.5-inch. diameter) tested in this study, consist of carbonate reservoir tight and cap rocks, which were extracted from Abu Dhabi producing oil fields. These samples were saturated with medium (290 API) crude oil in an EK specially designed core flood setup. Initially, electrokinetics was applied using a constant voltage gradient (2V/cm) on the core-plugs with acids of varying concentrations from 0.125 upto 1.2% HCl injected at the anode at 0.25 ml/min (consistent with average reservoir flow rate of 1 ft/D) and transported by electrokinetics to the target producer (cathode). However, the second experiment was repeated with conventional acidizing without the application of EK. The reservoir rock permeability and ultimate oil recovery were measured before and after each experiment to quantify the success of the process.

Several correlations related to acid concentration, recovery factor and permeability enhancement are presented here for both water-wet and oil-wet conditions. The experimental results at ambient conditions have shown that the recovery factor increases by 59-85%, and permeability increases by 28-45% in water-wet rocks as the acid concentration increases from 0.125% to 1%. EK-assisted acidizing results in higher oil recovery by 17-19% and higher permeability enhancement by 9-15% as compared to conventional acidizing, due to the fracturing of tight rocks in a precise and targeted manner. This could be promising for water swept and oil-wet reservoirs due to in-situ stimulation by co-generation of the free acid at the anode as well as high performance EK transport of the injected acid. Consequently, it also reduces the amount of acid injected in the presence of electrokinetics by about 20-41%. Under specific unique circumstances, there could be a point where the free generation of acid at the anode maybe sufficient for the acidization job without the need for additional acid injection. Targeting the development of a novel efficient and green approach for reservoir stimulation by reducing corrosion problems at surface, drilling facilities and wellbore tubing due to lower frequency/volume of acid injected.

**Electroremediation of Polluted Soil with Hydrocarbon**

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In recent years, the problem of hydrocarbon-contaminated soil has generated interest from government and private institutions through legislation and remediation of these sites, due to recalcitrant compounds being discharged into the environment.

Technologies have been developed to help solve this problem. To select the most appropriate technology for contaminated site remediation, the type of pollutant, its concentration, and site conditions must be taken into account. Contamination site remediation treatments are biological, physicochemical and thermal; electroremediation is a physicochemical process.

Soil electroremediation has been reported using different configurations of electrodes connected in series or in parallel, face-to-face, or using a rectangular or circular arrangement, among others. This research shows the electroremediation of hydrocarbon - contaminated soil using different electrode configurations, a method which uses an electric field to remove contaminants. Finally, the circular configuration showed the best electroremotion of hydrocarbon from soil in laboratory, and this configuration was scaled to apply the electrokinetic process in situ.
Enhanced Electrokinetic Remediation of Cadmium-Contaminated Natural Clay by Phosphonates and EDTA

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Soil contamination by heavy metals is a worsening worldwide environmental problem. Electrokinetic extraction is a promising technology for in-situ remediation of contaminated soils of low hydraulic permeability. However, the extraction of heavy metals is usually hindered by the high acid/base buffer capacity of natural soils. EDTA is a strong metal chelate widely studied in the enhancement of electrokinetic remediation. In this study, batch desorption experiments and bench-scale electrokinetic extraction experiments were carried out to study the effect of two phosphonates, i.e. EDTMP and NTMP, and EDTA on the extraction of cadmium from a natural clay from Shanghai, China. The results of the batch experiments indicate that it is very difficult to extract the cadmium sorbed on soil particle surfaces when the soil pH is above 7.0 without any enhancement. However, with the addition of 0.1 M phosphonates or EDTA, more than 75% of the sorbed cadmium could be dissolved into solution in the pH range of 2.0-11.0. The results of the electrokinetic extraction experiment indicate that the cadmium spiked in the specimen can be transported towards the anode with the enhancement of EDTA, EDTMP, or NTMP. Although phosphonates are not as efficient as EDTA in solubilization of cadmium, accumulation of cadmium in the vicinity of the anode was not observed as in the case of EDTA. The average removal efficiencies of cadmium from the soil samples collected after approximately 5 days of electrokinetic extraction enhanced by 0.1 M EDTMP and NTMP were 22.4% and 22.8%, respectively, higher than the 15.1% by 0.1 M EDTA under similar conditions.

Enhancement of Heavy Metals Remediation from Abu Dhabi Offshore Muds by Electrokinetics Coupled with Nano-Sized Particles and Chemicals

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There have been many field studies on the accumulation of heavy metals in the sediments around offshore oil and gas production facilities. It was shown that electroremediation is feasible for in-situ removal of heavy metals from offshore muds [Haroun, 2009, 2010 and Sanghee 2011]. Due to its recent promising results, this emerging environmental initiative can be engineered to develop into a leading in-situ decontamination approach. The optimization of this technique to remove specific heavy metals, such as As, Cd, Cr, Pb, Hg, Sr and Zn, with the use of EK assisted by Nano-Particles (CuO) and Chemicals (ABC) will be discussed. The objective of this study is to figure out the smartest coupling agents with EK in remediation of heavy metals from offshore mud. The scope of this research aims to identify the optimum operating conditions, which will allow for extraction of specific contaminants that exist in abundance in Abu Dhabi coastal areas. The experimental setup consisted of a 50cm-long by 5cm diameter sample chamber, which had two electrode chambers on either side, acting as the anode and cathode. A varying DC electrical voltage gradient of 1 to 2V/cm was applied in all tests for 72h.
After the in-situ electrochemical test was performed with Abu Dhabi seawater, removal efficiency of the metal ions from soil were determined by their concentration (Fig. 1). However, the removal efficiencies was influenced by the overall effects of the characteristics of the soils, the specific behaviors of metals in soils, the initial concentrations and speciation of metal contaminants as well as the velocity of electromigration. It also depends on the coupling materials and current density sustained. For example, Sr and Cr removal rates were higher in case of EK coupled with Nano CuO, whereas As and Pb were better with chemical ABC.

Other parameters including pH, conductivity, ORP, current and power were recorded and evaluated. These results enable us to identify the optimum operating conditions required in the up-scaling process, while maximizing the removal efficiency of targeted heavy metals. We are also able to determine a process of reducing electrode reactions, injected volume and power consumption to reduce the amount of energy and cost associated with this process. This process would in turn give us an understanding of the feasibility of sustainable in-situ electroremediation of heavy metals in high salinity environments.

Figure 1. Heavy metals’ concentration in EK with Chemical ABC/ Nano CuO mixed with Abu Dhabi seawater of offshore mud after 72 hours of treatment
Enhancing electrokinetic remediation of molinate contaminated soil using zero valent iron nanoparticles

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Molinate is a selective herbicide widely used in paddy rice fields. Electrokinetic (EK) remediation of molinate-contaminated soil was successfully achieved and modeled by Ribeiro et al. [1]. Molinate can also be degraded, through an oxidative pathway, by zero valent iron nanoparticles (nZVI) in aqueous solutions [2,3]. It is possible to use EK to enhance the transport of iron nanoparticles in low permeability fine-grain soils [4-6] and also improve the remediation effectiveness for different contaminants [7,9]. This work proposes the combined use of electrokinetics and nZVI to increase the degradation of molinate in the soil and enhance the nanoparticles transport.

Numerous studies showed the nZVI success in the degradation of diverse contaminants in aqueous media, but little is known on their performance for soil-sorbed contaminants. Before the EK experiments, batch degradation tests were carried out in two different soils (low and high organic matter content) spiked with molinate to assess if the addition of nZVI was effective.

A set of EK laboratory experiments with the injection of nZVI was carried out. The EK cell used has two electrode compartments and a central one. This one was modified at FCT-UNL in order to facilitate the introduction of the nZVI. The soils used were sampled in an industrial park and near a sanitary landfill in central Portugal. They were saturated with deionized water before placed in the cell. A set of five cellulose filters papers was used as passive membrane to assure the separation between the electrode compartments and the central one. The electrolyte used was 10−2 M NaNO3 with pH 7, with no recirculation. Daily injections of 1 mL of the zero valent iron slurry NANOFER 25S from NANO IRON, s.r.o. were made in the nZVI reservoir of the EK cell.

The results of the batch tests show that molinate absorbs more strongly in the soil with higher organic matter, as expected. The addition of nZVI contributes to the molinate degradation, both in the aqueous solution and in the soil (statistically significant, p=0.05, one-way ANOVA).

Preliminary results of the EK tests showed that nZVI can enhance molinate degradation, but further research is needed on the direct current enhanced transport of nanoparticles and the mechanisms involved.

References


**Evaluation of the Chemical Remotion of Mercury in Presence of Different Removing Agents from Polluted Bentonite and Quartz using Anodic Stripping Voltammetry**

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Heavy metals are necessary for live organisms; nevertheless, in high concentrations they represent a serious toxicity problem, being among the most dangerous Cadmium, Lead, Chromium and Mercury. The quantitative determination of heavy metals define the concentration in samples and it is necessary due to its toxicity, since, contrary to the organic residuals, the metals are not degraded and they accumulate in water, soils and silts.

Mercury in the environment is a threat to human health because it is a metal with bioaccumulation ability, affecting the brain and central nervous system and resulting in mental impairment. Thus, the determination of metals as Mercury is essential for the organism, and its maximum level of concentration in farming soil is 25 mg Kg$^{-1}$ dry soil.

Conventional methods to determine metals in liquid and solid matrix as Atomic Absorption (AA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) suffer from some disadvantages, such as high cost, long analysis time, requirement for sample pretreatment, and in some cases low sensitivity and selectivity. Compared with other methods, electrochemical methods are characterized by simplicity, high sensitivity, good stability, low-cost instrumentation, and small dimensions.

In consequence, diverse electro-analytical techniques have been reported to determine heavy metals in minerals such as the differential polarography of pulses with Drop of Mercury like the Electrode (DME). A sequential injection is reported
by Square Wave Anodic Voltammetry (SWAV), Square Wave Anodic Voltammetry Redisolution (SWAVR) and Anodic Stripping Voltammetry (ASV) for the simultaneous determination of ions as As$^{3+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, and Hg$^{2+}$ in potable water, minerals and soils previous acid digestion.

In this research, we show the evaluation of the chemical remotion of Mercury from polluted Bentonite and Quartz using ASV, where samples of Quartz and Calcium Bentonite were polluted with HgCl$_2$ 25 mg L$^{-1}$ to remove the Hg$^{2+}$ from the solid matrix using eight removing agents reported in the literature previously, which were evaluated to remove the major quantity of Mercury in aqueous solution. The removing agents proved were: KI 0.1 M, KCl 0.1 M; KOH 0.1 M, HCl 0.1 M, EDTA 0.1 M, hydroxypropyl-β-cyclodextrine (HPCD) 10 %, EDTA + Cysteine + NaCl 275 mg L$^{-1}$ / 1.15 % / 0.5 %, and Chitosan 0.01 M.

In order of the results obtained during the chemical remotion of Mercury with the different removing agents, the highest remotion of Hg$^{2+}$ after 1h from polluted Bentonite was using EDTA (17 %), and from polluted Quartz was using Chitosan (55 %). The efficient removal of Mercury contaminants observed under these conditions is attributed to electromigration of the coordination complexes that form between the terminal hydroxyl groups in EDTA and Chitosan in presence of the divalent Mercury (Hg$^{2+}$), which is probably strengthened by supramolecular interactions between unshared electrons at EDTA and Chitosan’s tertiary amino and Hg+2.

**Field Application of In-Situ Electrokinetic Remediation for Multi-Metal Contaminated Site**

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Electrokinetic remediation is an innovative technology to remove metals from the contaminated site in Korea because soil quality is regulated by pseudo-total concentration of metals extracted by aqua-regia. Additionally, the process could be applied to a site with high portion of fine grained soil where soil washing process, a common choice to remediate metal-contaminated soil in Korea, is not effective to be applied. Therefore, paddy rice field is one of most suitable site to apply electrokinetic remediation in Korea. We have tried to apply in-situ electrokinetic remediation to a site which was a former refinery plant and highly contaminated with As to 1.5 m in depth and with Cu and Pb to 1.0 m in depth. We installed conventional 1-dimensional electrode configuration and 2-dimensional hexagonal electrode configuration. In this study, we investigated difference in the removal of metals and time courses of operation parameters including current change and temperature change according to electrode configuration. Additionally we evaluated changes in fractionation of metals.

**Field Scale Pilot Demonstration of Electrokinetic-Enhanced Bioremediation (EK-Bio) of a PCE Source in Low Permeability Materials**

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Background/Objectives. The success of in situ remediation technologies, such as in situ bioremediation, requires effective and uniform delivery of remediation reagents through the target treatment area. Traditional amendment delivery techniques are generally based on hydraulic advection mechanisms, which are often faced with limitations in areas with low-permeability materials and/or highly heterogeneous geology. Transport of ionic substances such as lactate in an electric field is relatively independent of hydraulic properties and fluid flow. Therefore, effective amendment delivery using electrokinetics can be achieved in areas where permeability is limited and heterogeneous.

Approach/Activities. A field application was completed at a former industrial site to assess the ability of the EK-BIO technology to treat tetrachloroethene (PCE) dense non-aqueous phase liquid (DNAPL) source materials in interbedded deposits of sand and clay till. The highest PCE concentrations (up to 21,000 mg PCE/kg) have been observed in clay till between 3 and 8 meters below ground surface. The EK-BIO pilot test was performed and designed with the objective to demonstrate effective transport of lactate, the viability and migration of augmented Dehalococcoides, and PCE dechlorination within the test area. The field application consisted of a network of electrode wells with a spacing of approximately 1 meter by 3 meters. The design includes 3 pairs of anodes and cathodes, 3 amendment delivery wells, 4 monitoring wells, and 4 multilevel well systems to allow detailed performance monitoring.

Results/Lessons Learned. The results of the field application show that EK can facilitate the transport of amendments (lactate and KB-1TM) through clay soils. Dehalococcoides and vinyl chloride reductase (vcrA) levels increased significantly across the test area compared to baseline levels. Increases in vcrA counts within the clayey materials in the test area confirmed that EK operation was successful in distributing the microorganisms capable of PCE dechlorination to ethene. Significant reductive dechlorination of PCE to cis-1,2-DCE, VC and ethene was observed within groundwater samples and clay soil cores, indicating that PCE dechlorination to ethene can be achieved by EK-BIO with KB-1TM bioaugmentation. EK-Bio was chosen to treat the remaining contaminated are because the success of pilot demonstration.

Heavy Metal Decontamination in Abu Dhabi Offshore-Muds Generated from Refineries by Optimizing Electroremediation

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Offshore mud decontamination by electroremediation is an increasingly promising technology in the field of environmental indemnity. This emerging environmental initiative can be engineered to develop into a leading in-situ decontamination approach due to recent optimistic results. The optimization of this technique to remove specific heavy metals such as As, Cr, Pb and Zn is the scope of this research, which aims to identify optimum operating conditions which will allow the extraction of specific contaminants that exist in abundance in Abu Dhabi coastal areas.

In this study, contaminated offshore mud samples were collected from two locations that are considered to be the sinks to chemical disposal sources in Abu Dhabi. The 50, 80, 90 and 100 cm samples were consolidated before assembling the Electrokinetic (PI-EK-Env) apparatus cells. These EK cells were then subjected to both 2 and 3 V/cm for a fixed treatment time of 96 hours. Physiochemical properties of offshore mud were determined before and after EK treatment to determine the level of decontamination that was achieved. All samples showed a rather considerable extent of removal.
efficiency after the completion of continuous EK treatment by the application of D.C. Further experiments were conducted on samples with the same mineralogical nature and degree of contamination to determine the optimum operating conditions that will target specific heavy metal decontamination. Other parameters including pH, temperature, and current density were recorded and evaluated.

The offshore mud samples showed that there were high initial concentrations of heavy metals such as Tin, Scandium, Copper, Lead and Aluminum. After the samples were subjected to EK treatment, it was found that a high percentage of removal of Scandium, Copper, Lead and Palladium (60-100% removal) was achieved. Throughout the experiment, Chlorine gas was generated at the anode, due to oxidation of the chlorine anions, which was kept in solution as a form of pH control. These results enable us to identify the optimum operating conditions required in the up-scaling of both voltage gradient and sample length, while maximizing the removal efficiency of targeted heavy metals. We are also able to determine a process of reducing electrode reactions and power consumption to reduce the amount of energy and cost associated with this process. This process would in turn give us an understanding of the feasibility of sustainable in-situ electroremediation of heavy metals in high salinity environments.

**Impact of DC field on Clostridium perfringens spore**

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The objective of this study was investigating an impact of low gradient DC field on Clostridium perfringens spore in anaerobically treated sludge.

Anaerobic digestion (AnD) is a series of biological processes which permit on break down biodegradable material into methane (CH4) and carbon dioxide (CO2) in an oxygen free environment. The AnD process also generates a stabilized liquid effluent that contains water, minerals and approximately half of the carbon from the incoming materials and several groups of microorganisms. The AnD inactivates many microorganisms, however, some of them have ability to form spores to survive inconvenient conditions. Clostridium perfringens, a Gram-positive bacterium, is one of them. It is an endospore-forming, rod-shaped, non-motile anaerobic bacterium that can tolerate only 5 percent of oxygen, and is known to be the most widely distributed pathogen in nature. C. perfringens is a ubiquitous organism and a normal oral of human and animal gastrointestinal (GI) tract and can be found in sewage.

During extreme conditions, C. perfringens undergoes a differentiation process (in seven stages) and forms single oval sub-terminal spores with a diameter of 0.05) impact on its mean viability. However at lower gradient, the spores showed germination.

To estimate the extent of electric field-induced germination of C. perfringens spores, the biosolids was examined for viable counts before and after exposure to DC field for one hour. The differences in viable spore counts between before and after EK treatment indicated a meager spore reduction. However, this decline was significant for the same suspension of spores after 40 minutes incubation at 45oC. These results showed that although spores are highly resistant to EK treatment, they can be activated and germinate under the influence of electric field. The incubation time was necessary for the spore to pass the activation, outgrowth and germination stage.
Representative micrographs of thin sections of C. perfringens spore reveals appearance of linear phase in the spore survival curves, where firstly, breaks in spore coat along with destructions in the cortex and spore shape are produced, following by an obvious germination. It was concluded that electrokinetic phenomena can control survival organisms in AnD sludge including those resistant to disinfections.

Impact of Electrical Field on Substrate Utilization Rate and Microbial Revitalization in Bio-Electrochemical Cells

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The impact of electrical field on chemical oxygen demand (COD) utilization rate and microbial revitalization, indicated by the change in the volatile suspended solids (MLVSS), has been investigated in bio-electrochemical batch reactors. Each batch reactor contained 800 ml of the acclimated sludge and was fed with synthetic wastewater (initial COD = 1016 mg/l) once at the very start of the experiments. The acclimated sludge was aerated in order to provide the necessary oxygen for aerobic microbial growth and for mixing the sludge. The biomass in two reactors was exposed differently to DC electrical field; they were operated in intermittent electrical mode: a) 5 min. ON: 10 min. OFF and b) 5 min. ON: 15 min. OFF, whilst one reactor was continuously exposed to electrical field of 15 A/m². The aluminium flat anode and the stainless steel cathode were applied. For comparative purposes; a control bioreactor with no electrodes was operated simultaneously. The experiment was carried out for 122 h and several parameters were monitored. Samples were taken from the middle of each batch reactor and analyzed for COD (using Hach COD TNT vials), and MLVSS (using 0.45 μm glass fiber filters). A Hach HQ30d single-input multi-meter probe was used to monitor dissolved oxygen, pH, temperature, and electrical conductivity. The concentrations of biomass (MLVSS) and substrate (COD) over time were reported. The studies showed that the rate of substrate utilization in the electrobioreactors was significantly rapid, thus increasing the substrate bioavailability when compared to the bioreactor without DC. Furthermore, the microbial revitalization was also observed when electrical field was disconnected. Authors suggested that some of the microorganisms were adversely affected by the presence of the electrical field; however, other types might have been stimulated. It could be concluded that the application of an adequate electrical field in any biological media would create required conditions for the living microorganisms and therefore enhance the removal of organics (defined as COD) from the wastewaters through a combination of electrochemical and biological processes.

Improvement of sludge electro-dewatering process using pretreatment techniques

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Activated sludge processes that are extensively used in municipal wastewater treatment plants have a major drawback of producing huge amounts of waste sludge with high water content (95-99%). In order to create a sludge cake, water must be removed and the solids content increased. This can be carried out by centrifugation, belt or filter presses. The problem with any of these technologies is that the water that can be extracted from the sludge by hydraulic means is limited. This is because of the way in which water is bound to the sludge particles or flocs. During the electrokinetic (EK) dewatering (or electro-dewatering) process, the applied direct electric current results in increased water removal from the sludge. Electro-osmosis, which is the movement of capillary water because of the formation of the electrical double layer at the interface of water and the solid surface, is the major phenomenon occurring during such treatment. Usually,
sludge has a negative zeta potential, thus the direction of the electro-osmotic flow is always towards the cathode. The positive effect of electroosmotic dewatering of sludge has been known for several years. However, the technology has not yet been successfully applied in industry. It is because there are several technological barriers to the commercial exploitation of the technology that are yet to be resolved. One of these barriers is a scientifically robust design methodology.

Different modes of operation have been studied like keeping the voltage, current or electric field constant or allowing it to vary with time. Factors like salts, flocculants, suspension types, conductivity, various electrodes materials, electrode surface area, etc. have also been investigated. Currently, there is a strong urge to improve the existing EK-design methodology using sludge pretreatment techniques. A lab-scale EK dewatering configuration investigated the effects of various pretreatment methods like heating, ultrasonic, freeze/thaw and nano-particles. It seems that all these techniques could increase the dewatering efficiency and reduce the electro-dewatering time. The highest total solid content was achieved with the highest voltage and heating pre-treatment.

Mesoscale Modelling of the Water Adsorption and Transport Properties of Concrete
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The highly porous nature of concrete allows the adsorption of a large quantity of water within its microstructure. The presence of this water allows the movement through the concrete of dissolved ions, which may be harmful to the concrete, to reinforcing materials within it, or to users of the concrete.

Understanding the diffusive and electrokinetic transport of these dissolved ions requires an accurate model of the water content of concrete. Additionally, the transport properties are crucial in determining the electro-osmotic response of the system. To correctly model water transport through concrete, it is necessary to consider the multiscale structure of the pore network: for instance, transport takes place predominately in large (e.g. capillary) pores, yet the transport rate is dominated by the effect of the small (e.g. gel) pores that make up a bottleneck in the transport process.

We present a model of water adsorption and transport in concrete, in which pore radii are drawn from a bimodal distribution. Water can move through these pores by vapour diffusion and also by liquid flow. The existence of two distinct transport mechanisms means that the rate of water transport is strongly dependent on local water content. Furthermore, the calculation of local water content requires not simply an application of an equilibrium humidity to water content relation, but also the consideration of pore blocking leading to trapped water remaining in a pore even when the emptied pore is a lower free energy state.

Accounting for these complicating factors provides a significant advantage over simpler models that use parameters held constant throughout the sample and assumed to depend only on global properties such as environmental humidity or total mass of adsorbed water. It thus enables a more confident prediction of where water, and hence dissolved ions, will be located in a concrete sample that has been exposed to complicated environmental conditions.

Mobility and bioavailability of nutrients and microbial electron acceptors in bioelectroremediation processes in soils
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One of the major limitations of the biological degradation processes in polluted soils is the low interaction possibility between the three most important elements than are involved in the metabolism process of the pollutant: microorganisms, nutrients and pollutant. In the recent years it has increased the interest in an innovative technology, based in the application of a direct electric current to the soil in order to increase the mobility of the charged species present in the soil and therefore the possibility of interactions between them.

The overall aim of this study is to investigate the mobility of different nutrients and microbial electron acceptors as function of voltage gradients and soil texture.

Electrokinetic mobility of nitrates, phosphates, ammonium and oxygen was studied in a laboratory cell, in which the soils were introduced between two graphite electrodes. The soils used in this study were silica sand and kaolinite, both synthetic and free of pollutants. The nutrients solution was homogenously mixed with the soils. The same nutrients solution was added in the anodic and cathodic compartments. The bicarbonate buffer was selected to control the changes in the pH caused by the water electrolysis reactions and it was also added in the nutrients solution. The duration of the experiments was two weeks, during which the nutrients concentrations were measured in different points homogeneously distributed throughout the soil section.

The most relevant results were obtained for oxygen and nitrates. The obtaining of ammonium and phosphate concentrations was affected by parallel reactions that these species might be suffering (such as precipitation reactions of phosphate salts or ammonium decomposition into gaseous ammonia). Therefore, the obtained results for these last species were not representative.

In the obtained results in the experiments with the sandy soil it can be appreciated that the gradient of nutrients concentration is less pronounced when it is used a very high permeability soil. In this way, it is not observed significant differences between the different sampling points when a low voltage electric field is applied (0,5 V/cm). However, when the applied voltage increases (1V/cm), the differences between the sampling point closest to the cathode and the sampling point closest to the anode are more significant. It can be observed that the oxygen concentration is higher in the point closest to the anode because the water oxidation electrolysis reaction that takes place on the surface of the anodic electrode increases the concentration of dissolved oxygen that can diffuse throughout the soil. On the other hand, it can be observed small differences in the nitrate concentration between the sampling points when it is applied the lower voltage, so the quantity of nitrates is slightly bigger in the point closest to the anode. In the same way, when it is applied the biggest gradient voltage, the concentration of nitrate is lower in all the points of the soil section, so this species is being removed of the soil by electromigration and it is accumulating in the anodic compartment.

When it is used the clay soil, because its very low permeability, there are no differences in the oxygen concentration values obtained in the different sampling points and using different voltage gradients. However, it can be observed important differences in the nitrate concentration between the sampling points when it is applied voltage. Nitrates are almost completely eliminated in the sections closest to the cathode, accumulating in the points closest to the anode. This phenomenon is more pronounced when working with higher voltage, since the phenomenon of electromigration is more pronounced.
Multivariable analysis of electrodialytic remediation of contaminated harbor sediments

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Large amounts of sediments are annually dredged around the world in order to meet the demands of harbor development (e.g. maintaining or increasing navigational depths), and/or to meet the demands of governmental acts to improve the aquatic environment of harbors. Dredged, contaminated harbor sediments are, in most countries, considered as hazardous waste and are treated accordingly. The most common way of dealing with dredged contaminated sediments is disposal at licensed landfills (on land or deep sea), and in some cases solidification/stabilization of the sediments, e.g. in new harbor constructions. There is an increasing need to develop more cost-efficient methods for remediating the contamination to levels at which sediments are available for reuse. Electrodialytic remediation (EDR) provides such a method, and has been proven a liable method for remediating heavy metals from contaminated harbor sediments.

The focus of this study is however not to further develop and optimize the EDR method for harbor sediments, but to take a step back and conduct multivariable analyses of the existing data and hence form a better foundation for the later development and optimization of the method. The existing data-set spans a large geographical area and includes EDR results of harbor sediments from Denmark, Greenland and Norway.

The first step in the multivariable analyses is to perform principal component analysis (PCA) of the sediment characteristics in order to visualize the variation of the different sediments. Sediment characteristics include pH, grain size distribution, carbonate content, conductivity, metal concentrations and content of organic matter.

The second step of the multivariable analyses is to perform projection to latent structures analysis (PLS) in which relations between two matrices, X and Y, are determined. In this study, the X matrix consists of the sediment characteristics and the experimental variables. The latter include the remediation time, the current density, the liquid-solid ratio, rotation velocity of the suspended sediment and suspension liquid. The Y matrix consists of the responses, i.e. the remediation levels of the heavy metals cadmium, copper, lead and zinc. The PLS analysis determines whether the variation in the sediment characteristics and experimental variables are related to the variation in the remediation levels. If the PLS analysis shows a relation between the X and Y matrices, it is possible to statistically predict the remediation levels of a contaminated sediment with given characteristics and given experimental variables (operating within the given experimental space).

The third step of the multivariable analysis is to perform an inverse PLS analysis in which the X matrix consists of the remediation levels and the Y matrix consists of the experimental settings (variables and sediment characteristics). If the inverse PLS analysis shows a relation between the X and Y matrices, a scenario, in which a given contaminated sediment has to be remediated to a specified concentration, the experimental variables can be determined, is made possible. It is however important to stress that some caution of the results of an inverse PLS analysis should be taken, since the dimensions of the X matrix are lower than those of the Y matrix which could result in an undetermined system. The method can however provide valuable new ideas for future experiments.
The results of this study provide a good foundation for future experimental work, including optimizing the EDR method using multivariable methods (design and optimization). In addition it provides a good starting point for new experiments covering other important pollutants when dealing with harbor sediments such as arsenic, chromium, mercury, nickel, PAHs, PCBs, TBT and oil products.

Optimization of Electrodialytic Separation of Heavy Metals and Phosphorous during Domestic Wastewater Treatment

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Electrodialysis (ED) has mainly been developed as a remediation method for heavy metal polluted soils, harbor sludge and waste streams. Over recent years studies on treatment methods for both domestic and industrial waste streams have shifted their focus from purely remediation efforts to the recovery of valuable resources and nutrients: urban mining. ED followed a similar trend. The main reason for this development is decreasing availability and quality of important nutrients from primary sources, e.g. phosphorous [Cordell et al. 2009]. Therefore, alternative sources need to be found, in case of phosphorous this could be domestic wastewater.

During treatment of domestic wastewater, chemical coagulants are commonly used to remove phosphates which are not removable through biological processes. ED could be used to extract these phosphates instead, resulting in high quality resources and the reduced need of chemical coagulants. Consequently, this would lower sludge production and improve phosphorous availability for plants in the remaining sludge or sewage sludge ash. Simultaneous removal of heavy metals during ED, when concentrations exceed legislative standards will enable application of the initially polluted sludge in, for example, agriculture.

Source treatment of concentrated domestic wastewater, for the recovery of phosphorus through ED, has already shown to be effective [Fukumoto and Haga, 2004, Pronk et al. 2006], but would require extensive adjustments to existing wastewater gathering and treatment systems. Phosphorous removal through ED compared to conventional wastewater treatment techniques, such as biological treatment and chemical coagulation, is often considered non-profitable and leaves room for improvement [Keelley et al. 2012]. Heavy metal removal by ED in centralized wastewater treatment systems has mostly been studied for anaerobic digested sludge [Jakobsen et al. 2004, Ottosen et al. 2007, Kim et al. 2002].

The aim of this study is to investigate the efficiency of extracting phosphorous and heavy metals using ED in different stages of domestic wastewater treatment, e.g. ED treatment of raw sewage, aged sludge and anaerobically digested sludge. Furthermore, the possibility to correlate ED extraction of phosphorus and heavy metals to important parameters, e.g. organic matter content and pH, will be investigated. These correlations are obtained either from literature or experiments. Lab experiments are performed using an ED treatment cell, where the wastewater sludge is separated from the electrode compartments with ion-exchange membranes.

References:


Precipitation-Filtering Technology for Uranium Waste Solution Generated on Washing-Electrokinetic Decontamination

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A great volume of uranium electrokinetic waste solution has been generated during the operation of the washing-electrokinetic decontamination equipment to remove uranium from radioactive soil. The treatment technology for uranium waste solution generated on washing-electrokinetic decontamination was developed. First, a treatment process suitable to the contamination characteristics of washing-electrokinetic waste solution was proposed. Second, optimal treatment conditions for precipitation-filtration were selected through many experiments.

A process to reuse waste solution generated on washing-electrokinetic decontamination was developed. When the waste solution reuse process was applied on washing-electrokinetic decontamination, about waste solution volume of 70% was reduced. In order for the pH of a precipitate solution to reach 10, the calcium hydroxide needed to be 10ml/100ml(waste solution volume), the sodium hydroxide needed to be 1.4ml/100ml, and the calcium oxide needed to be 2.0ml/100ml. Dissolution velocity of calcium hydroxide was faster than that of calcium oxide, but volume of the generated waste solution on using calcium hydroxide increased 8ml/100ml more than that on using calcium oxide.

The total metal precipitation rate by sodium hydroxide in supernatant was the highest at pH 9. Only, some K(I) ions remained after precipitation. Meanwhile, the concentration of uranium in supernatant was below 0.2ppm. But, at pH=12, the concentration of uranium in supernatant increased. Some Al(III) and K(I) ions remained. Also, at pH=9, the concentration of uranium in filtrate after precipitation-filtration was below 0.2ppm. Some Ca(II), K(I), Mg(II) ions remained.

Full-size treatment equipments were manufactured for waste solution generated on washing-electrokinetic decontamination, which can treat 1,500 L of waste solution by a batch. When NaOH was injected as a precipitant, the uranium concentration in treated solution was the lowest of three precipitants and the dried sludge volume was the
smallest. But, when the treated solution is reused as washing solution or electrolyte, K(I) ions can be accumulated in treated solution. Meanwhile, when Ca(OH)2 was injected as a precipitant, the volume of generated waste solution will be increased and on treatment of the generated waste solution, the additional sludge will be generated.

Reactive transport modeling. Coupling chemical kinetics and chemical equilibrium in electrokinetic phenomena

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The computer-aid solution of mathematical models for reactive-transport phenomena, i.e. transport processes with chemical reaction, is not easy. Two main difficulties may be identified: First, the kinetic laws are normally unknown and the reaction mechanisms may change for different multi-species systems. Second, chemical reaction rates of simultaneous reactions may differ in several orders of magnitude, leading to numerical problems such as singularity of matrices.

The most practical reactive-transport models have been implemented accepting the so-called local chemical equilibrium assumption. In this context, any representative control volume (including solid, liquid and gas phases) is assumed to keep the chemical equilibrium condition of all species, even when consecutive control volumes of the spatial domain are not in equilibrium between each other.

In general, the local chemical equilibrium condition is an accurate approximation if the chemical rates for the reversible reactions in both the direct and reverse directions are significantly faster than the transport rates. In the case of the transport phenomena in electrokinetic treatments, that the main transport mechanisms are accepted to be chemical diffusion, ionic migration and advection, being the latter a combination of terms such as electroosmosis, electrophoresis and transport of the fluid media due to gradients of degree of water saturation or hydraulic pressures.

Homogeneous aqueous reactions, such as acids and bases dissociation, inorganic complexation or the self-ionization of water, are significantly faster than the aforementioned transport rates. However, heterogeneous reactions, such as precipitation/dissolution or adsorption/desorption processes, may have chemical rates comparable or even slower than the transport rates. Therefore, models assuming local equilibrium condition for heterogeneous reactions may have low prediction capability due to overestimation of the chemical rates regarding, for example, to the release of the target contaminants from the solid matrix.

In the present work, a physicochemical model has been developed to describe multi-species reactive transport of matter through porous media. The model has been adapted for simulating electrokinetic soil remediation and electro-desalination treatments. Local equilibrium condition is assumed for homogeneous aqueous reactions. For the case of heterogeneous reactions, generalized simplified kinetic laws are proposed and solved as part of the Nernst-Planck-Poisson system of equations.
Remediation of subsurface mercury contamination using the iodide-assisted electrokinetic process

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The objective of this lab-scale study was to evaluate the feasibility of remediating subsurface mercury contamination using the iodide-assisted electrokinetic process. Due to negligence, beginning 1994 a building complex was built on a mercury-contaminated site in Taiwan before the regulatory authority noticed the problem of soil and groundwater contamination thereat. To resolve this problem, the potassium iodide-assisted electrokinetic (KI-assisted EK) process was proposed in this research. In this work an EK remediation system, including a gas-tight sand-box reactor with monitoring wells & caps, DC power supply, and electrodes of various materials, was first installed. Then an actual Hg-contaminated soil (Hg concentration of 3,000 to 5,000 mg/kg) was collected, characterized, and filled in the soil compartment of sand-box reactor simulating the unsaturated zone and saturated zone. In addition, 0.1 M KI lixiviant and/or actual groundwater were used as anolyte, catholyte and soil pore water. At this stage, an electric field was applied to the EK remediation system using a constant voltage mode (i.e., 1 V/cm) or constant current mode (i.e., 20 mA) for eight tests with different remediation time ranging from 1 to 14 days. The following are the research findings obtained using the KI-assisted EK process in this work: (1) migration of HgI$_4^{2-}$ (originated from chemical reaction of Hg and KI in aqueous solution) toward the anode is the primary mechanism for Hg removal, whereas the transport of dissolved Hg$_2$I$_2$ toward the cathode end by electroosmotic flow is considered the secondary removal mechanism for Hg; (2) through the mass balance of total Hg in the sand-box reactor, it is postulated that there might exist a mechanism relevant to Hg stabilization rendering the formation of unknown residual metallic Hg compound that is non-dissolvable by aqua regia digestion and for subsequent chemical analysis; (3) the emission of Hg vapor would not take place in the KI-assisted EK process; (4) the KI-assisted EK process is considered to be technically and economically feasible as compared with other Hg remediation technologies. However, it is believed that further studies are needed before the KI-assisted EK process could be implemented in the real world.

Removal of Perchlorate from Water by Catalytic Electrochemical Processes

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Perchlorate is an emerging contaminant. Based on report by National Academy of Science, the maximum perchlorate concentration in drinking water is 4 ppb. Perchlorate is a stable ion that it is rather difficult to be reduced chemically, especially under ambient conditions of temperature, pressure and concentration commonly found in natural water. We have studied the chemical reduction of perchlorate under ambient conditions using catalytic electrochemical reduction method. A total of 18 catalysts from the first, the second and the third row of the periodic table were prepared and tested for their effectiveness in catalyzing the reduction of perchlorate in dilute aqueous solutions. The metallic catalysts that were coated on the surface of stainless steel mesh using electrophoretic deposition process. The metallic catalysts were in the size of 50-80 nm. Results indicated that the electrochemical catalysis system was able to reduce perchlorate. The reduction reaction followed a zero-order rate law, which is readily described by the Langmuir-Hinsheldwood kinetics in that the adsorption of perchlorate onto the catalytic membrane constitutes the first step of the reaction. The weakly adsorbed perchlorate reacts with the freshly generated hydrogen atoms yielding a series of
chloro-oxy anions, namely, ClO₃⁻, ClO₂⁻, and ClO⁻, and eventually Cl⁻. The reduction reaction was completed with a simple 1:1 stoichiometry observed between ClO₄⁻ reduced and Cl⁻ produced. Results indicated that Ti, Sn, Cr, Mo, Cd and Pt were the most effective in catalyzing perchlorate reduction. The specific rate constants were in the range of 10⁻³ M⁻¹ g⁻¹ h⁻¹. Specifically, it is possible to have a greater than 90% perchlorate removal in 6 h at an initial perchlorate concentration of 10 ppm under ambient conditions. Results also showed that the optimal surface density of catalyst was 0.65 mg/g (catalyst/support); percent of perchlorate removed decreased drastically when the surface density was greater or less than this value. It appears that a clean technology for the removal of perchlorate from water is feasible using catalytic electrochemical process.

**Simulated electroremediation of drilling muds using both oxidants and surfactants**

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Drilling mud sited in the south of Algeria give rise to an important pollution due to the presence of hydrocarbons and PAH'S. The remediation of these components is more difficult regarding the various species which exist and the interactions which occur between them. In this work, after the analysis of a sample of a real drilling mud, electrokinetic remediations of simulated samples have been tested. Two routes have been tested: oxidants and surfactants. In effect, knowing that hydrocarbons are hydrophobic, neutral and ionic surfactants are added to facilitate their transport through electroosmosis and electromigration (for ionic surfactants). Oxidants have also been added to test their ability to reduce the toxicity of some components by their reduction. A first study is carried out using diesel for the simulation. Then, the effect of the facilitating agents has been studied component by component with their successive addition in a simulated sludge. Aliphatic compound, and aromatic compound are considered.

Electrokinetic tests were carried out in a cylindrical cell in Glass where the central compartment of 1 liter (inner diameter = 2.5 cm) containing 300 grams of a simulated drilling mud is separated from cathodic and anodic sides by a filter paper (Whatman N°5) inserted between a grid of rigid nylon (mesh size = 2mm) and fibers ion exchange FIBAN A6 (OH⁻ form) and Fiban K1(H⁺ form) or ion exchange membranes. The circulation of the catholyte and the anolyte is ensured by a peristaltic pump (Watson Marlow 313S) from graduated reservoirs (250 ml each) at a flow rate of 15 ml.min⁻¹ which allows the escape of generated gas near the electrodes. In the two extremities there are two graphite electrodes. The variation of the composition of the sample is followed by analyses using Infrared spectroscopy, Gas Chromatography coupled to Mass Spectra and UV spectroscopy. The applied voltage is delivered by a power supply and maintained constant in all the runs.

The influence of some parameters is examined as current density, pH and conductivity. The role of the concentration of facilitating agent is also shown and the various results obtained are discussed and allow a solution for the treatment of drilling mud.

**Simultaneous Removal of Pb, Cd and Zn from Heavily Contaminated Mine Tailing Soil Using Enhanced Electrochemical Process**

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This research focused on electro-kinetic removal of heavy metals from heavily contaminated mine tailing soils. The removal efficiency was examined with and without the aid of a solubilizing agent as the mixing fluid, Na2EDTA. The soil contained high concentrations of the target metal contaminants (Cd = 34347 mg kg\(^{-1}\), Pb = 16381 mg kg\(^{-1}\), and Zn = 49248 mg kg\(^{-1}\)). The electrochemical tests were carried out in a specially designed electro-kinetic reactor with two intermediate aqueous collection locations within the soil chamber. First tap water and then 0.05 M solution of Na2EDTA were used as the pre-mixing agents of the contaminated soil. A constant DC voltage of 20 V (0.625 V/cm) was applied across the working electrodes in all the experiments for a treatment time of 48 h. The concentration accumulation of the metal species in the anode, cathode and the intermediate collection chambers were measured over time, as well as pH, conductivity and ORP. The removal efficiency was reported in percentage as the summation of the cumulative metal mass removed into all collection chambers in aqueous form, normalized to the initial mass of the metal in the soil.

The total removal efficiency of the metal ions from soil mixed with tap water were determined 35.60%, 78.79% and 55.09% for Pb, Cd and Zn, respectively. Figure 1 below shows the sequential distribution of the three metals removed into the various collection points over time with applied electrical field and tap water. At the high pH and low ORP environment at cathode, the metal ions that electromigrate into the catholyte precipitate as hydroxide salts. Due to electrochemical precipitation, the aqueous metal mass in the cathode compartment attained a constant equilibrium value after a short rise at the start of the treatment. Similar trends were observed in the intermediate collections sites where in fact the pH remained mostly stable slightly below the starting value of about 7. In contrast, the anionic complexes of the metals formed at low pH and high ORP environment at anode remain in solution when they electromigrate into the anolyte.

With 0.05 M Na2EDTA mixing solution, the removal efficiency of the metal ions from soil were determined as 32.25%, 55.04% and 28.79% for Pb, Cd and Zn, respectively. The Pb removal did not change appreciably, while Cd decreased in the anolyte and showed no change in the catholyte and the intermediate collection sites. The most appreciable change occurred with Zn, where more of the Zn remained in aqueous form in the catholyte and less of it migrated into the anolyte, as shown in Figure 2.

The removal efficiencies appeared to be influenced by the overall effects of the characteristics of the soils, the specific behaviors of metals in soils, the initial concentrations and speciation of metal contaminants, and the distribution of pH and ORP.
Figure 1. Distribution of aqueous metal concentration over time in EK test of contaminated mine tailing soil mixed with tap water.

Figure 2. Distribution of aqueous metal concentration over time in EK test of contaminated mine tailing soil mixed with 0.05M Na₂EDTA solution.
Sustainability evaluation of electrokinetics and other remediation alternatives for a contaminated site: A case study

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The project site, located in Greater Chicago area, was used from 1969 to 2004 for an electrical generation peaker station, which is currently in a stage of decommissioning. The site is contaminated by multiple spills of fuel oil, fuel lubricant, diesel fuel, and other petroleum associated compounds during the electrical generation operations.

During the site investigation, 96 soil borings were drilled and 6 monitoring wells were installed to determine subsurface soil and groundwater conditions and environmental impacts. The geology of the site is mostly clay deposits overlain by concrete and fill from previous site activity at some locations. The groundwater table is 3 to 12 feet below the ground surface. The soil and groundwater samples were tested for 41 potential contaminants, including BTEX, polychlorinated biphenyl (PCBs), polycyclic aromatic hydrocarbons (PAHs), ethylene glycol, pesticides, and heavy metals. The results showed that several locations of the site were contaminated with BTEX, PAHs, PCBs, and metals.

Baseline risk assessment is performed to assess the risks that the site contamination will pose to the potential receptors as well as determine the remedial goals. The test results on soil samples are compared to the IEPA’s Tiered Approach to Corrective Action Objectives (TACO) Tier 1 Remediation Objectives (RO) with the residential standard. Based on this assessment, some locations had benzene, naphthalene, PCB, and arsenic at levels above the TACO Tier 1 ROs, and some other locations had five PAHs at unacceptable levels. Overall, three locations are identified where soil remediation is required. The contaminants of concern are: naphthalene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene, Aroclor 1254, arsenic, benzene, and total chromium. TACO Tier 1 ROs are used as remediation goals for impacted soils. The contaminant concentrations in groundwater did not exceed the Class I remediation objectives of TACO Tier I on groundwater. Thus, it is concluded that the groundwater of the site had not been impacted.

Many alternatives were identified for the remediation of contaminated soils, and, ultimately, three alternatives were selected for further analysis: electrokinetics with ISCO injections, phytoremediation, and excavation/disposal. These alternatives were assessed against a variety of criteria: cost, remediation time, and sustainability. In order to assess sustainability, the Green Remediation Evaluation Matrix (GREM) was used to perform a qualitative assessment and SiteWise tool was used for a quantitative assessment of the three remedial alternatives. Based on this analysis, electrokinetics is shown to be the most sustainable option, followed by phytoremediation and then excavation/disposal.

Based on the contaminant concentrations, seven hot spots were identified. A geometric square of 10,000 ft2 was reasonably assumed for each hot spot. For each hot spot area, a preliminary electrokinetic system design, consisting of rows of cathodes and anodes, is proposed. A balance between the operating voltage and the spacing of electrodes is necessary to maximize contamination removal and site remediation economics. A chelate is recommended to be the enhancement solution in the electrokinetics to avoid premature precipitation of metals at the cathodes when pH
changes in soil. For organic contaminants, in-situ chemical oxidation is recommended along with electrokinetics to simultaneously oxidize organic hazardous materials and remove heavy metals. Fenton’s agent, composed of hydrogen peroxide and native iron catalyst, is recommended for chemical oxidation. When the concentrations of the contaminants are reduced to the remediation objectives, the electrokinetics system can be turned off. Continued monitoring will be applied for two years to determine if any rebound has occurred in the soils. Once the site is clean, electrodes will be removed and wells abandoned. The site will then be ready for use by the neighboring school and the community.

**Water Purification and Brine Concentration by Shock Electrodialysis**

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We investigate the experimentally and theoretically the possibility of exploiting deionization shocks in porous media for water purification and brine concentration by “shock electrodialysis”. The basic idea of this new approach is to drive an over-limiting current (faster than diffusion) through a charged porous medium sandwiched between two cation-exchange membranes, perpendicular to a pressure-driven cross flow, which produces a sharp “shock” in the salt concentration profile between deionized and concentrated streams, which are separated at the outlet. In contrast to classical electrodialysis, only one membrane type is needed to trigger the phenomenon, and the separation is effectively “membraneless” within the porous medium. Boundary layer analysis, generalizing the Leveque solution for over-limiting current, provides useful engineering principles. We demonstrate the principles of shock ED experimentally in a sequence of prototypes, initially using copper electrodes and copper sulfate solution, which can be replaced by electrode streams sustaining the current by water electrolysis, as on traditional ED. The results show reasonable efficiency and unique separation capabilities that may find applications in compact water treatment and brine concentration.

Note to the organizers: The talk of M. Z. Bazant on “Nonlinear Electrokinetic Separations in Porous Media” provides the necessary background for this talk and should come first.
POSTER ABSTRACTS

A Comparison Study on Electrokinetic Removal of Cadmium from Municipal Sewage Sludge with and without Improved Catholyte Circulation

Jie Gao, Qishi Luo, Changbo Zhang, Bingzhi Li, Liang Meng - Shanghai Academy of Environmental Sciences, China

Electrokinetic transport processes have been proved a potential way to effectively remove heavy metals including Cd from municipal sewage sludge. A comparative study of electrokinetic processes for remediation of contaminated sludge with and without improved catholyte circulation was conducted. In improved circulation system, the cadmium ions migrated into liquid can be prevented from re-entering into sludge by using three layers of anion exchange resin installed between the anode compartment and contaminated sludge which avoided deterioration of its performance by replacing each layer regularly. The effect of improved catholyte circulation on removal of Cd from municipal sewage sludge was evaluated through bench-scale electrokinetic tests. Results showed that EK-C (with improved circulation) treatment is more stable when compared with EK-N (without circulation) system. In the first 12 hours, the current of EK-C system increased to 46 mA rapidly compared with 108 hours for EK-N system. In EK-C system, pore water transportation and electroosmosis rate increased, and the pH in sludge and cathode reservoir was controlled between 7.09 and 8.66. The removal efficiency of Cd in EK-N treatment increased from 33.5% of to 53.5%. Sequential extraction analysis revealed that the reducible and oxidizable Cd had higher removal efficiency after being treated with EK-C system, and the percentage of residual Cd in sludge was enhanced, which meant that the bioavailability of Cd in sludge was reduced. The improved catholyte circulation assisted electrokinetic treatment was proven to be a promising way for cadmium contaminated sewage sludge.

Alternative carbon materials for electrochemical remediation

Eric Gil, Fernando Miguel de Amorim Lino, Muril Felisbino - Federal University of Goiás, Brazil

The electrochemical remediation technologies involve different approaches, whose complexity is mainly driven by the pollutant nature. Thus, while inorganic contaminants have been effective and efficiently removed from waste waters by electrochemical adsorption, organic pollutants are generally converted into less hazardous compounds. Such conversion is based on complex reactions steps, in which the efficiency of electrodic material is always determinant. Furthermore, the overall cost may be decisive in the choice of remediation treatment. Thus, the research on alternative materials, including the recyclable ones is very attractive. Therefore, the aim of our work was to evaluate carbon bat materials of piles as working electrode in electrochemical remediation of phenolic pollutants. The applied potential, hydrodynamic conditions, electrolyte and also some surface treatment were evaluated, in order to make a preliminary optimization of remediation process. The percentage of decay was measured by means of UV spectrophotometry and peak currents.

It was found that phenolic compounds are strongly adsorbed at potentials above 0.8 V, Nevertheless, the electro adsorption is followed by formation of passivating film, which grows leading to the blockade of electrodic surface. Thus, since the electrochemical reaction reaches less than nano scale, the removal of organic species is insignificant.
Meanwhile, at potentials higher than 1.5 V, such materials showed great potential to produce oxidizing species, i.e. hydroxyl radical and peroxide which leads to the oxidation of organic compounds. In turn, such materials showed good potential as support for immobilization of enzymes, such as laccase, a polyphenoloxidase commonly used in bioremediation of phenolic pollutants. Other potentialities of such recyclable carbon materials were also evaluated, including the surface modification with noble metals and conducting films.

Assessing the feasibility of the EKR of soils contaminated by heavy metals by titration curves

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J.M. Paz- García - Technical University of Denmark, Denmark

The pH is one of the key parameters that determine heavy metal mobility and fate in soils and sediments. It is well known that the resistance of soil to a change in pH strongly affects the mobilization of heavy metals in the soil. Different single and sequential extraction tests and pHstat leaching tests (at constant pH) have been developed for the study of the influence of a pH-decrease on the heavy metal release from the soil. Nevertheless, the acid-base reactions in a soil-water mixture are not as fast as those that take place in the aqueous phase. This kinetic control makes that the determination of the buffer capacity of the soil (usually the acid neutralization capacity, ANC) cannot be obtained as straightforward as an acid-base titration.

The buffer capacity of a soil is usually determined by the addition of different amounts of acid to several aliquots of a soil-water mixture. The slurries pHs and heavy metal concentration in the aqueous phase are determined after a nominal time at which the equilibrium is assumed to be reached (from 24 to 72 hours). As for the pHstat leaching test, the acid neutralizing capacity (ANC) corresponds to the amount of acid added to a soil-water suspension to keep the pH at a predefined constant value, so an ANC is obtained for each reference pH. The main inconvenience of the latter approach is that the acid neutralization can be slow at certain pH values and therefore, the acid addition rate should be adequately modified, leading to longer tests (from 24 to 96 hours).

This work aims the study of the influence of the pH on the retention of lead in a soil from the mining district of Linares (Spain) contaminated by heavy metals. The methodology used here is similar to the aforementioned ones, but in this case, the acid addition rate is predefined to a value more than 3 times higher than a threshold value above which the pH versus time curve is independent of the rate of acid addition. The feasibility of the electrokinetic technique for the remediation of this soil is assessed from the results obtained with three different acid solutions (nitric, acetic or EDTA) and the lead fractionation in the soil, according to the BCR method, at the end of each experiment.

The experimental system used basically consists of a 2 L reaction vessel with flat flange and mechanical agitator that contains the initial water/soil mixture (1.2 L/0.4 kg). The reactor is closed with a glass lid with flat flange and 5 ground-glass necks. Two of these necks allow the assembling of a pH electrode and of a sampling system for the withdrawal of aqueous samples. Through a third neck of the reactor lid, the desired reagent solution is added at the predefined rate, while the evolution over time of pH values in the water-soil mixture is registered. At selected times; samples of 10 mL were withdrawn for the determination of Pb concentrations in the aqueous phase.
The results indicate that the solubilization of the 40% of the lead present in the soil is achieved at pH values of about 6.5, 5 and 2.5 for Na2EDTA, acetic- and nitric- acid respectively.

Acknowledgements

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Comparing the effect of electrodialytic upgrading on semidry, dry and wet air pollution control residues

Lisbeth M. Ottosen, Pernille E. Jensen, Gunvor M. Kirkelund - Technical University of Denmark, Denmark

A major challenge of municipal solid waste incineration (MSWI) technology is the residue generated during the burning, and especially the air pollution control (APC) residue. In Denmark incineration with energy recovery is the chosen strategy for handling municipal solid waste except for a few fractions like glass, paper, cardboard, metal and hazardous waste which is sorted out at the source. Around 150,000 ton of APC residue is produced annually and exported as hazardous waste to Norway and Germany. The hazard arises from high amounts of mobile toxic elements, salts as well as trace quantities of very toxic organic compounds and the highly alkaline pH. The European waste strategy is in line with the current Danish practice on solid waste incineration of fractions that cannot be reused, and an increased European production of MSWI APC can be expected in the future.

Electrodialysis of semidry APC residue has shown potential for reduction of leaching of toxic elements and salts to produce a material feasible for substitution of cement in mortar. During the electrodialytic process, elements of potential value are concentrated in the concentrate stream which implies a reduction in the volume of hazardous material and a potential for regeneration. In this work, results of ten pilot-scale experiments are reported. In the experiments 8kg APC residue and 80 l water were mixed in suspension that was continuously treated in the electrodialytic set-up. The experiments were made with different APC’s from dry, semidry and wet fluegas cleaning system and the results from these varying APC residues were compared directly for the first time. Treatment times (5–10 h) and current densities (0 – 11.3 mA/cm2) were also varied. Significant reduction in leaching of the critical elements Pb, Zn and Cl was obtained. Leaching reduction depended somewhat on current density and treatment time, as a high current density and long residence time gave operational problems in the set-up.

Key words: Electrodialysis, municipal solid waste, air pollution control residue, urban mining, current density.

Comparison on Environmental Footprints of Electrokinetic Remediation and Soil Washing

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There are several remediation technologies for heavy metal contaminated site. It can be ex situ technology such as soil washing including excavation, physical separation and chemical extraction, or in situ technology such as electro-kinetic, and integration technology with soil washing and electro-kinetic. Even though EK and soil washing technologies are most
effective to cleanup for heavy metal contaminated site, however, that could produce the environmental footprints such as air emissions and waste water on the remediation process.

Recently, green and sustainable remediation (GSR) has been environmental issue because of environmental footprints such as CO2 on the remediation process. Environmental assessment is tool to analyze the environmental impacts such as footprints on the remediation process. In this study, environmental assessment was conducted to analyze environmental footprints and calculate the relative contribution of each process and compare 4 remedial alternatives for multi metal contaminated site using GSR tool.

Effect of pH control during electrokinetic bioremediation of a natural tropical soil

Maria Cláudia Barbosa, Leonardo Deotti, Jonathan Tenório de Lima, Márcio de Souza Soares de Almeida - COPPE, Federal University of Rio de Janeiro, Brazil

Electrokinetic remediation is an emerging technique for in situ treatment of contaminated soils. Applications coupled with bioremediation intend to inject nutrients in the soil to enhance contaminant degradation by microbial activity. However in some cases bacterial growth is reduced whereas pH gradients develop within the soil and compounds may precipitate on cathode due to its pH higher than 11. This work presents the results of pH control on soil properties and bacterial development during electrokinetic bioremediation of a clayey soil formed from a limestone matrix contaminated with hydrocarbon. The survey is based on 1D laboratory scale tests applying a total potential difference of 10 V during 48 h. Two different solutions were used: (1) a buffer solution of di-sodium hydrogen phosphate (Na2HPO4) and potassium hydrogen phosphate (KH2PO4) and (2) a solution of sodium chloride. The inversion of the EK field during the test was also applied as a third alternative for pH control. A few arrangements were elaborated for every experiment set up varying boundary and initial conditions. The goal for pH control was to prevent soil acidification in the anode vicinity, which has a negative impact on bacterial population. For this purpose anode and cathode reservoirs were filled with a saline solution with a known pH. Results demonstrated that bacterial population decrease was minimized under pH control. Electrodes degradation was also prevented and nutrient injection succeeded for most nutrients. It was observed that phosphate was rapidly precipitated close to the electrodes. Electric potential was lower in experiments with pH control when compared to a standard experiment. Electric field varied from 0.2 to 0.4 V/cm and upper values are related to more saline solutions. The laboratory tests showed that pH control may improve soil treatment but field tests are still necessary.

Effects of Anodic O2 on Pd-catalytic Hydrodechlorination of Chlorinated Solvent in Groundwater Using Cathodic H2

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Songhu Yuan - China University of Geosciences, China

Chlorinated solvents contamination is a world-wide environmental problem; development of innovative, high efficient and sustainable remediation methods is necessity to overcome this problem. Pd-catalytic hydrodechlorination by cathodic H2 is a promising method for clean-up chlorinated solvents in environmental media including contaminated groundwater. In the Pd-containing electrolyte, hydrodechlorination occurs on the surface of palladium using cathodic
hydrogen (1). However, the efficiency and the hydrodechlorination kinetics are as affected by the simultaneous production of anodic oxygen, which is an \( \text{H}_2 \)-utilizing competitive compound (2).

\[
\text{TCE (C}_2\text{HCl}_3) + 4\text{H}_2 = \text{Ethane (C}_2\text{H}_6) + 3\text{HCl} \quad (1)
\]

\[
\text{O}_2 + \text{H}_2 = \text{H}_2\text{O}_2 \quad (2)
\]

In this study, divided and undivided electrolyte batch experiments are conducted to evaluate the effects of anodic \( \text{O}_2 \) on Pd-catalytic hydrodechlorination of different contaminants using cathodic \( \text{H}_2 \). Trichloroethylene (TCE) and tetrachloroethylene (PCE) are used as representative contaminants in groundwater. In the presence of anodic oxygen, TCE (26.3 mg/L) and PCE (27.5 mg/L) are hydrodechlorinated up to 60.8% and 40.4%, respectively, within 90 min at 50 mA in a pseudo-first-order kinetics. In the absence of anodic oxygen, TCE is completely hydrodechlorinated within 20 min in a pseudo-zero-order kinetics, and PCE is hydrodchlorinated up to 98.1% within 20 min in a pseudo-zero-order kinetics initially followed by a pseudo-first-order kinetics. Anodic oxygen is detrimental to Pd-catalytic hydrodechlorination of chlorinated solvents.

**Effects of electrokinetic treatment of contaminated sludge on migration and transformation of cadmium, nickel and zinc based on chemical speciation**

*Jie Gao, Qishi Luo, Changbo Zhang, Bingzhi Li, Yue Zhu; Shanghai Academy of Environmental Sciences, China*

This study assesses the influence of electrokinetic treatments on the migrations and speciation of different heavy metals in sludge samples. The variations of sludge properties and distribution of Cd, Zn and Ni after electrokinetic treatments were examined, and the transformation of Cd, Zn and Ni is discussed. Bench scale electrokinetic experiments were conducted over the durations of 24 h, 48 h, 96 h and 144 h and subjected to a voltage gradient of 1 VDC/cm. The migration of the contaminants after the electrokinetic treatment was determined for each sample. Sequential extractions were performed on the contaminated sludge before and after electrokinetic treatment to determine the distribution of the contaminants in the sludge. The initial concentrations of Cd, Zn and Ni were 99.08, 2771.5 and 2953.7 mg/kg, respectively. The highest Electrokinetic removal of heavy metals from an agricultural soil efficiencies of Cd (33.5%), Zn (32.5%) and Ni (47.6%) were attained in the sample that was treated for a duration of 144 h, which was directly affected by the species distributions in the sludge. The application of voltage caused noticeable changes on the average speciation fractions of Cd, Zn and Ni: the speciation fraction of oxidizable heavy metals increased, whereas the reducible fraction decreased. With the exception of the oxidizable form, Cd did not have any statistically significant relationships with sludge parameters or duration. Bivariate correlation analysis indicated that speciation fractions of Zn and Ni were significantly correlated with the treatment durations and resistance at P

**EKR of copper mine residues with modified electric field**

*Adrián Rojo, Henrik K. Hansen, Paula Inostroza - Federico Santa María Technical University, Chile*

In Chile copper mining generates significant resources to the country’s economy, however, also generates large quantities of waste due to the tasks for exploiting its minerals. Annually, only the mineral processing generates large quantities of waste, some of them are transported and disposed as pulps forms in conditioned sites called mine tailing ponds. In these places, mine waste not only have a damaging effect on water resources by the natural leaching of heavy
metals and chemicals, but also generate effects on flora, fauna and air quality by the generation of fugitive emissions of fine particles. In this work an electrokinetic remediation (EKR) cell for copper mine waste using modified electric field (sinusoidal type) was analyzed, which seeks to remove the heavy metals presents in the waste. In this experimental scale only copper was monitored.

**Electroabsorption of fluorine and chloride ions using carbon-impregnated TiO2 nanotube electrode**

*Xuhui Mao, Yijia Yang - Wuhan University, China*

Groundwater containing fluorine ions needs to be treated before its being used as a drinking water source. Electroabsorption is a promising technology for defluorination and desalination of groundwater. In this study, a novel electrode material is developed for the electroabsorption of aqueous fluorine ions. The electrode was prepared by a two-step method. A titanium plate was anodize in an acid solution, so that a nanotube array can form on the electrode surface and huge surface area can be achieved. The second step is to impregnate the carbon precursor solution into the hollow nanotubes using a specially designed vacuum system. The carbon materials formed when the electrode was sintered under nitrogen atmosphere for 2hours at an elevated temperature. According to the preliminary results, the electrode showed good performance for the electroadsorption of flurione ions. Further study on the operating parameters and regeneration of the materials is underway.

**Electrochemical behavior of FeNbC based iron ternary alloys in non-deaerated solution 10-3M NaHCO3 and 10-3M Na2SO4. Effect of sodium molybdate**

*Sif-Eddine Amara, Farida Haddad, Rafika Kesri - University of Science and Technology Houari Boumediene (USTHB), Algeria*

In this work, the electrochemical behavior of four FeNbC based-iron ternary alloys, of variable compositions of iron, niobium and carbon, is studied by potentiodynamic polarization in absence and presence of sodium molybdate as corrosion inhibitor. These alloys are immersed in a non deaerated solution NaHCO3 10-3M + Na2SO4 10-3M. According to the obtained results, it seems that the corrosion resistance of the some alloys is better than other’s one, depending of composition, in presence of sodium molybdate.

In addition, an alloy with the composition 12.85 wt.% Nb, and 0.47 wt.% C has overall the lowest corrosion current densities, in particular at a concentration of 10-2 M of sodium molybdate. Note that this alloy has the highest niobium content and the least carbon content. For these reasons, the corrosion resistance of this alloy is studied in presence of sodium molybdate (10-2 M) at 25, 35, 45 and 55°C.

Several techniques (such as potentiodynamic polarization, polarization resistance and electrochemical impedance spectroscopy) are applied for this purpose. The results indicate that the temperature rise from 25 to 35°C leads to a decrease of corrosion current density. This can be interpreted by the fact that the effect of the diminution of O2 and CO2 concentrations overrides the opposite effect of the temperature rise. Moreover, beyond 35 °C, the corrosion current density increases. This is allotted to the constant kinetics augmentation.
Finally, the interpretation of the results obtained from the electrochemical methods used shows that the obtained parameters have the same tendency.

**Electrodialytic remediation of incinerated sewage sludge - Influence of natural weathering**

*Alexandra B. Ribeiro* - University of Lisboa, Portugal  
*Paula Guedes,* *Nazaré Couto* - University of Lisboa, Portugal  
*and CENSE, New and Technical University of Denmark, Denmark*

There is an increase tendency of incinerating sewage sludge produced at waste water treatment plants rather than its landfill or agricultural application. However, although sewage sludge ashes (SSA) can enclose elements of high value like phosphorus, due to the presence of leachable heavy metals, SSA cannot be applied to soil without previous treatment.

The present work aimed to survey how the exposure of SSA to weather conditions affects the electrodialytic (ED) process. For that a detailed characterization of SSA was carried out. As there is presently no Danish legislation about the use of SSA in agriculture, the limiting heavy metal concentrations for sewage sludge were used for comparison. Obtained results showed that Cd, Ni and Pb were above the limiting values whether Cr, Cu and Zn were below.

ED treatment was applied for 3, 7 and 14 days treating the SSA samples as stirred suspensions. At the end of 14 days the ash collected immediately after incineration presented slightly higher remediation efficiencies (here defined as the percentage of metals that were effectively removed from the ash towards the cathode and anode end) for Ni and Cd but lower for Pb when compared with the weathered ash. Preliminary results showed that, although Cd concentration was reduced in ca. 70%, the mean value is still slightly above the limiting concentration in both ashes. Ni and Pb were also still above the Danish legislation thresholds. Further studies should be carried out in order to increase heavy metals removal from SSA aiming its further valorisation as soil amendment.

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**Electrodialytic remediation of phosphorus containing soils**

*Henrik Hansen* - Federico Santa María Technical University, Chile

Phosphorus is an important element for life, is part of the basic structures for life and as plant nutrient. There is concern about the high demand associated with the production of fertilizers, so alternatives are needed to recover and reuse phosphorus.

This work concentrates in the use of electric current to recover phosphorus – specifically the electrodialytic remediation method (EDR). Eight EDR experiments were carried out with different soil types, soil particle size distribution, duration of treatment and phosphorus content in the soil. This was done in order to evaluate the feasibility of this treatment to
remove and recover the element. Three soil samples were analyzed: sand, clay and fertile agricultural soil. Prior to
treatment, the soil is characterized with texture analysis and measurement of organic material, which was tested
according to the type of soil particles for sand and clay. In the case of fertile soil, the sample is a mixture of both. The
measurement of organic matter was expected, very low for clay and sand, and medium to fertile soil. The experiment
were carried out constant voltage drop (20 [V]).

Comparing the EDR results it can be concluded that there is indeed a subsequent removal and recovery of phosphorus,
although the values do not reach significantly high removal rates in any of the experiments carried out. On the other
hand, an important redistribution of phosphorus within the soli matrices can be observed. For soils used, sand allows
easy migration of ions of the matrix structure, the clay tends to retain and prevent the passage of chemical species and
fertile soil a mixture of both properties, since it is a set of both matrices.

**Electrokinetic Remediation Combined with Reactive Barrier For As-Contaminated Soil**

_Eun-Ki Jeon, Kitae Baek; Chonbuk National University, South Korea_

Electrokinetic process has been applied to remediate contaminated-soil, sediments and sludge. However, the process is
a separation technique, and the separated pollutants should be treated properly. Reactive barrier could remove
pollutants by using several mechanisms including sorption, precipitation and chemical reaction in groundwater. In this
study, we investigated a potential of electrokinetic remediation combined with reactive barrier to separate metals from
soil. Alum sludge from water treatment process and Fe-loaded sludge from treatment plant for acid mine drainage were
used as reactive materials because they have high adsorption capacity for As. In this study, we evaluated a combined
process of electrokinetic remediation and permeable reactive barrier to remove As from a real contaminated site.

**Electrokinetic Remediation for Removal of Alkali Metal Ions from Contaminated Soil by Tsunami**

_Yasuhiro Akemoto, Masahiko Kan, Shunitz Tanaka - Hokkaido University, Japan_

**INTRODUCTION**

Japan has still now pollution problems of water and soil by the mega earthquake and tsunami on March 11, 2011. In the
accident of Fukushima Daiichi nuclear power plants, the various radionuclides such as cesium or strontium were
released and contaminated water and soil around Fukushima prefecture. Furthermore, the tsunami brought a large
quantity of salts into agricultural field. As a result, saline concentration in the soil increased and plants could not grow
well in the soil contaminated with salts. Since water does not penetrate through clayey soil, it is difficult to remove salts
from clayey soil by water flow. Electrokinetic remediation becomes a useful method to remove salts in clayey soil.

In this study, EKR treatment was demonstrated to remove salts from a model clayey soil prepared with garden soil and
kaolin. We investigated the distribution of alkali metal ions in the model soil after EKR treatment. We also compared the
effectiveness of EKR treatment with that of desalination with water flow.

**EXPERIMENTAL**
Two kinds of soil were used in this experiment. One is the commercial available kaolin (Wako Pure Chemical Co. Tokyo, Japan). Another is the mixture of garden soil and kaolin. An EKR cell made from acrylic resin was used as a migration chamber (3.0 cm in diameter and 10 cm length) having two electrode chambers at both ends. Two meshed Ti electrodes coated with Pt were used as the electrode. 0.1 M KCl was used as electrolyte. The effluent by EOF was collected in a measuring cylinder and stored for analysis. A constant voltage of 10 V was applied between the two electrodes for 72 h. The saline contaminated soil was prepared by adding the sodium chloride solution to the soil to be 2.00 mg (Na+)/g soil. After the EKR treatment, the soil sample was removed from the migration chamber and sliced into five sections. pH and EC and the concentration of sodium ion of each sections were measured by pH meter, electrical conductivity meter, and AAS, respectively. In the case of desalination with water flow, the same size column filled with the same soil as that of EKR was used, pure water is introduced into the column only by the gravity.

RESULTS AND DISCUSSION

The removal rate of sodium ion from the soil after EKR treatment was about 90 % and 67 %, in 50 % and 100 % kaolin clay soil, respectively. On the other hand, the removal rate of sodium ion by desalination with water flow was about 18 % and 11 %, in 50 % and 100 % kaolin clay soil, respectively. Since water cannot penetrate into clayey soil, desalination by water flow is not effective in this condition.

Therefore, EKR treatment was more effective than desalination with water flow for the removal of salts from highly clayey soil.

**Electrokinetic removal of Cr, Cu and Zn from sediment by pulsed electric field**

*Ljiljana Rajić, Božo Dalmacija, Dejan Krčmar, Milena Bečelić-Tomin, Svetlana Ugarčina Perović, Vesna Pešić, Malcolm Watson - University of Novi Sad, Serbia*

In this study we investigated improving the electrokinetic treatment of Cr, Cu and Zn contaminated sediment using a pulsed electric field. The influences of different ON/OFF ratios (3, 1 and 0.3) within 1 cycle/h as well as the number of cycles/h (1, 0.5 and 0.25) at a fixed ON/OFF ratio on metals removal efficacy were investigated. It was found that significant removal efficacies were achieved in comparison to conventional treatment for all target metals after using the pulsed field with ON/OFF ratios of 1 and 3. This indicates that ion diffusion during the OFF interval highly affects the metal ions removal efficacy. Removal efficacies achieved at an ON/OFF ratio of 0.3 were the similar to those achieved after conventional treatment. Since diffused metal ions can re-adsorb on sediment particles it is essential to optimize the OFF interval duration. Results indicate that decreasing the number of cycles/h at ON/OFF=3 decreases the removal efficacies for all target metals. It can be concluded that the pulsed technique can be used as an enhanced electrokinetic treatment without any additional costs but it is essential to optimize the conditions applied.

**Electrokinetic removal of heavy metals from an agricultural soil**

*Claudio Cameselle, Susana Gouveia - University of Vigo, Spain
Arylein Figerora, Henrik Hansen - Federico Santa María Technical University, Chile*

In this study, an agricultural soil sampled in Galicia (NW of Spain) was spiked with as Cu+2, Cr(VI), Pb+2, Zn+2 and Hg+2. The soil was stored in the darkness for 1 year to ensure the aging of the contaminants. The objective of this process was
to ensure a similar behavior of the spiked soil to that of a real polluted soil. The soil was analyzed before it was used in the electrokinetic experiments. The final metal concentration into the soil was as follows: Cd: 209.58 mg/kg; Co: 290.22 mg/kg; Cr: 1837.39 mg/kg; Cu: 2906.27 mg/kg; Hg: 1340.93 mg/kg; Pb: 1975.18 mg/kg; Zn: 1846.35 mg/kg.

Three electrokinetic tests were carried out to evaluate the ability of the electrokinetic treatment in the removal of the heavy metals from the soil. The first experiment did not use any enhancing agent in the electrode chambers or into the soil. DI water was used in the electrode chambers and the pH in catholite and anolite was the result of the electrolytic generation of H+ and OH- ions. The second experiment was carried out with citric acid 0.1 M as catholite and DI water as anolite. The third experiment was carried out with EDTA as catholite. In order to favor the complexation of heavy metals with EDTA, NaOH 0.1 M was used as catholite.

In general, heavy metals are effectively transported by the electric field through the agricultural soil sample, but the actual removal results largely depended on the extractant agents and the pH into the soil. Thus, in the experiment 1, the soil pH profile continuously increases from the anode side (pH= 2.1) to the cathode side (pH=8.5). In these conditions, heavy metals migrate towards the cathode and they accumulated into the soil close to the cathode side, except Cu and Cr that accumulated in the center of the soil specimen. The global removal in the soil for each metal was lower than 10%. The use of citric acid as a complexing agent clearly increased the removal of all the heavy metals, specially the removal of Zn (28%), Co (27%), Cd (19%) and Hg (17%). The profile of heavy metals concentration in the soil specimen, suggest that heavy metals migrated as cations towards the cathode, but the citrate in the catholite complexed the metals that are transported towards the anode. So, most of the metals were accumulated in the center of the soil specimen. The experiment 3, with EDTA in the catholite and NaOH in the anolite resulted in a different concentration profile. Heavy metals are mainly transported towards the anode. Partial removal can be found in the sections of soil close to the cathode, but no significant removal was detected on the anode side.

Overall, it can be concluded that the use of EDTA or citric acid can be used in the removal of heavy metals from the agricultural soil. The results suggested that longer treatment time is necessary to increase the removal of the heavy metals.

Electrokinetic surfactant enhanced remediation of a tropical silty clay soil contaminated with crude oil

Maria Cláudia Barbosa, Jonathan Lima, Márcio de Souza Soares de Almeida - COPPE, Federal University of Rio de Janeiro, Brazil

Electrokinetic remediation is being used for fine low-permeability heterogeneous and anisotropic contaminated soils treatment especially clays. Several studies have demonstrated its feasibility in laboratory and in situ applications for different contaminants mainly heavy metals. Recently it has also been employed for soils contaminated with NAPLs which are rather hydrophobic than hydrophilic and thus surfactants can be used together with more traditional techniques to aid removal. Surfactants have unique characteristics which increase the solubility of organic compounds and their further mobility and extraction. This work presents the results of an attempt to enhance electroremediation of PAHs with sodium dodecyl sulfate. Soil samples were collected from Sarapuí river (Rio de Janeiro/Brazil) and artificially contaminated with crude oil to 10g/kg of dry soil. The samples have an average specific gravity of 2.01 g/cm³, 8.1% of
organic matter content and a total cation exchange capacity of 32.38 cmolc/kg. It can classified as a silty clay. Two different laboratory experiments arrangements were fulfilled. For every sample it was applied a 10V total electric potential difference during 48h and the electrosmotic flow took place from anode to cathode. 1D and 3D experiments showed that electric field and direct current varied between 0.16 and 0.54 V/cm and 0.55 and 0.59 mA respectively. Temperature fluctuated from 21°C to about 26°C on 3D tests and may have influenced equilibrium reactions. It was verified that surfactants may improve contaminant migration in about 50% when compared to experiments without surfactants. Organic compounds mobility varied among the tests performed, however most of them were successfully removed up to 75% in 3D tests. There is evidence of mass flux inversion during some of the tests such the presence of oil on anode and fluid density increase. Some samples presented higher concentration values in the middle slice than in its boundaries probably due to flow reversal. That may imply a limitation for oil extraction in field application.

**Electromagnetic Separation of Iron Nanoparticles Modeled by Adsorption**

*Henrik Hansen - Federico Santa María Technical University, Chile*

The pyrometallurgic copper processing releases large amounts of arsenic, the wastewater treatment can be summarized in the process of oxidation, precipitation, filtration, and calcination.

Electrocoagulation of arsenic using iron nanoparticles has been shown to be an efficient arsenic removal process. A process to reduce the wastewater arsenic content from 0.5 g/L to 1 ppm, using pH adjustment, electrocoagulation, magnetic enhance sedimentation and magnetic filtration of iron nanoparticles embed with arsenic is proposed.

Magnetic separators used on the industrial scale are overwhelmingly high gradient systems which function as a column in continuous flow operations. At lab scale, many authors have developed high gradient magnetic separators (1 to 2 T) for iron or coated iron nanoparticles showing capture efficiencies of over 90%. Besides the construction of the filter and its proper functioning, understanding the physical phenomenon behind the magnetic separation is a relevant issue, especially when the scaling up is needed.

For successful collection of magnetic particles by high gradient magnetic separation (HGMS), the magnetic force attracting particles toward the wires must dominate the fluid drag, gravitational, inertial, and diffusional forces as the particle suspension flows through the separator. HGMS have been modeled extensively by numerous authors considering these forces. This work proposes the modeling of magnetic separation from the point of view of a well-known chemical engineering process, the adsorption process.

The magnetic separation system was considered to be analog to a fixed-bed adsorber, due to the adsorption in a fixed-bed column is the adhesion of particles from a gas, liquid, or dissolved solid to a surface of a porous media, creating a film of the adsorbate on the surface of the adsorbent, and the possibility of particle diffusion into the porous. In this case, the steel wool is looked at as porous media where the particles are adsorbed in its surface and create a film.

The magnetic field is assumed as the force that generates the adsorption process, where:

- The particles moves along the intraparticle spaces following a porous media flow (Darcy Flow) or a plug flow.
The trapping of iron nanoparticles on the steel wool as the adsorption rate, where diffusion or kinetics mechanisms are modeled.

- Axial dispersion of iron nanoparticles and its clogging phenomena are neglected on a first approach and then considered in the final model.
- The bulk flow velocity is assumed as constant and is modeled as the interstitial velocity.
- For the solid phase, a mass transfer coefficient will be established, neglecting the intra-pore adsorbate transport because the wires are not porous.
- The equilibrium is represented with Linear, Langmuir, Freundlich, Langmuir-Freundlich, and BET isotherms as common approximations.

The concentration of the iron nanoparticles is predicted to generate the breakthrough curve, in order to analyze the impact of the main variables, such as liquid residence time, iron nanoparticles concentration and magnetic field.

A magnetic filter was built to test the process and the experimental data are used to fit the parameters of the model, with the purpose to scale up this process to industrial size.

The experimental tests were run on the magnetic filter to determine the following variables:

- Saturation capacity retention and porosity of the steel wool.
- Outlet concentration depending on magnetic field and flow velocity.

This paper presents the model and the impact on its different parameters. The results of the fitting will be the feasibility of associate magnetic parameters with adsorption, making the modeling and scaling up of the magnetic filter relatively easy to perform.

**Electromagnetic Separation of Iron Nanoparticles using a Coil as a Filter**

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Arsenic is toxic heavy metal. To remedy arsenic contamination, several methods are used including precipitation, electrochemical reduction, adsorption, ion exchange, solvent extraction, nanofiltration and reverse osmosis. In Chili, the pyrometallurgic copper processing releases large amounts of arsenic. Specifically in the Codelco El Teniente copper smelter, the wastewater treatment can be summarized in the process of oxidation, precipitation, filtration, and calcination. Since the Chilean norm for wastewater discharge in rivers is 0.5 [mg/L] and the internal Codelco norm for wastewater reuse as process water is 1 [mg/L], in some cases the wastewater has to be recirculated back into the treatment process or reused with a higher content of arsenic. Both of these options are undesirable for the copper smelter.

Electrocoagulation of arsenic with iron nanoparticles has been shown to be efficient for arsenic removal from different water streams. The use of iron nanoparticles has its justification of their small particle size and large surface area to volume ratio to trap the arsenic, and because they can be easily removed from solution in a gradient magnetic field. Hence, the proposal for arsenic elimination is the electrocoagulation with nanoparticles follow with a magnetic filter.

Magnetic separators used on the industrial scale are overwhelmingly high gradient systems which function as a column in continuous flow operations. At lab scale, many authors have developed high gradient magnetic separators (1 to 2 T)
for iron or coated iron nanoparticles showing capture efficiencies of over 90%. However they always have used huge permanent magnets almost 3 or 4 times the size of the filter.

In the present work, a stainless steel tube inside a coil and filled with fine-grade steel wool is used as a new configuration of a magnetic filter for nanoscale zero valent iron nanoparticles suspended in water. The coil has the advantage of being an easy and cheap medium for producing a uniform magnetic field but, since for generating magnetic force acting over the particles, a spatial gradient of the magnetic field is needed, so the wool fibers were placed perpendicular to the magnetic field lines for accomplishing this.

The filter was 40 cm length and 4.2 cm of internal radius. It was packed with an average of 74 g of fine-grade steel wool. The coil was placed at the center of the filter and was 25 cm length. The coil was formed by 600 m of 16 BWG enameled copper wire resulting in 16 layers of 250 turns. The magnetic separation was carried out in continuous flow operation varying flow velocity (5 to 30 mL/s), electric current (0 to 5.5 A) traduced in magnetic field (0 to 0.07 T), inlet concentration of nanoparticles (1 to 10 g/L) and spatial arrangement of steel wool fibers (perpendicular and longitudinal to the magnetic field).

The longitudinal configuration of the steel wool fibers could retain almost nothing of the nanoparticles, so the next results correspond to the perpendicular arrangement. The maximum magnetic field used was 0.07 T because it was shown that with only 0.05 T the filter reached a 99% of capture efficiency for all inlet concentration at 15 mL/s. The average solute concentration in the wool steel was 0.43 g nanoparticles/ g wool steel, and at saturation 0.51 g nanoparticles/ g wool steel.

It can be concluded that the coil combined with the correct spatial arrangement of the fibers is a feasible medium to create a magnetic field capable for separating nanoparticles from water, even reaching 99% capture efficiencies.

**Electro-osmotic transport of nano zero-valent iron in Boom Clay: nZVI distribution and effect in the clay**

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**Introduction**

Nano zero-valent iron (nZVI) has attracted much attention for its potential to treat and degrade various soil contaminants, e.g. chlorinated compounds and pesticides. Nanoparticles are traditionally injected under pressure and/or by gravity to the contaminated plume where treatment is needed (1). However, rapid aggregation and sedimentation limit bare nZVI migration in subsurface systems, limiting the successful delivery of the nanoparticles to the contaminant source zone (2).

To overcome the limitations, a combined technique using nZVI and electrokinetics is actually being developed (1-2). Electrokinetic remediation is a process in which a low-voltage direct-current electric field is applied across a section of contaminated soil to remediate contaminants. Specifically, electro-osmosis (EO) may be utilised to transport oxidising or reducing agents into low permeability zones, facilitating the remediation of these contaminants.
The aim of this work is the study of the transport of nano zero-valent iron (nZVI) under electric field through Boom clay, a low permeability tertiary clay from Mol, Belgium, and its distribution.

Results and Discussion

The transport experiments were carried out in an electro-osmotic cell previously developed (3) (Figure 1). Several studies were done. The clay properties (cations content, etc.) and the distribution of the nZVI and different cations in the soil was determined using micro-XRF.

The presence of nZVI in the Boom clay affects the electro-osmotic flow by decreasing it. The bare nZVI limits the transport due to its natural tendency to form an oxide coating and aggregate. Even though nanoparticles coated with a non-ionic surfactant (Tween) were used, the formation of large aggregates clogs the transport routes and prevents particle transport completely, decreasing the electro-osmotic flow.

There is an increase of the current intensity with time due to the electrolysis of water in the neighborhood of electrodes. This may be due to the generation of H+ and OH- near the anode and cathode, respectively and enhanced release of other cations present in the soil (Ca2+, Mg2+). Moreover, the release of divalent cations (e.g., Ca2+ and Mg2+) and their presence in groundwater have an effect on compression of the electric double layer (EDL) of colloidal particles resulting in lower colloidal stability and higher filtration probability (4).

The pH in the soil reached more extreme values when nZVI was employed. Due to the electrolysis of water in the neighborhood of electrodes, the pH behavior in the anode and cathode reservoir approaches about 1.8 and 12.8, respectively, in all the experiments with nZVI. Once the small buffer capacity of the clay was used up, the acidification and subsequent coagulation and cation exchange in the clay takes place, and this effect increases with the increase in nanoparticle concentration.

According to the Micro-XRF (Figure 2) and cation analysis in the soils there is a cation exchange in the clay and the exchanged cations migrate towards the cathode. The formation of an acidic front affects the nanoparticles presence and it may cause the precipitation of the iron near the cathode, preventing it to reach the target (catholyte).

The reactivity of the nZVI was modified during the transport due to side reactions but the presence of reactive nZVI in the soil after the transport experiments was verified by analysis of hydrogen production.

Improvement of the transport is feasible. The research is ongoing and new assays are being developed.

Acknowledgments

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Estimation on the remediation cost of in-situ electrokinetic process for multi-metal contaminated site

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Economic consideration is major parameter to select remediation technology of contaminated sites. Generally, cost for electrokinetic process is higher than that of other remediation technologies. Alshawabkeh et al. reported cost for electric energy accounts approximately 25% of total cost in EK process. However, there was no report on details for the cost estimation on in situ EK process of multi-metal contaminated site. In this study, we carried out cost estimation of in situ EK process for multi-metal contaminated site based on a pilot scale field application.

Interpretation of the titration and solubility curves of a soil contaminated by heavy metals using freeware chemical equilibrium speciation software

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The buffer capacity of the soil is one of the most important parameters in assessing the feasibility of different remediation techniques of soils contaminated by heavy metals (washing, flushing, electroremediation, etc.). In another work presented in this conference, we study the influence of the pH on the retention of lead in a soil from the mining district of Linares (Spain) contaminated by heavy metals. Two types of curves, the soil titration with different acid solutions and the resultant aqueous concentration of Pb, were simultaneously obtained in that work. It was observed that those curves strongly depend on the nature of the acid used and on the rate of addition of acid solutions.

It is well known that the phenomena involved in the titration of a soil-water mixture are usually under kinetic control (mass transfer- or sorption- kinetics). This fact was observed in the experimental results, in which the titration curves obtained with each acid strongly depend on the addition rate of the acid solution. Nevertheless, when this rate is high enough, reproducible results and almost indistinguishable curves are obtained, this is, the results are no longer affected by the acid addition rate. This could indicate that the experimental results thus obtained involve only the fast processes, which probably are very close to the equilibrium conditions. The validity of this assumption can be assessed by the comparison of the experimental results with the corresponding simulation ones obtained under equilibrium conditions.

In the current work, this assumption is studied in the soil contaminated from the mining district of Linares. In this case, the influence of the pH on the retention of lead under equilibrium conditions is obtained by the simulation of the aforementioned experimental results using two different freeware chemical equilibrium speciation software: Hydra-Medusa and Visual MINTEQ.

In these simulations, different lead species were considered according to the main cations and anions presented in that soil (Ca, Mg, Fe, Mn, carbonates, etc) and to the species added during the titration (nitrate, acetic or EDTA). The shapes of the titration curves obtained by the simulation under equilibrium conditions are similar to the corresponding experimental ones. Nevertheless, the kinetics of the dissolution-neutralization processes affects significantly the locations of the inflection points and of the plateau on those curves.
The solubility curves of lead in the aqueous phase of the slurry, the simulations performed with the two software programs reproduce adequately the amount of lead dissolved as a function of the pH (solubility curves). Nevertheless, these programs do not predict the behavior observed at the final part of the experiments, in which the total dissolution of Pb does not occur. This amount of the Pb presented in the soil that cannot be dissolved, is only predicted by Visual MINTEQ if the Pb adsorption on the hydrous manganese oxide is considered using the diffuse layer model (DLM) and the dlm_Tonkin database provided by this software.

Finally, the BCR fractionation of the lead in the soil after the titration experiments is also adequately reproduced by the Visual MINTEQ software.

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Ion transport in Nafion as studied by NMR

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Salt can be removed from materials, e.g. soils or construction materials, by applying a potential difference across it. This process is normally accompanied by high pH gradients within the material due to the electrochemically enhanced water-splitting at the electrodes, which results in an increased hydrogen ion concentration at the positive electrode and an increased hydroxyl ion concentration at the negative electrodes. These acidic and alkaline regions cannot only lead to deterioration of the materials, but also affect the salt ion transport [1]. To block the ingress of the acidic and alkaline regions ion exchange membranes adjacent to the electrodes can be used (see fig. 1 and ref. [2]).

For the cation exchange membrane Nafion can be used with a typical a thickness of 100-400 μm. In this study we focus on the ion transport within these membranes itself as a function of the current density. In order to do so we have casted Nafion into cylinders of 10-40 mm in height, and monitored the ion profiles across the cylinders as a function of time and position for various currents with Nuclear Magnetic Resonance (NMR). To this end a specially designed NMR setup for ion measurement was used in this study. With this instrument we can non-destructively measure the ion-profiles with a high spatial resolution in the order of 2-4 mm, while we have an electrical current through the Nafion. The measured profiles have been compared with a model based on the Maxwell-Stefan equations. To verify the model we have looked at two cations with total different properties, i.e., Na and Li, during their transport through the Nafion. It was found that the model results compare well with the experimental observations.

Lab scale study of the influence of the acid strength over the performance of an acid-enhanced electrokinetic remediation

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It is widely accepted that, when an electrokinetic remediation (EKR) is performed for the cleanup of most toxic metals, an enhancement is needed. During the unenhanced EKR the reactions at the electrodes, probably water electrolysis, result in the production of hydroxides, at the cathode, and hydroniums, at the anode, that migrate towards the opposite electrode. Most toxic metals are recovered as cations, and in their way towards the cathode will meet the hydroxides, with different problems arising. The most typical enhancement is the addition of an acid over the catholyte, which results in the replacement of the hydroxides for the corresponding anion of the specific acid. This anion will also migrate towards the anode, so the decision about which acid should be used can be quite important.

Several previous works have tried the use of acids of different strength, but no definitive conclusions have been derived from these works, probably due to the experimental procedure used. Most research at the lab scale is performed at constant voltage drop, which is a reasonable decision based on the most likely design at the field scale. Nevertheless, the obtainment of reproducible results is difficult with this design because, at any time, a small difference in the conductivity will lead to an increase of the amount of hydroniums that will enter the soil, and this will feed back the initial difference of conductivity, leading to the divergence of the results. Instead, the use of a lab design based on constant current intensity allows a very good reproducibility, mostly when the experimental work is performed in different columns connected in series. For these cases, one can be sure that the amount of charge circulated through the soil is exactly the same for both columns, and is directly proportional to the experimental time.

We have applied the acid-enhanced EKR to a real soil with an important lead pollution (4.5 % of the dry mass), which was obtained at 400 m downstream of the slag heaps of a lead mine of Linares (southern Spain). This soil is alkaline and has an important amount of carbonates (8.5 %). We have tried nitric and acetic acids and both experiments were duplicated. All the experiments were ended once a 30 % of the initial lead was removed. A BCR sequential extraction procedure was performed in a “before and after” way to analyze the changes on the mobility that occurred during the remediation. The soil samples after the treatment were split into two slices, to observe the differences that could arise between the soil regions closer to each electrode compartment.

The results indicate that the reproducibility of the duplicates is very good. Also the BCR results obtained for the treated soil were quite similar for both acids, indicating that, by the time we decided the end of the experiments, more than 90 % of the lead was removed from the soil closer to the anode, an important accumulation is found in the soil closer to the cathode and the distribution of lead among the different fractions of the BCR was not depending on the acid selection. Nevertheless, the acetic acid required a larger amount of moles, but the time (and charge circulated) required for the same remediation efficiency was more than double for the nitric acid, due to the formation of acetic acid resulting in a larger fraction of the electric current being transported by the remaining ions.

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Modeling of electrodialytic removal of phosphorous from soil
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Phosphorous is one of the main constituents in natural soil. Electrokinetic soil remediation treatments irreversibly produce the migration of phosphorous compounds, as well as chemical composition changes in the minerals containing this element. The concentration and composition of phosphorous compounds may have an important role in the efficiency of electrokinetic remediation techniques. It may exist in either organic or inorganic forms, and both types of phosphorous compounds affect, for example, to the buffering capacity of the soil and, therefore, to the optimal pH for the remediation.

Apart for all those aspects than justified the study of phosphorous migration during electrokinetic treatments during other contaminants remediation, the feasibility study of the concentration and recuperation of phosphorous to be reused for agricultural purposes may be of interests, due to the increasing demand of phosphorus as a fertilizer agent.

In this work, a simulation-based study of the migration of phosphates and other phosphorous species during electrodialytic soil remediation processes is considered. The model is based on the finite element solution of a system of partial differential continuity equations for the chemical concentrations (Nernst-Planck-Poisson system). As external electric field, a constant difference of electric potential of 20 V between electrodes is established. The model includes the different permselectivities of cations and anions through the ionic exchange membranes used in the electrodialytic process to separate the treated soil to the accumulation and the electrode compartments.

The transport of phosphorous strongly depends on the chemical speciation. Important differences are observed depending on the proportion of organic or inorganic phosphorous. The chemical affinity with respect to calcium ions, forming aqueous complexes and apatite minerals, is remarkable. Accordingly, the model includes a comprehensive set of feasible chemical reactions involving phosphorous in different oxidation states. Both homogeneous aqueous complexation and heterogeneous precipitation and dissolution reactions are included.

The study is completed by means of a comparison with experimental results for the validation of the model and the estimation of the model parameters.

Modeling of transport processes through ion exchange membranes
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Semi-permeable membranes are used in several separation processes in chemical, biochemical and environmental engineering fields. In electrokinetic remediation, ion exchange membranes are receiving considerable attention, as they
produce a selective separation with low energy consumption. This kind of membranes is the base for the electrodialytic remediation processes. Moreover, membranes are also used for different purposes, as e.g. to control the pH of the media by preventing the acidic or alkaline front to penetrate the system, to create electrolyte compartments between the treated body and the electrode compartments for the selective recuperation of the contaminants, or to avoid contaminants to reach the electrode surface producing competitive electrochemical reactions.

Models for electrokinetic remediation treatments using membranes have to include the special behavior of the transport of the chemicals though the membranes. Different approximations have been proposed for modeling ionic exchange membranes. The simplest models treat the membranes as a gate that allows or inhibits the transport of ions depending on their charge. More sophisticated models incorporate the aging and saturation of the membrane and the selective efficiency depending on the transferred ion.

In the work presented here, a model for the transport of chemical species through membranes is presented. The model is based on a finite element integration of the transient Nernst-Planck-Poisson system incorporating different chemical aspects. Simulations are presented for the electroremediation treatment of a Pb contaminated soil, in which a set of membranes is used at the anode and cathode compartments for the acid-enhancement of the treatment.

**Potential of electrokinetic process to upgrade an antimony and arsenic contaminated soil - Suitability of coupled technologies**

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Soil metal contamination arising from mining operations can be considered as a major threat to land use. Concerning concentrations of antimony (Sb) and arsenic (As) are presented in several spots worldwide. The remediation of these contaminated matrices are of vital importance to restore environmental equilibrium.

The present work aims to survey optimized conditions for electrokinetic (EK) process as an efficient tool for removing Sb and As from contaminated soils. A soil was sampled in a mine area located in southern Hunan Province (China). Applying a low level direct current, EK promotes the movement of species out of the contaminated matrix, towards one of the electrode compartments, where they are concentrated and may be removed. The EK process was carried out in laboratory cells using a special set-up developed at ISSCAS. The removal of contaminants out of the soil was evaluated with and without phosphate addition, as well as pH adjustment of electrolyte solution. In parallel, experiments coupling EK with phytoremediation were tested in greenhouse conditions, evaluating the effect of an hyperaccumulator (Brassica juncea) and a non-hyperaccumulator (Lolium perenne) plant species in the enhanced removal of Sb and As from the soil.

The potential and applicability of EK and EK-assisted phytoremediation to promote soil remediation is discussed, regarding remediation of mine areas contaminated with Sb and As.

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ELECTROACROSS - Electrokinetics across disciplines and continents: an integrated approach to finding new strategies for
Reducing the hydroxyl ion penetration in sediment during electroremediation

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This study investigates certain techniques for reducing hydroxyl ion penetration during the electrokinetic treatment of sediment and its influence on Cr, Cu and Zn removal efficacies. Hydroxyl ions can cause accumulation of metal hydroxides in the cathode region of sediment. They can also cause organic mater dissolution which leads to formation of metal complexes with organic anions and changes in the ion migration path (accumulation at the anode region of the sediment). In addition to the conventional treatment (CON), the following techniques were investigated: auxiliary anode utilization (AA), circulation of electrolytes (CIRK) and use of the NEOCHIM cathode (NEO). The electric potential between the anode and the auxiliary electrode was fixed while that between the cathode and the auxiliary electrode was controlled to make the auxiliary electrode the secondary anode. Circulation of anolyte to catholyte at a rate 1.5 ml/min was used to decrease catholyte pH. With the NEOCHIM cathode technology, hydroxyl ions are retained in the inner compartment of the two-compartment electrode and are thus prevented from reaching the sediment. The sediment pH values at the cathode region were: 9.50, 8.07, 7.77 and 8.45, after CON, AA, CIRK and NEO, respectively. This suggest the techniques used were effective in reducing the OH- ions penetration into the sediment. Controlling the alkaline conditions in the sediment affected the metals distribution through the sediment causing a significant increase in the overall removal efficacies observed for all target metals.

Relationship microstructure-electrochemical behavior of alloys FeCoC

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This study deals with the effect of sodium molybdate on electrochemical behavior of some FeCoC based-iron ternary alloys by potentiodynamic polarization technique.

The corrosive medium used for the considered alloys (noted Co2, Co3, Co6 and Co8) is a non deaerated solution containing 10-3M NaHCO3 and 10-3M Na2SO4.

The results indicate that the Co6 and Co8 corrosion current densities are close and much higher than those of Co2 and Co3 alloys. A further study is carried out on Co6 alloys at a concentration of 10-2 M of sodium molybdate and at different temperatures (25, 35, 45 and 55°C) using potentiodynamic polarization, polarization resistance and electrochemical impedance spectroscopy techniques. In fact, a low value of corrosion current density and a presence of a passive plateau are observed at this concentration. The examination of the electrochemical parameters of the Co6 alloy shows that the corrosion current density decreases at 35°C. However, at 45 and 55°C, the corrosion current densities are multiplied by about 7 compared to the current density at 25 °C. In addition, the interpretation of the obtained results using different electrochemical methods shows that the determined parameters have the same tendency.
Removal of heavy metals from an agricultural soil

The intensive use of agricultural soils may result in the increase in the contaminant concentration. Contaminants can reach the soil through the additives used in agriculture: chemical fertilizers, pesticides and other organic wastes used as a source of nutrients. The high organic matter content in agricultural soils tends to complex and retains contaminants such as heavy metals. The removal of heavy metals from soils can be carried out by electrokinetic remediation but the high organic content in the soil makes the removal difficult.

In this study, an agricultural soil sampled in Galicia (NW of Spain) was spiked with Cu+2, Cr(VI), Pb+2, Zn+2 and Hg+2 up to a concentration of 1000 mg/kg, and Cd+2 up to a concentration of 140 mg/L, and Co+2 up to a concentration of 185 mg/kg. After the spiking process, the soil was stored in plastic bag in the darkness for 1 year to ensure the aging of the contaminants. The objective of this process was to ensure a similar behavior of the spiked soil to that of a real polluted soil. The soil was analyzed before it was used in the experiments and the final metal concentration into the soil was as follows: Cd: 209.58 mg/kg; Co: 290.22 mg/kg; Cr: 1837.39 mg/kg; Cu: 2906.27 mg/kg; Hg: 1340.93 mg/kg; Pb: 1975.18 mg/kg; Zn: 1846.35 mg/kg.

Several extracting agents were used for the removal of heavy metals from the soil. The results depended on the chemical nature of the extractant and its chemical affinity for the metal. In general, oxalic acid, citric acid, EDTA and sulfuric acid showed the best results in the removal of the target contaminants.

Cd was more effectively removed by sulfuric acid (81%), followed by citric acid and EDTA (59%) and oxalic acid (46%).

Co showed the best removal with sulfuric and citric acid (84%), followed by EDTA (73%) and oxalic acid (72%).

Cr showed the best removal with oxalic acid (77%) followed by sulfuric acid (48%) and citric acid (20%). EDTA showed a minor Cr removal of 6%.

Cu showed the best removal with sulfuric acid (87%) followed by EDTA (59%), oxalic acid (58%) and citric acid (46%).

Zn showed the best removal with sulfuric acid (90%) followed by oxalic (72%) and citric acid (61%), and EDTA (61%).

Pb showed only a significant removal with EDTA (31%) and oxalic acid (18%). Citric acid (8%) and sulfuric acid (7%) only showed minor removal efficiency.

Hg was the most difficult metal to be removed by extraction. Sulfuric acid was the extractant with the best removal efficiency (27%), followed by oxalic acid (19%), EDTA (15%) and citric acid (6%).

Those results confirm the feasibility of extraction of heavy metals from an agricultural soil. Although most of the metal content was added to the soil in the laboratory, the aging of the contaminants for a year it is expected to be representative of a real contaminated soil. Those results will be used in the design of enhanced electrokinetic tests.
Simultaneous removal of fuel hydrocarbons and heavy metals from a railroad soil using electrokinetic remediation

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The feasibility of the electrokinetic (EK) process for remediation of railroad soil contaminated simultaneously with organic and inorganic contaminants was studied. Also, the effect of pH conditioning during EK process on the system’s performance was evaluated. The target soil collected near a maintenance facility of railroad was contaminated with various heavy metals including As, Cd, Cu, Pb and Zn, as well as fuel hydrocarbons, over 12,000 mg/kg of total petroleum hydrocarbon (TPH). Although it was reported around 30% of polluted sites were known to be mixed contaminated, there have been few techniques to remove both of organic and inorganic contaminants successfully. In this study, EK remediation process was applied with pH-conditioning in catholyte using nitric acid in order to enhance the removal of heavy metals and TPH. 0 M to 1.0 M of nitric acid and 0.01 M of Na2HPO4 was supplied into catholyte and anolyte tank, respectively for 15 days of operation. System parameter including electrical density variation, electrolyte pH profile and electroosmotic flow (EOF) was evaluated during operation and soil moisture content, soil pH, residual content of each pollutant were analyzed. As results, it was observed that the higher concentration of nitric acid applied into EK system, the higher electrical density and reverse electroosmotic flow. Catholyte pH stayed around pH 2 when over 0.5 M of nitric acid was used as catholyte and acidic environment established in soil enhanced increased degree of reverse EOF as well as mobility of cationic heavy metals such as Cd, Cu, Pb and Zn. Using 1 M of nitric acid as catholyte, the average removal of Cd, Cu, Pb and Zn were 91.1 %, 74.1 %, 88.9 % and 90.0 %, respectively. On the other hand, As and TPH showed lower removal efficiencies in acidic condition, where the highest removal of As and TPH were 12.6 % and 26.5 % for control test without nitric acid in catholyte tank. In conclusion, EK remediation process is available to remove organic and inorganic pollutants and pH conditioning could dramatically enhance the removal of cationic heavy metals.

Solar Cell-Based Electrokinetic Remediation of Heavy metal Contaminated Soil

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Soil contamination has been a serious environmental issue in Korea and in the world because of rapid industrialization and urbanization. Electrokinetic remediation is one of in-situ technology to remove metals and/or organic contaminants from soils, sediments, and sludges. However, electrical energy consumption is a major barrier to apply the technique to a real field because energy costs account for 25% of total operation costs. Recently, renewable energy sources including solar energy and wind power have been interested in the remediation field due to requirement on green remediation. We evaluated solar cell-based electrokinetic remediation technique to treat heavy metals-contaminated soil. Basically, the overall performance is highly dependent on the energy supplied to system in electrokinetic remediation, however, solar power could provide similar effects with pulsed power to the system. We compared two different power sources in this study: solar power and normal power supply. Additionally, we evaluated the effects of additives in two systems.

Study of the behavior of an acid-enhanced electrokinetic remediation performed with a real soil spiked with lead

Since the 1980s decade there has been a sharp increase in the research for the development of new techniques for the remediation of contaminates sites, because one after another country realized that the economic budget that would require the recovery of all these sites is simply unaffordable. Most countries have developed criteria to prioritize the remediation of those sites that were bearing the most severe risks for humans or the environment. Also an important effort has been done in order to make available new techniques more economic.

Regarding both, the risk assessment and the development of new techniques, the most typical research approaches at the lab-scale are either the use of an already contaminated soil or the use of a model soil in which the contaminant is spiked. In the first case, the complexity of the soil matrix makes the derivation of conclusions applicable to other soils quite difficult. In the second case, the simplicity of the soil matrix can make the results more reproducible at different labs, but may be also of limited interest for the real contaminated soils, since that simplicity will be found in very few real cases.

Furthermore, the contact time between the contaminants and the real contaminated soils is usually larger than several months and can even be in the order of centuries. Obviously this contact time may not be used in the experiments at the lab scale. In these cases, typically, in the most favorable case, a series of experiments of different contact time are carried out, which range from some minutes or few hours to several days or even weeks. Then a comparison is made from which the conclusion is usually that a contact time of several hours or few days is large enough to assure that the different equilibria are reached. Nevertheless, it is also widely known that the transport of contaminants through the soil matrix can be very slow. Also that it can be difficult to distinguish between the pseudo-steady states that can control the partitioning between different soil compartments and the real thermodynamic partitioning.

Thus, there is a clear lack of experimental results obtained for soils that are spiked with a certain contaminant and allowed a variable contact time (ageing) ranging from weeks to years. In this work we present the first results that we have obtained for a soil that presents a moderate background concentration of lead, and was spiked with an additional amount of lead nitrate. The mobility of lead is studied by the BCR sequential extraction procedure, which divides the lead concentration into three fractions (weak acid soluble, reducible and oxidizable), besides the residual fraction that is obtained to investigate the mass balance, and support the quality of the analysis. It has been shown in the literature that the BCR fractionation can be used, together with mathematical models, to do reliable predictions about the maximum removal yield that can be obtained from several remediation techniques, including the electrokinetic remediation. In this paper we present the results of an early stage of the ageing process. The electrokinetic experiment is performed in a duplicated lab column assay using a constant current density and the disposition of the two columns electrically in series, to allow the maximum reproducibility of the results.

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Using of electrochemistry in the study of FeVTiC alloys

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The main purpose of this work is to identify all the carbides formed in FeVTiC alloys. EDS microanalysis have shown that their composition cannot be determined accurately because of the presence of carbon and of the small size of these phases. The identification of the observed phases permits, in a first hand, the establishment of the respective cooling paths. In a second hand, it can contribute to the understanding of the solidification behaviour of these kinds of alloys.

Our alloys were melted in an arc furnace under an argon flux. The identification of the carbides has been done of two different manners. The first one consists in extracting the carbides by electrochemical method before analyze them using X rays diffraction.

The second one is a direct analysis by EDS of each of these phases, including the iron matrix. The results obtained by these two methods are compared.

Three types of carbides were identified (V,Ti)C$_{1-x}$, (Ti,V)C$_{1-x}$ and VC$_{1-x}$ in our alloys. Cooling paths proposed for these alloys are issued from the results of the differential thermal analysis.

The mutual solubility between carbides of vanadium and titanium is due to the presence of a continue solid solution at high temperature. This strong solubility falls when the temperature is dropping, to lead to a nearly pure VC$_{1-x}$ carbide, in the rich vanadium region.

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Electrochemical dechlorination of TCE in a simulated karst aquifer

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A lab-scale Limestone block is proposed to simulate a karst aquifer for the remediation of TCE in ground water. The system contains a cast iron anode, which produces a reductive environment through generating ferrous ions, and a porous copper cathode, which reduces TCE to nontoxic ethene and ethane. The effect of different factors such as initial concentration of TCE (1 and 2 mg/L), applied current (30,60, and 90 mA), and flow rate (1 and 2 mL/min) on the remediation efficiency is evaluated. Longer retention time and higher current increased the removal rates. However, these conditions caused high precipitation. The maximum rate is obtained as 60% under the optimal conditions of 1 mL/min, 90 mA, and 1 mg/L. Another acrylic column with the same dimension is also employed for TCE remediation, comparing how various types of material can affect remediation performance.

KEYWORDS: Karst aquifer, Electrochemical process, TCE, Iron anode, Ground water remediation.

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Electrodialytic decontamination of fly ash from small scale waste incinerators in Greenland

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In Greenland waste has traditionally been dumped at open disposal sites combined with uncontrolled incineration. In the mid 1990’s the first waste strategy was implemented and as a result simple and small municipal solid waste incineration (MSWI) plants were taken into use in towns and settlements primarily to minimize the amount of waste at the disposal sites. Between 200–900 tons of toxic MSWI fly ash is every year shipped and deposited in Norway, since the Greenlandic disposal sites are not safe for disposal of this hazardous material. The MSWI fly ash could have value as a secondary resource in building materials, construction work or be deposited in Greenland, if the toxicity is lowered. This would contribute to solve the expensive problem of disposal abroad.

The aim of this study was to apply electrodialysis to fly ash suspension to evaluate the potential for reducing the heavy metal (Al, As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn) toxicity of the fly ash. Seven experiments were made with three different fly ashes in bench scale; treating 1 – 2.5 kg of fly ash in a suspension with 10 L distilled water. Compared to the traditional electrodialytic remediation cell design, the fly ashes were treated in a membrane stack which consists of several ion exchange membranes, concentrate and fly ash solution compartments. Experiments were made with varying remediation time, current densities and liquid-to-solid (L/S) ratios.

The removal of heavy metals from the fly ash suspension to the concentrate occurred within hours and the electrical conductivity of the fly ash suspensions decreased continuously during the treatment, showing a net removal of ions from the solution. Low L/S ratios of the fly ash suspension resulted in problems with clogging of fly ash compartments in the membrane stack. This also influenced the removal of heavy metals, which was less efficient than at the higher L/S ratios. A high current density over the membrane stack could not be kept constant. Both these factors influenced the operation of the membrane stack during the treatment and the results. Leaching of heavy metals after the electrodialytic experiments decreased compared to the initial leaching in all experiments.

Based on the oxide, mineral and chloride content of the electrodialytically treated fly ashes, recycling options such as replacement for cement in concrete, stabilization of fine-grained materials in the construction of roads and construction and enrichment of asphalt could be possible. Al, Si, Fe, and Ca oxides and minerals increased in concentration due to the electrodialytic treatment as a result of the dissolution and removal of soluble salts and metals.

The results show potential for applying electrodialytic treatment for decontamination of these fly ashes and the treated fly ashes could possibly be reused instead of being disposed of.

Electrosorption/Electrodesorption of Arsenic on a Granular Activated Carbon in the Presence of Other Heavy Metals

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The adsorption, electrosorption, and electrodesorption of aqueous, inorganic arsenic on the granular activated carbon (GAC), DARCO® 12×20 GAC was investigated in solutions containing arsenic as the only contaminant, as well as with chromium, nickel and iron. Darco 1220 was selected for these investigations primarily because it is relatively ineffective as a normal (unassisted) arsenic adsorbent in the chosen electrolytes at the low loadings used. It is shown that the application of anodic potentials in the 1.0 – 1.5V range, however, result in enhanced uptake, most probably due to
charging of the electrochemical double-layer at the electrode surface. 100% regeneration of electrosorbed arsenic was achieved via electrodesorption at a cathodic potential of 1.50V. The presence of ad–metal ions was observed to have a significant and complex effect on arsenic adsorption, electrosorption, and electrodesorption. In particular, the Cr:As ratio was shown to have complex effects, decreasing adsorption uptake when present as 3:2, but enhancing adsorption when present as 5:1. Nickel was found to have less of an effect than chromium except at the highest anodic potential used of 1.50V, where it exhibited better performance than chromium. The presence of iron significantly enhanced uptake. With a 1.50V anodic potential, the bulk arsenic concentration was reduced to less than detectable limits, well below the USEPA MCL for drinking water. Regeneration efficiency by electrodesorption for the As–Fe system was greater than about 90%.

Response of indigenous microorganisms to bio-electrokinetics applied to remediation of soil contaminated with PAH and metals

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Thirty percent of contaminated site in Montreal contain PAH and other thirty percent contains both PAH and metals. The soil remediation is such cases should target all contaminants for effective results. Electrokinetically enhanced bioremediation focuses on bio-augmentation of microbial biomass in order to accelerate the pollutants biodegradation processes. Electrokinetically transported nutrients and electron acceptors have been proved to be effective in situ soil remediation for various hydrocarbons. Generally, during the biodegradation process microorganisms produce biosurfactants (e.g. rhamnolipid). It is production crucial for successful hydrocarbon-bioremediation process. From other hand, rhamnolipids solubilize metals and make them more mobile within a natural system, which might be useful to electrokinetic transport.

The objective of this study was to investigate efficiency of rhamnolipid production by bacteria in the area where bio-electrokinetics was applied in-situ. A series electrokinetic (EK) cells containing natural contaminated soil was subjected to bio-electrokinetics process for over a moth under different DC voltage gradient. Mineralogical analyses showed than soil was mostly containing muscovite, chlorite and quartz. Nutrients and electron acceptors were supplied through electrokinetic phenomena excited in EK cells. After the end of experiment, soil between electrodes was sliced, samples taken and analysed.

Results showed that microorganisms are not affected by acid front and bioaugmentation was observed. However, a decrease of microorganisms, counting was found in the cathode area. Nevertheless, analyses of rhamnolipid showed it uniform distribution between electrodes showing effectiveness of the bio-electrokinetics in situ. Furthermore, chemical analysis also showed reduction of pollutants proportionally to the rhamnolipid concentration. In was concluded that bio-electrokinetic can be successfully applied to mix contaminated soil.

The Behavior of Metal Ion Concentrations in Solution During Co-electrodeposition

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The quantitative and qualitative behavior of the co-electrodeposition of metal ions from solution mixtures differs significantly from that in the individual single-metal solutions, primarily due to metal displacement reactions. The primary mechanisms of import in electrowinning multiple metals from complex acidic mixtures for remediation, as well
as other applications, are presented and discussed, specifically with respect to the co-removal of copper and nickel from aqueous solution mixtures. However, the resultant general approach can be applied to a number of other metals as well.

A numerical model of co-electrodeposition, metal corrosion, metal displacement, and mass transfer in a batch electrowinning environment is presented and demonstrated to describe the behavior of experimental copper/nickel co-electrodeposition in a spouted particulate electrode (SPE) very well as a function of pH, temperature, and dissolved oxygen concentration. The electrochemical model is based upon a general approach for modeling recirculating electrochemical reactors in single metal solutions, extended to simulate the co-removal of copper and nickel behavior with pH and temperature.

The model and data show that copper deposits first and nickel second, consistent with their respective standard reduction potentials. However, copper deposits much more rapidly than when it is present alone in solution, and nickel exhibits a maximum that does not occur when it is present alone in solution. The nickel maxima are due to the displacement reaction between copper ion and nickel metal. In addition to the effects observed during electrodeposition, the effects of the metal displacement reaction are also quite evident in metal corrosion experiments where the cathodic feeder current is turned off, and the deposited metals are allowed to re-dissolve into solution. Under these conditions, it is observed that the copper cation concentration can exhibit two regimes of behavior, depending on the relative magnitudes of the corrosion and displacement rates – that is, corrosion rate-control, where the copper cation concentration increases with time, and displacement rate control, where the copper cation concentration decreases with time. The location of these regimes is dependent on temperature, pH, and copper cation concentration at the time of current shut-off. In these binary solutions, however, the nickel cation concentration can only increase with time after current shut-off.

The metal displacement reaction serves to “spread out” the removal of copper and nickel in time. This characteristic produces regions in the metal concentration-time history where there is preferential copper removal or nickel removal. This behavior allows the development of strategies for the concentration of each metal, or separation, in addition to just removal.
TOUR INFORMATION

Under preparation.
BOSTON ATTRACTIONS

General Information
Boston, first incorporated as a town in 1630, and as a city in 1822, is one of America’s oldest cities. One of the best ways of navigating Boston’s historic sites is the Freedom Trail. The Trail takes the visitor to 16 historical sites in the course of two or three hours and covers two and a half centuries of America’s most significant past. A red brick or painted line connects the sites on the Trail and serves as a guide. Since the past and the present live alongside the Trail, its visitors have the opportunity to see the City as it truly is. Some of the historical sites included in the Freedom Trail are the Boston Common, State House, Park Street Church, Granary Burying Ground, Old South Meeting House, Old State House, Site of the Boston Massacre, Faneuil Hall, Paul Revere House, Old North Church, Copp’s Hill Burying Ground, USS Constitution, and the Bunker Hill Monument.

In addition to Northeastern University, Boston has many other colleges and universities that are available to visit, including scientific and engineering-focused schools such as Harvard University, Massachusetts Institute of Technology, Boston University, Boston College, Tufts University, and Wentworth Institute of Technology. Other prominent institutions are Berklee College of Music, Massachusetts College of Art and Design, Emerson College, New England Conservatory, and many more. More than a quarter million students attend colleges and universities in Boston alone making Boston a very young, energetic, and inspiring city.

For more information about activities in and around Boston please contact the Greater Boston Convention and Visitors Bureau at (888) SEE-BOSTON (888-733-2678).

Getting Around Boston
Walking: Chances are you’ve heard Boston referred to as “the walking city.” The City of Boston works hard to live up to this title. Its Public Works and Transportation Departments are constantly marking crosswalks, performing regular maintenance of traffic signals and pedestrian pushbuttons, and using innovative pedestrian safety signs at busy locations in downtown Boston.

Driving: The City of Boston has partnered with local company Zipcar to promote car-sharing in an effort to reduce congestion and promote sustainable transportation alternatives.

Commuter Rail/Subway/Bus: Thousands of residents and visitors use the extensive MBTA system of subways, commuter trains, and buses to get in and around Boston. Visit www.mbta.com for information on schedules and fares and to access the trip planner tool.

Taxis: Boston’s taxis are regulated by the Boston Police Department’s Hackney Carriage Unit. The Department has been working to promote greener, fuel-efficient taxis through the Clean Air Cab program, providing online services to improve customer experience, and implementing the use of credit fare readers.
Shopping and Dining
In the Back Bay, visitors can walk the length of Newbury Street for some of Boston’s most chic, fashionable stores. Boylston Street (which runs parallel to Newbury Street) has a number of fine department stores. There are several shopping centers in the heart of the city; the Shops at the Prudential Center connects by walkway to Copley Place, an enclosed mall full of upscale stores and restaurants. Downtown Crossing has the full range of national department stores, boutiques and pushcarts, which offer both the familiarity of home and local Boston souvenirs.

From comfort food to gourmet cuisine, there’s something in Massachusetts to satisfy everyone’s inner foodie. State specialties include fresh Atlantic seafood, authentic Italian in Boston’s North End, and farm-to-table freshness from our numerous farmers’ markets. And of course, that one-of-a-kind New England "clam chowda."

Entertainment
Museums: Boston has museums to suit almost every interest. The Museum of Fine Arts offers one of the largest art collections in the world. Also offering contemporary art is the Institute for Contemporary Art, newly-relocated to the Waterfront district. The Isabella Stewart Gardner Museum has a garden courtyard blooming with life in all seasons, surrounded by three floors of galleries. The Museum of Science offers hands-on exhibits, laser shows and IMAX films that are fun for all ages, while the newly-renovated Children’s Museum can entertain and educate children and their parents.

Shows and Concerts: Boston has a strong tradition of performing arts. In the theatre district, there are the Opera House, Colonial Theatre, Wilbur Theatre, Shubert Theatre and the Wang Center for the Performing Arts. Dance performances remain a cultural strong point and the Boston Ballet is one of the best in the world. The world-renowned Boston Symphony Orchestra and the Boston Pops perform at Symphony Hall.

Parks: Boston has multiple park systems within the city, including the Emerald Necklace, a 1,100-acre chain of nine parks, including the Public Garden and the Boston Common. In the summer, the Boston Common’s Frog Pond features a spray pool for children and the Swan Boats at the Public Garden. Just a short ferry ride from the city, you can visit the Boston Harbor Islands, the country’s newest National Park. Visitors to the Harbor Islands can enjoy full or half-day trips for swimming, boating, island tours, hiking, fishing and bird watching.

Sports: Boston is home to several well-known franchises, most especially the Boston Red Sox, who won the 2004 and 2007 World Series Championships.
MAPS