出國報告（出國類別：國際研討會）

2016 年各類有機與無機污染物氧化與還原整治技術進展
（2016 Advances in Oxidation and Reduction Technologies for Remediation of DNAPL, LNAPL and Various Organic and Inorganic Contaminants）

服務機關： 行政院環境保護署

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摘　要

本次赴美國亞特蘭大參加「2016 年各類有機與無機污染物氧化與還原整治技術進展（2016 Advances in Oxidation and Reduction Technologies for Remediation of DNAPL, LNAPL and Various Organic and Inorganic Contaminants）」國際研討會，辦理日期為民國 105 年 11 月 14 日至 105 年 11 月 17 日，為期 4 天，係由 Redox Technologies, Inc.公司主辦，並由美國、加拿大、歐洲及南美洲數個顧問公司及學術單位籌組協會共同協助辦理。總計共有 39 篇口頭論文發表，研討會與會人員包括相關領域之專家學者、工程師、學生及美國環保署官員等約 50 人。

本次研討會共分為 10 個子題於同一會議室內依序進行專題研討，分別為現地及離地化學氧化、DNAPL 調查與處理、整合性整治技術、DNAPL 與 LNAPL 之化學氧化與還原技術、現地整治之注藥系統、生物轉換、低通水性介質之整治、場址復原與管理、甲烷蒸氣控制技術等議題。

目前各類整治及調查技術之研發、商業化或實作成果大部分散佈於全球各地之產業界、學術界及政府機構，因此，本次研討會係提供一專業之溝通平台，供各界專業人士一同參與經驗交流與討論，同時藉由本次研討會之參與，可瞭解目前國際間對於 NAPL 污染物整治及調查技術之發展與相關應用。整體而言，國際間目前技術發展與應用層面，與我國相差不遠，但國外對於污染場址管理及整治策略思維，均納入不同程度風險管理或風險溝通之概念，進而加速完成污染場址整治、解列、開發再利用等不同目的，有效達到土壤環境永續發展之最終目標，此為我國未來需參考並持續努力之方向。此外，亦經由研討會之參與，加強與國外專家學者之交流，並與國際接軌及增加我國於國際土水界之能見度，促成未來各類型國際合作之可能性。

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一、目的

是否存有重質非水相液體（DNAPL）通常為土壤、地下水污染場址調查或整治時之重要因子之一，因污染場址特性不同，DNAPL 之分布情形、對地下水污染均有不同程度影響，尤其 DNAPL 會持續釋出溶解態污染物至地下水中，在經費與時間雙向考量下，能將場址成功解列成為一大挑戰。有鑑於此，過去 30 年間，許多新穎技術已被發明並成功應用於實場中，對目前許多 DNAPL 污染場址之調查或整治有著極大助益。

但即使針對 DNAPL 污染源積極進行移除或整治工程，仍然可能無法將污染物濃度成功降至管制標準下，使得許多污染改善者對於 DNAPL 整治相當猶豫，而導致 DNAPL 整治無法順利執行之主要原因不外乎為場址調查結果、整治成效判斷及替代整治目標接受程度所帶來之各種不確定性，因此，如何以最符合經濟效益且有效管控風險責任來規劃適當之整治策略為目前國際間普遍納入考量之因素之一。此外，近年來污染土地開發及再利用為全球各界關注議題之一，若能發展更有效率之調查或整治技術，將能更快速並以較低成本完成場址解列，使受污染土地能夠活化再被充分使用，以達到土地永續發展之目的。

我國自土污法公告實施以來，已公告列管 6,515 餘處污染場址，其中約 3,224 多處已成功解除列管，但未解除列管場址仍多達 3,291 多處，其中近 100 處場址可能具有非水相液體（NAPL）污染物存在。為掌握目前污染調查及整治技術發展趨勢，以藉此提升我國對於 NAPL 污染物調查及整治技術能力，及早發現潛在污染，並加速完成污染改善，故藉由本次國際研討會，持續汲取各國先進技術及經驗，作為我國未來污染場址管理之參考依據。此外，我國作為亞洲土水調查整治技術及法規政策管理制度之重要輸出樞紐，有必要持續加強我國與歐美各國間之學術與經驗交流，除可有效增加我國能見度外，亦可促成未來各種國際合作之可能性，建立起任何可行之互惠互助之國際合作機制。

二、過程

本次「2016 年各類有機與無機污染物氧化與還原整治技術進展（2016 Advances in Oxidation and Reduction Technologies for Remediation of DNAPL, LNAPL and Various Organic and Inorganic Contaminants）」國際研討會於美國亞特蘭大舉行，係由 Redox Technologies, Inc.公司主辦，並由美國、加拿大、歐洲及南美洲數個顧問公司及學術單位籌組協會共同協助辦理。會議日期為民國 105 年 11 月 14 日至 105 年 11 月 17 日，為期 4 天。研討會共有 39 篇口頭論文發表，並分為 10 個子題，依不同子題內容於同一會議室內依序進行專題研討，詳細議程請詳見附錄一。本次參與研討會行程如表 1 所示，研討會現場照片如圖 1 所示。10 個子題分別為：

（一）現地及離地化學氧化（In-Situ and Ex-Situ Chemical Oxidation）

（二）現地化學氧化（In-Situ Chemical Oxidation）

（三）DNAPL 調查與處理（DNAPL Characterization and Treatment）

（四）整合性整治技術（Combined Remediation Technologies）

（五）DNAPL 與 LNAPL 之化學氧化與還原技術（Oxidation and Reduction Technologies for DNAPL and LNAPL Treatment）

（六）現地整治之注藥系統（Delivery Systems for In-Situ Remediation）

（七）生物轉換（Biotransformation）

（八）低通水性介質之整治（Remediation in a Low Permeability Media）

（九）場址復原與管理（Site Rehabilitation and Management）

（十）甲烷蒸氣控制技術（Controlling Methanogenesis/Oxidation Technologies）

透過研討會之口頭論文發表可得知目前 NAPL 污染整治及調查技術，大部份我國已普遍使用中，整體而論，國內與國外技術層面相去不甚太遠、無明顯落差。而在應用方面，國內礙於場址數量、常見污染物型態、水文地質狀況及污染行為人經濟狀況等原因，成功案例數量或比例則遠不及國外。以下茲針對國內較少見之技術、整治決策思維或實作案例重點摘要說明如下，詳細論文摘要內容請詳見附錄二。

1. 以整合式微生物與化學氧化反應進行污染物轉換（Combined Microbial-Chemical Redox Reactions for Contaminant Transformation）

   生物整治雖然可有效將污染物降解為無害或較為無害之副產物，但細胞反應過程常需較長時間才能完成，因此，本篇研究係說明生物整治與化學氧化法如何相互搭配使用於有機與無機污染物之整治，以及如何促進不同微生物族群之生長，進而讓目標污染物轉換為較無害之型態。在研究過程中，於實驗室結果可觀察到在微生物經過一段時間馴養後，再透過不同化學氧化機制，可有效促進微生物族群生長，並有效將爆炸性物質、重金屬、類金屬、放射性核種、含氯有機物等污染物進行降解。此外，同樣概念也可使用化學氧化物將污染物優先進行轉換，再透過生物轉換將殘餘之污染物進行降解，但此作法需要較成熟之經驗與技術，以避免抑制生物轉換反應之發生。

2. 最先進與最通用之化學氧化還原技術（State of the Practice versus State of the Art in Chemical Oxidation/Reduction Technologies）

   此篇論文發表之主要目的為目前進行整治時一些常被忽略之盲點，包括理論與實際執行面之差異，以計算藥劑所需總量為例，雖然係以現地數據進行計算，但整治成效仍不如預期，主要原因極可能為地表下優勢水流路徑，導致大部分藥劑都流至某些區域，使得其他區域仍無法改善。此外，本論文另一重點則強調無論何種整治技術，均會經過一定成熟發展的演進模式，包括從一開始的研發，至後面市場上被普遍接受、技術持續成熟穩定，到最後大幅降價及相互競爭。而目前大部分整治技術（例如化學氧化還原技術）發展至今，都已經邁入削價競爭之階段，因此，目前業界多以價錢決定最通用之整治工法，導致整治成效之不確定性上升，最終有可能需要花費更多經費來達到原先設定之整治成效，甚至與最新先進技術（剛完成研發之新技術）所需經費相較不遠。最後，本論文從是否可達到整治目標與整體所需經費等角度，以幾個不同案例說明最先進與最通用技術間之差異性。

3. 放射性核種及無機污染物污染場址之調查與整治執行方式（Characterization and Remediation Approaches for Radionuclide, Inorganic Co-contaminated Subsurface Sites）

位於不飽和層之污染物為持續造成地下水污染之貢獻來源之一，因此，針對此類型之污染源，必須仔細規劃較長期之調查及整治策略。本篇論文以美國一能源部之場址為例，說明該場址早期因廢棄物不當處置，造成未飽和層土壤具有無機、重金屬及放射性物質等污染，再藉由土壤入滲機制，進而造成地下水污染。由於場址污染物種類多且複雜，若採完全整治方案（所有污染物全數整治至管制標準以下），所需經費可能極高，故建議採取多種不同整治方案同時進行之方案，包括 A.監測式自然衰減；B.依據準確之污染物宿命與傳輸模式，並配合基線健康風險評估結果，控制污染物入滲至地下水中之流量與速率，換言之，本場址主要採自然衰減方式，並配合適當之風險管理作為，以最符合經濟效益之方式，達到長期保護場址周遭受體之目的。

4. 巴西里約舊工業區含氯污染場址復原工程（Rehabilitation of Old Industrial Area in Rio de Janeiro, Brazil Contaminated by Chlorinated Compounds）

污染土地開發再利用為近年受到各界極度關注話題之一，如何將位於巴西里約舊工業區內之含氯污染場址快速解列，並完成開發為巴西政府重點工作，因有急需進行開發之需求，故化學氧化法為主要選取之整治工法。該污染場址首先使用界面活性劑（Rentaltech 500®）沖排技術，將土壤中之污染物進行移除，爾後再使用螯合劑（METALDOWN®）與氧化劑（Oxytech®）加速完成污染物之氧化/沉澱反應。整治工程完成後，巴西政府特將場址現況進一步進行分析，由數據結果發現所採用之整合性整治工法成效良好，將 PCE 污染物濃度有效降至管制標準以下，此外，場址殘餘之污染物濃度與各種藥劑經評估後，亦確認不會對人體健康與環境生態產生任何風險危害，依此確認該場址可更進一步進行後續開發行為。

5. 全面且創新之 DNAPL 場址調查與整治指引：最新 ITRC 出版物簡述（Comprehensive and Innovative Guidance for DNAPL Site Characterization and Remediation: Overview of Recent ITRC Products）

美國州際科技及法規委員會（The Interstate Technology & Regulatory Council, ITRC）長期致力於研擬新穎之 DNAPL 污染場址調查、整治或管理相關之技術或規範指引，該單位特別透過本次研討會發表近年最新完成研擬之參考指引：

（1）整合性 DNAPL 污染場址策略：以流程圖方式提供 DNAPL 污染場址管理及污染整治整體架構，從場址概念模式、整治工法評估與選取、到最後整治成效及替代方案評估等。

（2）DNAPL 污染場址調查：主要說明目前運用 DNAPL 污染宿命與傳輸於場址概念模式之最新觀念，包括 DNAPL 基礎特性、DNAPL 生命週期、整合性場址調查方法等，此指引另依據不同調查目的、環境介質、資料品質，提供可供下載之完整工具集與 EXCEL 檔案，以協助選取及評估適當之 DNAPL 場址評估工具與技術。

（3）質量通量與質量釋出估算：此指引彙整質量通量與釋出之基本概念，並說明如何協助於污染場址管理，此外，另說明質量通量與釋出之完整計算方式，以及如何預估實施整治後之相關污染狀況及整治所需時程等。

（4）含氯乙烯類污染物現地生物整治：最後一份指引主要呈現並詳細說明運用現地生物整治法進行含氯乙烯類 DNAPL 污染物整治時之相關技術規範，同時亦說明使用現地生物整治時之優點。

表1　本次參與研討會行程

日　期	工作內容概要
105 年 11 月 12 日	去程，出發至美國亞特蘭大
105 年 11 月 13 日	抵達美國亞特蘭大，辦理研討會報到註冊事宜
105 年 11 月 14 日 ~ 105 年 11 月 17 日	參加「2016 年各類有機與無機污染物先進氧化與還原整治技術」研討會議
105 年 11 月 18 日 ~ 105 年 11 月 19 日	回程，返回台北

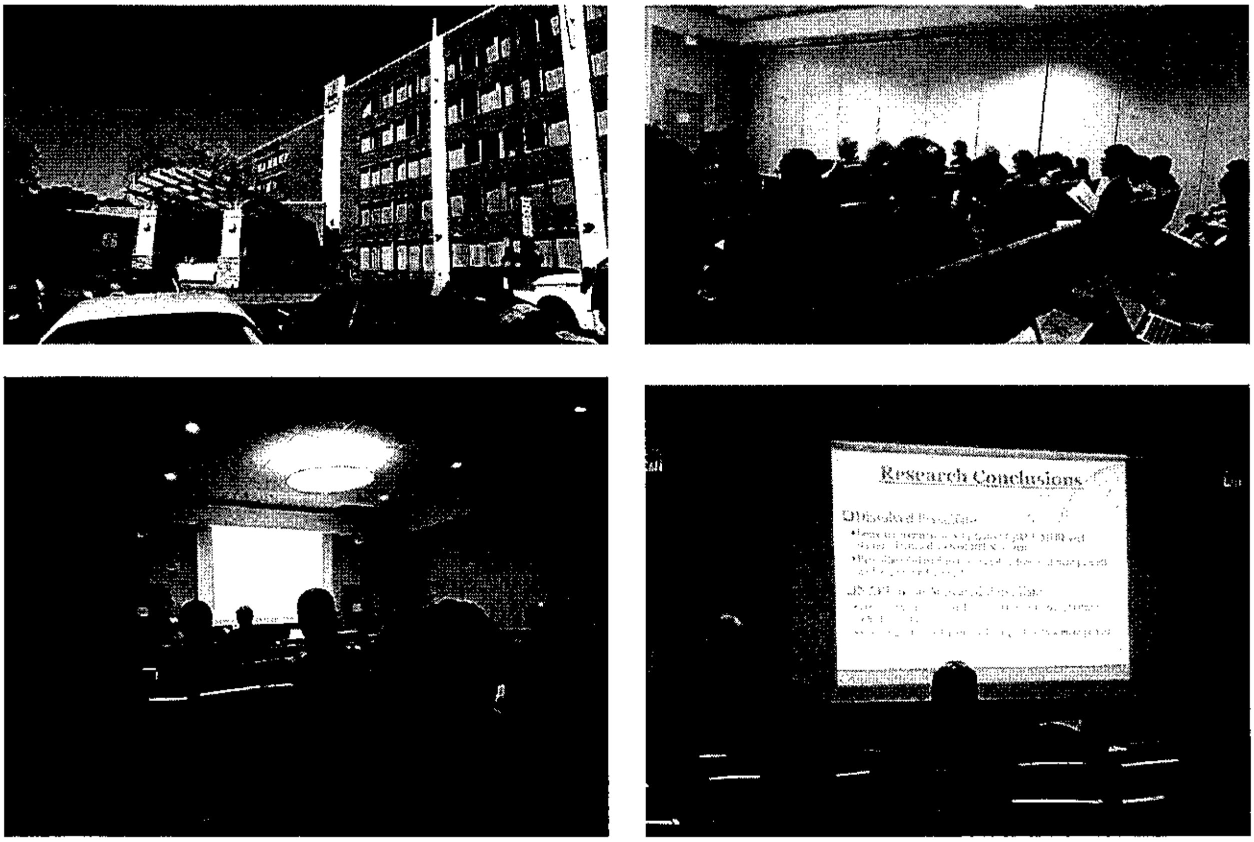

圖1　研討會現場相關照片

三、心得與建議

（一）我國土污法自施行以來，已公告列管約 3,291 餘處污染場址，現階段大多數場址正進行或即將規劃進行污染改善作業，經由本次研討會中，多位專家學者提供之實際案例均可發現，目前業界普遍將經費視為整治方案最關鍵因素，並作為主要規劃依據。此類情形於國內更為常見，多數污染行為人抱著得過且過之心態，僅願花費最少經費讓場址可以順利解列，導致污染改善前應詳細執行之補充調查作業均無仔細執行，就因未完整掌握場址資訊，導致改善工法成效不彰，更嚴重的是讓污染團擴大、污染濃度持續攀升或造成二次污染，最終導致所花費成本遠高於當初所預估。為徹底改善此現象，除應將國外概念與經驗導入國內市場外，主管機關亦應於計畫書審查階段嚴格把關，確認整體經費是否過高或過低，同時，亦應透過不同場合持續教育污染行為人、工程施作單位或工程顧問公司，價錢不是可成功、快速完成整治之主要；亦不是唯一之關鍵決定因素。

（二）污染土地再利用或循環經濟等皆為國內近年來極度被關注之環保議題，而國內許多場址常因污染情形過於嚴重、污染範圍過大或污染改善整體經費過高，使得這些場址之污染改善進度滯礙不前，如何將這些萬年場址解除列管並加速完成開發為目前各界急需努力之重點。環保署雖然已將風險管理相關之污染場址管理策略帶入國內，但民眾對於把污染物留在現場之作法普遍無法接受，一般均認為污染物濃度需處理至管制標準以下，方為可接受之方式，但忽略處理至管理標準以下所需之經費及時間可能遠超出可接受範圍，而多餘的整治行為對環境無形之衝擊亦有可能無法量化，因此，認為國內應持續針對污染場址周界居民，加強教育及宣導有關於國外對於污染場址改善之觀念及方法，如何有效將最佳管理措施（BMP）與永續觀念導入污染場址改善作業，並配合風險管理與風險溝通，以達成保護環境及各生物體之目的，加速完成場址解除以及完成土地再開發。

（三）本次出國主要目的除汲取國外最新技術與工作經驗外，亦希望加強與國外學者或政府機關之交流，藉此宣揚我國長期致力於土壤及地下水污染調查與整治之努力成效。會議期間，主辦單位曾多次表達希望未來可於臺灣辦理類似本次研討會性質之強烈意願，廣邀亞太地區專家學者、政府官員或顧問公司與會，增加多方各界交流之機會。由於臺灣土水技術與法規發展位屬亞太地區較為領先之地位，因此建議我國可持續與主辦單位保持聯繫，爭取合作（或協助牽線國內各產官學單位）辦理此類型大型國際研討會之寶貴機會，一方面增加我國於土水領域之曝光率，另一方面亦可讓我國保有亞太地區土水技術主要輸出樞紐之重要地位，擴大臺灣於亞洲區域之影響力，依此提昇國內產業於土壤及地下水污染整治市場的國際競爭力，並且逐步轉換成為我國進入國際市場之跳板。

附錄一、研討會議程

Session I : *In-Situ* and *Ex-Situ* Chemical Oxidation

Combined Microbial-Chemical Redox Reactions for Contaminant Transformation

Kevin T. Finneran
Clemson University Environmental Engineering
Owner and Principal, Finneran Environmental Consulting

State of the Practice versus State of the Art in Chemical Oxidation / Reduction Technologies

Michael C. Marley
XDD Environmental, USA

Treatment of Emerging Contaminants in Water Reuse Applications

Yiqing Liu[1], Ying Huang[1], Susan D. Richardson[2]and
Dionysios D. Dionysiou[1*]
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Mechanisms of Oxidations by Peroxomonosulfate

Dan Meyerstein
Chemical Sciences Department, Ariel University, Ariel, Israel

Engineering Electrochemical Oxidation Processes for the Removal of Emerging Contaminants

Xiaoyang Meng and John Crittenden
Brook Byer Institute of sustainable system, Georgia Institute of Technology, USA

Chlorine Atom Chemistry within an AOT

Stephen P. Mezyk
California State University, Long Beach, USA

Session II: In-Situ Chemical Oxidation

Development of Novel In Situ Chemical Oxidation (ISCO) Technologies for the Cleanup of Contaminated Soil and Groundwater

Anh Pham
Department of Civil and Environmental Engineering, Carleton, Canada

Use of ZVI Catalyzed Hydroxyl & Sulfate Free Radicals to Address BTEX Contamination via In-Situ Chemical Oxidation Followed by Intrinsic Facultative, Biologically Mediated Processes

Michael Scalzi and Antonis Karachalios
Innovative Environmental Technology, Inc. (IET) Pipersville, Pennsylvania, USA

Using Klozur® KP (Potassium Persulfate) as an Extended Release Oxidant and Permeable Reactive Barrier
Brant A. Smith[1] and Pat Hicks[1], Brianna Desjardins[2] and Sandra Owen[2]
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Trichlorfon Removal from Veterinary Wastewater through Chemical Photooxidation
Rosalina González, Juan P. Merchán, Natalia Sanchez
Department of Environmental and Sanitary Engineering, La Salle University, Bogota, Colombia

Case Study: Treatment of a TCE Plume Using ISCO at an Active Manufacturing Facility in Spartanburg, South Carolina
Ed Hollifield and Jennifer Byrd
Environmental Resources Management, Charlotte, North Carolina, USA

Reactive Transport Modeling: A New Paradigm in Design of ISCO and ISCR Systems
Robert D. Mutch, Jr., and Richard F. Carbonaro
Mutch Associates, LLC, Ramsey, NJ, USA

Session III: DNAPL Characterization and Treatment

Comprehensive and Innovative Guidance for DNAPL Site Characterization and Remediation: Overview of Recent ITRC Products
Ryan Wymore
CDM Smith, USA

Adaptive Long Term Remediation of a Chlorinated Solvents Plume in Georgia
Jennifer Byrd and Ed Hollifield
Environmental Resources Management, Charlotte, North Carolina, USA

Successful Modification of a Poorly Performing Biorecirculation System for DNAPL Source Area Treatment
Kent Sorenson
CDM Smith, USA

Surprising Efficacy of "Sipping" Heavy DNAPL without Disturbing Formations, Using Low-Flow Positive-Displacement Piston Pumps
Mark Bertane
Blackhawk Technology Company, USA

Innovative Surfactant System Formulations for LNAPL Recovery
Mark Kluger[1], Jeffrey H. Harwell[2], Mark Hasegawa[3], Gary Birk[4] and David Alden[4]
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[2]University of Oklahoma, Norman, OK, USA
[3]Hasegawa Engineering, Lethbridge AB, Canada
[4]Tersus Environmental, Wake Forest, NC, USA

Session IV: Combined Remediation Technologies

Reducing Treatment Costs by Optimizing a Combined Remedy using Traditional Techniques and High-Resolution Site Characterization
Shanna Thompson[1], Andrew Montgomery[1], Whitney Law[1], John Jenkins[2] and Carol King[2]
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Safer, More Effective ISCO Remedial Actions using Non-Extreme Persulfate Activation plus Sustained Secondary Biotreatment
Jim Mueller, Matt Geary and Greg Booth
Provectus Environmental Products, Inc.

Dual Anaerobic-Aerobic Cultures Bioaugmented on GAC for Treatment of Chlorinated Benzenes in Contaminated Groundwater and Sediments
Michelle M. Lorah[1], Emily H. Majcher[1], Denise M. Akob[2], Edward J. Bouwer[3], Steven Chow[3], Neal Durant[4], and Amar Wadhawan[4]
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[2]U.S. Geological Survey, Reston, Virginia, USA
[3]Johns Hopkins University, Baltimore, Maryland, USA
[4]Geosyntec Consultants, Columbia, Maryland, USA

Multi-Component Treatment Strategy for Chlorinated Ethene and Chlorinated Benzene DNAPL Source Area
Ryan Wymore
CDM Smith, USA

Field Demonstration of Vadose 1,4-Dioxane Remediation by Extrême Soil Vapor Extraction (XSVE)

Isabel Green[1], Rob Hinchee[2], David Burris[3], Kimiye Touchi[4] and Paul Dahlen[5]
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[3]IST, Panama City, FL USA
[4]AECOM, Sacramento, CA USA
[5]ASU, Tempe, AZ USA

Session V: Oxidation and Reduction Technologies for DNAPL and LNAPL Treatment

Using the Availability of Natural Organic Carbon as a Metric for Selecting Oxidative or Reductive Remedies for DNAPL and LNAPL Cleanup

Francis H. Chapelle[1] and Mark A. Widdowson[2]
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[2]Derpatment of Civil and Environmental Engineering, Virginia Tech, USA

Four Years of Chemical Reduction to Achieve Treatment Standards for Carbon Tetrachloride/Chloroform at an Industrial Site in Brazil

Jack Sheldon
Antea Group, West Des Moines, IA, USA

Enabling NAPL Removal using Surfactants and Hydrogen Peroxide

Geeta Dahal, Dan Socci and Jen Holcomb
EthicalChem, USA

Session VI: Delivery Systems for In-Situ Remediation

Gravity Feed Delivery of Oxidant to a Dilute PCP Plume

Jennifer Byrd and Greg Jirak
Environmental Resources Management, Atlanta, Georgia, USA

Highly Successful ERD Pilot Evaluation Utilizing a Simple Additive Delivery Approach

Kent C. Armstrong[1] and Jim Romeo[2]
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[2]ITB, Inc., Merritt Island, Florida, USA

Highly Successful ERD Pilot via Simple Additive Delivery System Lead to Full-Scale Biostimulation Strategy for Destruction of Residual cVOCs
Kent C. Armstrong[1] and Geoff Bell[2]
[1]BioStryke Remediation Products LLC, Andover New Hampshire, USA
[2]G2S Environmental, Inc. Burlington, Ontario, Canada

Session VII: Biotransformation

Biogeophysical Analysis of Hexavalent Chromium Biotransformation: Column Studies
Brady Lee, Kayla Johnson, Jonathan Thomle, Timothy Johnson,
Edmundo Pacencia-Gomez and M. Hope Lee
Pacific Northwest National Laboratory, Richland, WA, USA

Successful On-Site Treatability Study Evaluating Feasibility of Biostimulation to Enhance Microbial Degradation of 1,3,5-Trimethylbenzene Under Anaerobic Conditions
Kent C Armstrong[1] and Cynthia L. Cason[2]
[1]TerraStryke Products LLC, Andover NH, USA
[2]ET Technologies, Parker CO, USA

Optimization-Based Monitoring of a Fluidized Bed Biofilm Reactor Operated as Part of the 200 West Area Pump and Treat Facility at the Hanford Site
Brady D. Lee, Elsa A. Cordova, Sabrina D. Saurey, Danielle Saunders,
Emalee E. Eisenhauer, Mark A. Carlson, and M. Hope Lee
Pacific Northwest National Laboratory, Richland, WA, USA

Session VIII: Remediation in a Low Permeability Media

A Rigorous Demonstration of Permeability Enhancement Technology for In Situ Remediation of Low Permeability Media
Kent Sorenson
CDM Smith, USA

Pilot Study - Reductive Dechlorination Results Review
W. Russell Kestle, Jr.
Superfund Resoration and Sustainability Section, Superfund Division, Atlanta, Georgia, USA

Session IX: Site Rehabilitation and Management

In Situ Geochemical Immobilization Technology for DNAPL Management

Jim Mueller[1], Jim Erickson[2], Mike Slenska[3], and Mitchell Brourman[3]
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[2]TetraTech, USA
[3]Beazer East, Inc., USA

Rehabilitation of Old Industrial Area in Rio de Janeiro / Brazil Contaminated by Chlorinated Compounds

Marcos Sillos, Silvia C. Nascimento, Antonio Passarelli,
Raphael G.R.Oliveira and Samuel B. De Souza
VALGO, Brazil

Characterization and Remediation Approaches for Radionuclide, Inorganic Co-contaminated Subsurface Sites

Hope Lee, Mike Truex, Brady Lee
Pacific Northwest National Laboratory, Richland, WA USA

Session X : Controlling Methanogenesis / Oxidation Technologies

Reasons and Technology for Controlling Excessive Methanogenesis during Remedial Actions: Case Studies and Remedial Alternatives

Jim Mueller, Matt Geary and Greg Booth
Provectus Environmental Products Inc, USA

Supercritical Water Oxidation of Toxic Waste Generated in Academic Veterinary Practices

Rosalina González, Paula Cárdenas, Andrea Landinez
Department of Environmental and Sanitary Engineering, La Salle University, Bogota, Colombia

Fenton and Photo-Fenton Technologies Modified with Tartaric Acid for the Treatment of the Wastewaters from a Urea-Formaldehyde Resin Production Process

Jessica Gordón-Tulcán, Jady Pérez, William Villacís and Florinella Muñoz
Laboratorio de Aguas y Microbiología, Departamento de Ciencias Nucleares, Facultad de Ingeniería Química y Agroindustria, Escuela Politécnica Nacional, Quito, Ecuador

附錄二、研討會論文摘要全集

Sesssion I: In-Situ and Ex-Situ Chemical Oxidation

Combined Microbial-Chemical Redox Reactions for Contaminant Transformation

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Owner and Principal, Finneran Environmental Consulting
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Bioremediation has generally been predicated on stimulating strictly microbial reactions, in which the cells must directly interact with the contaminant(s) to transform it. While this can be effective and efficient, there are times when direct cellular interactions are slow, incomplete, or completely impossible. We have been investigating combined microbial-chemical reactions for both organic and inorganic contaminants, and how to best promote different microbial populations for increasing the rate and extent of attenuation. One effective approach has been microbially mediated reactions, which promote secondary chemical reactions that transform contaminants of concern. This has been particularly effective with explosives, energetics, and metals/metalloids. The cells reduce electron acceptors including Fe(III) or reducible natural organic matter (humic substances), and the reduced Fe(II) or humic material chemically transfers electrons to molecules such as the cyclic nitramines explosives (e.g. RDX and HMX), aromatic explosives (e.g. dinitroanisole), metals (e.g. Cr(VI)), and metalloids (e.g. arsenate). This process has been referred to as extracellular electron shuttling, but in reality is more of an understanding of how electron transfer takes place within contaminated water/solid environments. We will discuss new approaches in this technology including electron transfer via activated carbon. An alternative approach is when chemical treatment precedes microbial treatment, such as when chemical oxidants or reductants are applied for contaminant transformation, and microbial activity is then promoted to degrade residual contamination. This strategy requires finesse as not to inhibit secondary microbial reactions, once the chemical treatment has been applied. Finally, these microbial-chemical interactions have led to a greater understanding of the dynamics amongst disparate microbial populations, including the *Dehalococcoides* like microbes and Fe(III)-reducing microbes. We will discuss how to simultaneously promote these populations for accelerating chlorinating solvent remediation.

State of the Practice versus State of the Art in Chemical Oxidation / Reduction Technologies

Michael C. Marley
XDD Environmental, USA

Through practising in the development, design and implementation of remediation technologies from the early 1980's, there has been a noticeable cyclical pattern in the maturation of the technologies. From soil vapor extraction, through sparging, bioremediation, chemical oxidization and reduction, pressures to provide these technologies to the market quickly and at the lowest possible cost have resulted in a broad range in the state of the practice. Additionally, for the most part, short-term economic considerations result in the state of the practice plateauing well below the level of the state of the art.

For technologies such as soil vapor extraction and sparging, initial success is evident; however, it can take years of operation before system failure to meet remedial goals or system design limitations come to light. For other technologies such as chemical oxidation and reduction, the failures and limitations are more likely to present themselves in the near-term.

The purpose of this presentation will be to highlight this pattern in the cycle of technology development / maturation for chemical oxidation / reduction. Again, pressure in the industry for low cost solutions is a major driver in the state of the practice. With the low cost driver, uncertainties associated with reaching the desired remedial goals can be high. This approach ultimately can result in higher cost to meet the remedial goals due to multiple remedy applications and evaluations, than may be achieved using a state of the art approach. Case studies will be used to illustrate the difference between state of the practice and state of the art with respect to meeting remedial goals, and ultimately cost.

Treatment of Emerging Contaminants in Water Reuse Applications

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A major issue with water reuse is that most of the chemicals presented in wastewater cannot be efficiently removed by conventional treatment. Those untreated compounds, such as pharmaceuticals, pesticides, hormones, and musks, can enter ecosystem or drinking water supplies, which may have detrimental impacts on human health. This study aimed to apply UV based-advanced oxidation processes (AOPs) to simultaneously degrade seven emerging contaminants (ECs), including diclofenac (DCF), triclosan (TCS), estrone (E1), 17β-estradiol (E2), 17α-ethinyl estradiol (EE2), bisphenol A (BPA), and ibuprofen (IBP). UV-C alone, low-pressure (LP)-UV/H_2O_2 and mercury-free light-emitting diode (LED)-UV/H_2O_2 were evaluated and compared for the destruction of these target pollutants. In addition, the influence of initial concentration of H_2O_2, common anions (e.g., Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-), pH and natural organic matter (NOM) on the degradation of DCF and TCS by LP-UV/H_2O_2 was explored. The degradation kinetics of DCF and TCS were inhibited in real water samples. Structural destruction of DCF and TCS were then further evaluated by total organic carbon (TOC) and LC/MS/MS studies.

Preliminary controlled laboratory chlorination/bromination reactions were done on these ECs and some of their transformation products were identified via high resolution accurate mass liquid chromatography tandem mass spectrometry (LC-MS/MS) and high resolution accurate mass gas chromatography mass spectrometry (GC-MS). Chlorine- and bromine-containing by-products were identified from several ECs. Results from these studies will be presented.

Mechanisms of Oxidations by Peroxomonosulfate

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Peroxomonosulfate, HSO_5^-, is commonly used in a variety of advanced oxidation processes. However, the detailed mechanisms of its reaction with transition metal complexes was not reported. It is commonly assumed that these processes are initiated by the reaction

(1) $M^{II}(H_2O)_6^{2+} + HSO_5^- \rightarrow M^{III}(H_2O)_6^{3+} + SO_4^{\cdot -} + OH^-$.

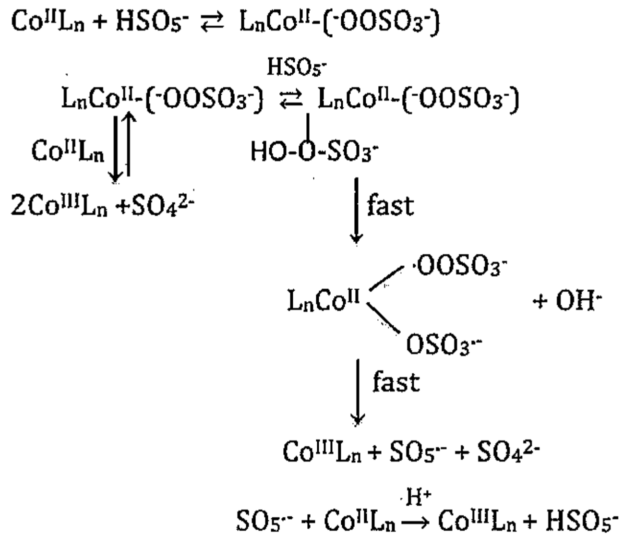
which is followed by:

(2) $M^{II}(H_2O)_6^{2+} + SO_4^{\cdot -} \rightarrow M^{III}(H_2O)_6^{3+} + SO_4^{2-}$

and by:

(3) $M^{III}(H_2O)_6^{3+} + HSO_5^- \rightarrow M^{II}(H_2O)_6^{2+} + SO_5^{\cdot -} + H^+$

The latter reaction does not occur for M = Fe as $E°(SO_5^{\cdot -}/HSO_5^-) = 1.1$ V.
Reaction (1) is endothermic for M = Co. However, in the presence of the ligands L, $L = P_2O_7^{4-}$; $P_3O_{10}^{5-}$ and ATP^{4-}, which stabilize $Co^{III}L_n$ the reaction is considerably more complex and proceeds via the following mechanism:



This mechanism proofs that the AOPs processes are considerably more complex than usually assumed.

Engineering Electrochemical Oxidation Processes for the Removal of Emerging Contaminants

Xiaoyang Meng and John Crittenden
Brook Byer Institute of sustainable system, Georgia Institute of Technology, USA

Electrochemical oxidation has been proposed as a sustainable wastewater treatment technology to remove emerging contaminants in aqueous phase. But it is hampered by high electrode fabrication cost, high energy consumption, anode fouling and low oxidation efficiency. Moreover, mass transfer limitation is another significant drawback for electrochemical oxidation in pilot scale applications. Therefore, it is important to make electrodes with high oxidation efficiency and investigate the impacts of mass transfer when fabricated electrodes are used in real type of reactors (e.g. plug flow reactor). In this work, we show a methodology of using band gap engineering to fabricate anodes. Our anode namely TiO_2 based SnO_2/Sb-polytetrafluoroethylene resin (FR)-PbO_2 is capable to generate powerful oxidant hydroxyl radical effectively. These electrophilic hydroxyl radicals can react with organic contaminants non-selectively and eventually mineralize them to CO_2 and H_2O. We also present a rational method for determining how much mass transfer influence destruction rate under different operational conditions in chosen type of reactor. The impact of mass transfer is quantified by deriving an effectiveness factor Ω. This effectiveness factor would allow us to predict observed destruction rate for different electrodes installed with different operational conditions, from bench scale to pilot scale.

Chlorine Atom Chemistry within an AOT

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Quantitative and cost-effective removal of all traces of residual pharmaceutical contaminants is essential before direct potable reuse of wastewater can be achieved. However, conventional wastewater primary and secondary water treatments that depend upon adsorptive and chemical-physical processes have been demonstrated to not be sufficient, and therefore additional treatment using radical-based advanced oxidation based technologies (AOTs) are now being considered. Most AOTs utilize the hydroxyl radical ($HO^\bullet$), as their primary oxidizer, this radical can be created using a variety of techniques including combinations of O_3/H_2O_2, O_3/UV-C, and H_2O_2/UV-C. Other AOTs include the light irradiation of titanium dioxide, sonolysis, or the irradiation of water via electron beams or γ rays produce a mixture of oxidizing hydroxyl and reducing (e.g. hydrated electron (e_{aq}^-) or hydrogen atoms ($H^\bullet$)) radicals.

The $HO^\bullet$ radical is very powerful oxidant and will non-selectively react with all organics. This results in its overall contaminant removal efficiency being significantly reduced by the presence of much higher levels of other water constituents, such as dissolved organic matter (DOM) and carbonate. Dissolved oxygen in the water will react with any AOT produced reducing species. Moreover, the deliberate addition of chemicals such as bleach (NaOCl) into the treatment train can generate anti-fouling species such as chloramines (NH_xCl_y) which can also interfere with the AOT efficiency through direct absorption of UV-light or scavenging of $HO^\bullet$ radicals. However, one mitigating factor for UV-based AOTs is that they can generate chlorine atoms ($Cl^\bullet$), by photolysis of both free chlorine (HOCl) and chloramines. Chlorine atoms are also oxidizing, and thus could assist with the $HO^\bullet$ removal of chemical contaminants. While this is a promising enhancement in the AOT treatment methodology the effectiveness of the $Cl^\bullet$ reactions must be fully established at the benchtop before its use at large scale. Both kinetics and reaction mechanisms are required to determine their effectiveness.

In recent studies we have performed electron pulse radiolysis measurements to determine reaction rate constants for $Cl^\bullet$ with a large number of DOM fractions, regular wastewater constituents, plus typical pharmaceutical contaminants such as antibiotics, estrogenic steroids, and nitrosamines. Reaction rate constants for only DOM were found to be about an order of magnitude slower than determined for the analogous $HO^\bullet$ radical reactions. The $Cl^\bullet$ radical's reactivity for contaminant pharmaceuticals varied over several orders of magnitude, but again overall was lower than for $HO^\bullet$. All these findings will be discussed, along with their predicted impact in real-world waters.

Session II: In-Situ Chemical Oxidation

Development of Novel In-Situ Chemical Oxidation (ISCO) Technologies for the Cleanup of Contaminated Soil and Groundwater

Anh Pham
Department of Civil and Environmental Engineering, Carleton

In Situ Chemical Oxidation (ISCO) is being increasingly used as a means of cleaning up contaminated soil and groundwater. In this remedial practice, strong oxidants such as hydrogen peroxide (H_2O_2) and persulfates ($Na_2S_2O_8$ and $NaHSO_5$) are injected into the subsurface to initiate radical reactions that can transform contaminants into less toxic/benign byproducts. The success of ISCO depends on a number of factors, including (1) the yield of radical species (i.e., hydroxyl and persulfate radicals) from the injected oxidants, and (2) the proper delivery of oxidants to the subsurface location where the contaminants exist.

This talk discusses some of our recent findings on the efficacy of the hydrogen peroxide- and persulfates-based ISCO, and approaches that potentially can improve the performance of these technologies in the field. The kinetics, efficiency, and mechanism of contaminant oxidation by H_2O_2, $Na_2S_2O_8$, and $NaHSO_5$ under different remediation scenarios are compared. A novel approach that can enhance the delivery and activation of persulfates is presented.

Use of ZVI Catalyzed Hydroxyl & Sulfate Free Radicals to Address BTEX Contamination via In-Situ Chemical Oxidation Followed by Intrinsic Facultative, Biologically Mediated Processes

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In situ chemical oxidation via zero valent iron activated sodium persulfate and hydrogen peroxide has been used in numerous sites across the country. Two specific sites are discussed specifically where the objective was to reduce the concentration of volatile organic compounds (VOCs) such as BTEX and trimethylbenzene in soil and groundwater. The first site was a former gasoline service station located in St. Augustine, Florida and the second site was a former gas station located in Clinton, New York.

The remedial design that was implemented in both sites managed to initial oxidize the targeted contaminants and then promote facultative biodegradation in the subsurface. The introduction of a unique mixture of hydroxyl, peroxyl and sulfate free radicals allows for both Fenton-like reactions and long-lived sulfate free radical oxidation. These reactions extend the oxidant and free radical residual, and further stimulate the biological mineralization of the petroleum compounds. Through the use of the oxidation byproducts, iron and sulfate, biological mineralization proceeds following the oxidation event. The sulfate ion produced as a consequence of the decomposition of the persulfate allows for the attenuation of the targeted contaminants under sulfate reducing conditions. In addition, the iron present in the subsurface provides terminal electron acceptors for continued biological mineralization.

Both remedial designs were implemented by Innovative Environmental Technologies, Inc. The injection in St. Augustine, Fl was performed in April 2008 and the one in Clinton, NY in October 2009. The three targeted wells in St. Augustine, Fl showed BTEX concentration decreases of 74%, 95% and 91% respectively, 12 months after the completion of the injection event. The site in Clinton, NY recorded a total decrease of 79% in BTEX concentrations, 17 months after the implementation of the remedial design. Compounds that are more readily biodegraded, such as xylene, readily disappeared and compounds that are more recalcitrant, such as benzene, were degraded at high rates and eventually disappeared. In Clinton, NY, trimethylbenzene compounds were targeted by the remedial design and were successfully reduced to standard within 12 months of the remedial event. Both sites have since received notices of "no further action".

Using Klozur® KP (Potassium Persulfate) as an Extended Release Oxidant and Permeable Reactive Barrier

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Klozur® KP is based upon the potassium persulfate molecule and is a new product to the environmental industry. Historically, environmental applications of persulfate have been based upon sodium persulfate (Klozur SP). Potassium persulfate releases the same remediation potential (persulfate anion) as sodium persulfate but has several different key characteristics that are beneficial for specific situations. Klozur KP has a theoretical solubility that is over an order of magnitude lower than sodium persulfate and the use of the potassium salt which would be beneficial at a limited number of sites that have regulatory guidance on sodium (Na) concentrations in groundwater.

This presentation will provide an update as to the application of potassium persulfate including the latest available bench and field applications. This will include column studies comparing the rate of release of the persulfate anion from Klozur KP and Klozur SP, longevity of solid state oxidant and destruction of common aqueous phase contaminants such as 1,4-dioxane and MTBE. The residence time required to treat each compound will also be discussed. The existing column study data show treatment of both 1,4-dioxane and MTBE to non-detect, a sustained consistent release rate of the persulfate anion and other key characteristics that can be used by design engineers and implementers for a variety of site specific applications.

Trichlorfon Removal from Veterinary Wastewater through Chemical Photooxidation

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It was found that veterinary places in Bogota city are discharging wastewater from the healthcare of pets without any control and/or treatment. This can cause health problems for presence of substances of health interest as anti-parasitic containing highly toxic active substances. To identify this, many surveys were conducted and it was found that Trichlorfon is frequently used (LC_{50} = 0.49 mg L^{-1} using Bocachico fingerlings as bio-indicator). Due this, it was decided to apply the technique of photo-oxidative destruction to remove this chemical because it is useful in this type of contaminants. To do that, a reactor of 6L was built and the Hydrogen Peroxide was selected as oxidizer. The initial concentration of Trichlorfon was around 700 mg L^{-1} of TOC (Total organic Carbon) and the best result obtained was 27 mg L^{-1} of TOC showing an effectiveness in the removal of this compound (96%). In addition, with this result the environmental law is fulfilled. This evidenced that is highly effective in removing organic material and the possibility of its use in any veterinary facility.

Key Words: Photooxidation, Wastewater, trichlorfon Organophosphate

Case Study: Treatment of a TCE Plume Using ISCO at an Active Manufacturing Facility in Spartanburg, South Carolina

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Background and Objectives. A Chlorinated Volatile Organic Compound (CVOC) plume originating from former degreasing operations extends over approximately 7 acres on-site at an active manufacturing facility in Spartanburg. South Carolina. The primary groundwater contaminant is Trichloroethene (TCE) with elevated concentrations near source areas (former degreaser and waste disposal areas) in the western section of the facility and extending west and off-site. The Site is located in the Inner Piedmont of the Piedmont Physiographic province of South Carolina, which is characterized by metamorphic and igneous rocks of varying age overlain in the uplands by saprolitic silty to clayey soils derived by weathered and variably decomposed bedrock. The three main piedmont aquifer zones generally encountered in the Piedmont are present at the site including the saprolite, partially weathered rock (PWR) and bedrock aquifer zones. CVOC groundwater contamination is present in each of the aquifer zones with the highest concentrations detected in the PWR zone. After completion of a remedial alternatives analysis, an in-situ chemical oxidation (ISCO) was selected as the primary technology used for groundwater treatment.

Approach and Activities. The corrective action approach utilized ISCO to remediate the CVOC affected saprolite, PWR and shallow bedrock aquifer zones from the source areas of the site to the western property boundary. ISCO treatment method consisted of two full rounds of sodium permanganate (NaMnO4) injection into the saprolite aquifer zone utilizing direct-push injection points (DPT). The initial injection was conducted in 2008 and used NaMnO4 delivered to the site utilizing 72 DPT points to deliver approximately 16,000 gallons of 5% sodium permanganate solution. Injection points were installed on 20-foot grid spicing, given an estimated radius of injection of 10 feet. Oxidant injection was accomplished by using DPT to advance an injection point to multiple discrete vertical intervals within the saturated surficial aquifer zones to depths ranging from approximately 27 to 55 feet below land surface (ft bls). This approach facilitated vertical distribution of oxidant through the saturated zone. The NaMnO4 solution has a specific gravity of approximately 1.1, and thus was expected to migrate vertically downward over time, allowing for treatment within the deeper PWR aquifer and the PWR / bedrock transition zone and shallow bedrock. A second full scale injection replicating the initial activities was conducted in June 2013 with post treatment monitoring since that time.

Results. CVOC concentrations in the historically most impacted on-site source areas have been treated with results of approximately 90 to100% reduction in contaminants since the last injection. CVOC concentrations in the on-site well cluster immediately downgradient of the ISCO treatment area shows an approximately 90 to 95% decrease in CVOC concentrations, further evidence that the site is effectively being treated using ISCO. No significant rebounding of site contaminants has been observed during the course of this treatment which is generally atypical of ISCO treatment in the upland Piedmont geology of South Carolina.

Reactive Transport Modeling: A New Paradigm in Design of ISCO and ISCR Systems

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Application of three-dimensional, numerical, reactive transport modeling is emerging, we believe, as a new paradigm in the design process of in situ treatment systems. Its rapid emergence as a design tool is reminiscent of the paradigm that began to appear in the early 1980s when use of numerical groundwater flow modeling started to become standard practice in the design of groundwater extraction systems (despite the now apparent limitations in software and hardware at the time). In the last few years, reactive transport modeling has been applied with great success to evaluation and design of in situ chemical oxidation (ISCO) and in situ chemical reduction (ISCR) systems. Experience has shown that it can help optimize the performance of ISCO and ISCR remedies, reduce the risk of outright failure, and save overall costs. A reactive transport model is built upon the foundation of a three-dimensional groundwater flow model and includes the ability to model the chemical interactions between injected chemicals and the contaminants of concern; between the injected chemicals and the aquifer skeleton; and other subsidiary reactions, such as the generation of Cr(VI) by ISCO systems. As with any numerical model, best results are obtained when the model is calibrated to laboratory and field data. Several case studies will be described where three-dimensional, reactive transport models were instrumental in the evaluation and design of full-scale ISCR and ISCO systems.

Session III: DNAPL Characterization and Treatment

Comprehensive and Innovative Guidance for DNAPL Site Characterization and Remediation: Overview of Recent ITRC Products

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Over the past several years, the Interstate Technology and Regulatory Council (ITRC) had developed cutting edge technical and regulatory guidance for characterization, remediation, and management of sites contaminated with Dense Non-Aqueous Phase Liquids (DNAPLs). Specifically, the ITRC has produced four guidance documents that will be presented:

- Integrated DNAPL Site Strategy: This guidance presents a framework for managing and remediating sites contaminated with DNAPL. The approach, structured as an iterative flowchart, includes emphasis on developing a comprehensive Conceptual Site Model (CSM), creating SMART objectives, appropriately applying and evaluating remedial technologies, and re-evaluating the remedy and modifying the approach as necessary.
- DNAPL Site Characterization: This guidance builds on the CSM component of the IDSS by introducing new concepts that are the foundation of current understanding of contaminant fate and transport at DNAPL sites. Concepts presented include fundamentals of DNAPL characteristics, the DNAPL life cycle, the 14 compartment model, and a new Integrated Site Characterization process. In addition, this guidance includes a stand-alone, comprehensive matrix that describes tools and techniques available for characterizing DNAPL sites. This Tools Table contains more than one hundred tools and is a downloadable Excel file that is segregated into categories and subcategories based on the characterization objective (geology, hydrogeology, or chemistry), type of media (unconsolidated or bedrock, saturated or unsaturated), and data quality (quantitative, semi-quantitative, qualitative).
- Measurement and Use of Mass Flux and Mass Discharge: This guidance summarizes the basic concepts of mass flux and mass discharge and describes how this information can improve the management of contaminated sites. The ITRC guidance includes a comprehensive presentation of the primary measurement and estimation techniques, including advantages and disadvantages of each. In addition, several case studies are presented as examples of applications of mass flux and mass discharge. These measurements can be helpful for predicting post-treatment plume conditions and remediation timeframes, as well for establishing measurable interim remedial action objectives to allow transitioning to less costly treatment strategies.
- In Situ Bioremediation of Chlorinated Ethenes: DNAPL Source Zones: This final ITRC document on DNAPLs presents technical and regulatory guidance for application of in situ bioremediation (ISB) in chlorinated ethene DNAPL source zones. ISB has several advantages compared to other technologies when applied in source zone because of two primary factors: 1) enhanced dissolution and/or desorption of nonaqueous- and/or sorbed-phase contaminant mass and 2) biological degradation to nontoxic end products. The ability of ISB to enhance the dissolution and desorption of nonaqueous-phase contaminants to the aqueous phase, where they can be degraded by the microbial population, is what makes the ISB technology applicable to DNAPL source zones. This typically results in faster remediation compared to traditional technologies that are limited by the NAPL dissolution rate (i.e., groundwater extraction).

Adaptive Long Term Remediation of a Chlorinated Solvents Plume in Georgia

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Background and Objectives. Chlorinated solvent impacts to groundwater were identified in 1991 at a former manufacturing facility in Georgia. Between 1992 and 1999 over 50 soil samples were collected to identify source areas and 80 groundwater monitoring wells were installed for horizontal and vertical delineation of the groundwater plume. Assessment results confirmed no presence of residual unsaturated soil contamination. Based on the groundwater data, two source areas were identified (the former dip tank area and the septic tank area). The remediation strategy for the site focused on source depletion, followed by treatment of the downgradient plume, as necessary.

Remediation activities began in 2002 with an ISCO pilot test utilizing potassium permanganate in the former dip tank area. Full scale ISCO injection of permanganate, which focused oxidant delivery to the two identified source areas via permanent injection wells, began in 2003. Annual ISCO injections were conducted between 2003 and 2010 resulting in the delivery of 266,700 gallons of oxidant solution to the two identified source areas.

In 2008, a soil vapor extraction (SVE) system was installed to reduce mass flux to groundwater by treating the capillary fringe. As with the ISCO injection program, the SVE system focused on treatment of the two source areas. Between 2008 and 2012, a total of 608 pounds of VOCs were removed from the subsurface by the SVE system.

Anaerobic bioremediation was selected as a potential remedy for the more dilute downgradient portion of the plume. The first pilot test injection was conducted in 2011. Contaminant concentrations in the bioremediation pilot test area wells were an order of magnitude higher than expected.

Approach and Activities. Due partially to the unexpectedly high contaminant concentrations in the downgradient bioremediation pilot test area, a detailed review of the site history was conducted in 2012 to refine the site conceptual model (SCM) and, based on the refined SCM, revise the site remediation plan. A detailed review of site assessment data and historic sources resulted in the identification of several data gaps and potential secondary source areas. Chemical speciation analysis and 3D modeling provided evidence that the 1,500 foot long groundwater plume extending from the site was likely the result of several small spills as opposed to releases from two large distinct source areas as previously thought. Rebound of source area contaminant concentrations, formerly attributed to matrix diffusion, may have been the result of contaminant flux from previously unidentified secondary source areas. In addition, the existing remediation system infrastructure was no longer in the areas with the highest contaminant concentrations.

Results. Additional site investigation activities conducted in October 2012 confirmed the presence of several secondary source areas. Based on the site investigation results, the source area ISCO injection strategy was modified and the August 2013 injection event focused on oxidant delivery to the newly identified secondary source areas. In addition, several new groundwater monitoring wells were installed throughout the footprint of the plume to refine the preferential flow paths migrating from the newly identified source areas. The data provided by the new wells identified a long narrow preferential flow path extending from the site. The revised off-site remediation strategy focuses on addressing the preferential flow path which greatly reduces the area requiring active remediation.

Lessons Learned from Successful Modification of a Poorly Performing Biorecirculation Pilot

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Background/Objectives. Combining recirculation and bioremediation can be a highly effective way to accelerate cleanup of impacted source zones in groundwater. A combined bioremediation and recirculation pilot study was recently performed at an industrial site in Southern California to evaluate the ability to reduce source TCE mass in a semi-confined aquifer. The pilot study was met with multiple challenges including permitting delays with the local agency, biofouling, proper amendment selection, and re-injection strategy.

Approach/Activities. In order to evaluate the efficacy of bioremediation to treat TCE in groundwater with concentrations in excess of 100 mg/L (indicating a high likelihood of the presence of dense nonaqueous phase liquid), a pilot study was conducted using combined recirculation and bioremediation. Initially, extracted groundwater was constantly amended with emulsified vegetable oil (EVO) and reinjected to enhance reducing conditions within the study area. After this method failed, a revised strategy was implemented using sodium lactate as the amendment, pulsing the amendment during recirculation, and bioaugmenting once geochemical conditions would promote *Dehalococcoides* growth.

Results/Lessons Learned. Following the initial phase of the pilot study (constant EVO addition), TCE was quickly converted to cis-1,2-DCE but further dechlorination was not observed. Additionally, the performance of the injection well decreased significantly over the course of a few months. After working closely with the local agency, the new injection method was adopted by intermittently pulsing sodium lactate into the constant recirculation stream. Frequent measurement of TOC and geochemical conditions were used to determine that bioaugmentation could be performed after only 1½ months following restarting the system. Within 5 months of bioaugmentation, TCE concentrations of over 100 mg/L were completely converted to ethene (>99.9% reduction of chlorinated ethenes) throughout the monitoring network, including cross-gradient wells 30-40 feet away from the recirculation line. In addition, the biofouling observed during the initial pilot testing was largely avoided. Over 6 months after shutting down the recirculation system, results indicate that desorption of TCE has not impacted groundwater concentrations and the 99.9% reduction has been sustained. Based on these remarkable results, a full-scale system is now being designed for the facility.

Surprising Efficacy of "Sipping" Heavy DNAPL without Disturbing Formations, Using Low-Flow Positive-Displacement Piston Pumps

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Remediation pumping of DNAPL product prone to subsurface migration, such as coal tar, creosote, No. 6 fuel oil and other heavy hydrocarbons, typically extracts a magnitude percentage of effluent compared with a small amount of the actual contaminant product.

Transporting and treating the effluent is often difficult and expensive with little to show for the effort.

Instead of increasing pump flows to boost recovery, or backing off the effort in frustration, several remediation sites have gone in another direction. They are opting to use small, low-flow piston pumps to "sip" heavy DNAPL from the formations in which it resides, extracting far higher percentages of product vs water per stroke, significantly reducing costs of operation, energy, transportation and treatment, and successfully reducing plumes.

This presentation will present results from three representative case studies and demonstrate the simple technologies of positive-displacement piston pumps, including power sources of pneumatic air, solar and grid electricity.

Case Study #1 – Midwestern U.S. municipal park

For many years, coal tar from an old utility company has been collecting in a bedrock depression 50 feet below the park's grass. The weight of the underground pond has been forcing tar into smaller bedrock fissures.

As a test, two top-head-drive piston pumps began sipping a cup of tar each twice an hour, six gallons a day. Because of the tar's high viscosity, shallow groundwater contaminated by lighter oil also collected in the underground pool above the tar. The site's ongoing recovery goal is to remove tar and oil but not groundwater. The tactical challenge addressed by the test was to bring up the product without roiling the formation.

The successful multi-month test, monitored by transducers, demonstrated the necessity of low-flow pumping in this application and the viability of piston pumps to handle difficult product. Data will support.

Case Study #2 – Australia steel plant works

In 2015, engineers discovered tar in an environmental-monitoring bore. As part of the investigation and plan for remediation, the company put in a 2-foot diameter, 12-foot-deep well, topped with a piston pump.

Engineers linked the discharge hose to a skip bin (dumpster). When filled, the bin is emptied by a vacuum truck and the tar is recycled.

In February, the pump began continuous operations. Roughly 10,000 liters (2,600+ gallons) were extracted in the four months. A 30-second video will show pump discharge viscosity and flow.

Case Study #3 – Lake Superior mixed-source Superfund site

The value of this study is the significant increase in free product recovery when electric piston pumps replaced common airlift pumps, even as total effluent rates remained steady. Contaminants at the Ashland, Wis., site found in sediment, groundwater, soil and a buried ravine include tar, oil and other waste consisting of PAHs, VOCs and metals.

During 78 weeks, 1,550 gallons of free product were recovered, 2.85 gal/day. Previous reported daily average and daily maximum rates ranged between 1.0 and 2.0 gal/day. Effluent totaled 392,800 gallons, a 5,035 gal/wk discharge rate, comparable with earlier reported averages. Cumulative summary tables will be presented.

Pumping technology

A discussion and animation will demonstrate how a piston pump works. Remediation piston pumps are miniaturized, next-generation versions of the century-old oilfield pump jack – simple, reliable and adaptable, with motor and controls cleanly at or above surface grade; easy to install and service, low maintenance, safer for workers and, virtually non-polluting. They pump almost anything flowable.

Innovative Surfactant System Formulations for LNAPL Recovery

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Background/Objectives. Based mostly on empirical experience, practitioners have concluded that NAPL solubilization was a necessary first step in the mobilization process and that surfactant concentration, up to a point, was generally proportional to performance. It is now understood, as evidenced by trends seen in the detergent industry that high efficiency products at lower concentrations meet the industry's requirements. These lower concentration formulations are not only as effective but work well at a variety of temperatures and water hardness conditions. That said, surfactants typically found in household cleaning systems, such as laundry detergent or shampoo, lower the interfacial tension (IFT) by about an order of magnitude. This is sufficient because mechanical energy can be added to laundry or shampooing to mobilize the trapped oil. In a porous medium, however, we must reduce the IFT by three or four orders of magnitude to reach our goals.

Approach/Activities. Technology developed at the University of Oklahoma, originally focused for enhanced oil recovery at petroleum reservoirs and subsequently adapted to the environmental arena, can lower the IFT sufficiently to allow physical mobilization of residual LNAPL with the limited production of thermodynamically stable emulsions. This talk will focus on the use of artfully formulated surfactant blends that reduce solubilization and simply allow LNAPLs in saturated soils to become mobile.

Results/Lessons learned. The presentation will include results and lessons learned from the latest field implementation where selecting an optimized surfactant blend minimized required flush water and costs for produced effluent fluids treatment.

Session IV: Combined Remediation Technologies

Reducing Treatment Costs by Optimizing a Combined Remedy using Traditional Techniques and High-Resolution Site Characterization

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Background/Objectives. The remediation team implemented and optimized a combined remedy for treating tetrachloroethene (PCE) in soil and groundwater at three properties related to a Region IV Superfund Site. The combined remedy includes in-situ chemical oxidation in the source area, enhanced in-situ bioremediation in the dilute plume along with soil vapor extraction and high vacuum remediation in the vadose zone. In addition to monthly system optimization and data evaluation to guide operations, the team implemented high-resolution site characterization (HRSC) techniques and low-cost system adaptations. The optimizations refined the applied remedy to the changing conditions of the PCE plume as it responds to the remedy.

Approach/Activities. During the remedial action, several different technologies were used to gain a better understanding of the Site geology, contaminant distribution, and the Site's response to the combined remedy. At the first property, soil sampling with a mobile laboratory was used to gather high resolution data and justify a small soil excavation in place of planned SVE system design/build. At the second property, several optimization strategies were used: (i) the vadose zone remedy was optimized by connecting former vacuum monitoring points into the SVE extraction piping to better target remaining PCE mass, (ii) the groundwater remedy was optimized by modifying the injection technique to mitigate daylighting, and (iii) the source area groundwater remedy was converted to the second stage of the treatment train (i.e., in-situ enhanced bioremediation, ISEB) early due to the positive response to ISEB observed in the dilute portion of the plume. At the third property, a Membrane Interface Probe (MIP) and Hydraulic Profiling Tool (HPT) investigation was used to understand the location of residual mass after completion of the soil vapor extraction (SVE) operations, and this residual PCE mass was then targeted with High Vacuum Recovery and densely spaced oxidant injection points.

Results/Lessons Learned. The combined remedy was optimized by making adjustments in O&M routine, filling Conceptual Site Model (CSM) data gaps, and phasing in new remediation techniques as the contaminant mass reduction of the original remediation technique reached an asymptotic state. Updating the CSM allowed the remediation team to refine the remedial action by understanding the changing conditions of the source area and groundwater plume in response to the combined remedy. The $30,000 investigation investment at the first property resulted in savings of over $300,000 in system design and operation cost. At the second property, the concentrations of PCE were reduced faster than planned, and the number of in-situ ISEB applications was reduced for an estimated $200,000 in cost savings. At the third site, using HRSC allowed the remediation team to identify changes in the plume and re-allocate the treatment efforts to the areas with remaining PCE mass in soil and groundwater. This case study is an example of how optimizing a remedy can reduce the overall cost of remediation.

Safer, More Effective ISCO Remedial Actions using Non-Extreme Persulfate Activation plus Sustained Secondary Biotreatment

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Provect-OX® is an *in situ* chemical oxidation (ISCO) / enhanced bioremediation reagent that rapidly oxidizes a wide variety of organic constituents of interest (COI) present in impacted soil, sediment and groundwater (including chlorinated solvents, petroleum hydrocarbons, and pesticides) while uniquely supporting long-term, sustained, secondary bioremediation processes. As such, it is the only ISCO technology designed to manage residuals and prevent contaminant rebound (COI rebound is a common problem encountered with conventional ISCO technologies). This is accomplished by using ferric iron (Fe III) as a safe and effective means of activating persulfate which quickly yields sulfate and ferrate radicals for ISCO treatment. The process also enhances subsequent utilization of sulfate and iron as terminal electron acceptors for facultative redox reactions for improved biodegradation of any residual COIs.

Alternative methods of stimulating secondary biodegradation processes using oxygen release compounds (such as calcium or magnesium oxyhydroxide) are limited in that they will remain active for only a few months, after which time their oxygen release potential is exhausted. Iron, on the other hand, will remain active for many years and the resultant iron/sulfide precipitates provide for additional reactive surfaces to help manage rebound. Moreover, oxygen release compounds inherently increase the local pH to extremely basic conditions (>10 pH units) which is simply not conducive to biological activity. Additional benefits include: i) Provect-OX will not generate excessive heat / off-gases, ii) nor will it mobilize heavy metals or lead to the generation of secondary impact issues such as elevated arsenic, chromium resulting from grossly elevated pH.

Provect-OX is a dry powder material that is pre-mixed (all in one bag). It can be easily injected into a subsurface environment in a variety of ways, based on site-specific designs. Application methods include direct mixing, hydraulic fracturing, pneumatic fracturing, and direct push injection of slurries or liquids. Direct placement in trenches and excavations are also reliable application methods. Data from full-scale field applications will be presented to demonstrate effective *in situ* groundwater treatment for petroleum hydrocarbons (salinity levels variable) along with detailed cost analysis for the remedial actions.

Dual Anaerobic-Aerobic Cultures Bioaugmented on GAC for Treatment of Chlorinated Benzenes in Contaminated Groundwater and Sediments

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Bioremediation of mixtures of chlorinated benzenes can be achieved most efficiently using sequential or combined anaerobic and aerobic degradation processes because of the typical recalcitrance of monochlorobenzene and possible benzene accumulation under strictly anaerobic conditions. The presence of DNAPL (dense non-aqueous phase liquid) concentrations of chlorobenzenes, especially in shallow sediment where flowpaths to exposure points are short, further complicates *in situ* bioremediation. In this study at a Superfund site contaminated with trichlorobenzenes, dichlorobenzenes, and monochlorobenzene, we are testing the use of anaerobic and aerobic chlorobenzene-degrading cultures bioaugmented together on granular activated carbon (GAC) as a method to sequester the chlorinated benzenes and simultaneously facilitate their complete biotransformation through combined reductive dechlorination and aerobic (or microaerophilic) oxidation pathways. Two application methods of the dual-culture GAC are being tested in laboratory experiments and small-scale field pilot tests— one method with bioaugmented GAC mixed into sand placed on the sediment surface for a reactive cap and a second with direct mixing of the GAC into shallow sediments. The cultures utilized include an aerobic culture (15B) enriched from the site wetland sediment and an anaerobic dechlorinating culture (WBC-2) that was previously developed from another wetland site.

Microcosms with the WBC-2 and 15B cultures bioaugmented on GAC and mixed with sand (6 percent GAC by dry weight) removed about 85 percent of the amended 1,2- and 1,4-dichlorobenzene in 24 hours, which was greater than removal in controls without the biofilms. A low but significant increase in monochlorobenzene and benzene in sediment-GAC mixtures analyzed from anaerobic microcosms mixed in wetland sediment provided evidence that reductive dechlorination of the tri- and di-chlorobenzenes occurred, although concentrations were below detection in the water in the microcosms. Column experiments showed lower monochlorobenzene concentrations in effluent water and overall greater removal of chlorinated benzenes in columns constructed with both cultures bioaugmented on the GAC compared to columns containing GAC bioaugmented only with the anaerobic WBC-2 culture. These laboratory results indicated that removal occurred by biodegradation in addition to sorption and that aerobic biodegradation processes were important in increasing overall contaminant removal. Initial results of the field pilot tests, which contain both cultures bioaugmented on GAC, show substantial removal of chlorinated benzenes (1 to 3 orders of magnitude decrease) in the sediment and groundwater within the reactive zones compared to controls. Thus, the combined field and laboratory data indicate that the dual-bioaugmented GAC will provide a feasible remediation for the shallow groundwater and sediments.

Multi-Component Treatment Strategy for Chlorinated Ethene and Chlorinated Benzene DNAPL Source area

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The results of the treatability study conducted at Hunters Point Naval Shipyard indicate that the integrated, multi-component treatment strategy performs significantly better than either of the individual technologies alone to remove large amounts of a mixed chlorinated benzene, ethene and ethane DNAPL mass in a short timeframe, and establish a treatment system that more effectively achieves stringent groundwater cleanup criteria. The integration of in situ thermal remediation (ISTR) and in situ bioremediation (ISB) resulted in removal of DNAPL and an 86-99.9% reduction in soil contaminant mass quickly (4 months). Due to logistical and technology-specific constraints, it was infeasible for the ISTR technology to remove sufficient contaminant mass to meet stringent groundwater criteria. Therefore, CDM Smith integrated ISTR with ISB to reduce the footprint of energy-intensive and expensive ISTR, used heat generated to improve ISB mass removal rates, and polished remaining contaminants post-ISTR. The research conducted by CDM Smith resulted in a novel system that emplaced ISB amendments prior to ISTR to take advantage of heat generated to accelerate treatment rates using ISB (measured kinetic degradation rates were double post-ISTR compared to pre-ISTR). Therefore, this established ISB system, remediated contaminants before, during and after ISTR within the DNAPL source area and dissolved phase contaminant plume. Within a year of the polish, groundwater contaminant concentrations were reduced by 2 to 5 orders of magnitude representing an average of 86 to nearly 100% reductions of the dissolved chlorinated solvent parent compounds within the former DNAPL source area.

Field Demonstration of Vadose 1,4-Dioxane Remediation by Extreme Soil Vapor Extraction (XSVE)

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1,4-Dioxane is a volatile organic solvent mostly used as a stabilizer for other chlorinated solvents such as TCA when stored in aluminum containers. Though owning a vapor pressure (30 mm Hg at 20 °C) in similar range of TCA and Benzene, 1,4-dioxane is proven difficult to treat with conventional soil vapor extraction (SVE) remediation due to its high solubility. After SVE, 1,4-dioxane can linger on and continue to leach into groundwater. To solve this problem, a method of Extreme Soil Vapor Extraction (XSVE) is proposed, where heated dry air injection is added at high flow rates to enhance SVE performance for 1,4-dioxane removal.

A field site at the former McClellan AFB in California, US with 1,4-dioxane existence in vadose zone was selected for this project. The objective of the study is to demonstrate the idea of XSVE and assess its performance towards 1,4-dioxane removal in the vadose zone. The site had an existing SVE system in operation aimed at removing volatile solvents from the vadose zone. At the time of starting of this XSVE project, the original SVE project is nearing completion at treating other solvents but was inefficient at removing 1,4-dioxane in the same time period.
The XSVE system was designed to treat the residual 1,4-dioxane. Pre-XSVE soil borings confirmed the location of significant concentrations of 1,4-dioxane in the vadose zone and determined treatment zone location to be approximately 38-68 ft below ground surface (bgs).

The XSVE system was configured with four injection wells in square pattern around a central extraction well, and off-gas was treated with an existing treatment system. Soil vapor monitoring probes, temperature, and soil moisture sensors were installed at various distances between the injection and extraction wells within the treatment zone. In addition, temperature and soil moisture sensors were also installed below the treatment zone to detect potential downward migration of 1,4-dioxane due to condensation. Air heated by in-line heaters were injected into each injection well and maintained a flow rate of ~85 scfm. The system operated with little downtime for ~1 year, during which the treatment zone was periodically monitored.

At completion time, the treatment zone soil temperature reached as high as 90°C and soil moisture sensor readings reached as low as zero near the injection wells. Final soil boring showed XSVE was able to effectively reduce treatment zone soil 1,4-dioxane concentrations by 95%. Extraction well monitoring showed that most of 1,4-dioxane removal occurred before soil temperature in the treatment zone increased substantially, indicating that enhanced air flow is the primary facilitator. This demonstration confirmed that XSVE can provide a cost-effective and easily-implemented remedial option for vadose zone 1,4-dioxane.

Session V: Oxidation and Reduction Technologies for DNAPL and LNAPL Treatment

Using the Availability of Natural Organic Carbon as a Metric for Selecting Oxidative or Reductive Remedies for DNAPL and LNAPL Cleanup

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All aquifer systems contain organic carbon, which exists in the particulate, adsorbed or dissolved phases. This organic carbon has the capacity to drive the reductive dechlorination of chlorinated solvents (DNAPLs) or inhibit the oxidation petroleum hydrocarbons (LNAPLs). However, the amount and bioavailability of organic carbon varies enormously between different hydrologic settings. Thus, concentrations of organic carbon in aquifer sediments is a key factor in selecting oxidative or reductive remediation strategies for chlorinated solvent or petroleum hydrocarbon contamination of groundwater systems.

We measured concentrations of potentially bioavailable organic carbon (PBOC) and total organic carbon (TOC) in aquifer sediments at fifteen naval facilities located throughout the United States, many of which exhibit both LNAP and DNAPL contamination. Concentrations of PBOC were linearly related to TOC concentrations, but on average PBOC concentrations were five times lower than TOC concentrations. As expected, the reductive dechlorination potential of sediments from these sites was directly proportional to PBOC and TOC concentrations. Conversely, concentrations of dissolved oxygen were inversely related to concentrations of PBOC and TOC. The collective experience with oxidative remediation strategies (such as Fenton's reagent addition), or reductive remediation strategies (such as emulsified vegetable oil addition) at these sites suggests the following general observations:

1. Oxidative strategies for both LNAPL and DNAPL were more successful at sites with low PBOC (< 200 mg/kg) or TOC (< 1,000 mg/kg) concentrations.
2. Reductive strategies for DNAPL were more successful at sites with low PBOC (< 200 mg/kg) or TOC (< 1,000 mg/kg) concentrations.
3. Reductive strategies for DNAPL were less successful at sites with high PBOC (> 200 mg/kg) or TOC (> 1,000 mg/kg) concentrations.

These results suggest that measuring sediment concentrations of PBOC or TOC are a useful and quantitative metric for deciding between oxidative or reductive remediation strategies at LNAPL and DNAPL sites.

Four Years of Chemical Reduction to Achieve Treatment Standards for Carbon Tetrachloride/Chloroform at an Industrial Site in Brazil

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In situ chemical reduction (ISCR) continues to be a successful remediation technology in Brazil. Exceptionally warm groundwater temperatures and viable microbial populations foster rapid biodegradation kinetics. Carbon Tet and its daughter product, chloroform, can be further degraded using chemical reductants.

In São Paulo, Brazil, ISCR has been used at a former adhesives manufacturing site where carbon tetrachloride was once used as a raw material. Two source areas were identified and the groundwater plume has migrated off-site to neighboring properties and under a minor highway. A cometabolic bioremediation system using butane was previously implemented and has success reducing carbon tetrachloride concentrations. The system failed to significantly reduce chloroform concentrations.

A pilot test was undertaken using a hybrid amendment consisting of a carbon source and microscale zero valent iron was applied to low permeability silts/clays using pneumatic fracturing, trenching, direct push, and soil mixing techniques (depending on the varied lithology in the area). Significant reductions of carbon tetrachloride and chloroform were quickly observed, with changes in field parameters and geochemistry. Information on injection spacing was also developed. A description of and data from the pilot test will be summarized for this presentation.

Over the last four years, a full scale application of the hybrid amendment was completed at 30 locations across three properties using a combination of techniques for different site scenarios and post-injection were data collected. Significant reductions of parent/daughter compounds have been documented with corresponding changes in field parameters and geochemistry. Changes in mass, concentration and plume geometry will be presented over the course of remediation. Remediation is in its final stages and much of the site has met commercial treatment standards and is close to residential standards with the exception of a few monitoring wells. Observations from the life cycle of remediation will be presented and the final path forward described.

Enabling NAPL Removal using Surfactants and Hydrogen Peroxide

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Non-aqueous phase liquid (NAPL) is the source of groundwater and soil contamination at many sites and is a technically challenging problem to address in the subsurface. Conventional In-Situ Chemical Oxidation (ISCO) implementations are limited to aqueous phase reactions and are unable to address bulk NAPL plumes cost-effectively, typically requiring very large amounts of oxidant and multiple treatments to meet cleanup goals. Pump-and-treat approaches for NAPL removal produce very gradual, continuous contaminant extraction and are designed to be in place for many years. These systems tend to exhibit diminishing yields and reduced effectiveness through time.

This presentation will focus on simultaneous application of low doses of optimized surfactant blends and hydrogen peroxide to enhance NAPL removal using SEPR (Surfactant Enhanced Product Recovery) technology which greatly improves the economics and performance compared traditional contaminant removal approaches. Surfactants used in the SEPR™ process lower interfacial tension and decrease the capillary forces which keep the NAPL in place, resulting in greater mobility of the NAPL phase. Additionally, the simultaneously injected hydrogen peroxide helps loosen the NAPL and provides buoyancy, facilitating NAPL transport towards recovery wells. A SEPR alone treatment typically will suffice if the endpoint criteria is NAPL mass removal or NAPL removal to sheen and/or no measureable free product in the monitoring wells A follow up S-ISCO® (Surfactant enhanced In-Situ Chemical Oxidation) treatment is recommended when low soil and groundwater remediation criteria are required. Bulk NAPL removal in the preceding SEPR phase, provides improved cost/performance of subsequent surfactant enhanced oxidation of the residual soil contamination. Background on the benefit of surfactants in remediation will be presented, along with field case studies demonstrating the significant advantages of surfactant use for in-situ remediation, particularly for heavy hydrocarbons and NAPL.

Session VI: Delivery Systems for In-Situ Remediation

Gravity Feed Delivery of Oxidant to a Dilute PCP Plume

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Background and Objectives. Groundwater at a former wood preserving facility in Georgia has been affected by releases of pentachlorophenol (PCP). The source of the PCP in groundwater was a dip tank that was used to apply solutions to lumber to control surface staining. The highest concentration of PCP identified on-site is 7,900 ug/L of PCP.

An in-situ chemical oxidation (ISCO) pilot test was conducted at the site in 2009. A total of 1,900 gallons of 6.5% sodium permanganate was delivered to three injection wells in the pilot test area. The target treatment area is relatively shallow (10 to 20 feet below ground surface) with a depth to water of approximately 5 feet in the injection area. Decreases in PCP concentration of up to 95% were observed during the pilot test, however, pressurized injection resulted in slow injection rates and surfacing of oxidant in in the pilot test area.

Based on the results of the pilot test, additional pressurized injection wells were installed as part of the full scale implementation of ISCO. Similar issues with slow injection rates and surfacing of oxidant were encountered outside of the pilot test area during full scale implementation. As a result, gravity feed injection through infiltration galleries was selected as an alternative delivery method for oxidant injection.

Approach and Activities. In March and April 2014, a total of 300 feet of infiltration gallery trench was installed for gravity feed delivery of oxidant in and around the source area.. Four 30 foot long infiltration gallery trenches were installed in the source area (Trenches 2 through 5). One 105 foot long infiltration gallery trench was installed between the source area and the western site property boundary to prevent off-site contaminant migration (Trench 1) and one 75 foot long trench was installed downgradient of the source area to mitigate contaminant migration outside of the source area (Trench 6). Infiltration gallery trench construction included the installation of a 4 inch diameter perforated pipe placed within 16 inches of number 57 stone. Each trench was installed in 15 foot segments with a threaded connector on the upgradient end to accept oxidant and a bolted manhole cover on the downgradient end for observation and cleanout (as necessary). The trenches were installed at the top of the water table, between 2 and 5 feet below ground surface. Between July and August 2014, a total of 14,250 gallons of 5% sodium permanganate were allowed to gravity feed into the infiltration galleries.

Results. Contaminant concentration trends in downgradient monitoring wells, which prior to injection showed a steep increasing trend, have decreased more than 50%. The impact of oxidant delivery, as evidenced by a 92% decrease in contaminant concentration, was been observed 120 feet downgradient from the closest infiltration gallery. Contaminant concentration trends in remaining site wells are exhibiting decreasing trends with reductions in PCP concentration of up to 95%. Based on the site data collected to date, gravity feed delivery of oxidant through a series of infiltration galleries appears to be cost effective and technically viable method of oxidant delivery at this site.

Highly Successful ERD Pilot Evaluation Utilizing a Simple Additive Delivery Approach

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Groundwater at the NASA Stennis Space Center facility has trichloroethene (TCE) in deep water bearing units outside the influence of existing pump and treat recovery systems. In an effort to identify a cost-effective and sustainable solution, enhanced reductive dechlorination was evaluated as a site remedy using **ERD**ENHANCED™, a patented carbohydrate-based formulation containing macro-micro nutrients, proven to biostimulate native microbials and enhance chlorinated alkene contaminant destruction. An *in-situ* pilot evaluation was implemented from July 17, 2013 to October 21, 2014 to confirm additive efficacy and collect full-scale pre-design remediation data. Passive Release Sock (PRS) units were deployed in test-well 06-12 MW to passively amend the groundwater and create a limited area of influence (AOI).

Over the 15-month period, groundwater from test well 06-12 MW realized a >96.9%REDUCTION in TCE concentrations with a >81.9%REDUCTION in the parent-daughter ratio indicating enhanced reductive dechlorination. With regards to *cis*-1,2-dichloroethene (*cis*-1,2-DCE), after an initial >85.5%REDUCTION a 1,530%INCREASE was observed at 4-months; followed by a >91.1%REDUCTION by evaluation end. No Vinyl chloride or Ethene was detected during this period.

Significant reduction in TCE concurrent with increased cis-1,2-DCE is consistent with biotic dechlorination. Indicator parameter data consistent with anaerobic, chemically reducing conditions were recorded, proceeding through sulfate reduction in test well 06-12 MW into which **ERD**ENHANCED™ containing PRS units were deployed.

An independent microcosm study was also performed, comparing **ERD**ENHANCED™ as sole electron donor to lactate, using site groundwater. Three microcosms spiked with SDC-9 dehalorespiring bacterial were established; one with **ERD**ENHANCED™, second lactate, the third Control with no amendment. Over 10-day period **ERD**ENHANCED™ amended microcosm outperformed lactate realizing complete biotransformation of parent TCE and both daughter products cis-1,2 DCE and VC.

Highly Successful ERD Pilot via Simple Additive Delivery System Lead to Full-Scale Biostimulation Strategy for Destruction of Residual cVOCs

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The Site, a former dry cleaner in Burlington Ontario, Canada; is currently vacant, zoned commercial/residential and desirous for redevelopment. Since 2006, investigations document chlorinated volatile organic compound (cVOC) impacts to soil/groundwater. Contaminant-of-Concern (COC), Tetrachloroethylene (PCE), present at concentrations above Ministry of Environmental & Climate Change (MOECC) Table 3 Site Condition Standards (SCS). Concentrations cVOC daughter products Trichloroethylene (TCE) and Dichloroethylene (DCE) low, with Parent:Parent Daughter (P:PD) molar ratios ≈100%, indicative of minimal dehalorespiration.

A Pilot-Study approved by MOECC, using Passive Release Sock (PRS) deployment units filled with ERDenhanced™, a biostimulation additive by BioStryke®, began in March 2011 to determine if native dehalorespiring populations could be stimulated to realize enhanced reductive dechlorination. PRS units are suspended vertically within screen interval of existing 2-inch monitoring well (MW-2) passively amending the impacted saturated soil column. Units were replaced 3-times at ≈8-week intervals; performance groundwater monitoring/sampling performed concurrently, four events completed with final additive replacement week-20 of ≈26-week evaluation.

Results confirm ERDenhanced™ stimulated native dehalorespiring bacteria within treatment zone. Supportive evidence include: reductions in groundwater ORP, expedited terminal electron scavenging, expedited solubilization of residual mass (additive enhanced co-solvent effect) followed by increased bioavailability and enhanced reductive dechlorination of parent/daughter cVOCs. Specifically, [PCE] decreased 46.9% by week-8, increased 233.3% by week 14 to decrease 89.6% by week-26. Total [cVOCs] decreased 49.6%, then increased 282.6% to decrease 77.4% at week-26; reductions in P:PD ratio ≈70.9%, from 100% to 29.1%.

In July 2013, under MOECC approval, a full-scale remediation strategy combining source removal and biostimulation with ERDenhanced™ to address residual cVOC contaminants began. Approximately 90 m^2 (250 m^3) of subslab cVOC impacted soils were removed to ≈3 meters bgs. Structural constraints limited additional excavation. An injection gallery was installed in the excavation footprint using clear stone and 6-inch slotted PVC pipe placed 2-3 meters bgs (GW elevation ≈3meters). In March and July 2014 a ≈9% ERDenhanced™ slurry was gravity fed into the gallery using 990kg and 840 kg of additive, respectively, with 1,100L make-up water.

Since March 2014, 5-rounds of groundwater monitoring completed (through October 2015), confirming four downgradient locations (MW-2, MW-209, MW-3 and MW-6) demonstrated positive effects form additive deployment. Each located 15-20 meters downgradient from the gallery, changes in geochemical metrics confirm enhanced reducing conditions achieved, with reduced ORP values, increased methanogenic conditions and [Total Organic Carbon] (TOC) remaining >100 mg/L. Dramatic changes in [cVOC] and P:PD were also observed. Specifically, [PCE] reduced 99.9% (MW-2), 95.0% (MW-3), and 97.9% (MW-6); total [cVOC] reduced 89.7% (MW-2), 75.8% (MW-3), and 88.1% (MW-6). No recorded [VC]. P:PD ratios reduced 99.0% (MW-2), 87.7% (MW-3), and 90.0% (MW-6) due to introduction of ERDenhanced™.

The Pilot and full-scale biostimulation strategy confirms sustainable, cost-effective and safe in-situ cVOC remediation is feasible making similar sites suitable for redevelopment, occupancy, and productive utilization.

Session VII: Biotransformation

Biogeophysical Analysis of Hexavalent Chromium Biotransformation: Column Studies

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Biogeophysics is a relatively new field of study that focuses on the relationship between geophysical signatures and subsurface microbial activities. Field evaluations at DOE and DoD field sites over the past years have seen distinct signatures in geophysical measurements that fell outside of what was expected; in one case, a year after injection of a carbon source. These responses are thought to be caused by precipitation, microbial activity, the formation of a microbial biofilm, and sorption. Spectral induced polarization is a geophysical technique that measures phase shift and electrical conductivity. This series of experiments were designed to attempt to simulate biogeochemical reactions that would occur in the environment, similar to a site during and after carbon injection for bioremediation.

A series of continuous flow columns were filled with sterilized fine sand sourced from the Hanford Site in southeastern Washington State, USA. Synthetic Groundwater Media with hexavalent chromium (Cr(VI)) was used in an attempt to replicate *in situ* conditions. The bacterium *Cellulomonas* sp. strain ES6, isolated from the Hanford Site, is known to have the ability to reduce Cr(VI) to trivalent chromium (Cr(III)) in anaerobic conditions. One column was inoculated with ES6 in order to facilitate the reaction under controlled conditions. Each column contained a different experimental condition; no amendment, Cr(VI) added to media, Cr(VI) and lactate added to media, and Cr(VI) and lactate added to media with ES6 culture inoculated sand. Lactate was added to a cell-free control column to track the conductivity change associated with amendment addition. In the inoculated column lactate was provided as the primary carbon source for ES6. Columns were continuously monitored to calculate the frequency-dependent complex impedance using spectral induced polarization. Column effluent was analyzed for Cr(VI) content, bacterial cell count, and activity using molecular biological tools.

A distinct electrochemical polarization was observed in the columns containing Cr(VI) only. This is a possible indication of the abiotic reduction of Cr(VI) to Cr(III). In the columns containing the ES6 culture as well as lactate, a distinct electrochemical polarization was also observed. This polarization is potentially associated with biotransformation of the Cr(VI), as total Cr increased on the surface of the sand in columns where carbon was added. The geophysical signatures aligned closely with the data generated from the effluent analysis further supporting the findings.

Successful On-Site Treatability Study Evaluating Feasibility of Biostimulation to Enhance Microbial Degradation of 1,3,5-Trimethylbenzene Under Anaerobic Conditions

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The Site, a bulk fuel supply facility, has maintained underground storage tanks (USTs) containing petroleum hydrocarbon products since the 1960s. Site characterization indicated no soil contamination in excess of state risk-based screening levels (RBSLs) above the water table, however, one constituent - 1,3,5-Trimethylbenzene (1,3,5-TMB) - was detected in groundwater at levels in excess of the state standard of 0.07 mg/L.

In February 2014, the inferred area of groundwater impacted by concentrations of 1,3,5-TMB above the state standard extended 270-ft downgradient from the source area. The plume extends 60-ft laterally with a 15-ft vertical thickness. The impact zone is inclusive of monitoring wells MW-5 (source) and downgradient wells MW-4 and MW-7; roughly 60 feet and 180 feet downgradient from MW-5, respectively. Within the plume 1,3,5-TMB ranged from 0.37 mg/L to 0.75 mg/L. Extending >400 feet downgradient from MW-5 and inclusive of the 1,3,5-TMB plume, groundwater is characterized by dissolved oxygen (DO) levels of 0.72 mg/L to 1.98 mg/L, neutral pH and oxygen reduction potential (ORP) consistently less than 0.00 mV. Outside this area, DO ranged from greater than 3.6 mg/L to less than 7.4 mg/L and ORP readings were greater than 100 mV.

An onsite in-situ treatability evaluation approved by the Colorado Division of Oil and Public Safety (OPS) was implemented in September 2015. It's dual purpose was 1) to determine feasibility and sustainability of biostimulation; and 2) to evaluate the efficacy of TPHenhanced™ to promote 1,3,5-TMB degradation under anaerobic conditions. TPHenhanced™ provides macro-micro nutrients and alternative respiratory pathways to native microbial populations while maintaining anaerobic, low DO and low ORP conditions.

The additive was deployed using a GeoProbe DT7822 direct push 'Vista Clean Inject' system and injection tooling. Target depths were 15-ft to 30-ft below ground surface (BGS) with 2-foot injection intervals to layer distribution of TPHenhanced™. Three injection nodes were amended, one 15 feet upgradient and two 15 feet crossgradient of MW-5. Each node received approximately 160 pounds of biostimulant with 230-gallons water (3.82% additive slurry volume to pore space volume). Groundwater sampling was conducted sitewide prior to and twice after additive deployment.

Baseline 1,3,5-TMB at MW-5 (source) from October 2014 to June 2015 averaged 0.71 mg/L; downgradient, 1,3,5-TMB ranged from 0.35 mg/L at MW-4 to 0.32 mg/L at MW-7. In January 2016, four months post injection, 1,3,5-TMB at MW-5 had decreased 49.2% with observed increases in concentrations of dissolved iron (+1,081%), manganese (+1,356%), and a 72% decrease in nitrates. Downgradient at MW-4, dissolved iron/manganese increased 115%/131% with a 59% decrease in nitrates. Further downgradient at MW-7, dissolved iron/manganese increased 1,866% and 892% with a greater than 98% reduction in nitrates. Each secondary metric supports amendment influence, increased microbial respiration, and anaerobic non-assimilative destruction of 1,3,5-TMB.

In April 2016, seven months post deployment, additive influence appears to have diminished at MW-5 as reflected by a 55.2% increase in 1,3,5-TMB, complete depletion of nitrates, and slight decreases (<2.0% and 41%) in dissolved iron and manganese. Downgradient at MW-4 and MW-7, decreases in 1,3,5-TMB continued (-73.0% and -53.3%) while geochemically little to no changes occurred at MW-4. At MW-7 dissolved iron/manganese decreased 46.6% and 42.0% with nitrates remaining non-detectable. At all three locations ORP values declined, ranging from -142.5 mV (MW-5) to -211.9 mV (MW-4) while pH remained neutral and DO values decreased to <0.01 mg/L.

In summary, analytical and field monitoring data indicates amending 1,3,5-TMB-impacted groundwater with the biostimulant TPHenhanced™ positively influenced biogeochemical conditions to favor anaerobic microbial respiration and non-assimilatory contaminant degradation. Additional monitoring/sampling is scheduled and a second injection program, similar to the first, is being discussed for implementation in late summer 2016.

Optimization-Based Monitoring of a Fluidized Bed Biofilm Reactor Operated as Part of the 200 West Area Pump and Treat Facility at the Hanford Site

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The United States Department of Energy's 200 West Area Pump and Treat Facility is designed to collect and treat contaminated groundwater to reduce the mass of nitrate, carbon tetrachloride, trichloroethene, chromium (Cr III and Cr VI), technetium-99, and uranium. A fluidized bed biofilm reactor (FBBR) is incorporated in the treatment train for the purpose of removing nitrate, chromium and the chlorinated organics present in the groundwater. The FBBR was inoculated with a commercially available microbial culture capable of reducing or encapsulating these contaminants. Microbial growth and contaminant conversion was stimulated through the addition of organic carbon substrate (MicroCg™), phosphoric acid, and a micronutrient blend. Initial analytical results indicated the microorganisms effectively reduced many of the contaminants fed into the FBBR. Shortly after start-up, however, operational challenges related to overproduction of extracellular polymeric substance (EPS) leading to loss of the granular activated carbon (GAC) substrate from the FBBRs which impacted removal efficiency and negatively impacted downstream treatment processes. Adjustment of the macronutrients (carbon and phosphorus) and micronutrient mixture resulted in generation of significantly less EPS, but GAC was still being carried out of the bioreactors. For these reasons, samples of the FBBR media were characterized related to biofilm constituents, the microbial community present, as well as the macro- and micronutrient content. Results from these analyses were then compared to operational and performance parameters of the biological system. Analysis of the FBBR influent showed oxygen saturation requiring increased addition of macro- and micronutrients to establish optimal operation (nitrate and other contaminant reduction) and minimization of EPS production. Adjustments to the substrate feed to minimize processes adverse to operation lead to improved FBBR performance and establishment of optimal conditions for high nitrate removal efficiencies.

Session VIII: Remediation in a Low Permeability Media

A Rigorous Demonstration of Permeability Enhancement Technology for In Situ Remediation of Low Permeability Media

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Background/Objectives. Effective amendment delivery at low-permeability sites remains one of the most challenging obstacles in the remediation industry. Permeability enhancement technology (i.e., environmental fracturing) has been shown capable of improving amendment delivery and treatment effectiveness at many sites where conventional injection techniques are ineffective. However, limited guidance is available for proper design and implementation. ESTCP project ER-201430 was funded to provide comparisons of commercially available permeability enhancement technologies at three sites with differing lithologies, contaminant profiles, and remedial objectives. In addition, advanced monitoring techniques pertinent to the permeability enhancement technology were evaluated. This presentation will compare and contrast the results at the three sites, and provide recommendations for application of the various techniques.

Approach/Activities. Three DoD sites with challenging lithologies were selected for demonstration of the permeability enhancement technology. Site contamination had previously been addressed using conventional injection techniques such as in-well or direct-push injection with limited success. A comparison of the hydraulic and pneumatic approach to permeability enhancement technologies was performed at one of the sites with a silty clay and weathered shale lithology, whereas two different hydraulic permeability enhancement techniques were performed at the other two sites with a weathered sandstone/siltstone and glacial till lithology. A variety of advanced monitoring techniques including tiltmeter, electrical resistivity tomography (ERT), and electrical conductivity (EC) logging were performed. In addition, conventional soil and groundwater sampling techniques were performed to aid validation and confirmation of aforementioned monitoring tools.

Results/Lessons Learned. This presentation provides details regarding the application of the permeability enhancement technology at three low-permeability sites. In addition to the effective radius of influence and amendment delivery results for each of the approaches, lessons learned will be discussed. A variety of design factors will be discussed, including selection of the proper enhancement technique, amendment emplacement methodology, emplacement volume, well design and construction, and appropriate tools for real-time monitoring.

Pilot Study - Reductive Dechlorination Results Review

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This presentation will highlight the results of a pilot study conducted at a former manufacturing plant in Central Florida, a Superfund Site with an active groundwater remediation system. Chlorinated solvents, primarily tetrachloroethene (PCE) and trichloroethene (TCE) were detected in low permeability sediments beneath a former retention pond. These compounds, discharged to the basin in the 1950's and 1960's, migrated to a formation of interbedded silts, sands and clays which make up the base of the surficial aquifer at a depth of 40 to 45 feet below land surface. These compounds, detected in excess of 85,000 ug/l, were slowly releasing back into the aquifer which was the subject of a pump and treat remedial action. A Remedy Review recommended that enhanced natural attenuation, utilizing a controlled release electron donor (HRC-X) be used to accelerate cleanup in the interbedded silts, sands and clays. This compound, injected into and above the low permeability materials relied on the groundwater gradient and dispersion to stimulate reductive dechlorination across the impacted strata. Three years after injection the dechlorination process remains active and source area and downgradient wells have seen reductions of PCE concentrations ranging from 78% to 99%. Daughter products of the dechlorination (DCE and vinyl chloride) have peaked and declined in the source area wells and are being monitored in the downgradient wells. This presentation will review the processes involved in reductive dechlorination including the role of alternate terminal electron acceptors i.e., sulphate reduction, optimal ORP range, methanogenesis and degradation pathways.

Key Words: Dechlorination, Solvents, Oxidation-Reduction Potential (ORP)

Session IX: Site Rehabilitation and Management

In Situ Geochemical Immobilization Technology for DNAPL Management

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For several decades we have worked collaboratively to develop cost-efficient, effective strategies for managing large, complex sites impacted by free-phase hydrocarbons (such as coal tar, creosote, heavy oils and related compounds). One process we developed involved the use of modified solutions of permanganate ($NaMnO_4$) to affect *in situ* stabilization of dense non-aqueous phase liquids (DNAPLs). These reagents were designed to react with organic (and certain inorganic) constituents of interest (COIs) present as soil residuals (*e.g.*, DNAPL or ganglia) and physically encrust/immobilize them thereby offering long-term sequestration (LTS). Provect-GS™ represents our next-generation LTS technology. This improved reagent uniquely combines partial mass removal/destruction of the COI with other physicochemical processes to rapidly reduce aquifer permeability and sequester hydrophobic contaminants offering *in situ* geochemical immobilization (ISGI). These combined reactions improve remedial performance, predictably extend treatment longevity, and inherently increase the reliability of the overall approach for DNAPL management.

As relatively small amounts of the liquid reagent migrate horizontally and vertically through a targeted treatment area, various biological and chemical reactions rapidly remove COIs in the dissolved phase. This increases the release of COIs from NAPLs into the aqueous phase, with the more water soluble, lower-molecular-weight (LMW) constituents being removed at a proportionally higher rate thus leading to a "hardening" or "chemical weathering" of the NAPL as it steadily loses its more labile components. This increases the viscosity of the NAPL resulting in a more stable residual mass hence the flux of COI released into the dissolved phase is much reduced and natural attenuation processes are more easily capable of managing associated plumes. Furthermore, in the presence of Provect-GS, the permanganate oxidation reactions are modified to yield manganese dioxide-based precipitates which form at the organic interface and physically entomb NAPL residuals. These precipitates also decrease the permeability of the aquifer which further reduces the flux of COIs. Other ingredients unique to Provect-GS (*e.g.*, specially selected organoclays) further enhance these physical immobilization or sequestration reactions, and they even further decrease the permeability of more porous lithological aquifer features which typically harbor DNAPL. Within a few days, these aquifer intervals are sealed and disconnected, and the potential for DNAPL transport or migration is greatly reduced.

Laboratory tests demonstrated that Provect-GS reagents were effective in managing creosote DNAPL, and that the reagents could be prepared in a manner that yields a liquid suspension with a density and viscosity conducive to easy field applications (fluid transport and pumping, *etc*). A field-scale pilot-test (*ca.* 80 x 80 feet from 10 to 67 feet bgs) was performed in a well-delineated area of a former wood treating facility that was heavily impacted by creosote DNAPL. Detailed information on the LTS reagents and lessons learned during their field implementation will be presented along with results of field performance monitoring and application costs.

Rehabilitation of Old Industrial Area in Rio de Janeiro / Brazil Contaminated by Chlorinated Compounds

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Background/Objectives: The issue of contaminated areas and disabled areas have been hotly debated in business community because it involves high costs and many difficulties of legal character, communication and institutional. In addition, it creates problems for urban management for devaluing the property and its surroundings, deteriorate by the city's image before investors, public opinion, favor illegal waste disposal, and illegal occupation of land. In this process, this paper presents the main results in PCE decrease within a treatability test and in the field. The site is located in a very populated area downtown Rio de Janeiro city, Brazil. It used to be a Clothing Factory. The local geology consists of sandy sediments.

Approach/Activities. Chemical oxidation is becoming a popular remediation technology in Brazil especially at sites contaminated with chlorinated compounds. Short term and terminal solutions in remediation are important characteristics in places where residential redevelopment is required. Regulators are bringing up some questions such as lixiviation of metals in ISCO remediation, and this paper reports results in PCE decrease within a treatability test and in the field.

For the treatment of groundwater, it was used the technique of soil flushing by means of surfactants. After application of the surfactant product (Rentaltech 500®) observed that surfactant was effective in solubilizing contaminants adsorbed to the soil of this area. A chelated metal (METALDOWN ®) and oxidant (Activated Persulfate - Oxytech®) were used to improve oxidation/precipitation of metal ions.

Results: The analytical monitoring of groundwater showed that Persulfate (Oxytech®) oxidation was efficient and achieved the proposed goals for recovering site. The metals behavior during oxidation showed no significant variation in groundwater concentration, geochemical analyses and some Pourbaix diagrams showed very small change in pH x Eh relationship, indicating low mobilization.

Results/Lessons Learned. The technique combined in situ remediation presented efficiency/effectiveness indicating that the area is free from toxicological risk to human health and the environment. Surfactant acted in reducing the surface tension of the water/solvent interface, allowing the exposure to bio decomposition of the contaminant by the microorganisms present in the subsurface. The oxidative attack significantly reduced the PCE half-life and chelated metal acted in low metals mobilization.

Characterization and Remediation Approaches for Radionuclide, Inorganic Co-contaminated Subsurface Sites

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Contaminants in the vadose zone may be long-term sources of groundwater contamination and need to be considered in remedy as well as long-term strategy evaluations. In many cases, remediation decisions for the vadose zone will need to be made all or in part based on projected impacts to groundwater from these unknown, uncharacterized 'sources' that are migrating or have migrated through the vadose zone. Aqueous wastes containing inorganic (non-volatile), metals and radionuclides were disposed of at the land surface (i.e., directly to the ground in cribs, trenches, tile fields, etc.) at locations across the Central Plateau of the Department of Energy Hanford site, and have resulted in complex comingled plumes both within the vadose zone and in groundwater. Because of contaminant transport through the vadose zone, the temporal profile of contaminant concentrations entering the groundwater is different than the temporal profile of the aqueous waste disposal. Depending on the chemical characteristics of the contaminant, vadose zone transport mechanisms tend to decrease contaminant concentrations and limit the rate of contaminant movement. In these ways, contaminant concentrations are attenuated during transport through the vadose zone, processes which are complicated by the comingled nature and reactivity of the contaminants. There are significant natural attenuation processes inherent in vadose zone contaminant transport, including both hydrologic and biogeochemical processes that serve to retain contaminants within porous media and physical processes that slow the vertical rate of movement for disposed water and waste solutions. Several approaches have been developed that (a) use an adaptation of the established EPA Monitored Natural Attenuation evaluation approach, and (b) are based on conceptual models, which are focused on identifying and quantifying features and processes that control contaminant flux through the vadose zone. These framework approaches are being further developed to incorporate the complexities associated with comingled contaminants as well as coupling the latest understanding of the fate and transport of risk-driving contaminants such as Tc-99 and I-129 in the vadose zone and into groundwater. This work is bridging the development and validation of these frameworks to support evaluation of complex comingled contaminant fate and transport in the vadose zone to refinement of the site conceptual model, assessment of risk, and support for baseline risk assessment and remedy selection. Together with biogeochemical studies targeting the controlling and/or attenuation processes driving the transport, lateral and distal migration of comingled plumes, (primarily I-129, Tc-99, and inorganics such as nitrate), these approaches provide a much enhanced understanding of natural conditions, and more can be used to predict future impacts to receptors (groundwater). While these tools are primarily intended for evaluating contaminant transport under natural attenuation conditions, the approach can also be applied to identify types of, and targets for, mitigation approaches in the vadose zone that would reduce the temporal profile of contaminant concentrations in groundwater, if needed.

Session X: Controlling Methanogenesis / Oxidation Technologies

Reasons and Technology for Controlling Excessive Methanogenesis during Remedial Actions: Case Studies and Remedial Alternatives

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At many groundwater remediation sites, excessive production of methane has been observed following the addition of organic hydrogen donors such as (emulsified) oils/lecithin, sugars and conventional ISCR reagents. This is because methanogens are commonly the most ubiquitous indigenous microbes in anoxic aquifer settings. And given that methanogens replicate in 1 to 2 hours (whereas *Dehalococcoides* spp. for example double in 24 to 48 hours), they often bloom and dominate following the addition of organic hydrogen donors, thereby liberating large amounts of methane gas. There are at least three important consequences of this response:

i) <u>Cost</u> - by utilizing hydrogen, the methanogens compete with dechlorinating microbes thus making inefficient use of the amendment (just 20 ppm methane in groundwater represents about 35% "waste" of material – this is fact [not logically debatable] and represents common and tangible detriment);
ii) <u>Safety</u> - elevated methane concentrations can exceed current and pending regulations of < 1 to <28 ppm in groundwater, and/or <0.5% v/v methane in soil gas (*e.g.*, <10% of the LE); methane gas will induce vapor migration potentially causing indoor air issues of VOCs) and exceed LEL; and
iii) <u>Performance</u> - rapid growth of methanogens consumes alkalinity while generating acids increasing the potential for aquifer acidification (which may liberate heavy metals such as arsenic causing secondary contaminant issues).

Controlling methanogenesis during remedial actions is becoming commonplace among seasoned professionals as the positive effects on remedial performance, safety, regulatory compliance and sustainability become well understood. Provect-CH4® is as antimethanogenic reagent (AMR) that is highly relevant to the remediation industry. And Provect-IR® is an antimethanogenic ISCR reagent that uniquely combines multiple sources of nutrient-rich, engineered-release, hydrophilic carbon + ZVI + other reagents along with a source of natural statins as inhibitors of protein biosynthesis and activity of enzyme systems unique to Archaea (*i.e.*, methanogens). During the presentation the following topics will be discussed:

i) <u>What is the Problem with Methane</u>? – as explained thru definition and via project examples, participants will better understand why State and Federal (US EPA; US DoD) agencies have instituted programs to monitor methane production and regulate/guide the remediation industry.
ii) <u>How can we Control Methanogens</u>? – a detailed, yet easy to understand explanation of the nature and mode-of-action of natural antimethanogenic reagents (AMRs) will be presented, and technologies that specifically govern methanogens will be described
iii) <u>Cost and Benefit Analysis</u> – project examples (dry cleaning facilities in urban settings; industrial sites impacted by chlorinated solvents) will be used to present cost of using AMRs to actively control methanogenesis.

Supercritical Water Oxidation of Toxic Waste Generated in Academic Veterinary Practices

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The preservation of anatomical samples is a critical step in the veterinary practices. To make that, formaldehyde diluted in water is commonly used. It is deposited in large ponds where the pieces of animals are placed. In Colombia this chemical is considered as a pollutant of sanitary interest if it is no treated before to disposal, and is common that the anatomical labs do not have the appropriate infrastructure to treat the wastewater generate on them. This occurs because the conventional wastewater treatment systems that the country has do not permit the degradation of the chemical. For this reason, it was selected the supercritical oxidation technique because it is highly efficient in destruction of toxic organic compounds according to many authors. The samples were obtained from the Anatomical Lab of La Salle University in Bogotá-Colombia and a 2k factorial design was used; in which the temperature, oxidation time and excess of oxidant was handled as variables to study. The best result was an efficiency of destruction of 99.51% with the conditions used (500 °C, 5 min, 100 % H_2O_2 Excess). The initial COD of 9200 mg.L-1 and a final COD of 40 mg.L-1, indicating that the method is effective for the treatment of this kind of waste in a batch reactor.

Keywords: Formaldehyde, Supercritical water oxidation SCWO, Anatomical Labs waste

Fenton and Photo-Fenton Technologies Modified with Tartaric Acid for the Treatment of the Wastewaters from a Urea-Formaldehyde Resin Production Process

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Wastewaters associated to the production of the urea-formaldehyde resins by polymerization have a high contaminant potential, because they contain organic compounds that could be difficult to remove by conventional biological systems. Pollutants found in these wastewaters include solvent (e.g., xylene, toluene) and polymer residues, as well as formaldehyde itself. For the treatment of water containing such pollutants, the Advanced Oxidation Processes (AOPs) offer many advantages, including high removal efficiencies. Among the AOPs, Fenton and photo-Fenton technologies are widely applied for the treatment of industrial effluents. Therefore, in this work, these technologies were tested.

The characterization of the wastewater was the first step in this study. The pollutant load (i.e., the chemical oxygen demand, COD) measured in this study was ~173,000 mg/L, with a pH value of 3.2 and a content of Total Organic Carbon (TOC) of 53,490 mg/L. As usually happens for industrial effluents, the Biological Oxygen Demand (BOD_5) of this wastewater was zero, thus the biodegradability (BOD_5/COD) was also zero. Since tartaric acid is a low-cost reagent, and non-toxic for aquatic organisms, it can be used as chelate for Fe^{2+} in order to facilitate the production of hydroxyl radicals (·OH), which are a very strong oxidant agent. In addition, the incorporation of this chelate allows the oxidative reaction to take place, with a high efficiency, in a broad range of pH values.

The applied procedure is presented in the following. For the Fenton process, the iron complex with tartaric acid was prepared by mixing ferrous sulfate and tartaric acid in a molar ratio of 1:5 and stirred during 45 min. Two different concentrations for both ferrous complex (0.3 and 0.7 mM) and hydrogen peroxide (85 and 180 mM) were tested in batch experiments with a total time reaction of 45 min. The best results were obtained with a concentration of 0.7 mM of the complex and 180 mM of hydrogen peroxide. With these conditions, the COD removal was 92.51 %. The final pH value was 6.0 and the mineralization level was 87.01 %. In addition, the remaining components present in water after the treatment showed a biodegradability of 0.60.

The best conditions found for the Fenton process were applied for the photo-Fenton process. An UV-C lamp of 15 W was used for batch experiments (including a cooling system) and the COD removal was measured. The total time of reaction was 90 min and samples were collected every 15 min. After 45 minutes of reaction, no more changes were observed. The COD removal was 9 3.14 %, with a final pH value of 6.1. The estimated mineralization level was 88.14 % and the remaining components (after treatment) showed a biodegradability of 0.67.

The results indicate that a high proportion of the pollutants can be removed. Moreover, the remaining compounds in water could be removed in a subsequent biological treatment, because the biodegradability increases. In order to optimize the processes and the use water, the possibility of implementing the recirculation of treated water into the production process should not be ruled out.