Case Studies on Remediation for Soil Contamination Sites



Pro. Vision Environmental Engineering Corporation Web Site : www.pveec.com.tw Presenter : Joseph Fan GM

About PVEEC

- PVEEC has many highly experience employees, such as geological technicians, Doctors, contamination investigation and remediation experts.
- We have more than 22 years experience whether foreign or domestic in our region.
- According to our extensive experience, we provide accurate and real subsurface information as well as the best proposal of contamination and remediation about the works of geophysical investigation, geological drilling and prospecting, contamination investigation and remediation, etc.
- For each project, PVEEC treats with professional service and dedicated attitude, and we hope that everyone love and protect our mother-the Earth like us.











Our Vision



Cultivate the Earth's doctors that love and protect the Earth.



Restore the Earth that would be filled with health and happiness.



Accomplish the blessed mission that manage and restore the Earth.

Core Value



Our Service

- Soil and Groundwater Contamination Investigation and Restoration
- Environmental Site Assessment
- Aquifer Storage Recovery, ASR, and Water Resource Planning
- Geophysical Prospecting
 - (1) Subsurface Contamination and Waste Investigation
 - (2) Subsurface Structure Survey
 - (3) Hot spring and groundwater resource
 - (4) Sliding hillside, Colluvium or Alluvium
 - (5) Riverbed and Reservoir Sedimentation
 - (6) Subsurface pipelines
- Geological Drilling and Prospecting

Career Information – Joseph Fan

- BS, Civil Engineering, Tamkang University, Taiwan, 1987
- MS, Environmental Engineering, Colorado State University, 1992.
- Life Member of Taiwan Association of Soil and Groundwater Environmental Protection
- Over 23 years experience of Soil and groundwater investigation and remediation
- Directed environmental site assessment projects (Phase I & II, and EHS) for multinational companies.
- Managed several remedial projects for soils contaminated with petroleum hydrocarbons and received closure letters from USA government.
- Managed heat-enhanced bioremediation projects for soils containing crude oils, gasoline, diesel and kerosene.
- Developed the electro-kinetic treatment method for soil and groundwater contamination in porous media having low permeability.
- Managed and performed pilot tests to remove heavy metals from contaminated soil and extract selenium, boron and salts from groundwater.
- Directed and performed numerous in-situ soil and groundwater remediation involving LNAPL and DNAPL clean up, using a combination of biodegradation, heat-enhanced soil venting, air sparging, and electro-kinetic techniques.



Electro-kinetic Enhanced Bioventing Advanced Vapor Extraction Electro-kinetic Enhanced Soil Washing

Case 1:

Electro-kinetic enhanced bioventing of gasoline in clayey soil



Site Introduction

A 10,000 gallon of underground storage tank of gasoline was spill, in San Diego, California.

- The soil plume covers an area of about 2,400 (ft²) and to a depth of about 30 (ft).
- The depth of in surface from 0 to 15(ft) was clay, and the other was conglomerate sandstone.
- The soil was contaminated, but groundwater was not.
- Total gasoline in soil plume is estimate at about 1,000 pounds of gasoline in about 3,500 tone of soil.
- The gasoline concentration in the soil plum range from 100 to 2,200 (ppm) and the target cleanup level was below 100 (ppm).

Problem

Find problem

- Using open excavation pit was not an economic option.
- The conventional vapor extraction system would not work with the low permeability clay.

Solve problem

- The electro-kinetic enhanced bioventing method can be applied to treat this clayey soil.
- The electro-kinetic system was operated at electricity flow to dry out the gasoline in clayey soil.
- The technology provides a cost effective and minimum disruption to business operation.

EK Bench Scale Test

CLASSIC EK BENCH TEST 1A





LASSIC BENCH TEST 1C



CLASSIC BENCH TEST 1D







CLASSIC BENCH TEST 1E

ATER

ELECTRO-OSMOSIS DEWATERING





CLASSIC EK BENCH TEST 1F

DEWATERING (ELECTRO-OSMOSIS) ELECTROCHEMICAL OXIDATION





EK Bench Scale Test Result

TABLE 1

BENCH SCALE ELECTROCHEMICAL OXIDATION TEST RESULTS GASOLINE CONTAMINATED CLAYEY SOIL PEPBOYS SITE SAN DIEGO, CALIFORNIA

(Units in mg/Kg)

	Initial	After 8 Hours of Treatment		Destruction	
		EK-1	EK-2	Efficiency %	
TPH AS GASOLINE	230.00	ND(<5)	ND(<5)	97.82+	
BENZENE (B)	1.9	ND(<0.005)	ND(<0.005)	99.73+	
TOLUENE (T)	6.3	ND(<0.005)	ND(<0.005)	99.92+	
ETHYLBENZENE (E)	2.8	ND(<0.005)	ND(<0.005)	99.82+	
XYLENES (X)	13.0	ND(<0.005)	ND(<0.005)	99.96+	

Vapor Extraction Injection System Piping Diagram



Vapor Extraction System - Condensator



Piping and Equipment Layout



Pipe and Equipment Layout









Heat Enhanced Biovention System



Temperature Effects Microbe Growth Rate



Knock Out Moisture Trap

Removed moisture in the extracted air, Avoid condensation to block piping.



Ultraviolet (UV) Light Disinfection System

The UV system was to eliminate bacteria in the extracted air form contaminated plume.



Granular Activated Carbon (GAC) Adsorption

- Two 55 gallon drums of GAC were serially installed after UV light disinfection system.
- The closed loop recirculation setup could bypass GAC or through it to injection well.



Electro-kinetic Methodology – Electro-Osmotic Flow in Capillaries



Electro Installation Diagram



Electro-kinetic Treatment System

The 39 electrodes was connected to DC power supply.
Electricity flow was operated at about 10 to 15 ampere.



Field Analysis Data

VOCs Concentration



Confirmation Result

		IPH as				
	Sample ID	Gasoline	В	Т	E	Х
		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
	V1-10'	ND	ND	ND	ND	ND
	V1-15'	1.2	0.0079	0.039	0.0098	0.073
Confirmation Drilling	V1-20'	ND	ND	ND	ND	ND
	V1-25'	ND	ND	ND	ND	ND
	V1-26'	ND	ND	ND	ND	ND
Sampling depth intervals : 10, 15, 20, 25,						
and 20 (ft)		0.1	0.017	0.013	ND	ND
and 30 (ii)	V2-2-15'	1.7	0.048	0.062	0.015	0.069
	V2-3A-20'	ND	ND	ND	ND	ND
	V2-3B-20'	ND	ND	ND	ND	ND
	V2-4-26'	ND	ND	ND	ND	ND
	V2-5-30'	ND	ND	ND	ND	ND
	V3-1-10'	ND	ND	ND	ND	ND
	V3-2-15'	170	1	9	3.5	19
T	V3-3-20'	220	ND	1	2.5	18
	V3-4-31'	290	0.22	1.8	2.7	15
VW-1	V4-1-10'	ND	ND	ND	ND	ND
		1.3	0.033	0.15	0.03	0.22
2" Dia. PVC Electric Wire Conduit	V4-3-20'	4.4	0.047	0.3	0.099	0.72
	V4-4A-25.5'	12	ND	ND	ND	ND
	V4-4B-25.5'	11	ND	0.0087	0.05	0.42
Equipment PAD						
VW-2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	V5-1A-10'	ND	ND	ND	ND	ND
▲ V-4	V5-1B-10'	0.28	ND	ND	ND	ND
Vertication Sampling Location	V5-2A-15'	126	3.6	11	1.2	6.6
	V5-2B-15'	3.4	ND	0.09	0.046	0.27
Scale (feet)	V5-3-20'	14	ND	0.14	0.1	0.69
	V5-4-26	98	0.0085	1.4	1.6	12

Average

36.707

0.156 0.964

0.458

2.815

Conclusion

Two 120 cfm explosion proof blowers were operated with 35~70 cfm

- The remediation effort was completed about 90 days.
- The average concentration was below the proposed cleanup level 100 ppm.
- The cost of treatment is about \$50 per ton.
- The technology provides a cost effective and minimum disruption to business to operation.



January 18, 1995

President

2081 15th Street

Dear Mr. Loo:

Walter W. Loo, CEG, CEM

San Francisco, CA 94114

Environment & Technology Services

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Sincerely, Cern

Conference Director HAZMACON '95

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OAssociation of Bay Area Governmente

The HAZMACON award, an engraved plaque, will be presented to you or your representative at the HAZMACON luncheon at the San Jose Convention Center on Tuesday, April 4 at noon. Please let us know who will be accepting the award so that we may register that person for a complimentary three-day admission to conference sessions, April 4 - 6. At the awards ceremony, we will also present a check of \$280 for travel expenses. Please let us know to whom the check should be addressed. We will issue a press release about the award shortly, and will forward copies to you in case your organization would like to promote your success.

I am pleased to inform you that your Electrokinetic Enhanced In-Situ Bioventing at Former Automobile Dealership Facility project was selected as the HAZMACON award winner for exemplary technology development in site remediation.

If you have any questions, please do not hesitate to call me at (\$10) 464-7951. Congratulations, and I look forward to seeing you there.

Terry Bursztynsky, P.E.



For exemplary technology development in site remediation,

HAZMACON honors

Environment and Technology Services, for Electrokinetic Enhanced In-Situ Bioventing at a Former Automobile Dealership Facility

Presented at HAZMACON '95 San José, California April 4, 1995

Case 2:

Advanced vapor extraction system enhanced biodegradation of gasoline



Site Introduction

A 1,000 gallon of underground storage tank of waste oil was spill, in Anaheim, California.

- The soil plume covered an area of about 900 (ft²) and to a depth of about 15 (ft).
- The site was underlain by alluvial soils which were composed of loose sands.
- The soil was contaminated, but groundwater was not.

Total waste oil in the plume was estimated at about 12,000 pounds in about 700 tons of soil.
Site Introduction

- The TPH concentration in the soil plum was range from 7,100 to 15,000 (ppm).
- The target cleanup level: TPH as gasoline and TPH as diesel were 100(ppm), TPH as waste oil was 1,000(ppm).

Problem

Find problem

- Using open excavation pit was not an economic option.
- Operating Equipment Rental Site

Solve problem

The advanced vapor extraction could mediate the TPH concentration in the soil.

The technology provided a cost effective and minimum disruption of business operation.

Monitoring Well Installation



Well & Remedial System Layout



Piping and Vapor Extraction System







Ultraviolet (UV) Light Disinfection System

- Three UV light units were connected in series or parallel by switched control ball valves.
- The UV system was to eliminate bacteria in the extracted air from contaminated plume.



Granular Activated Carbon (GAC) Adsorption

- Two 55 gallon drums of GAC were serially installed after UV light disinfection system.
- The closed loop recirculation setup could bypass GAC or through it to injection well.



Confirmation Result

Confir	matic	on Drilling	Sample ID	TPH (ppm)			Tox (ppm)
		Shi Dhining	oumpie ib	Gasoline	Diesel	Oil	rox (ppiii)
Samplin	a dept	h intervals : 5, 10, and 15 (ft)	CS-1-05	ND	ND	ND	ND
	9 0 0 0 0		CS-1-10	ND	ND	ND	ND
			CS-1-15	ND	ND	210	ND
•		MW-1 MW-2					
			CS-2-05	ND	ND	ND	ND
			CS-2-10	ND	ND	ND	ND
N		Eormer Soil	CS-2-15	ND	ND	ND	ND
	Concrete	Plume					
		CS-1 CS-2	CS-3-05	ND	200	ND	ND
Asphalt		VW-1 VW-2 • CS-4	CS-3-10	ND	24	160	ND
Pavement			CS-3-15	ND	160	420	ND
		MW-3					
			CS-4-05	ND	ND	ND	ND
		Existing Garage	CS-4-10	ND	ND	ND	ND
			CS-4-15	ND	ND	ND	ND
l							
0 1 2		Monitoring wells	A.C.L	100	100	1,000	1
		 Vadose wells Confirmation Soil Borings 	Min. Ave.	ND	36.9	65.8	ND
Scale (feet)			Max. Ave.	ND	43.6	140.8	ND

Conclusion

- The remediation effort was completed about 90 days.
- The concentration was way below the proposed cleanup.
- The cost of treatment is about \$50 per ton.
- The technology provides a cost effective and minimum disruption to business to operation.

Case 3:

Electro-kinetic Enhanced Soil Washing For Heavy Metals Contaminated Soil



Soil Washing and EK for Heavy Metals – Vandenberg Air Force Base, CA









Site Introduction

- The experiment site was in Changhua county, Taiwan.
- The site was heavy metal contaminated farmland.
- The contaminants were Cd, Cr and Pb.





Electro-kinetic Methodology

Desorption of Heavy Metals :



Electro-kinetic Methodology

- Electrophoresis is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field.
- Electro-osmosis is the motion of liquid induced by an applied potential across a porous material, capillary tube, membrane, microchannel, or any other fluid conduit.
- Electrolysis is a technique that uses a DC current to drive an otherwise non-spontaneous chemical reaction.
- Ion Exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex.

Experimental Layout

 Study of electro-kinetic Enhanced Soil Washing for heavy metals contaminated soil

Two treatment cells (A and B) : _____ Leakage Collection Sump



Site Preparation





Collected Contaminated Soil

Treatment Cell Construction





Profile View



Treatment Cell Construction





The cathode electrode mesh set in a bottom of test cell





Electrode Control Box

Safety Fence



Experimental Process

Phase I (40 days)



Experimental Process

Phase II (90 days)



Electrolyte Leakage



Covered with Plastic Sheet



Leakage Collection Sump



Leakage Liquid



Confirmation Sampling



X : Soil Confirmation Sampling Location





Pb		Phase I		Phase II					
Date	6/26	7/8	7/18	8/25	9/17	10/9	11/25		
AC-1	6.80	3.82	3.80	5.89	3.57	4.51	1.48		
AC-2	6.70	4.96	2.00	5.75	4.83	4.78	2.56		
AC-3	6.60	6.16	6.20	5.72	4.55	4.22	2.56		
Ave.	6.70	4.98	4.00	5.79	4.32	4.50	2.20		
BC-1	6.70	3.18	6.10	5.67	2.74	3.02	1.19		
BC-2	6.70	5.77	5.80	6.27	3.91	3.72	1.77		
BC-3	6.90	6.01	5.90	6.16	5.14	4.29	2.33		
Ave.	6.77	4.99	5.93	6.03	3.93	3.68	1.76		



Pb	Phase I						Phase II							Removal	Total	
Date	6/26	7/8	7/18	7/29	Removal(%)	8/25	9/1	9/17	9/29	10/9	<mark>10/19</mark>	<mark>10/29</mark>	11/9	<mark>11/25</mark>	(%)	Removal(%)
AC-1	22.36	13.76	10.70	13.78	38.36	17.62	15.93	13.17	12.95	9.14	9.09	11.92	8.25	6.18	64.93	72.36
AC-2	19.48	15.13	9.62	14.07	27.80	18.94	16.89	16.93	26.34	11.96	11.66	16.38	11.07	7.99	57.81	58.98
AC-3	20.22	14.61	9.71	17.21	14.90	17.54	16.34	18.20	17.33	13.13	11.49	15.46	13.04	8.54	51.32	57.76
Ave.	20.69	14.50	10.01	15.02	27.40	<mark>18.03</mark>	<mark>16.39</mark>	<mark>16.10</mark>	<mark>18.87</mark>	11.41	<mark>10.75</mark>	<mark>14.59</mark>	<u>10.79</u>	7.57	58.02	63.41
BC-1	25.45	8.95	9.08	10.75	57.78	12.98	13.4	12.34	16.79	10.23	9.19	11.83	5.33	4.09	68.49	83.93
BC-2	23.30	14.40	10.40	11.69	49.85	17.88	13.46	13.12	17.75	12.66	12.09	14.89	11.48	6.26	64.98	73.13
BC-3	27.66	15.96	13.80	13.02	52.95	15.66	15.02	14.19	18.25	18.52	12.40	15.46	10.79	7.21	53.97	73.93
Ave.	25.47	13.10	11.09	11.82	53.61	15.51	13.96	13.22	17.60	13.8	11.14	14.06	9.20	5.85	62.25	77.02

HCL→Cd



Cd	Phase I					Phase II								Removal	Total	
Date	6/26	7/8	7/18	7/29	Removal(%)	8/25	9/1	9/17	9/29	10/9	<mark>10/19</mark>	<mark>10/29</mark>	11/9	11/25	(%)	Removal(%)
AC-1	1.84	1.56	1.44	1.11	39.84	1.85	1.33	1.40	0.83	0.77	0.64	0.27	0.42	0.26	85.91	85.87
AC-2	1.56	1.90	1.61	2.09	0.00	2.14	1.48	1.94	1.67	1.36	1.02	1.38	1.27	0.72	66.37	53.85
AC-3	1.65	1.69	1.87	2.18	0.00	1.86	1.95	1.82	1.85	1.29	0.87	1.56	0.93	0.79	57.55	52.12
Ave.	1.68	1.72	1.64	1.79	0.00	1.95	1.59	1.72	1.45	1.14	0.84	1.07	0.87	0.59	69.73	64.95
BC-1	2.28	1.73	1.24	1.11	51.18	1.91	1.61	1.49	0.67	0.45	0.41	0.64	0.27	0.12	93.72	94.74
BC-2	2.06	2.41	1.75	2.41	0.00	2.37	2.46	1.89	1.66	1.46	1.65	2.02	1.08	0.50	78.91	75.73
BC-3	2.74	2.47	2.54	3.08	0.00	2.17	2.75	2.58	1.97	1.73	1.93	1.65	1.55	0.89	58.99	67.52
Ave.	2.36	2.20	1.84	2.20	6.84	2.15	2.28	1.99	1.43	1.21	1.33	1.44	0.97	0.50	76.6	78.67

HCL→Cr



Cr	Phase I					Phase II							Removal	Total		
Date	6/26	7/8	7/18	7/29	Removal(%)	8/25	9/1	9/17	9/29	10/9	10/19	10/29	11/9	11/25	(%)	Removal(%)
AC-1	51.46	44.02	47.10	52.76	0.00	48.80	43.52	30.33	22.67	16.97	11.08	11.29	11.57	27.23	44.20	47.09
AC-2	32.74	30.70	29.90	26.09	20.31	55.29	45.19	49.73	32.65	17.58	16.75	15.14	13.41	16.02	71.02	51.07
AC-3	37.62	28.40	27.20	24.57	34.69	48.98	49.34	48.32	33.99	27.44	17.55	26.75	16.43	19.99	59.16	46.86
Ave.	40.61	34.37	34.73	34.47	15.1	<mark>51.01</mark>	<mark>46.02</mark>	<mark>42.79</mark>	<mark>29.77</mark>	20.66	<mark>15.13</mark>	17.73	13.80	21.08	58.68	48.09
BC-1	69.60	46.38	43.80	64.63	7.14	37.04	41.81	52.03	30.69	23.75	18.62	28.77	20.43	20.72	44.05	70.23
BC-2	57.49	34.38	31.50	41.48	27.85	65.75	41.22	53.80	30.75	28.40	27.49	21.56	18.75	28.35	56.88	50.69
BC-3	86.20	39.19	50.70	66.27	23.12	54.26	43.23	52.15	40.60	41.64	27.75	21.61	19.9	28.82	46.89	66.57
Ave.	71.1	39.98	42.00	57.46	19.18	52.35	42.09	52.66	34.01	31.27	24.62	23.98	19.69	25.96	50.40	63.48

Soil Fertility Analysis

	Experimental							
Analysis	ļ	4	В					
	Before	After	Before	After				
рН	6.7	2.2	6.77	1.76				
EC (dS/m)	0.48	NA	0.57	NA				
Organic(%)	4.4	4.1	5	5.1				
Nitrogen(%)	0.24	0.42	0.25	0.75				
Bray-1 P(mg/Kg)	42.3	10.6	49.77	66.2				
CEC (C mol/kg)	17.97	NA	19.4	NA				
Exchangeable Potassium (mg/kg)	51.47	61.5	61.9	63.2				

NA: Not Available

Heavy metals contaminated in liquid leakage

		4	В		
Analysis	Experi	mental	Experime	Sewage Standard	
	Before	After	Before	After	
рН	3.5	7.89	3.58	8.02	6.0~9.0
Cr	0.206	0.025	0.30	0.022	0.03
Pb	1.524	0.082	2.19	0.052	1
Cd	1.646	0.016	2.034	0.029	2

Unit: ppm

Conclusion

- The lower pH 2~3 in soil could be more effective desorption of heavy metals.
- Adding the desorbent could increase desorption heavy metal contaminants in soil and improved soil fertility.
- Exchanging the cathode and anode could increase desorption Cr elements in soil.
- The remediation experiment was completed about 140 days.
EK Remediation Case 4 -In-Situ Bioremediation with EK for TPH

- Bay Area, San Francisco, CA
- TPH-G and TPH-D
- Soil plume covered an area of 45m² with a depth of 3~3.5m
- GW plume covered an area of 240 m² with bsg 3.5~4.5m
- Clayey bay mud
- Soil TPH within 1.5 month from 3,900 ppm to 40 ppm
- After 9 months work, GW BTEX Concentration was lower than CA cleanup standards
- Installed total 59 electrodes with 5m longs

Site Layout











Site Preparation















Remediation Equipment



AS Air Compressor









Single Well Test - SVE



Single Well Test - AS



Single Well Test - EK





 PT-MW-2 is Anode(+), PT-SVE is Cathode, 6m apart.
 Anode injected ORC
 GW velocity was 0.45~1.85 m/yr, 6m needed 3.2 years
 Cathode DO was increased after EK turned on.

LNAPL Remediation Case 6 – Refinery Source Area Investigation





Refinery Pilot Test - MPE For Source Area

MPE System Test













Oil & Water Separator



Oil and Water Flow Meters





Transfer Pump





Thank You!

APOLL TECH Apollo Technology Co., Ltd.

Case Studies of Remediation of Mercury Contaminated Soil

Speaker: Yu-Ting (Phil) Wei, Ph. D.



APOLL TECH Apollo Technology Co., Ltd.

Background

Properties of Mercury

Mercury is the most hazardous metal for human health and environment.

Elemental mercury is a liquid at normal temperature.

- Industrial facilities use mercury in their processes / products such as chlor-alkali plants/ thermometers, barometers, fluorescent light.
- It has high toxicity, volatility and is tendency to bioaccumulate in human body.
- There are several kinds of mercury compounds in the environment.



Properties of Mercury Compounds

Compound Name	Elemental Mercury	Mercury(II) oxide	Mercury sulfide	Mercuric Chloride	Mercurous Chloride	Methyl- mercuric Chloride	Dimethyl Mercury
Molecular formula	Hg_0	HgO	HgS	HgCl ₂	Hg_2Cl_2	CH₃HgCl	C_2H_6Hg
Molecular weight	200.59	216.59	232.66	271.52	472.09	251.1	230.66
Solubility (g/L)	5.6 X 10 ⁻⁵	0.053	insoluble	69	2.0 X 10 ⁻³	0.100	1
Density (g/cm³)	13.534	11.14	8.10	5.4	7.15	4.06	3.1874
Boiling Point (°C)	357	Not available	Not available	302	384	Not available	93
Melting Point (°C)	-39	500	580	277	302	170	-43
Oxidation State	0	+2	+2	+2	+1	+2	+2



Mercury Species in Water

 $\rm Hg^{2+}$, $\rm HgCl^+$, $\rm HgCl_2$, $\rm HgCl_3^-$, $\rm HgOHCl$, $\rm Hg(OH)_2$, $\rm HgS_2^{2-}$, $\rm HOHS^-$, $\rm HgS(s)$, $\rm Hg(liq)$, $\rm Hg(OH)_2(s)$

The mechanism of heavy metals transport across microbial cells

→ Nutrient metal uptake systems

- Ligand associated with facilitated transport system (L), complexes metal for transport.
- Mⁿ⁺ can be "mistaken" for nutrient metals, e.g. Zn, Mn.

→ Passive diffusion through membrane

- Membrane permeable species diffuse passively through plasma membrane.
- Neutral species (e.g. M-Org) may be most permeable.



Ref : Biogeochemistry of Small Catchment: A Tool for Environmental Research, 13 Trace Metals Speciation and Cycling, 1994, by B. Moldan and J. Cemy.

APOLL TECH Apollo Technology Co., Ltd.

Treatment Technologies For Mercury

States I and the second second

Regulatory Considerations

- In Taiwan, the Soil and Groundwater Pollution Remediation Act (SGWPR Act) was promulgated on February 2, 2000.
- The soil pollution control standard of Hg was set to be 5 mg/kg for food crop farmland soils and 20 mg/kg for other soils.
- The groundwater pollution control standards of Hg was set to be 0.002 mg/L for category I and 0.02 mg/L for category II.
- Sediment quality criteria: upper limit 0.87 mg/kg; lower limit 0.23 mg/kg
- Workplace air quality criteria: 0.05 mg/m³ (mercury vapors), 0.01 mg/m³ (Organic mercury)
- Effluent water quality of Hg: 0.005 mg/L, Organic mercury: ND
- Drinking water quality of Hg: 0.002 mg/L
- TCLP criteria : 0.2 mg/L (Total mercury)

APOLL TECH Treatment Technologies For Mercury

Technology	Description
Solidification / Stabilization	Physically binds or encloses contaminants within a stabilized mass and chemically reduces the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms.
Soil Washing / Acid Extraction	Uses the principle that some contaminants preferentially adsorb onto the fines fraction of soil. The soil is suspended in a wash solution and the fines are separated from the suspension, thereby reducing the contaminant concentrations in the remaining soil. Acid extraction uses an extracting chemical, such as hydrochloric acid or sulfuric acid.
Thermal Desorption / Retorting	Application of heat and reduced pressure to volatilize mercury from the contaminated medium, followed by conversion of the mercury vapors into liquid elemental mercury by condensation. Off-gases may require further treatment through additional air pollution control devices such as carbon units. <i>9</i>

Ref: U.S. EPA, Treatment Technologies For Mercury in Soil, Waste, and Water, 2007

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Mercury Enrichment

Particle size		Sand		Silt	Clay			Mercury distribution		
		0.1 cm	0.01 cm	0.002 cm	400 Aº	50 Aº	10 Aº	total	Mass, mg	Concentration, ppm
Soil sample	Weight, g	40	30	15	10	3	2	100	20	200
	%	0.40	0.30	0.15	0.10	0.03	0.02	1	100 %	_
	Specific surface area, cm ² /gm	9.1	67.9	17.0	1.9×10 ⁴	4.5×10 ⁴	1.5×10 ⁵	21.4×10 ⁴	—	9.34×10 ⁻⁷ mg/cm ²
20 um screened	Weight, g	32	24	12	2	0.6	0.4	71 g	4.0	56
	%	0.45	0.34	0.17	0.028	0.007	0.005	1	20 %	_
	Specific surface area, cm ² /gm	10.2	77.0	192.5	0.53×10 ⁴	1.1×10 ⁴	3.8×10 ⁴	5.46×10 ⁴	—	9.34×10 ⁻⁷ mg/cm ²
overflow	Weight, g	8	6	3	8	2.4	1.6	29	16.0	552
	%	0.28	0.20	0.10	0.282	0.083	0.055	1	80 %	_
	Specific surface area, cm ² /gm	6.3	45.3	113.2	5.3×10 ⁴	12.5×10 ⁴	41.3×10 ⁴	59.1×10 ⁴	_	9.34×10 ⁻⁷ mg/cm ²
										10

For sand and silt, specific surface area =2.3/d; For clay, specific surface area = $0.75/\ell$

Detection and Site Characterization

- The most commonly used site characterization technique for mercury is field-based X-ray fluorescence (XRF) analyzers. It can detect mercury concentration in less than 3 minutes.
- MA-3000 Mercury Analyzer: MA-3000 determines total mercury in Solid, Liquid and Gaseous matrices using the principle of thermal decomposition, gold amalgamation, and atomic absorption in accordance with USEPA 7473, ASTM D-6722-01, without any sample preparation. It can directly detect mercury in only 7 minutes. The measurement range is between 0.002ng-2000ng of mercury.
- A model EMP-2 is designed for measuring of gaseous mercury in work environments. The EMP-2 has sensitivity limits down to 0.1 ug/m³.



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Case

Soil Washing Treatment





- ✤ Owner: Japan Kaneka Soda Co., Ltd. 日本鐘淵曹達株式會社
- Object: Supply Military material (Use Soda to dissolve Aluminum) (Use Bromine as anti-knock agent)
- Factory: Salt land 600 Ha Bromine Plant 500kg/D NaOH Plant 100T/D (Mercury electrode)
- Construction: 1940-1944
- Operation: 1944
- Shut down: 1944/10 (ruined by US Air force Bomb)

Ref: CPDC, Remediation of CPDC An-shun Site: An Introduction





1945-1964 (Mercury Pollution)

- Owner: Taiwan Soda Company
- Factory: NaOH Plant 50T/D (Mercury electrode)
- Product: 45% Soda solu. / Flake soda Liq.CL₂ / H² / NaClO₃ Solu. / HCl Solu.

H₂

Na Cl

16

Na Cl

B'

Cl₂

- Reconstruction: 1946
- Operation: 1946 3T/D
 1964 100T/D

Ref: CPDC, Remediation of CPDC An-shun Site: An Introduction <u>Wikipedia</u>,: Castner–Kellner process



- Owner: Taiwan Soda Company
- Factory: NaOH Plant 50T/D (Mercury electrode) Pentachlophenol plant 5T/D
- Product: 45% Soda solu. / Flake soda Liq.CL₂ / H² / NaClO₃ Solu. / HCl Solu. Na-PCP
- Shut down: 1982.07 (Mercury Pollution Problem)









* 1983-2009 (Mercury / PCP)

 Owner: China Petrochemical Develop. Company (CPDC)
 Before 1993 CPDC State-run After 1993 CPDC Private

Remediation:

- → 1989 PCP-polluted groundwater remediation
- → 2003 An investigation of Dioxin
- → 2003 promulgated as Remediation Site
- → 2008 Court judged CPDC's responsibility
- 2009 Remediation plan was approved by Tainan government, and started since May, 2009

Ref: CPDC, Remediation of CPDC An-shun Site: An Introduction





Cleaned Area

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> 2003
 Road 2-9 was excavated

ei

 \bigcirc

EPB

- → 2005-Fish ponds were monitored (27 ha.)
- → 2008 Chu-Fa-Gun Stream (6000 m³) was excavated



After 2009.05.06 by EPB

Remediation Criteria

promulgated in 2003

Soil

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→ Dioxin < 1000 ng-I-TEQ/KG
 Hg < 20 mg/kg

Sediment

➡ Dioxin < 150 ng-I-TEQ/KG Hg < 1 mg/kg</p>

Surrounding Air Quality

→ Total Hg < 150 ng/Nm³ (WHO: 1000 ng/Nm³) PM10 < 125 ug/Nm³


















Mercury Distribution in An-Shun Site

Highest concentrations detected

- ➡ In soil: 9,550 mg/kg (vs. 20 mg/kg standard)
- → In sediment: 1,410 mg/kg (vs. 1 mg/kg standard)

Total Hg mass estimated to be over 40 tons

- Some hot spots in soil have been removed and contained in temporary storage areas
- → The storage place zone contains highly contaminated soil

Mercury derivative

➡ React with CL₂/NaOH/S to form HgCl₂/Hg(OH)₂/amalgam/HgS



An-Shun Site

SWSP, Sea water storage pond CAP, Chlor-alkali plant area PCP, Pentachlorophenol-plant area LVA, Lime vegetation area GA, Grass area

Soil & sediment polluted: in 37.1 ha

Target contaminants: Mercury, Dioxin (and also Pentachlorophenol)

Mercury Transfer & Pollution Map

Mercury Transport Path



Mercury - Pollution Map





Chlor-alkali Plant Area

Hg (average: 33 mg/kg; max: 3370 mg/kg) Dioxin (average: 1281 ng-TEQ/kg)

Detection Value Table

Item	Hg (mg/kg)	Dioxin (ng-TEQ/kg)
Number of samples	696	151
Maximum	3,370	45,500
Minimum	0	1
Average	33	1,281
Standard deviation	152	3,935
95% of the upper limit of the trustworthiness	43	1,845
95% of the lower limit of the trustworthiness	23	717







mg/kg

Particle size distribution

No	Sampling	Material P	roportion (%)	No	Sampling	Material P	Proportion (%)
NO.	depth (cm)	Sand	Silt and clay	NO.	depth (cm)	Sand	Silt and clay
G19	50-100	94.2	5.80	G82	50-100	86.59	13.41
G39	200-250	95.12	4.88	G83	50-100	92.02	7.98
G43	50-100	92.54	7.46	G84	50-100	92.01	7.99
G47	200-250	93.91	6.09	G91	50-100	90.53	9.47
G48	50-100	93.28	6.72	G92	50-100	78.49	21.51
G38	50-100	88.10	11.90	G93	50-100	94.67	5.33
G129	50-100	87.19	12.81	G104	50-100	93.41	6.59
G81	50-100	84.47	15.53				





Mercury Map (depth: 3m)





Hg (average: 40 mg/kg) Dioxin (average: 205,222 ng-TEQ/kg) (max: 14,100,000 ng-TEQ/kg)

Detection Value Table

Item	Hg (mg/kg)	Dioxin (ng-TEQ/kg)
Number of samples	85	285
Maximum	444	14,100,000
Minimum	0	7
Average	40	205,222
Standard deviation	89	1,255,846
95% of the upper limit of the trustworthiness	56	336,223
95% of the lower limit of the trustworthiness	23	74,222



Particle size distribution

No	Sampling	Material P	Proportion (%)	No	Sampling	Material P	Proportion (%)
NO.	depth (cm)	Sand	Silt and clay	NO.	depth (cm)	Sand	Silt and clay
CS017	0-50	92.34	7.66	CS035	50-100	89.74	10.26
CS017	200-250	98.80	1.20	CS037	0-50	86.44	13.56
CS019	50-100	83.30	16.70	CS037	200-250	92.94	7.06
CS021	0-50	83.00	17.00	CS039	100-150	95.78	4.22
CS025	0-50	88.41	11.59	CS041	0-50	89.29	10.71
CS028	100-150	92.18	7.82	CS041	100-150	89.88	10.12
CS033	150-200	91.55	8.46	CS041	200-250	91.73	8.27
CS034	0-50	83.13	16.87				



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Sea Water Storage Pond A

Hg (average: 11 mg/kg) Dioxin (average: 611ng-TEQ/kg)

Detection Value Table

ltem	Hg (mg/kg)	Dioxin (ng-TEQ/kg)
Number of samples	129	46
Maximum	104	4,460
Minimum	1	2
Average	11	611
Standard deviation	18	934
95% of the upper limit of the trustworthiness	13	853
95% of the lower limit of the trustworthiness	8	368

Granulometry

No	Sampling	Material P	roportion (%)	
depth (cm)	Sand	Silt and clay		
A01	0-30	77.24	22.76	
A03	0-30	43.17	56.83	
A03	30-60	88.87	11.13	













Sea Water Storage Pond B

Hg (average: 42 mg/kg) Dioxin (average: 979 ng-TEQ/kg)

Detection Value Table

Item	Hg (mg/kg)	Dioxin (ng-TEQ/kg)
Number of samples	207	42
Maximum	1,410	6,560
Minimum	0	3
Average	42	979
Standard deviation	164	1,648
95% of the upper limit of the trustworthiness	62	1,427
95% of the lower limit of the trustworthiness	22	531

Particle size distribution

No	Sampling	Material P	roportion (%)	
dep	depth (cm)	Sand	Silt and clay	
B01	90-120	89.80	10.20	
B03	90-120	63.36	36.64	
B04	90-120	54.13	45.87	
B06	90-120	50.36	49.64	
B08	210-240	85.41	14.59	
B17	90-120	92.41	7.59	
B20	90-120	91.49	8.51	



mg/kg



How to treat?



Remediation Plan 2009-2024

Remediation Train Concept



APOLL TECH Quantities of Mercury Contaminated Soil / Sediment

Sedime	ent from Po	nd B	-	Sec	liment fron	n Pond A	
(34,000	0 m ³ ,54.0	00tons)		(21,	000 m ³ , 3	34,000tons)	
Depth (cm)	Volume(m ³)		海水池4區		Depth (cm)	Volume (m ³)	
0-30	9,200		Pond A	A c	0-30	21,000	
30-60	6,250				30-60	0	
60-90	6,250		赵 辰二二一 樹林	區	30-90	0	
90-150	7,000	→海水池8區	▶ 鱖氯上敞區 •Chloralkali Plant				
150-210	5,300	Pond B		//早 ^最 Soil fr	om Storag	e space	
0.11.0			暫存區	(20,0	$00 \text{ m}^3 \cdot 32$.,000tons)	
Soll from	n Chioraika	II Plant	Storage area	Area	Sources	Volume (r	m ³)
(30,000	m^3 , 48,00	0 tons)	五氯酚工廠區	A2-1~A2-12	2 Chloralkali F	Plant 10,000)
Depth (cm)	Volume (m ³)		PCP plant	A3-1~A3-7	Chloralkali F	Plant 5,500	
0-50	12,000						
50-100	8,000			I	Grass Are	ea 500	
100-150	4,000			K1~K2	Grass Are	a 4,000	
150-200	4,000	\leq 10	60 000 tons				
100 200							
200-250	2,000						
200-250	2,000					36	

Introduction of Soil Washing

- With the limited available storage space at An-shun site, China Petrochemical Development Corporation (CPDC) was considering economical and efficient methods for soil treatment.
- Soil with low mercury concentration and with dioxin below regulation standard is targeted for priority treatment.
- The goal is to reduce the amount of soil required for thermal treatment or more complicated treatment in the future, in hope to reduce the overall remediation cost for soil treatment.



The Concept of Soil Washing

Interpreting the mercury speciation in soil

- Implementing a sequential extraction process of different operationally defined fractions (mobile Hg, semi-mobile Hg and non-mobile Hg)
- Applying the adequate reagents and controlling the pH value to transform mercury species that are adhered to the soil surface into mercury complex, they would

dissolve in the water



APOLL TECH Mercury Analysis (Before Washing)

Samples	Mobile Hg (mg/kg)		Semimobile Hg (mg/kg)		Nonmobile Hg (mg/kg)	
	Conc.	%	Conc.	%	Conc.	%
Sea pond B	12.27	13%	30.82	34%	49.24	53%
Sea pond B	13.32	13%	30.66	31%	56.58	56%
Sea pond B	23.35	8%	138.9	51%	115.1	41%
Chlor-alkali area	11.66	22%	30.91	58%	11.07	20%
Grass area	5.37	15%	28.17	79%	2.06	6%
Grass area	3.42	10%	27.40	81%	3.00	9%



Samples	Mobile Hg (mg/kg)		Semimobile Hg (mg/kg)		Nonmobile Hg (mg/kg)	
	Conc.	%	Conc.	%	Conc.	%
Sea pond B	0.62	4%	14.31	85%	1.83	11%
Sea pond B	1.88	13%	10.62	72%	2.29	15%
Sea pond B	7.61	57%	4.37	33%	1.38	10%
Chlor- alkali area	2.93	56%	1.71	33%	0.61	12%
Grass area	4.77	43%	5.73	52%	0.53	5%
Grass area	4.09	46%	4.47	50%	0.34	4%

APOLL TECH The Feasibility Study -A Pilot Test

15 tons of mercury contaminated soil was treated by soil washing. The percentage of qualified treated soil is 78%. The unqualified soil includes wastewater mud cake, waste activated carbon and contaminated soil.



41

Mobile Shelter

Application

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- Special excavation
 *when PM10 or vapor
 Hg over regulation
- Low material cost
 *no steel-structure
- Dismantle & Buildup
 * in 20 min.

Protection

 Protect environment & human health









Building Soil Washing Plant

Land preparation



Concrete foundation



Physical washing equipment



Factory Installation







Pipeline installation



Commissioning





Physical washing

Chemical washing















- In sea pond area, dredging the sediment layer by layer according to the investigation data
- In Chlor-alkali and storage area, applying XRF to identify the available feed soil
- Weekly detect the dioxin concentration to control feed quality
- Three stages to qualify treated soil : self-quality control, self-verification and EPB verification



Sediment Transport



Dredging Boat





Cutter Suction



Pipeline on the pond



Pipeline on the ground



Feed location





Field XRF





MA-3000 mercury analyzer

EMP-2 mercury vapor analyzer





Dioxin Enrichment During Commissioning

* Soil

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Unit: ng-TEQ/kg	Input Dioxin	Output Dioxin				
Date	Feed	Silt and Clay (unqualified soil)	Washed Soil (qualified soil)			
2012/9/26	438	1,230	82.9			
2012/9/28	1,120	1,800	323			
2012/10/5	1,128	6,948	585			
2012/10/7	1,640	5,329	1,007			

Sediment

Unit: ng-TEQ/kg	Input Dioxin	Output Dioxin	
Date	Feed	Silt and Clay (unqualified soil)	Washed Soil (qualified soil)
101.11.21	11,800	6,900	504
101.11.26	1,020	6,000	274
101.11.28	7,180	16,200	702
101.11.30	28,500	16,200	222
101.12.04	328	5,400	217 56



Feed		Washed Soil Weight (tons)		
	Feed Weight (tons)	Self verified	Washed rock	
Soil	43,696.95	27,387.13	7,058.92	
Sediment	36,314.07	30,640.26		
subtotal	80,011.02	58,027.39	7,058.92	
Total	80,011.02	65,086.31		

The percentage of qualified treated soil =

 $\frac{65,086.31}{80,011.02} \times 100\% = 81\%$

EPB verified soil: 53,436 tons


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Case II

Thermal Treatment

Plan Overview - Ex-Shin Ya Light Bulb Plant

- 1969 Shin Ya Electronics started manufacturing light bulbs at XinZhung, Taipei County
- 1989 ceased operation
- 1997 business closed

TECH

- 2006 an investigations done by EPA on discarded plants, soil found contaminated with mercury
- 2007 on the watch list promulgated by EPB
- 2010 FarGlory won bid on land
- 2010 contamination investigation commissioned by FarGlory approved
- 2010 FarGlory commissioned ApolloTech in the execution of contamination remediation project
- 2012 Remediation completed by Apollo Tech



Aerial photograph of Ex-Shin Ya Light Bulb Plant

Pollution Distribution

- Contaminated soil: 21,043 m²
- After investigation: 16,300 m²
- Additional investigation: 10mx10m grids , taking 201 core samples in different depths, the total is 725 soil samples
- Contaminated depths: 0.5 to 2 meters below ground level
- Samples exceed the regulation standards: Mercury: 44 samples
 Copper: 16 samples
 Cadmium: 10 samples
 Chrome: 5 samples
 Arsenic: 2 samples













APOLL TECH Thermal Equipment



Indirect Fired Rotary Kiln



First Section 0.76m(dia.)x12.0m(L)



Second Section 0.95m(dia.)x12.0m(L)





Flue Gas (II)



Air Pollution Control System



Cyclone, Bag Filter and Ceramic Filter

Sulfur Enhanced Active Carbon Tank

 Adsorb the mercury vapor in the flue gas to comply with the air emission standard

Bag and Ceramic Filter

- Resistant to the high temperature flue gas
- Capacity: 45 m³/min
- Advantage: Avoid the mercury vapor being condensed on the dust



Mercury Recovery





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Fine Tube Condenser and Cyclone

- To condense and recover mercury
- Heat exchange capacity: 1,000,000 kcal/hr
 - Indirect heat exchange method to prevent the further pollution

Fine tube condenser

Ion Exchanger Resin Tower

- To remove the mercury from condensed water
- Advantage: high efficiency
- Compliance with the effluent water standards







Treatment	Amount	Notes		
Excavation	27,800 m ³	Investigated area was 11,500 m ² and 2 m depth Contaminated area was 4,800 m ² and 1 m depth		
Dry screening	15,100 m ³	Screened soil was 9,800 m ³ and soil contamination by other heavy metals was 5,300 m ³		
Wet screening (washing)	8,900 m ³	To reduce the amount of contaminated soil for further thermal treatment		



APOLL TECH Excavation and Backfill



Excavation



Excavation



Excavation



Backfill



Excavation







Dry screening



Pick up wastes



Dry screening

O





Pick up wastes



Dry screening





Washing feed



Washing



Washing feed



Water recycling



Washed soil discharge



Water recycling

APOLL®TECH Thermal Treatment



Control panel



Feed area



Temperature control



Discharge area





Quality Control



- Field-based X-ray fluorescence (XRF) analyzers It can detect mercury concentration in less than 3 minutes
- MA-3000 Mercury Analyzer: MA-3000 can directly detect mercury in only 7 minutes. The measurement range is between 0.002ng-2000ng of mercury
- A model EMP-2 is designed for measuring of gaseous mercury in work environments. The EMP-2 has sensitivity limits down to 0.1 ug/m³











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Washed soil



Thermal treated soil



Mixing dilution





Labtoratory test

Water Pollution Control

Grit chamber

Wastewater treatment

- Rain gutters are placed around the site perimeters. Runoffs are connected in the temporary grit chamber for recycling.
 Effluent water meet the runoff standards of construction sites.
- Excavation and backfill were done in sections to prevent extensive exposure of excavated areas and rain wash.
- Condensed water in thermal treatment was treated to reuse for cooling water and car wash.



Spray to prevent dust

Road wash

Cover by canvas



Dust network



Change the active carbon periodically

Flue Gas Monitoring

- Taiwan EPA Certified laboratory for analysis
- Monthly detect flue gas
- Weekly detect mercury vapor surrounding the thermal plant
- Using NIC EMP-2 to detect mercury vapor every day





) TECH Monitoring the Mercury ab urrounding thermal Plant

Four spots surrounding the thermal plant were chosen

Overall, 33 monitoring data were all less than 0.00022 mg/Nm³ *







VOCs and Odor Monitoring

 Taiwan EPA Certified laboratory for analysis

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 EPB also randomly monitored the odor on site







Items	Standards	Detected
Stack	1,000	733
Surrounding area	50	<10





Surrounding Area Monitoring

Groundwater
Effluent water
Air quality
Mercury vapor
Noise and vibration

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	items	Frequency
Air	TSP, PM10	Monthly
	Mercury	Weekly
Vibration		Monthly
Noise	Lmax, Leq	Monthly
Effluent water	pH, temperature, SS, COD, Mercury, Copper, Cadmium, Nickel	Monthly
Groundwater	Heavy metals and VOCs	Monthly

Quality Control Process

Quality Control Process

- Randomly select 20 samples to verify the treated soil
- Taiwan EPA Certified laboratory for analysis

* QC

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- → Mercury: ND 12.3 mg/kg
- → Copper: 8.22 232 mg/kg
- → Nickel: 17.0 67.1 mg/kg
- → Cadmium: ND 6.06 mg/kg
- ➡ Arsenic: 4.97 16.2 mg/kg
- → Chrome: 17.1 64.2 mg/kg
- → Lead: 10.8 192 mg/kg
- → Zinc: 49.6 487 mg/kg





Feed (input)			Treated Soil (output)		
Average Conc.	Amount	Mercury Mass	Average Conc.	Amount	Mercury Mass
37.5 mg/kg	4,700 ton	176.25 kg (100%)	1.5 mg/kg	2,820 ton	4.23 kg (2.4%)

Active Carbon Absorbed			Emission Gas		
Average Conc.	Amount	Mercury Mass	Average Conc.	Amount	Mercury Mass
18,800 mg/kg	6.5 ton	122.2 kg (69.3%)	300 µg/m ³	4,512,000 m ³	1.35 kg (0.77%)

Verification

Self-verification

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- Taiwan EPA Certified laboratory for analysis
- Randomly select 30 samples to verify the treated soil
- Quality control by XRF

Verified Data

- → Mercury: 0.36 8.44 mg/kg
- → Copper: 24.8 138 mg/kg
- → Nickel: 28.3 67.9 mg/kg
- → Cadmium: 0.06 4.74mg/kg
- → Arsenic: 5.70 14.1 mg/kg
- → Chrome: 21.5 55.9 mg/kg
- → Lead: 22.1 121 mg/kg
- → Zinc: 84.9 358 mg/kg

EPB Verification

- → Taiwan EPA Certified laboratory for analysis
- Randomly take 15 samples to verify the treated soil
- Verification results: all comply with the regulation standards



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Summary

Summary

XX:

- Two cases of mercury remediation are included in this report. Thermal treatment was completed, and the soil washing treatment is currently in process. Other than detection equipment, all other equipment are purchased locally for the flexibility and efficiency of maintenance and updates.
- Key to successful remediation not only depends on understanding the ppm concentration level of the contamination, but also on the soil properties. Due to the complexity of the soil, remediation techniques should be assessed and specialized case by case.
- While thermal treatment is a common practice, soil washing treatment could be another practice that can be used effectively in mercury remediation. Furthermore, if the two treatments can be combined in the remediation process, the results is not only effective, but economical.

Thank you for your attention

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Remediation techniques of soil contamination

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International Training Course March 21-28, 2016

Zueng-Sang Chen

Content

- Management of soil remediation project
- Development and application of soil remediation techniques
- In-situ (in site) remediation techniques and assessment of contaminated sites
- Ex-situ (off site) remediation techniques and assessment of contaminated sites
- Case studies
- Discussions









Conceptualization

USEPA

General soil remediation Techniques (since 1985)

- soil vapor extraction (13%)
- bioremediation (13%)
- <u>air stripping</u> (9%)
- soil washing (9%)
- immobilization) (solidification or stabilizing method) (9%)
- thermal desorption (5%)
- chemical oxidation (5%)
- radio/electric heating (5%)
Summary of soil remediations for rural soils

- Chemical methods a. extraction method b. reduced condition c. stabilization
 Engineering methods
 - a. removal contaminated soils and cover with clean soils
 - **b. cover with clean soils**
 - c. soil washing
 - d. electrokinetics
- Biological methods a. phytoremediation
 b. phytostabilization

in-situ physico-chemical method Solidification

- By adding the chemical materials to mix or react with the pollutants in the soil
- To solid the contaminated soil as very low release material under natural raining system
- To reduce the pollutants released from the solid materials.
- Cost effective?

in-situ physico-chemical method **Soil amendments**

- To reduce the bioavailability of metals treated with different non-toxic materials as soil amendments
- Reduce the bioavailability of metals in soils by addition of lime materials, phosphate materials, zeolite, hydrous metal oxides, or organic materials, etc.
- Cost-effective?
- Any other materials can be used?

in-situ physico-chemical method **Attenuation**

- To mixture and dilute the soils of whole soil depths
- Dilution the surface contaminated soils by mixing with the subsurface clean soils by machines. About 200 ha of Taiwan rural soils were cleaned up by this method.
- How to approve it is effective?
- What is the limit factor to apply this method?

in-situ physico-chemical method Soil Flushing

- The soils treated with different reagents or surfactants
- Only for contaminated sandy soils or course soil texture soils, not for sticky clay soils
- Need to treat the waste water
- Cost-effective?

in-situ physico-chemical method Soil Washing

- Treated with different acids including HCl, HNO₃, phosphoric acid, etc.
- Must be recycled of the chemical acids to reduce the remediation cost
- Need to treat the waste water to discharge into the environment
- Need to recovery the soil characteristics and soil function for crop productivity.
- Very high cost including remediation, waste water treatment and soil function recovery

in-situ physico-chemical method **Electrokinetics Separation (EK)**

- Electric current induced movement of ions to electrodes and to remove the pollutants.
- Need to evaluate the efficiency to remove the pollutants
- Cost-effective? High energy?
- Why it is not successful in the field site?



Schematic Diagram of One Electrode Configuration and Geometry Used in Field Implementation of Electrokinetic Remediation







Schematic View of Contaminated Plume Stopped by An Electrokinetic Fence

In-situ: electrokinetics and heating Vitrification

- Heating to produce a glass-like, nonporous materials.
- 300-600 degree C for Hg sites and pesticides sites
- More than 1000 degree C for high concentration of Hg sites and dioxin sites
- Very high cost techniques.

Vitrification



In-situ: biological method Phytostabilization

- To promote vegetative growth to immobilize metals of contamination site (eg. vetiver grass)
- To produce the green landscape and to stabilize the contaminated sites
- Can not significant remove the pollutants from the sites
- Very low cost (< US\$ 10/ton soil)
- ONLY recommendation for low contaminated sites

Phytostabilization Vetiver grass







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In-situ: biological method Phytoremediation (or phytoextraction)

- To significantly remove the metals by plants.
- 420 plant species found for different metals uptake
- Higher than 100 times of general plant species (>100 mg/kg for Cd, >1000 mg/kg for Cu, Cr, Ni, Pb, or >10000 mg/kg for Zn)
- Highly accepted by the local community for low contamination sites, especially for European Union.
- Very low cost (< US\$ 10/ton soil)
- ONLY recommendation for low contaminated sites
- Cost-effective ?

Phyto-stabilization (42 species tested in the field of Taoyuan, Taiwan)



12 species (total 24,000 plants) were studied in 1 ha of Cu, Zn, Cr and Ni-contaminated soils



(Lai et al., 2010)

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Hyperaccumulator Thlaspi caerulescens

Pb 8,500 mg/kg Cd 164-2,800 mg/kg Zn 27,000 mg/kg







in situ physico-chemical method for oil contaminated soils: Soil vapor extraction (SVE)

- Inject the air into deep contaminated soils of the site and pump out the pollutants from the site
- Install at the suitable depth of the contaminated soils of site
- Need to model the effectives of the SVE installation
- Need to evaluate the effectives and removal time of site
- Cost-effective
- Need to check to cut the pollution sources

Case study in semiconductor plant



Excavation or removal of high concentration area



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Soil vapor extraction (SVE)



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adsorption

Soil vapor extraction SVE

- vapor extraction
 - 300 M3/hr
 - Adsorption of the pollutants gas
- injection of air
 - To increase the VOC extraction rate
- PLC controller
 - Inter-mediate or regional vapor extraction



Vacuum pump

(資料摘自瑞昶科技顧問公司史麗芬於環保署演講內容, 2003)



Vacuum pump and active carbon adsorption



PLC controller

safety and health plan

- **Emergency in SVE**
- Monitoring Air quality in site
- Operator protection working in the site



室内施工人員之防護

(資料摘自瑞昶科技顧問公司史麗芬於環保署演講內容, 2003)



Monitoring Air quality in site



Operator protection working in the site

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Zueng-Sang Chen

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in situ physico-chemical method for oil contaminated soils (need new technology?)

- Attenuation: Dilute the pollutant concentration under natural soil condition.
- **Soil Flushing :** soil flushing with reagents or surfactants
- Oxygen Release Compound (ORCs): Adding the Calcium peroxide or other compounds to continuously release the oxygen gas

Soil vapor extraction: oil contaminated soils



in situ physico-chemical method

for oil contaminated soils: Soil Flushing

- Polluted soil treated with reagents or surfactants
- More suitable for course soil texture soils, not for cleyey soil
- The reagents are most chemcial trong acidic reagents
- High potential cost
- Need to pump and treat of the groundwater in the downriver

Soil Flushing: oil contaminated soils



Low Permeability Zone

U.S. EPA TIO

in situ physico-chemical method for organic contaminated soils **Permeable reactive barriers, PRB**

A Permeable Reactive Barrier (PRB):

- is a permeable zone containing or creating a reactive treatment area oriented to intercept and remediate a contaminant plume
- removes contaminants from the ground water flow system by physical, chemical, or biological processes

PRB Concept (USEPA, 2013)



In site: Permeable reactive barriers, PRB



PRBs – Introduction and Overview

Why Use a PRB?

- Treatment occurs in the subsurface
- Typical treatment is passive
- Lower costs than conventional methods
- Allows full economic use of a property
- Robust
- Monitoring can be focused

(USEPA, 2013)

Permeable reactive barriers, PRB

mechnisum
physical
chemical
biological

pollutants
VOCs
SVOCs
BTEX
Heavy metals
Inorganic salts

PRBs – Introduction and Overview

Contaminants Treated and Reactive Media Used

CONTAMINANT	BARRIERTYPE	REACTIVE MEDIA	STATUS
Organics - DCE, TCE, PCE - BTEX - nitrobenzene - DCA, TCA - PCBs, PAHs	Degradation	zero-valent iron iron(II) porphyrins resting-state microorganisms oxygen-releasing compound dithionite	commercial laboratory field field field
	Sorption	zeolite surfactant modified silicates organobentonites activated carbon	laboratory laboratory laboratory laboratory
Inorganics - heavy metals (Ni, Pb, Cd, Cr, V, Hg) - radioactive (U, Ra, Sr, Cs, Tc) - nitrate	Sorption	peat ferric oxyhydroxide bentonite zeolites and modified zeolites chitosan beads	laboratory field laboratory laboratory laboratory
	Precipitation	hydroxyapatite zero-valent iron dithionite lime or limestone	laboratory commercial field commercial
	Degradation	saw dust	field



Off site: physico-chemical methods -1

- Solidification : addition of a cementing agent to produce a hardened, nonporous materials.
- Soil Washing : Chelate or acid extraction
- Chemical /Solvent extraction : extraction by chemical reagents (EDTA, citric acid etc.) and separate the pollutants from the solution
- Chemical Oxidation : oxidation of organic materials to produce CO₂ and H₂O
Off site: physico-chemical methods -2

- Soil Flushing
- Soil vapor extraction (SVE)
- Particle-size segragation : selected removal of fine particle (clay) that have high concentration
- Soil excavation : soil removal and disposal.

in situ physico-chemical method for oil contaminated soils

- Soil vapor extraction (SVE): Sent air into deep soils of the site and pump out the pollutants from the site
- Attenuation: Dilute the conc. In the natural condition
- **Soil Flushing :** soil flushing with reagents or surfactants
- Oxygen Release Compound (ORCs): Adding the Calcium peroxide to release oxygen

Chemical remediation techniques

- acid washing or extraction method
- Stabilization or solidification
- chemical oxidation, reduction or neutralization)
- Electrokinetics

ISCO (In-Situ Chemical Oxidation)

 Put the oxidant into the soil to transfer or reduce the concentration, mass, mobility or toxicity of pollutants (contaminants of concern, COC) in soil or groundwater

Can combine with other treatments (ex. bioremediation

Benefit of ISCO method

- oxidation of DNAPL materials
- reduce the reaction time
- reduce the cost of pump and treatment
- do not change the building structure
- reduce the cost of excavation and treated soils

In situ chemical oxidation



SA17 Naval Training Center Orlando, Florida, USA



wash rack < storage area for waste fuel & oil -19,000 ft²

-Initial site investigations began in 1995



-Gasoline-range organics -CVOCs (TCE and VC) -maximum conc. 306,000µg/L for TCE 78,500µg/L for GRO





-remediation time

11/6-12/1, 2000

- -69 Injectors in 3 levels
- -8,700 gallons H₂O₂ (25%) 6,900 gallons Fe (II)

remediation results

CVOCs reduced from 306,000 µg/L to 27,000 µg/L (removal rate : 92%)
GRO removal from 78,500 µg/L to 9,190 µg/L (removal rate : 90%)

Target value:
500 µg/L → by addition of H₂O₂ injection

Chemical Stabilization/solidification method

- By adding the chemical materials to stabilize or react with the pollutants in the soil
- To solid the contaminated soil as very low release material under natural raining system
- To reduce the pollutants released from the solid materials.
- Cost effective?

Case study for *stabilization technology* in USEPA

Case studies for stabilization technologies (modified from U.S. EPA.10)

Site/ contractor	Contaminant (concentration)	Treatment volume	Physical form	Binder	Percentage binder(s) added	Treatment (batch/ continuous in situ)	Disposal (onsite/ offsite)	Volume increase, %	Scale of operation
Midwest, U.S. Plating Company, Envirite	Cu, Cr, Ni	16,000 yd ³	Sludge	Portland cement	20%	In situ	Onsite	> 0	Full scale
Marathon Steel Phoenix, AZ Silicate, Tech.	Pb, Cd	150,000 yd ³	Dry-landfill	Portland cement and silicates (Toxsorb) TM	Varied 7-15% (cement)	Concrete batch plant	Landfill	NA	Full scale
N.E. Refinery ENRECO	Oil sludges, Pb, Cr, As	100,000 yd ³	Sludges, variable	Kiln dust (high CaO content)	Varied, 15-30%	In situ	Onsite	> Varied, ~ 20% average	Full scale
Amoco Wood River Chemfix	Oil/solids Cd, Cr, Pb	90,000,000 gallons	Sludges	Chemfix proprietary	NA, proprietary	Continuous flow (proprietary process)	Onsite	Average 15%	Full scale (site delisted 1985)
Pepper Steel & Alloy, Miami, FL VFL Technology Corporation	Oil sat: soil Pb (1000 ppm) PCBs (200 ppm) As (1-200 ppm)	62,000 yd ³ (plus 5000 tons of surface debris)	Soils	Pozzolanic and proprietary	~ 30%	Continuous feed (mixer proprietary) design	Onsite	$\sim 1\%$	Full scale
Vickery, OH Chemical Waste Management	Waste acid PCBs (< 500 ppm), dioxins	~235,000 yd ³	Sludges (viscous)	Lime and kiln dust	\sim 15% CaO \sim 5% kiln dust	In situ	Onsite (TSCA cells)	>~9%+	Full scale
Wood Treating, Savannah, GA Geo-Con, Inc.	Creosote wastes	12,000 yd ³	Sludges	Kiln dust	20%	In situ	Onsite lined cells	>~ 14%	Full scale
Wyandotte, MI Treatment Plant Chem Met	Various/combined	20 million gal/yr	Various	Lime		Continuous	Offsite (secure landfill)		In-plant process
Chem Refinery, TX HAZCON	Combined metals, sulfur, oil sludges, etc.	90,000 gal. (445 yd ³)	Sludges (synthetic oil sludges)	Portland cement and proprietary	NA	Continuous flow	Onsite (secure landfill)	>Estimated 10%	Full scale
Metalplating, WI Geo-Con, Inc.	Al (9500 ppm) Ni (750 ppm) Cr (220 ppm) Cu (2000 ppm)	3000 yd ³	Sludges	Lime	10-25%	In situ	Onsite landfill	> 4-10%	Full scale

Case study for Reagents for stabilization in USEPA

Reagent applicability for waste stabilization

Waste component	Cement-based	Pozzolan-based	Thermoplastic	Organic polymer	
Nonpolar organics as: oil and grease, aromatic	May impede setting Decreases durability over a long time period.	May impede setting. Decreases durability over a long time period.	Organics may vaporize upon heating. Demonstrated	May impede setting. Demonstrated effectiveness under certain	
hydrocarbons, halogenated hydrocarbons, PCBs Volatiles may escape upon mixing Demonstrated effectiveness under certain conditions. ^a		Volatiles may escape upon mixing. Demonstrated effectiveness under certain conditions. ^b	effectiveness under certain conditions. ^C	conditions. ^d	
Polar organics as: alcohols, phenols, organic acids, glycols	Phenol will significantly retard setting and will decrease durability in the short run. Decreases durability over a long time period. ^e	Phenol will significantly relard setting and will decrease durability in the short run. Alcohols may retard setting. Decreases durability over a long time period.	Organics may vaporize upon heating.	No significiant effect on setting.	
Acids as: hydrochloric acid, hydrofluoric acid	No significant effect on setting. Cement will neutralize acids. Types II and IV portland cement demonstrate better durability charactenstics than Type I. Demonstrated effectiveness. ^{1,g}	No significant effect on setting. Compatible, will neutralize acids. Demonstrated effectiveness ^{1,g}	Can be neutralized before incorporation.	Can be neutralized before incorporation. Ureaformaldehyde demonstrated to be effective. ¹	
Oxidizers as: sodium Compatible hypochlorate, potassium permanganate, nitric acid, potassium dichromate		Compatible	May cause matrix breakdown, fire.	May cause matrix breakdown, fire.	
Salts as: sulfates, halides, nitrates, cyanides	Increase setting times. Decrease durability. Sullates may retard setting and cause spalling unless special cement is used. Sullates accelerate other reactions	Halides are easily leached and retard setting. Halides may retard setting, most are easily leached. Sulfates can retard or accelerate reactions.	Sulfates and halides may dehydrate and rehydrate. causing splitting.	Compatible ^h	
Heavy metals as: lead, chromium, cadmium, arsenic, mercury	Compatible. Can increase set time. Demonstrated effectiveness under certain conditions. ¹	Compatible. Demonstrated effectiveness on certain species (lead, cadmium, chromium). ^d .	Compatible. Demonstrated effectiveness on certain species (copper, arsenic,	Compatible. Demonstrated effectiveness with arsenic. ^d	
1 //www.actional.com/actional			chromium).d		
Radioactive materials	Compatible	Compatible	Compatible	Compatible	
^a Tittlebaum and Seals 1985; Vi	in Keuren et al. 1987, JACA 1985; U.S.	EPA 1986: Jones 1986	¹ JACA 1985.		
b Musser and Smith 1984; U.S.	EPA 1984; Kyles, Malinowski, and Stan	9 Van Keuren et al. 1987.			
^c Tittlebaum and Seals 1985; JA	CA 1985.	h Musser and Smith 1984.			
d Tittlebaum and Seals 1985.		¹ Federal Register 1988, Kyles, Malinowski, and Stanczyk 1987.			
^e Kolvites and Bisbop 1987.		1 U.S. EPA 1984.			

^e Kolvites and Bishop 1987.

Model demonstration of chemical stabilization



Off site : Heating

- Vitrification: heating to produce a glass-like, nonporous materials (<600 degree C) (soil properties will be changed
- Incineration: heating the organic pollutants to remove the pollutants
- Pyrolysis: heating the organic pollutants to remove the pollutants in no oxygen conditions (>1000 degree C)
- Thermal desorption : heating the organic pollutants to remove the pollutants in low or high temperature conditions

Bioremediation: biological treated methods

- oxidation and reduction decomposed by microorganisms
- biofilm treatment, biological adsorption, etc
- bio-restoration

Bioremediation treatments -1

- Best benefit: stable and no side effects
- suitable for organic pollutants: TCE or gasoline
- Different remediation types :
 - oxidized and reduced methods
 - in-situ and ex-situ
 - microbiological approach and microbial ecology approach

Bioremediation treatments -2

- General methods: bioventing, slurry reactor, land farming, composting, enhanced in-site bioremediation, etc.
- Most sites were treated by in-situ for biological decomposition process

Indicators of Natural attenuation by microorganisms

key factors: collected the information of bio-transportation and the evidence of effective biological activity.

three evidences : (1) reduce the conc. of pollutants, (2) do have the biological reactions, and (3) have by-product produced through reactions

Off site : **biological** method

 Land farming: The excavation materials were filled on the land surface for biological decomposition

 remediation for oil pollution



U.S. EPA TIO

Suitability of natural bioremediation

Evidences of natural bioremediation)
Total assimilative capacity can be used for the decomposition of BTEX comp
Structural analysis of pollution plume

Non-technical factors

budget and time
idea of communities
layout of the site and surrounding area
target value of soil remediation

Summary of remediation techniques used in Taiwan

- Phytostabilization (** field scale)
- Dilution attenuation (*field scale) : heavy metals pollution
- Soil amendments (soil addition) (pilot scale)
- Soil washing (by acidic solution) : (*field scale)
- Soil vapor extraction (SVE) (*field scale)
- Thermal desorption (*field scale) (pesticides)
- Solidification (pilot): (in pilot) :heavy metals pollution
- Chemical oxidation (gas station pollution) (*field scale)
- Electrokinetics separation (EK) (pilot)
- Bioremediation (oil pollution) (*field scale)
- Land farming (oil pollution sites) (*field scale)

Analysis of soil remediation techniques and regulations -1

- **The reasonable soil remediation procedurescy makers**
- Cut the pollution sources
- Is the cleanup the sediment of irrigation water, then do the soil remediation project ?
- How to recover the minimum soil fertility requirements fo crop productivity after the soil remediation?
- How to establish the standard operation procedures (SOP) to evaluate the soil condition after soil remediation project ?

Analysis of soil remediation techniques and regulations -2

- How to recover the minimum soil fertility requirements fo crop productivity after the soil remediation?
- Do we have other evaluation methods to evaluate the status of soil pollution by bioavailability extraction methods?
- Where is the pollution sources in the contaminated sites by environmental forensics?

Analysis of remediation techniques and regulations of oil pollution-1

- Risk-based assessment approach
- **Remediation target**
- Remediation strategy, and
- Budget consideration

Analysis of remediation techniques and regulations of oil pollution-2

- How to establish the "technical guidelines" to be followed?
- How to finish the remediation project in a reasonable time?

Factors to select the suitable remediation techniques

- Technical consideration : evaluated on performance, reliability, implementability, time, and safety
- Environmental concerns : environmental standard of pollutants, short and long term effects, irreversible commitments of resources, and their costs
- Public health concerns : site evaluation and analysis of human exposure to site, comparisons of projected clean up level, and ability to be removed
- Institutional concerns : the effects of national and local government standards and other institutional considerations of each alternative techniques
- Costs : include operation and maintenance (O&M) costs

Factors affecting the options of remediation

- Safety
- Reliability
- Reduce the toxicity, volume and mobility (20% of cost to reduce 80% risk)
- Necessity for process proof monitoring
- Treatment rate
- Treatment by-product
- Acceptability to regulators and local residents,
- Reclamation cost

Procedure to select the good remediation techniques

- Remedial Goal (Health Risk assessment)
- Identification of response action
- Screening of soil remediation technology
- Development and screening of remedial action alternatives
- Detailed evaluation

Factors for selecting remediation techniques of contaminated soils by heavy metals

- conc. of heavy metals
- soil texture
- depth of groundwater level
- the efficiency
- budget and benefits
- time
- opinion of people)

Conclusions

The soil remediation techniques and their development for rural soil contaminated by heavy metals and oil.

- Technical and non-technical factors
- The regulations should be revised
- Problems and statistic analysis of techniques and regulation







Case studies of Bioremediation and Phytoremediation on PetroleumContaminated Site

侯善麟 Frank S. L. Hou 台灣中油 CPC Corporation, Taiwan 中國醫藥大學 China Medical University



Bioremediation

 Using subsurface microorganisms to transform hazardous contaminants into relatively harmless byproducts, such as ethene and water

- Biodegrade
- Mineralize
- Biotransform
- Techniques or types of bioremediation:
 - A component of Natural Attenuation
 - Enhanced Bioremediation
 - Bioaugmentation



Bioremediation Background

- Natural Attenuation is Not fast enough, Not complete enough, Not frequently occurring enough to be broadly used for some compounds, especially chlorinated solvents
- The current trend is to stimulate/enhance a site's indigenous subsurface microorganisms by the addition of nutrients and electron donor
- In some cases, bioaugmentation is necessary when metabolic capabilities are not naturally present.


Soil and Subsurface Contaminants

- Benzene and related fuel components (BTEX)
- Pyrene and other polynuclear aromatics
- Chlorinated aromatics and solvents
- Herbicides and pesticides
- Nitroaromatic explosives and plasticizers







Current Water Issues Associated with Gasoline Use • Widespread contamination • Major threat to drinking water resources Components of fuels are known carcinogens Current fuel oxygenate, MTBE, very mobile and not very degradable • Ethanol is due to replace MTBE, but its behavior in the subsurface is not yet understood



Typical Fuel (BTEX) Spill





Treatment Techniques

Soil Extraction Pump and Treat O Physical and/or reactive barriers • Air and Hydrogen Sparging Biological (microbes) • Chemical (surfactants)



Why Bioremediation?

• No additional disposal costs • Low maintenance • Does not create an eyesore Capable of impacting source zones and thus, decreasing site clean-up time



Source Zone Treatment vs. Plume Treatment





Fundamentals of Biodegradation

• All organics are biodegradable, BUT biodegradation requires specific conditions

- There is no Superbug
- Contaminants must be bioavailable
- Biodegradation rate and extent is controlled by a "limiting factor"



Biotic Transformations

- Result of metabolic activity of microbes
- Aerobic and anaerobic biodegradation
- Reduces aqueous concentrations of contaminant
- Reduction of contaminant mass
- Most significant process resulting in reduction of contaminant mass in a system



Bioremediation Processes

- Conversion of contaminants to mineralized (e.g. CO₂, H₂O, and salts) end-products via biological mechanisms
- Biotransformation refers to a biological process where the end-products are not minerals (e.g., transforming TCE to DCE)
- Biodegradation involves the process of extracting energy from organic chemicals via oxidation of the organic chemicals



How Microbes Use the Contaminant

• Contaminants may serve as: Primary substrate enough available to be the sole energy source Secondary substrate provides energy, not available in high enough concentration Cometabolic substrate fortuitous transformation of a compound by a microbe relying on some other primary substrate





Electron Exchange



Aerobic v. Anaerobic

- If oxygen is the terminal electron acceptor, the process is called aerobic biodegradation
- All other biological degradation processes are classified as anaerobic biodegradation
- In most cases, bacteria can only use one terminal electron acceptor
- Facultative aerobes use oxygen, but can switch to nitrate in the absence of oxygen



Bacterial Metabolism

Aerobic

Anaerobic

Oxidation Cometabolism

Denitrification Manganese reduction Iron reduction Sulfate reduction Methanogenesis



Electron Acceptor Zones

- After O₂ is depleted, begin using NO₃⁻
- Continue down the list in this order



Electron Acceptor Condition





Bioremediation Practice

- Understand physical and chemical characteristics of the contaminants of interest
- Understand the possible catabolic pathways of metabolism and the organisms that possess that capability
- Understand the environmental conditions required to:
 - Promote growth of desirable organisms
 - Provide for the expression of needed organisms
- Engineer the environmental conditions needed to establish favorable conditions and contact organisms and contaminants



Oxygen is of Primary Importance

- Most of the time oxygen is the primary factor limiting *in situ* biodegradation
- In most cases if adequate oxygen can be supplied then biodegradation rates are adequate for remediation
- Other limiting factors exist, but are usually secondary to oxygen

Degradation for Benzene: $C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$



Oxygen Supply is the Key to Aerobic In Situ Bioremediation

• Two ways to introduce oxygen in situ Dissolved in water : Actively pumped: H₂O₂, aerated water Passively: ORC ®, membrane, aeration In gaseous form, usually air Bioventing above the water table Air sparging below the water table



Electron Donors

- Alcohols and acids
- Almost any common fermentable compound
- Hydrogen apparently universal electron donor, but no universal substrate
- Laboratory or small-scale field studies required to determine if particular substrate will support dechlorination at particular site



Electron Donors

Acetate Acetic acid Benzoate Butyrate Cheese whey Chicken manure Corn steep liquor Ethanol Glucose Hydrocarbon contaminants Hydrogen biochemical electrochemical gas sparge Humic acids naturally occurring Isopropanol Lactate Lactic acid Methanol Molasses Mulch

Pickle liquor Polylactate esters Propionate Propionic acid Sucrose Surfactants -Terigitol5-S-12 Witconol 2722 Tetraalkoxsilanes Wastewater Yeast extract



Enhanced Bioattenuation

Technology	Petroleum Hydrocarbons (e ⁻ acceptor)	Chlorinated Solvents (e ⁻ donor)
Liquid Delivery	Oxygen Nitrate Sulfate	Benzoate Lactate Molasses Carbohydrates
Biosparge	Air (oxygen)	Ammonia Hydrogen Propane
Slow-release 台灣中油股份有限公司 CPC Corporation, Taiwan	Oxygen (ORC)	Hydrogen (HRC)





Phytoremediation is the use of higher plants to bioremediate contamination in soil, water, or sediments. Variations of phytoremediation that have been used in the past include wetlands to treat municipal sewage or neutralize acidic mine drainage.

Currently, phytoremediation is proposed for remediation of both organic and inorganic contaminants in soil, sediments and water.



Plants may transport oxygen into the subsurface; lower the water table by transpiration, thereby pulling oxygen into the soil from the atmosphere; and increase hydraulic conductivity of the soil as roots produce channels in soil.

Flood-tolerant and wetland plants are especially efficient at transporting oxygen into the subsurface. These processes are thought to enhance aerobic biodegradation by increasing oxygen in the subsurface.

As plants transpire, the movement of water through the plant also carries along dissolved components. Dissolved contaminants such as chlorinated solvents can be removed from the soil in the transpiration stream and emitted to the atmosphere through the plant leaves. This type of "remediation" could be undesirable





- ≈350 plant species naturally take up toxic materials
 - Sunflowers used to remove radioactive cesium and strontium from Chrenobyl site
 - Water hyacinths used to remove arsenic from water supplies in Bangladesh, India







Drawbacks Only surface soil (root zone) can be treated Cleanup takes several years



SITE REMEDIATION

PROCEDURES

- SITE CHARACTERIZATION
 REMEDIAL ALTERNATIVES ANALYSIS
- DESIGN, CONSTRUCT AND OPERATE



GOALS OF SITE CHARACTERIZATION

- The goals of site characterization are to:
- 1. Determine the extent and magnitude of contamination
- 2. Identify contaminant transport pathways and receptors
- 3. Determine risk of exposure



Zones of Contamination





Identification of Receptors and Pathways





METHODS OF SITE CHARACTERIZATION

Remote Methods

- Seismic Survey
- Soil Resistivity
- Ground Penetrating Radar
- Magnetometer
 Survey

Direct Methods

- Auger Drilling
 Detery Drilling
- Rotary Drilling
- Soil Excavation



DIRECT SUBSURFACE SAMPLING

Auger Drilling Useful in unconsolidated geologic materials. • Sample collection easy, intact **Rod inside** samples can be collected with hollow stem hollow-stem auger. for removing plug Cannot be used where significant consolidated rock is Flight present. Removable Does not alter subsurface geo-Plug chemistry. **Drill Bit**



SPECIAL CONCERNS FOR DIRECT SUBSURFACE CHARACTERIZATION

Drilling through confining layers may allow the spread of contamination from one hydrologic unit to another.




SOIL CHARACTERIZATION

Soil Contaminant Sampling

- Performed during drilling or excavation.
- Collection of samples from several depths within the soil profile.
- •Where volatile compounds are present, sampling should be done in air-tight glass containers. No headspace should be left in the containers.
- Samples should be chilled for transportation to the laboratory.



GROUNDWATER CHARACTERIZATION

Extent of Contamination:

Successive wells should be drilled until the extent of the groundwater contaminant plume is defined.





DEVELOPMENT OF ALTERNATIVES

Identify general response to actions for each objective

- Characterise media to be remediated
- Identify potential technologies
- Screen the potential technologies
- Assemble the screened technologies into alternatives



ALTERNATIVE SELECTION

Long term effectiveness
 Long term reliability
 Implementability
 Short term effectiveness
 Cost



TREATMENT ALTERNATIVES

On site

- In situ
- Ex situ (Excavation)

Off site (Excavation & Transportation)



In-Situ Biodegradation - Natural Attenuation





Natural Attenuation of Contaminants





In-Situ Biodegradation - Engineered Systems

Air-sparging/nutrient addition system





7

In-Situ Biodegradation - Engineered Systems

Combination air injection/extraction system





Ex-Situ Biodegradation - Pump and treat





Ex-Situ Biodegradation - Biofiltration





Ex-Situ Biodegradation - Biopiles



Ex-Situ Biodegradation - Landfarming

Procedures:

- Excavated soils are spread onto the ground surface to a depth of less than 0.5 meters.
- Underlying soils should be low permeability, or a clay liner or impermeable membrane should be used to prevent contaminant migration to groundwater.
- Landfarmed soils should be tilled every 2-3 months and kept moist.



Gasoline Station Bioremediation

SUNDCO

The gas station at Phillip and Columbia Street was sold to a new company and any soil and groundwater contamination of the site

due to its previous operation by Sunceo had to be removed

Excavation and Tank Removal

The old gasoline tanks were removed and holes bored to detect gasoline and then a deeper excavation was done to the groundwater level to check for this contamination





The water surface showed visible signs of oil contamination.





These pipes had perforated sections spanning the soil and groundwater regions and going a few feet below the water table

The larger pipes surrounded the contaminated areas and were all then joined to the vacuum pumping systems



The soil that was contaminated was excavated and removed to a secure landfill site

To remove, or at least reduce, the contamination of the groundwater below the soil, holes were drilled and pipes were installed around the edge of the contaminated zone

Gasoline removal

The pipes were joined together at the surface and pumps were attached to these pipes. The pumping systems pumped a mixture of groundwater, pure gasoline product floating on the surface of the groundwater and soluble products from gasoline that had entered the groundwater. These soluble products would have included benzene, ethylbenzene, toluene and xylenes. The mixture of gasoline, soluble products from gasoline products and water was pumped into a tanker truck on the property and disposed of after separation into the two phases of water and gasoline. The water would have contained the water-soluble components.











Phillip Street



Cross Sectional Diagram of excavation and wells



Final Operations

Pumping continued for some months until most of the free product and soluble components had been removed from the immediate vicinity of the site. Pumping also ensured that no more migration of the soluble components in the groundwater could occur. A negative gradient was established during pumping so that surrounding contaminated water flowed into the site and not away from it.

Pumping would have to have been continued for many years if ALL of the soluble components in the groundwater needed removal through this "pump & treat" methodology.

□ The residual soluble components were assumed to have been remediated through biological mechanisms in the groundwater.

□ In this particular case, bioremediation was used as a final cleanup operation, but the bulk of the materials were removed via the pump and treat method. This is often referred to as "polishing" – that is, removal of the residual, low levels of soluble components through bioremediation activities performed by indigenous microorganisms



Petroleum Contaminated Sites

Service Stations
Tank Farms
Oil Spill Sites













Petroleum Contaminated Soil

(Soil and Groundwater Pollution Remediation Act)

土壤管制項目及管制標準 Clean-up Standards for Petroleum Contaminated Soil Remediation	
管制標準項目/Item	單位Unit(毫克/公斤mg/kg)
苯 (Benzene)	5
甲苯 (Toluene)	500
乙苯 (Ethyl benzene)	250
二甲苯 (Xylene)	500
總石油碳氫化合物(TPH)	1000



Events of Oil Spill, Leakage

加油站地下儲槽及管線系統洩漏 UST leakage at M. L. Service Station May 2000, 200立方米(m³) Soil Excavation



Events of Oil Spill, Leakage

加油站地下儲槽及管線系統洩漏 UST leakage at L. C. Service Station Aug. 2000, 5197立方米(m³) Soil Excavation





地下輸油管線系統洩漏 Underground Pipeline Oil Spill at K. M. Island Oct. 2002, 2570立方米(m³) Petroleum Contaminated Soil





地下輸油管線系統洩漏 Underground Pipeline Oil Spill at Tainan Apr. 2003, 7500立方米(m³) Soil Excavation



地下輸油管線系統洩漏 Underground Pipeline Oil Spill at Tainan Apr. 2003, 7500立方米(m³) Soil Excavation



Remediation Strategy/Technologies for Petroleum Contaminated Soil Treatment

現地復育 In-situ Remediation 離場復育 Ex-situ Remediation 生物復育法 Bioremediation (Landfarming, Biopile) ---(A) 植物復育法 Phytoremediation --(B) 自然衰減法 N.A. ----生物復育法+植物復育法(A+B) 生物復育法+植物復育法+自然衰減法(A+B+C)



Factors influencing biodegradation of hydrocarbons in soil:

- •Contaminant type
- •Bioavailability
- •Toxicity
- •Temperature
- •Moisture, pH, nutrients and soil type









Treatment Facilities (Tainan)



Treatment Facilities (Taichung)











// CPC Corporation, Taiwan

Soil : Diesel & Gasoline Contaminated Soil From A Pipeline Leakage Site Near Tainan

- Volume: 644m³
- Method : Land farming & Biopile
- Results : Soil TPH degrade from 6000 mg/kg to150mg/kg in 240 days.







Remediation Operation













Remediation Operation















Soil Remediation Project at a Tank **Truck Accident Site** Soil : Diesel Contaminated Soil Volume: 13 m3 (Ex-situ) **Method** : Land farming **Results : Soil TPH degrade from** 3000 mg/kg to 200mg/kg in 300 days.








Remediation Operation













Remediation Operation

















CHINESE PETROLEUM CORP.