An investigation into the treatment of co-mingled saline-hydrocarbon affected soil and groundwater

by:

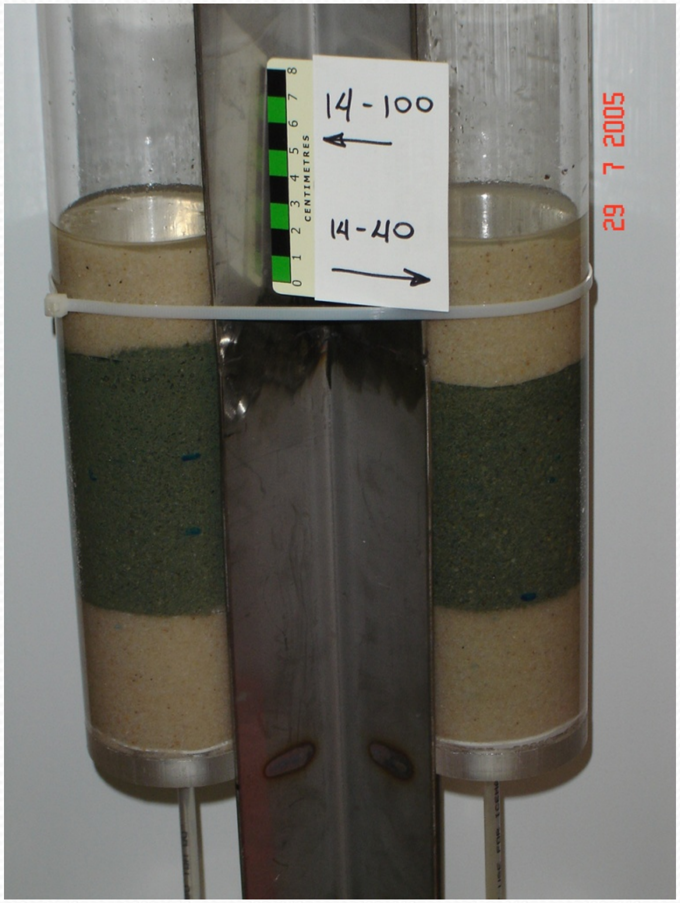
Gordon H. Bures, M.Eng., P.Eng.
Frac Rite Environmental Ltd.

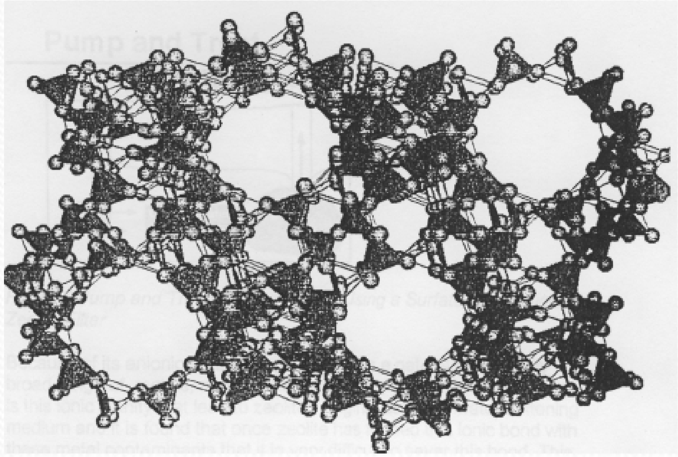
Dr. Edwin Liem, Ph.D.,
Black Earth Humates Ltd.

Outline

- What are Zeolites and Humates?
- Existing environmental applications
- Rationale for column testing
- Column testing and results
- Conceptual field pilot application

Zeolites





- Naturally occurring, crystalline, porous aluminosilicate structure
- Anionic framework, high CEC
- Open structure, molecular "sieve" - traps contaminants

Zeolite Column Test Results: 2005

TABLE 3 –
Column Test Salinity Parameters

PORE VOLUMES:	Cl (mg/L)	EC (uS/cm)	SO_4 (mg/L)	TDS (mg/L)	pH	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SAR
	COLUMN 1: DISCHARGE WATER SALINITY (-14 + 100 MESH ZEOLITE)									
PRE-TEST	9630	19500	439	13600	7.0	2430	66.0	579	2410	11.4
0-2	8920	17500	378	12200	6.9	3230	260.0	496	1080	4.7
20-22	9590	19000	405	13300	7.2	2430	232.0	565	2310	11.0
40-42	9660	19300	395	13500	7.2	2380	168.0	565	2350	11.2
60-62	9770	19900	401	14000	7.3	2430	129.0	571	2400	11.4
80-82	9670	19400	373	13600	7.4	2320	90.4	547	2280	11.1
100-102	9840	19500	477	13600	7.5	2460	95.6	578	2440	11.5
120-122	9910	19700	412	13800	7.6	2580	96.0	602	2540	11.7
PORE	COLUMN 2: DISCHARGE WATER SALINITY (-14 + 40 MESH ZEOLITE)									
VOLUMES:	Cl (mg/L)	EC (uS/cm)	SO_4 (mg/L)	TDS (mg/L)	pH	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SAR
PRE-TEST	9630	19500	439	13600	7.0	2430	66.0	579	2410	11.4
0-2	8200	17000	321	11900	7.0	2860	239.0	436	1200	5.5
20-22	9450	19300	386	13500	7.2	2490	218.0	578	2340	11.0
40-42	9610	19500	383	13600	7.3	2450	156.0	570	2370	11.2
60-62	9580	19300	386	13500	7.5	2250	129.0	533	2230	11.0
80-82	9640	19500	410	13600	7.4	2350	122.0	552	2310	11.2
100-102	9570	19800	374	13800	7.5	2390	101.0	560	2360	11.3
120-122	9680	19400	400	13600	7.5	2400	98.5	562	2360	11.3
140-142	9790	19500	394	13600	7.6	2570	114.0	609	2550	11.7
POST	ZEOLITE SALINITY AFTER TESTING									
TEST ZEOLITE:	Cl (mg/L)	EC (dS/m)	SO_4 (mg/L)	SPECIFIC GRAVITY	pH	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	SAR
US MESH :										
-14 + 100	6070	17.9	334	1.49	7.5	1920	71	176	1980	11.6
-14 + 40	4070	13.0	226	1.25	7.7	1120	60	96	1490	11.5

<u>Note:</u> Cl – chloride; EC – Electrical Conductivity; SO_4 – sulphate; TDS – Total Dissolved Solids; Ca – calcium; K – potassium; Mg – magnesium; Na – sodium; SAR – Sodium Adsorption Ratio.

TABLE 1 –
Column Test Specifications

Parameter	*Specifications (actual)*	
	-14 + 100 zeolite test column	- 14 + 40 zeolite test column
Dry weight	324 g	300 g
Wet weight	330 g	330 g
Pore volume	249 cm^3	209 cm^3
Sample dimensions (saturated)	101 mm Height x 67.5 mm Diameter	88 mm Height x 67.5 mm Diameter
Consolidation Pressure	60 kPa	60 kPa
Water feed rate	10 ml/min $\pm$ 15%	10 ml/min $\pm$ 15%
Column water head	1 m $\pm$ 10%	1 m $\pm$ 10%
Sampling frequency	7.60 hrs	6.25 hrs
No. of samples taken	7	8
Total test volume	30.4 litres	29.7 litres
Test duration	53.2 hrs	50 hrs

- High permeability: $K = 10^{-4}$ m/s
- Na reduced 60%
- Cl reduced 15%
- SAR reduced from 11.4 to 4.7

Humates

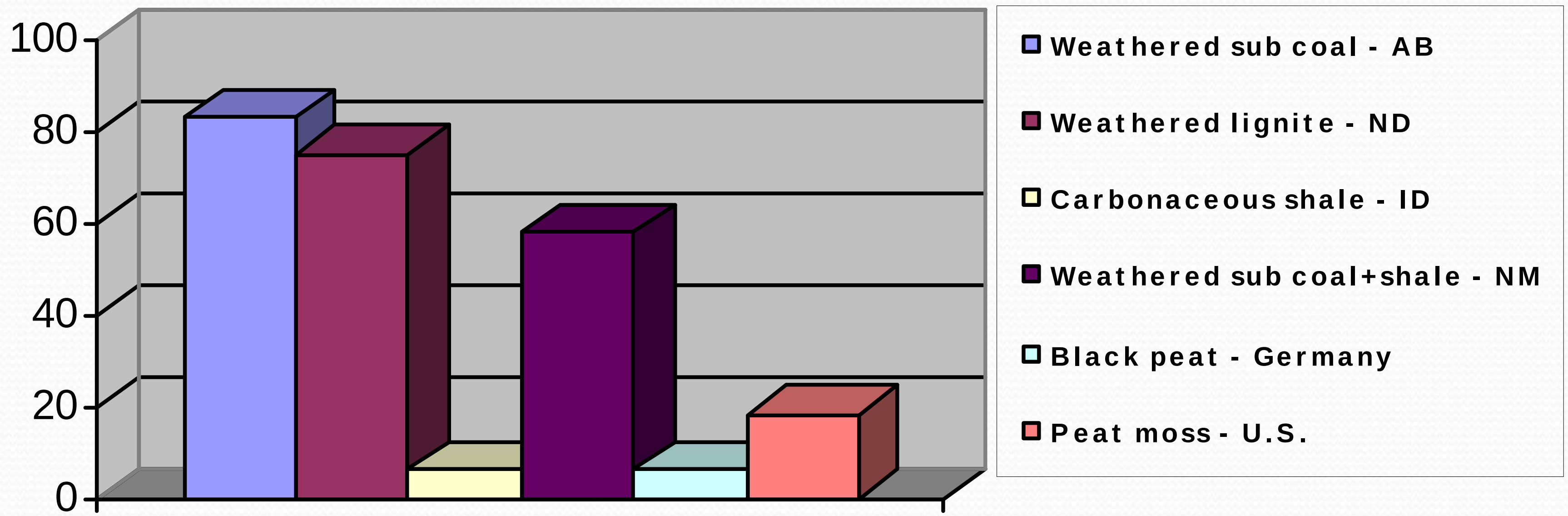
HUMATES: Organic material formed from the decay of plant and animal residues. Large organic molecules with many functional groups.

- Comprised of 90% C and O
- 10% H, N, S and trace elements
- Two main components of Humates are HUMIC and FULVIC acid

- ATTRIBUTES:

- Chelator to fixate sodium
- Increases solubility of PHCs
- Provides carbon for Microbes to convert PHCs to acids and sugars
- Cation and water retention

HUMATE COMPARISONS
% Total Humic Acids - Dry Matter



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Present Remedial Applications

- Mine tailings remediation for metals reduction (humates)
- Treatment of co-produced saline formation waters in oil and gas industry (zeolites)
- Phytoremediation (humates and zeolites)
- Treatment of saline-hydrocarbon drilling mud returns (humates and zeolites)
- Treatment of sodic soils in dry land farming (humates)

Rationale for Treatability Testing

Zeolites/humates have been used in reclamation to remediate surficial soils, but …

There isn't yet a commonly used *in situ* approach to cost-effectively treat deeper impacted subsoils.

- Co-mingled saline-hydrocarbon impacts reside at many existing and former facilities for which a passive and cost-effective *in situ* remedial approach is needed, especially in deeper subsoils.
- This approach needs to address both soil and groundwater impacts

Humate and Zeolite Column Testing

- Concept evolved from 2005 zeolite column study on sodic/saline impacted groundwater to include treatment of co-mingled petroleum hydrocarbons
- IRAP supported column study was prepared in 2009-2010 to study potential for using combination of humates and zeolites to remediate petroleum hydrocarbons concurrently with salts through physical attenuation mechanisms
- Humates also facilitate biodegradation of PHCs, which was not examined in column study

Test Objectives

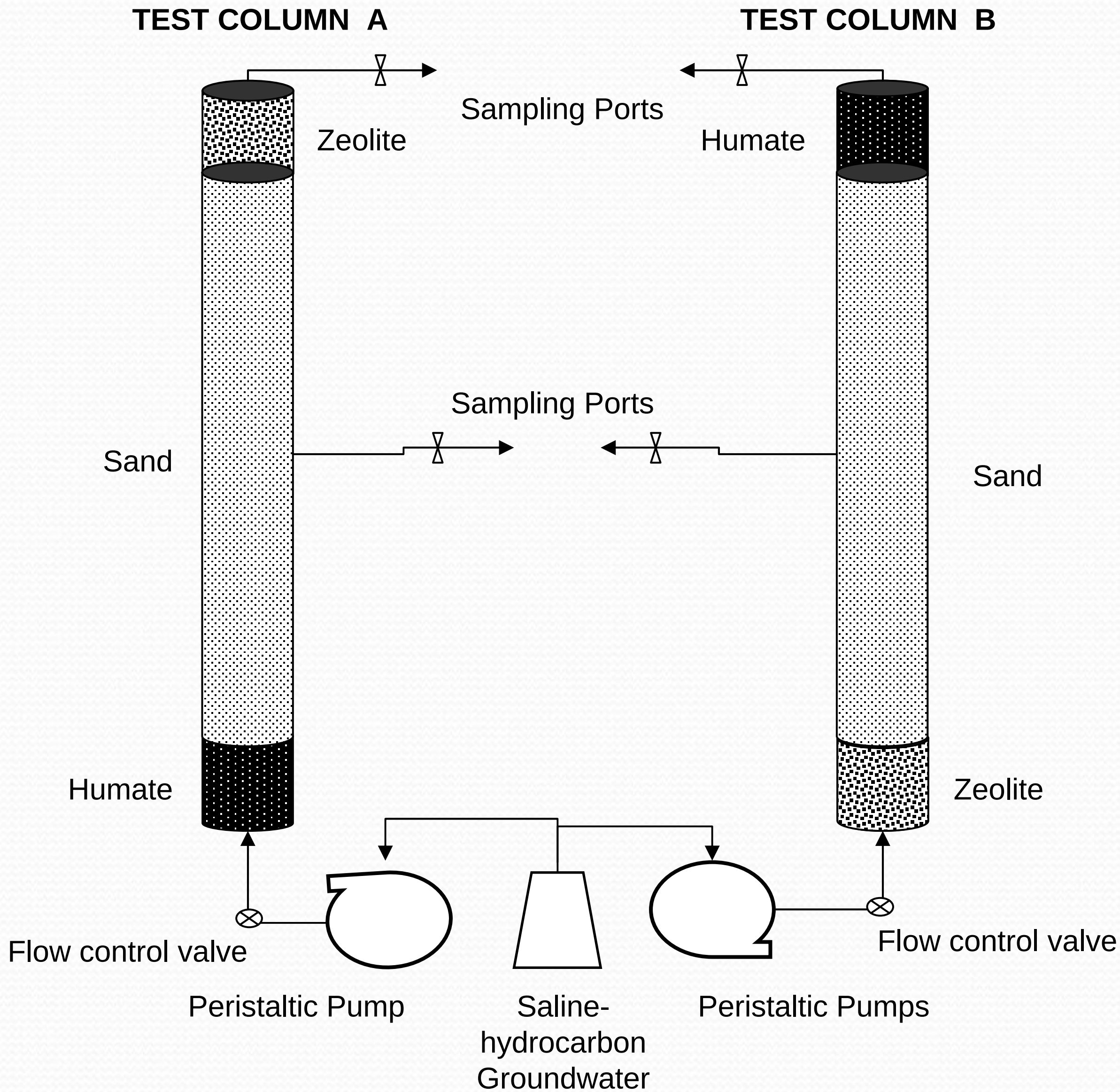
The specific objectives of the laboratory testing program were to evaluate the performance of the combination of amendments with respect to:

- Reduction in salinity indicator parameters;
- Reduction in sodium and chloride concentrations;
- Reduction petroleum hydrocarbon constituents (i.e. BTEX, F1, F2);
- Remediation effectiveness relative to the *sequence of treatment* in the test columns;
- Sodium and salinity retention as measured by Sodium Adsorption Ratio (SAR) and Electrical Conductivity, respectively; and,
- Efficacy for implementation of zeolites and humates in the field for passive treatment of saline-hydrocarbon impacted soil and groundwater.

Configuration of Test Columns

Column Test Specifications

Parameter	*Specifications (actual)*	
	Column A	Column B
Sand weight	3,654.9 g	3,674.5 g
Humates weight	959.0 g	1,015.2 g
Zeolites weight	1,212.9 g	1,137.1 g
Configuration bottom-top	Humates - Zeolites	Zeolites - Humates
Humate Dimensions	300 mm Height x 68.5 mm Diameter	320 mm Height x 68.5 mm Diameter
Zeolite Dimensions	320 mm Height x 68.5 mm Diameter	300 mm Height x 68.5 mm Diameter
Total column pore volume	2,000 cm^3	2,000 cm^3
Flow rate	50 ml/min	Variable: 5-59ml/min
Sampling frequency	40min	variable
No. of samples taken	11 water, 2 “soil”	8 water, 2 “soil”
Total test volume	13 litres	14 litres
Test duration	4:41	16:47



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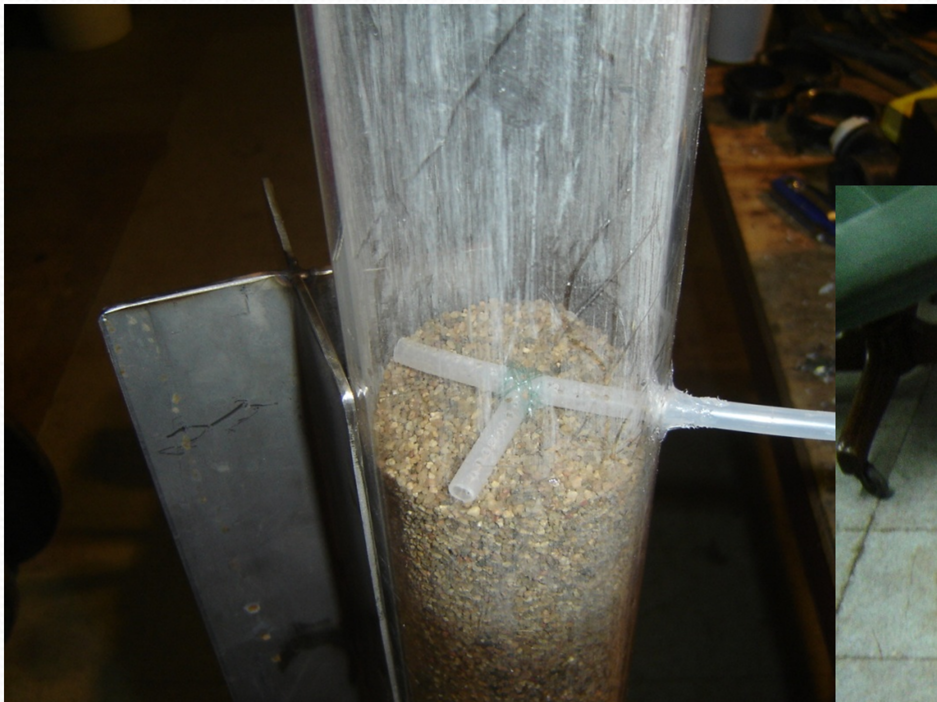
Column Construction and Apparatus



Mid – column sampling port construction

Peristaltic flow pumps and saline groundwater source

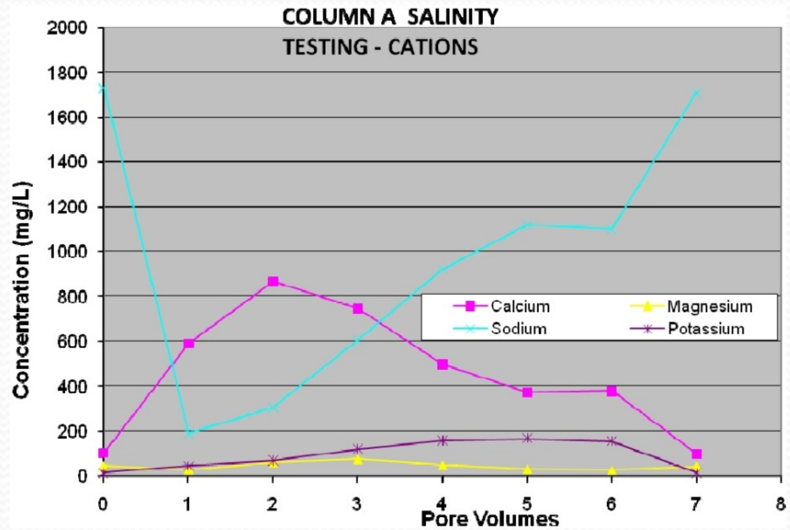
Geotechnical Properties

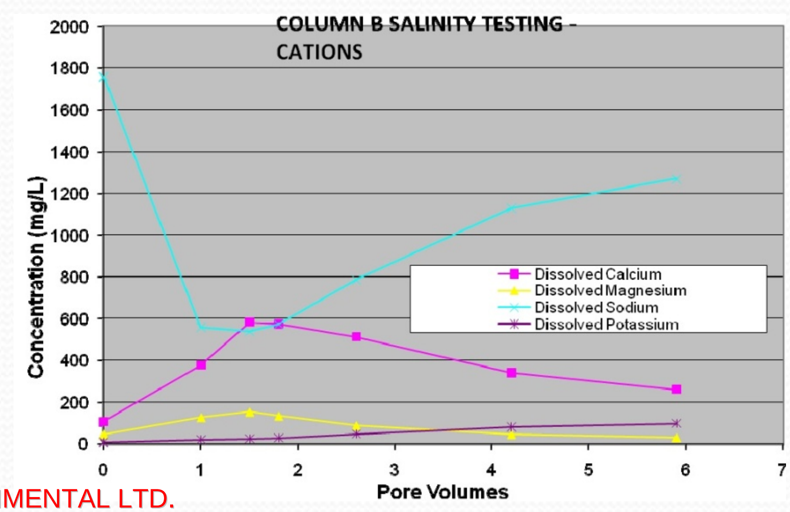
Test Parameter	*Geotechnical Properties*		
	Humate **-10+40 mesh** **“leonardite”**	**Zeolite** **-14+40 mesh** **“clinoptilolite”**	**Silica Sand** **-16+40 mesh**
Specific gravity	1.3	2.3	2.6
Porosity (%)	29	58	36

Results – Sodium Reduction

Maximum reduction in sodium concentration after 2-3 pore volumes:

- Cation exchange manifested as substitution of calcium for sodium in zeolite latice structure
- Column A (Humate-Zeolite) treatment sequence had greatest sodium removal (89%)

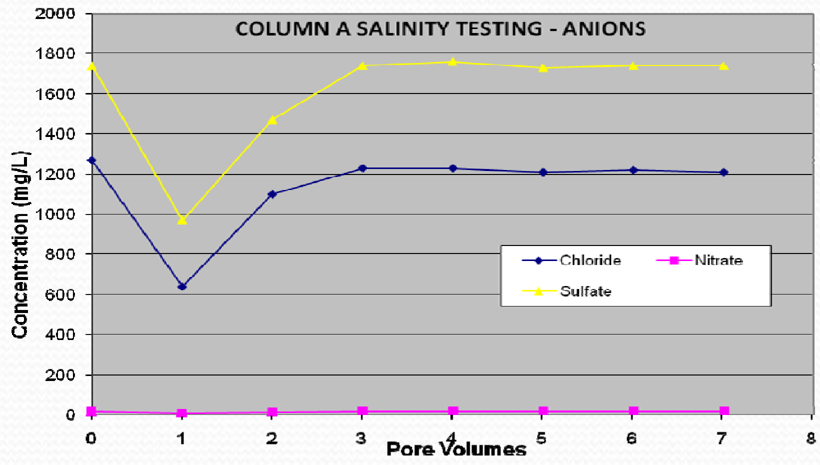


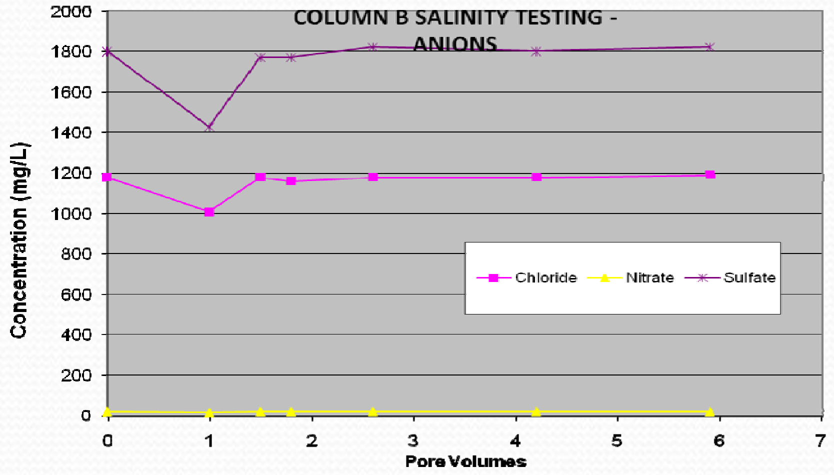


Results – Chloride Reduction

Maximum reduction in chloride concentration after <u>1 pore volume</u>:

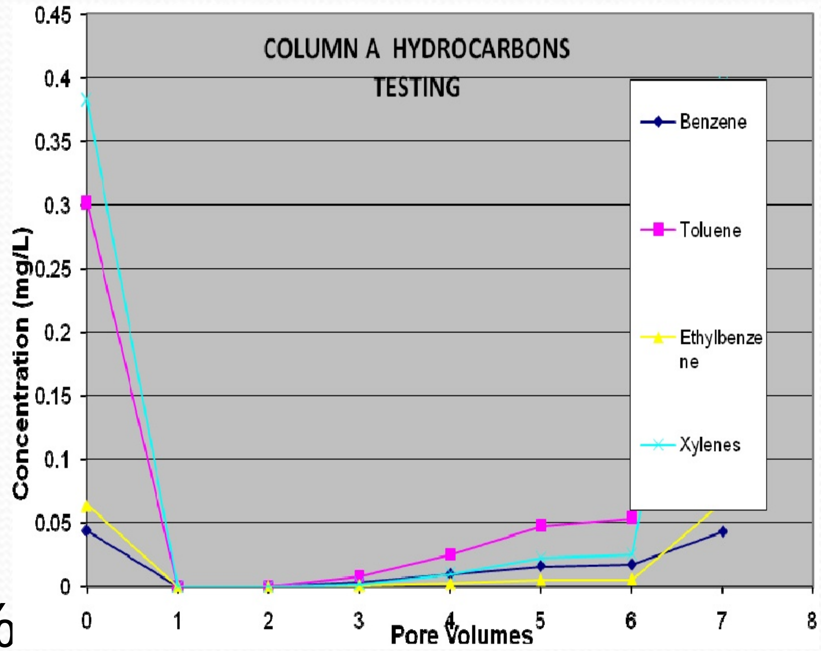
- Column A (Humate-Zeolite) treatment sequence had greatest chloride removal (50%)
- 35% of chloride attenuation attributable to humates, and 15% to zeolites



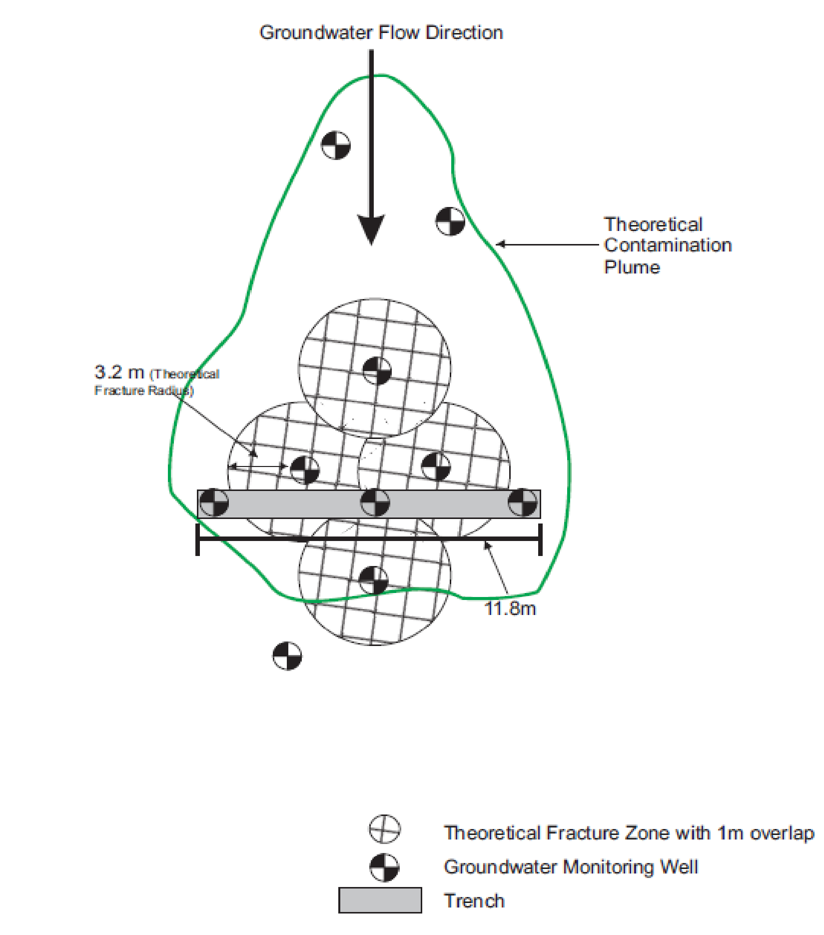


Results – BTEX Reduction

- Significant reduction in BTEX concentration after <u>2-6 pore volumes</u> (Column A)
- Concentrations of BTEX in effluent stream reduced to ND concentrations at 1 – 2 pore volumes
- Humates responsible for ≥ 87% of BTEX adsorption



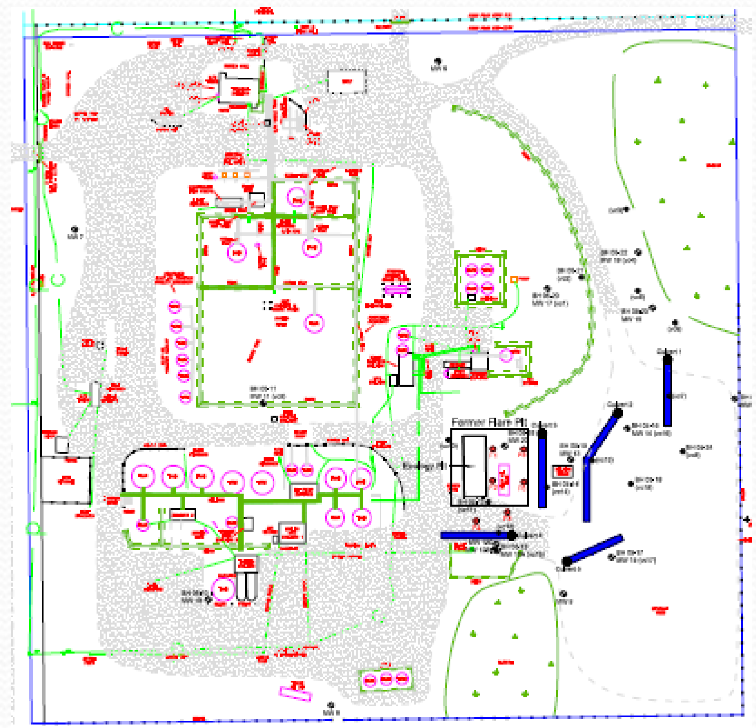
Conceptual Salt – Hydrocarbon Treatment Barrier



- Hydraulic Fractures create a network of interconnected sand drainage pathways to direct flow in a low permeability soil towards a zeolite/humate treatment trench.
- System can be easily scaled up to include captive deionizations or reverse osmosis.

(2012 IRAP Phase 2 Field Pilot)

Salt Remediation using Interceptor Trenches



Objective:

Create a network of sand drainage fractures to connect with interceptor trenches for enhancing salt capture and treatment using reverse osmosis.

Conclusions

- Most effective treatment results for salinity and petroleum hydrocarbon constituents were in Column A, i.e. humate treatment followed by zeolite treatment.

- Chloride reduction also noted in this configuration, possibly attributable to attenuation of chloride compounds in solution.

- Column test results are conservative in that they don't consider bioremediation processes

- Column test results can be used in design of treatment trench to conduct a field pilot