Two Wrongs Can Make a Right

A Novel Approach to the Biochemical Neutralization and Remediation of Cement-Impacted Soils

RemTech 2024

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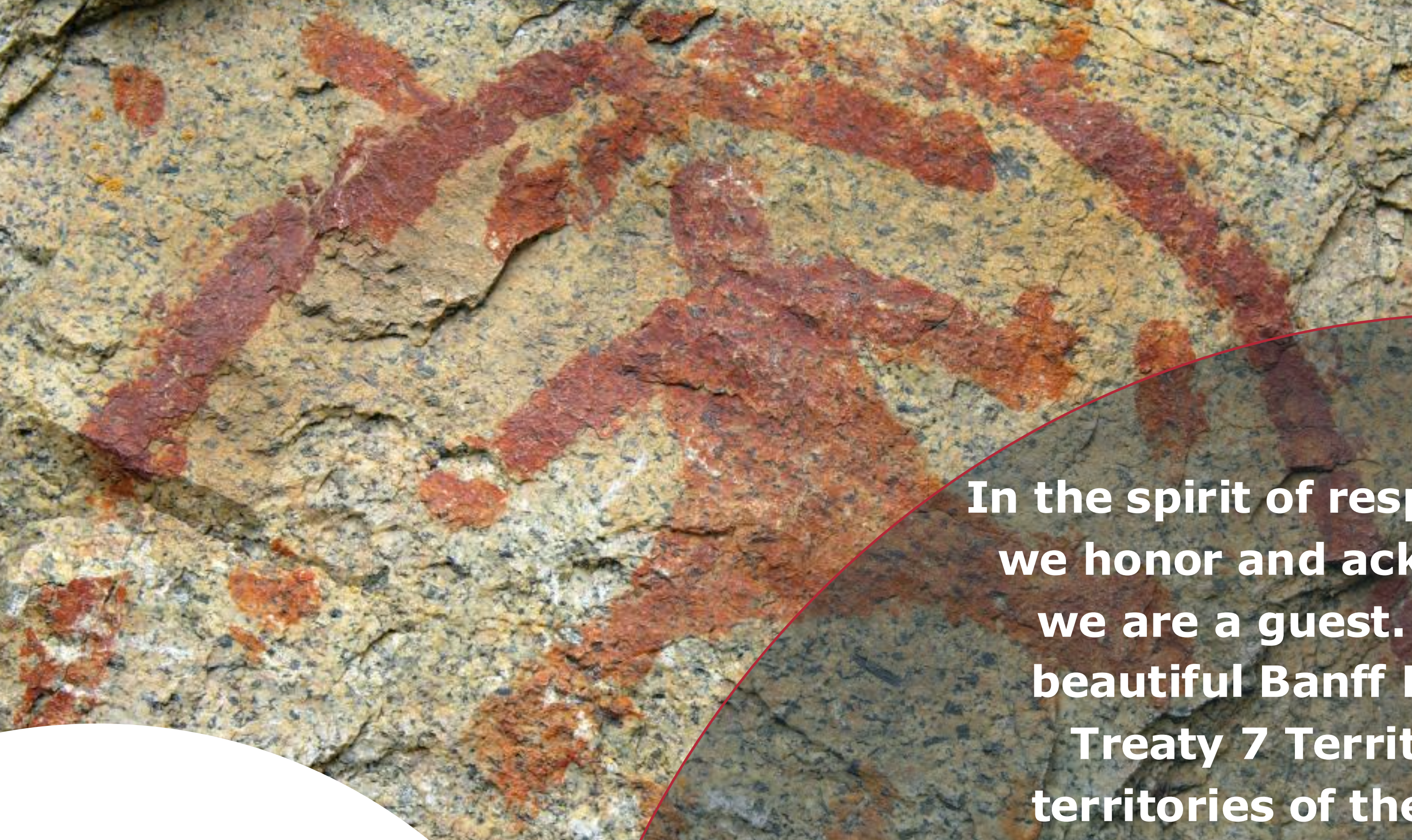
16 October 2024

worley consulting



Progressive Aboriginal RELATIONS COMMITTED

Canadian Council for Aboriginal Business

In the spirit of respect, reciprocity, and truth, we honor and acknowledge the land where we are a guest. Today we are located in beautiful Banff National Park which is in Treaty 7 Territory and the traditional territories of the Iyarhe Nakoda Nations (Bearspaw, Chiniki and Goodstoney), the Blackfoot Confederacy (Siksika, Kainai and Piikani) and Tsuut’sina First Nation. These lands have also long been traditionally important to the Ktunaxa, Secwépemc, Mountain Cree, Dene and Métis Peoples.

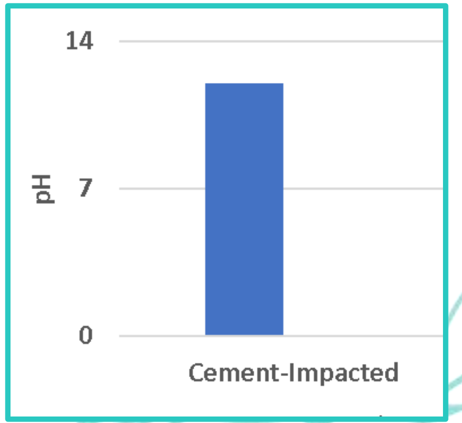
Outline

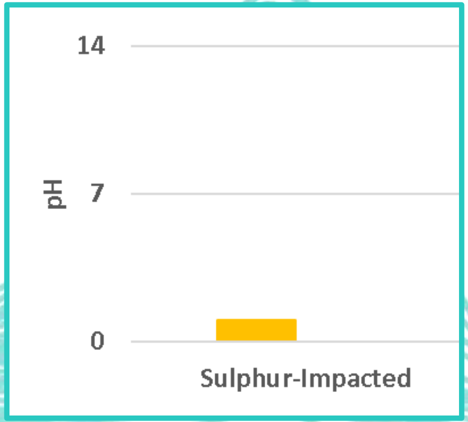
- Study Purpose and Objectives
- Conceptual Site Model
- Bench Scale Testing and Results
- Hydrogeochemical Conceptual Model
- Modelling Tools
- Unsaturated Flow Modelling
- Geochemical Modelling
- Transport Modelling
- Conclusions
- Q&A

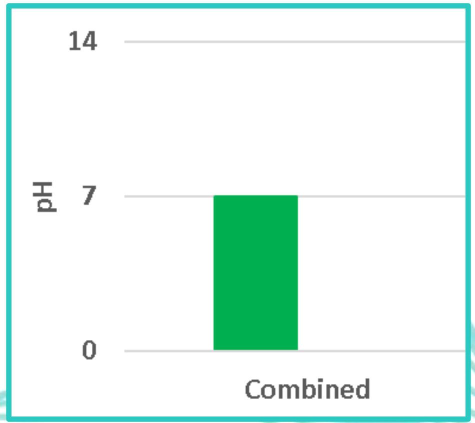
Remedial Magic?

Could this novel remediation approach effectively turn "waste" into "resource" for two contaminated sites?

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH$ + $H_2SO_4 \rightarrow 2H+ + SO_4^{2-}$ ⇒ $2H_2O + 2CaSO_4$







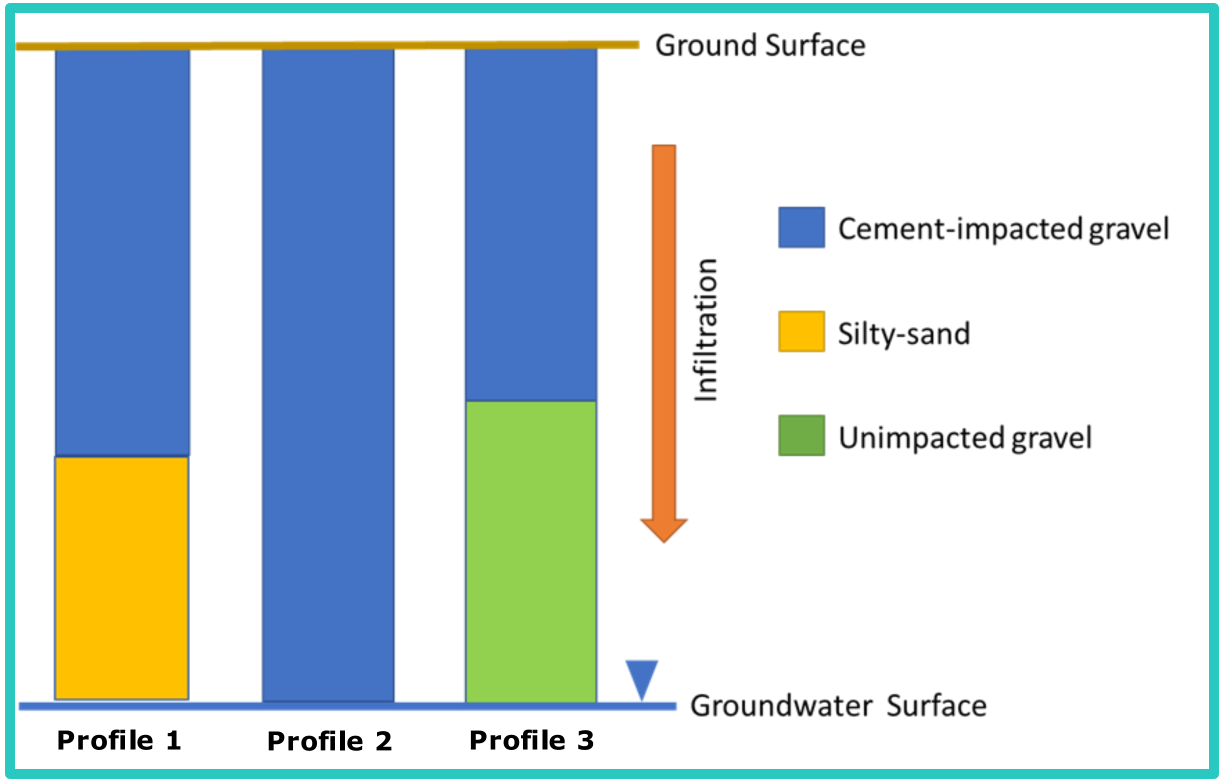
Study Objectives

1. Proof of concept
2. Confirm that mixing the two soils would not:
    a) Impact the ongoing sulphur oxidation
    b) Generate leachate that could result in “new” impacts
3. Estimate remediation timeframe.
4. Provide recommendations for a field-trial remediation program

Conceptual Site Model

- Brownfield site
- Commercial land use
- Excavation is not practical
- Remediation ongoing during development

Conceptual Site Model



Cement-Impacted Site

- Site Stratigraphy:
  - Cement-impacted gravel
  - Silty-sand
  - Unimpacted gravel
- Located within 100m of a surface water body
- Groundwater flow towards the southeast
- pH values in some areas were as high as 12.5
- Impacts are generally highest between surface to 1 mbgs

Sulphur-Impacted Site

- Collected from areas with known sulphur impacts
- pH values in some samples were lower than 1.68
- Elemental sulphur concentrations ranged from 30,000 to >40000 mg/Kg

Bench-Scale Testing and Analyses

Soil samples from both sites underwent a battery of batch tests and analytical procedures to develop a body of evidence that could be used to support future field trials of this remedial approach and form the basis of the hydrogeochemical model.

Petrological Assessment

X-ray Diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS)

Microcosm Testing

Simulated field application under various conditions

General Soil Chemistry

Individual and composite samples analysed for salinity, sulphur and metals parameters

Shake Flask Testing

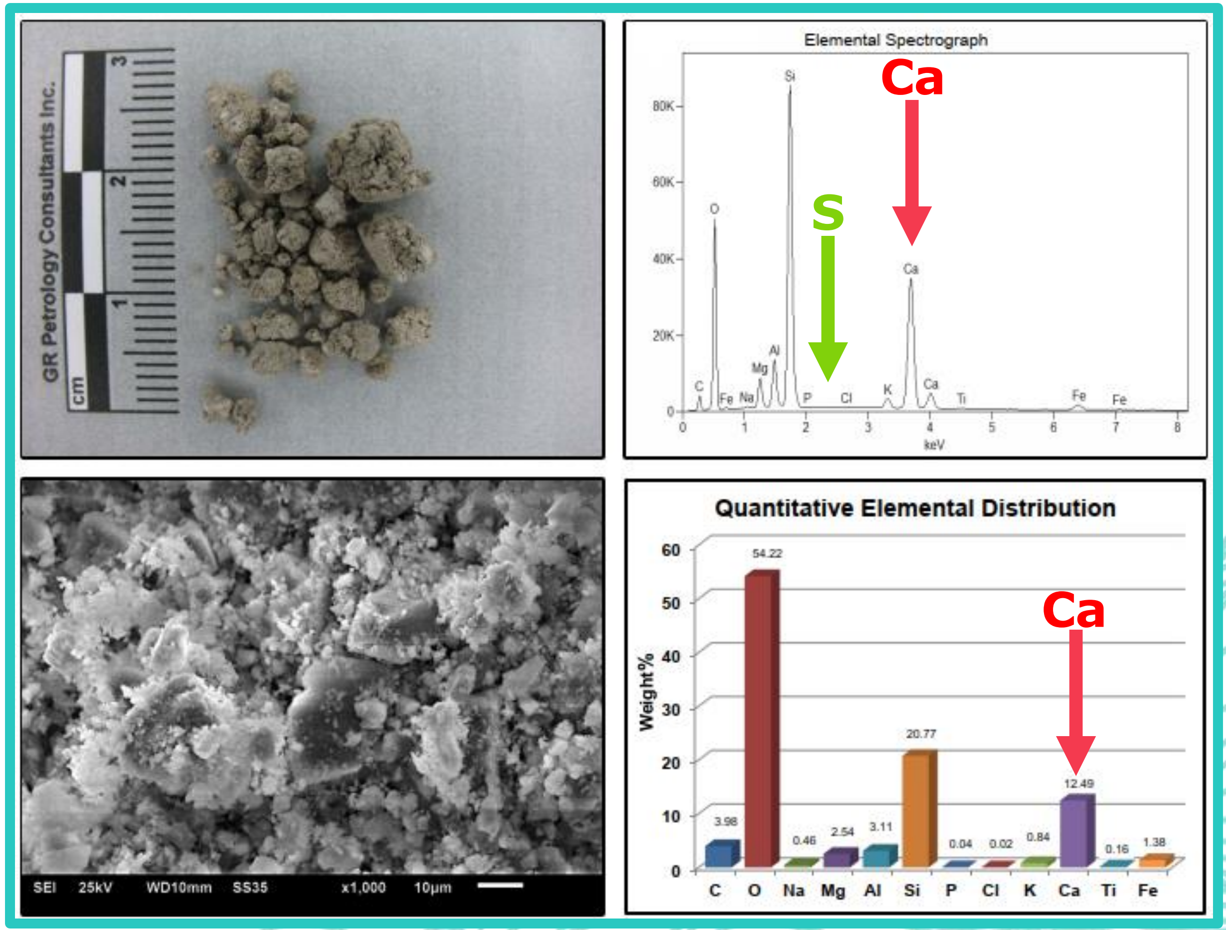
Performed modified shake tests to assess equilibrium porewater chemistry

Acid-Base Accounting

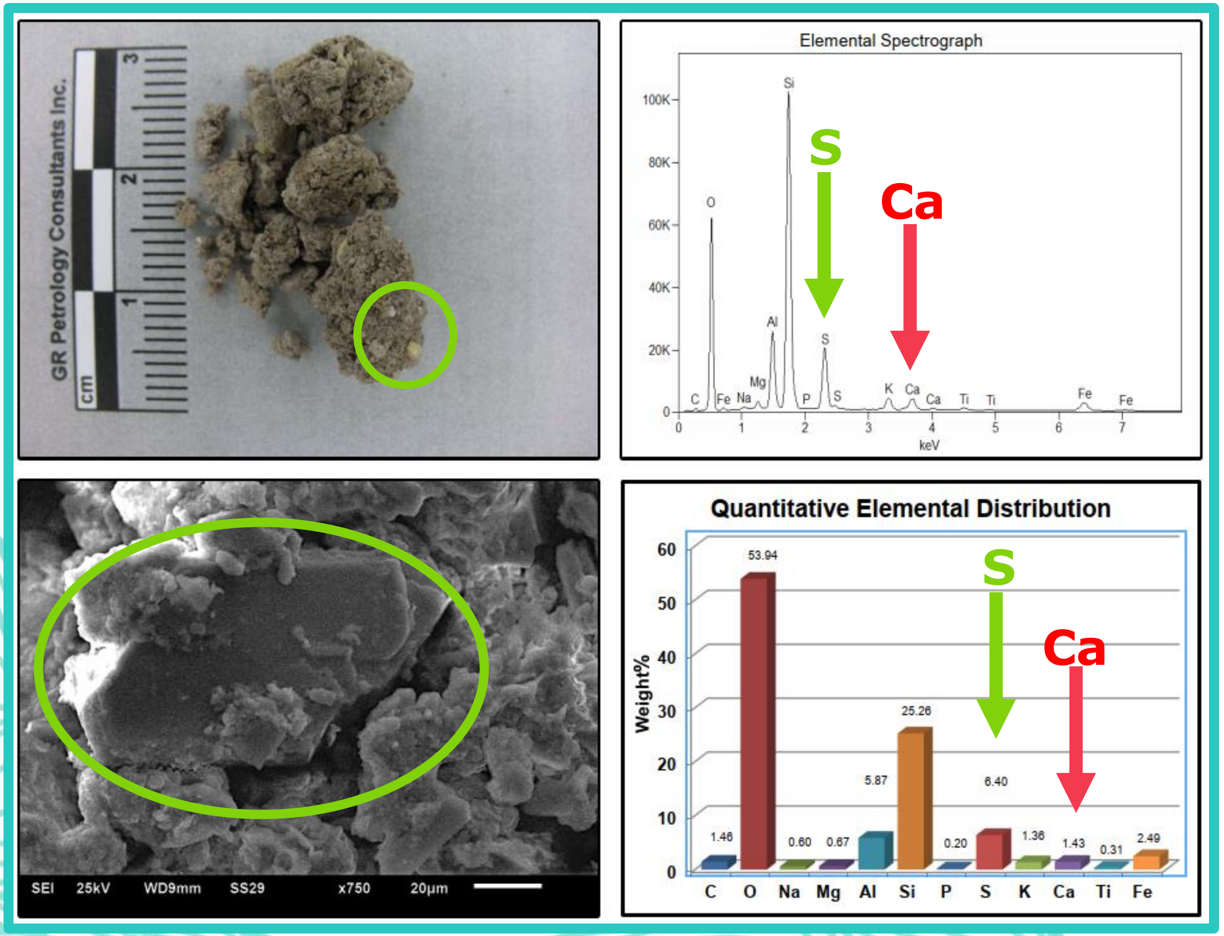
Selected soils analyzed for acid generation potential (AP) and neutralization potential (NP)

Petrology

Cement-Impacted Soil



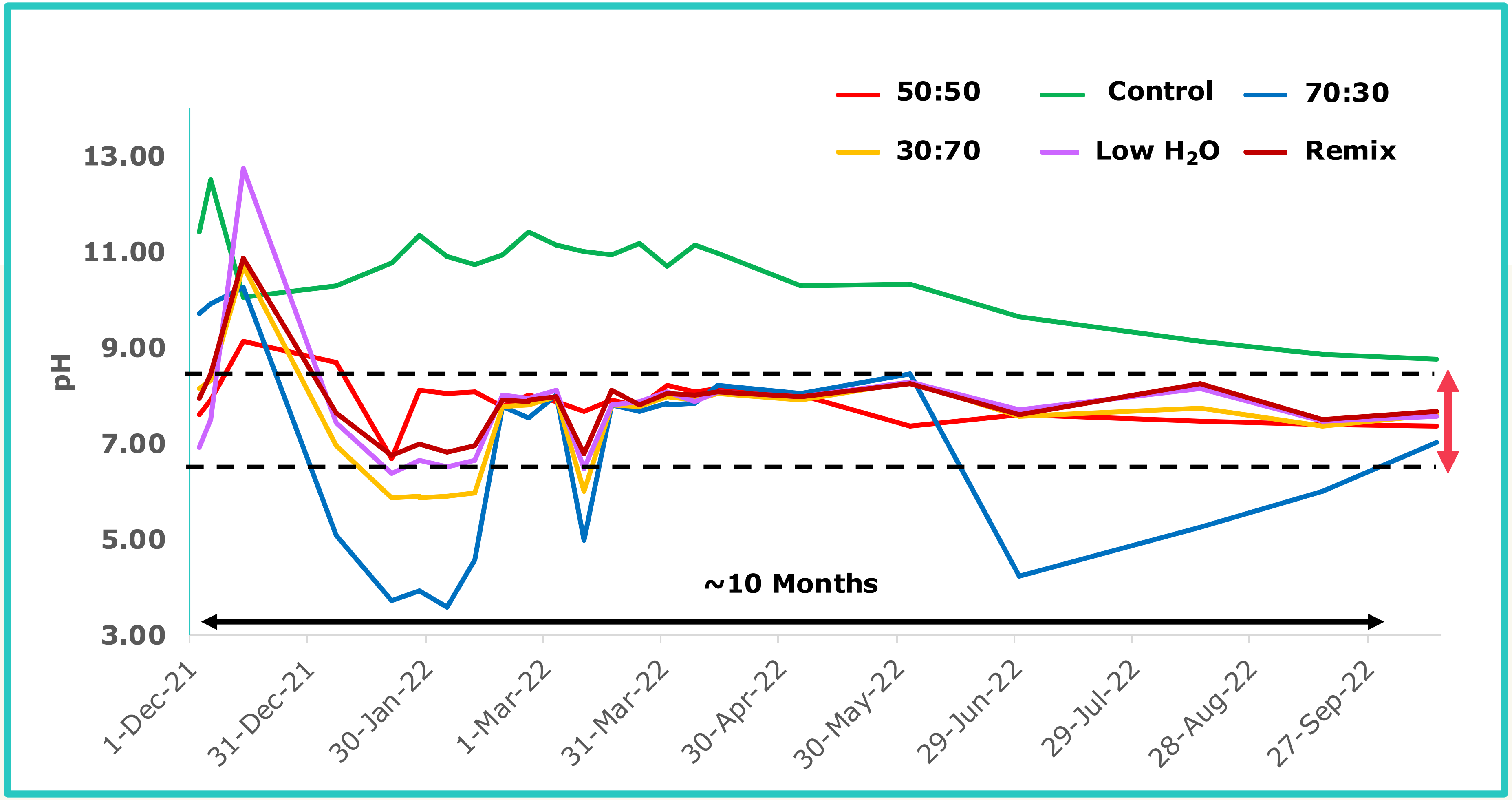
Sulphur-Impacted Soil



Microcosms

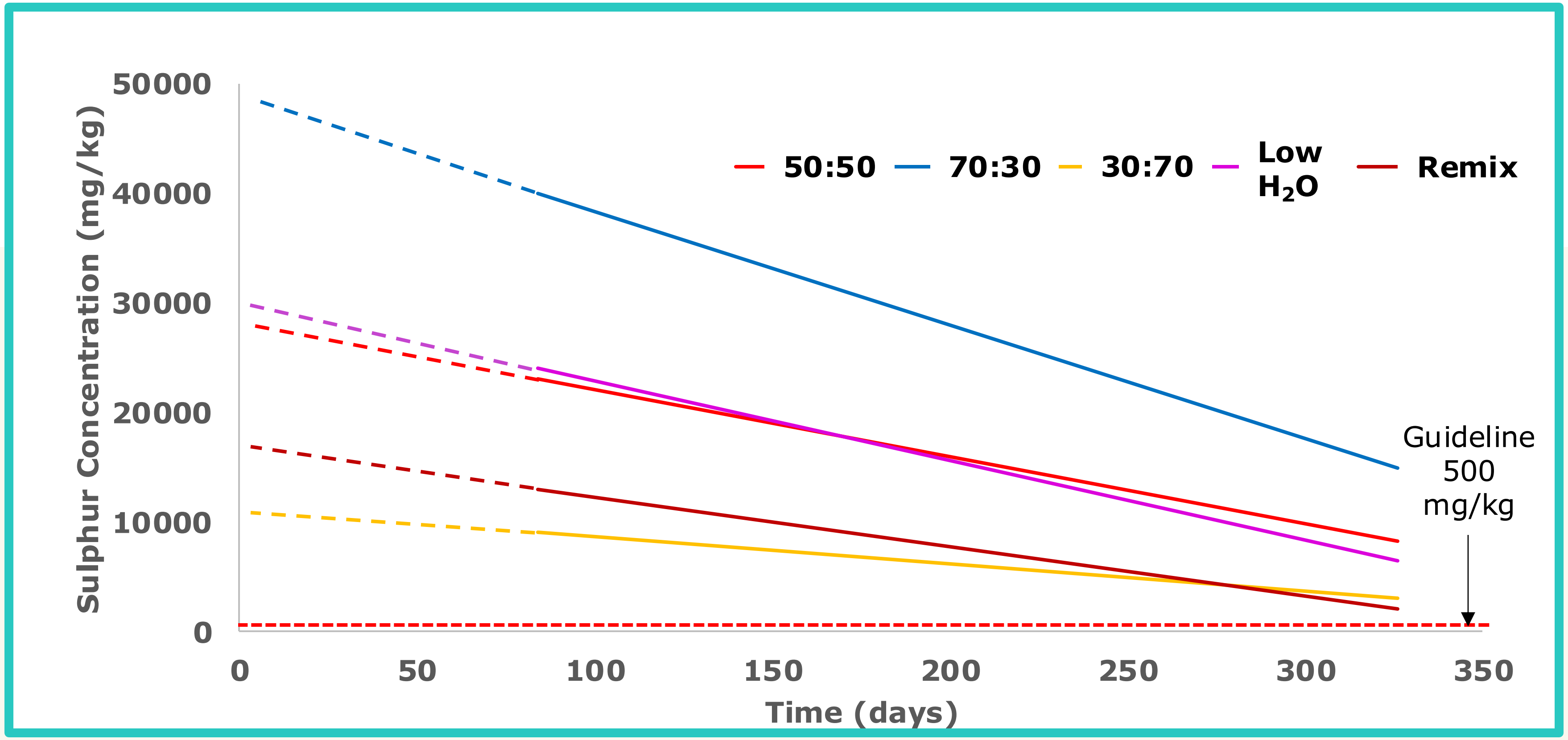
Microcosm ID (S:Cement)	% Sulphur-Impacted Soil	% Cement-Impacted Soil	Target Moisture Content (%)	Target Temperature (°C)	Mixing
50:50	46	54	20	20	N
Control	0	100	20	20	N
70:30	71	29	20	20	N
30:70	32	68	20	20	N
50:50 w/Low Water Content	46	54	5	20	N
50:50 w/ Remixing	46	54	20	20	Y

Microcosms



50:50
Control
70:30
30:70
Low H_2O
Remix
13.00
11.00
9.00
7.00
5.00
3.00
pH
~10 Months
1-Dec-21
31-Dec-21
30-Jan-22
1-Mar-22
31-Mar-22
30-Apr-22
30-May-22
29-Jun-22
29-Jul-22
28-Aug-22
27-Sep-22

Microcosms



Sulphur Concentration (mg/kg)
50000
40000
30000
20000
10000
0
0
50
100
150
200
250
300
350
Time (days)
50:50
70:30
30:70
Low H_2O
Remix
Guideline
500
mg/kg

Sulphate
Organic Carbon
Calcium Carbonate Equivalent

Eureka!

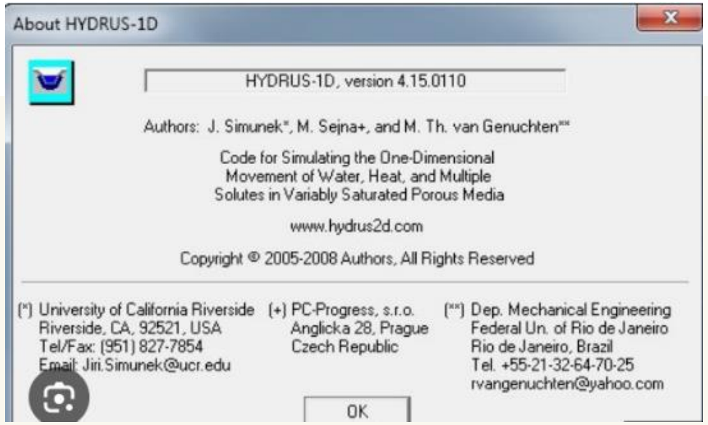
1. Proof of concept
2. Confirm that mixing the two soils would not:
    a) Impact the ongoing sulphur oxidation
    b) Generate leachate that could result in "new" impacts
3. Estimate remediation timeframe.
4. Provide recommendations for a field-trial remediation program

Hydrogeochemical Modelling Objectives

- Determine the optimal mixing ratio of sulphur- and cement-impacted soils for future neutralization field trials.
- Estimate the time frame for neutralization of cement-impacted soils at the Site.
- Determine whether the treatment could introduce any new environmental risks.

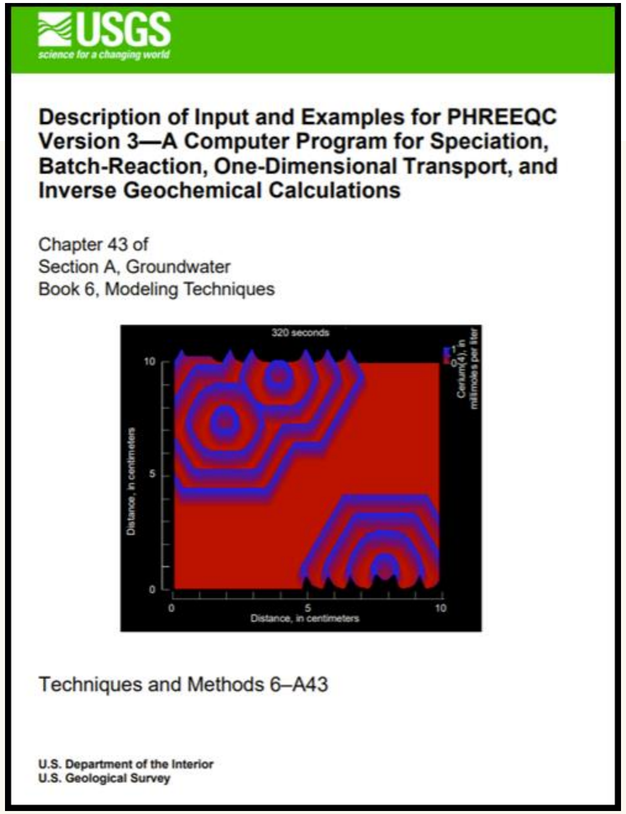
Modelling Tools

Unsaturated Flow Modelling with Hydrus and FEFLOW



DHI-WASY Software
FEFLOW®

Geochemical Modelling with PhreeqC


USGS
science for a changing world

Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations

Chapter 43 of
Section A, Groundwater
Book 6, Modeling Techniques

Techniques and Methods 6–A43

U.S. Department of the Interior
U.S. Geological Survey

Transport Modelling with the Domenico Analytical Solution

$$DF4 = \frac{4}{exp(A) \times erfc(B) \times [erf(C) - erf(D)]}$$

$$A = \frac{x}{2D_x}\left\{1 - \left(1 + \frac{4L_sD_x}{v}\right)^{1/2}\right\}$$

$$L_s = \frac{0.6931}{t_{1/2s}}\left(e^{-0.07d}\right)$$

$$v = \frac{V}{\theta_t R_s}$$

$$B = \frac{x - vt\left(1 + \frac{4L_sD_x}{v}\right)^{1/2}}{2(D_x vt)^{1/2}}$$

$$R_s = 1 + \frac{\rho_b K_{oc} f_{oc}}{\theta_t}$$

$$C = \frac{y + Y/2}{2(D_y x)^{1/2}}$$

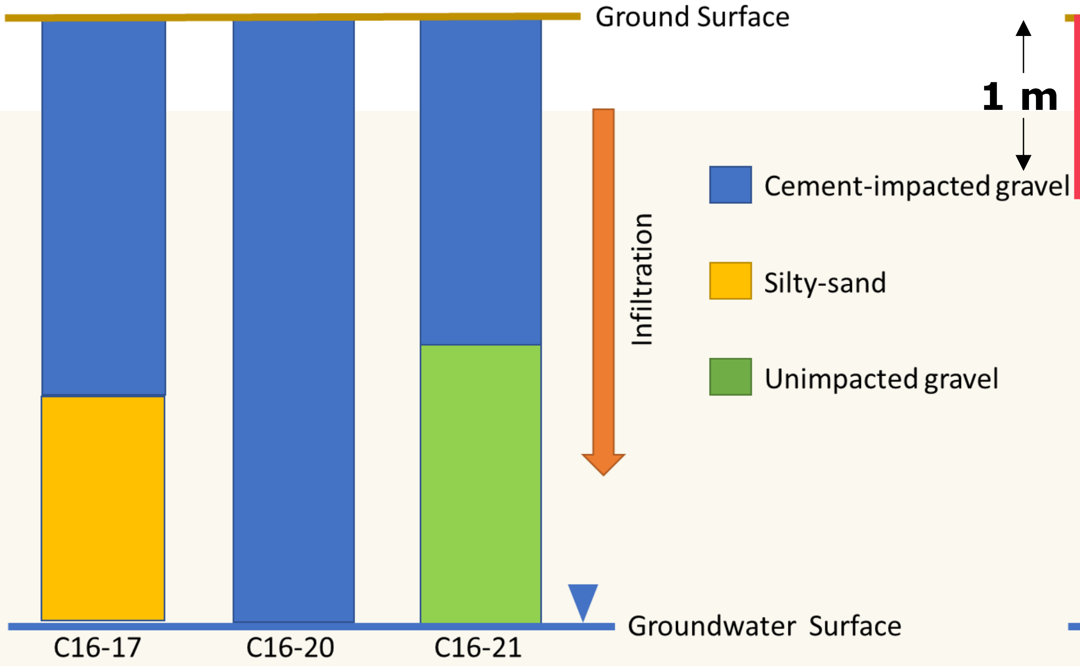
$$D_x = 0.1x$$

$$D = \frac{y - Y/2}{2(D_y x)^{1/2}}$$

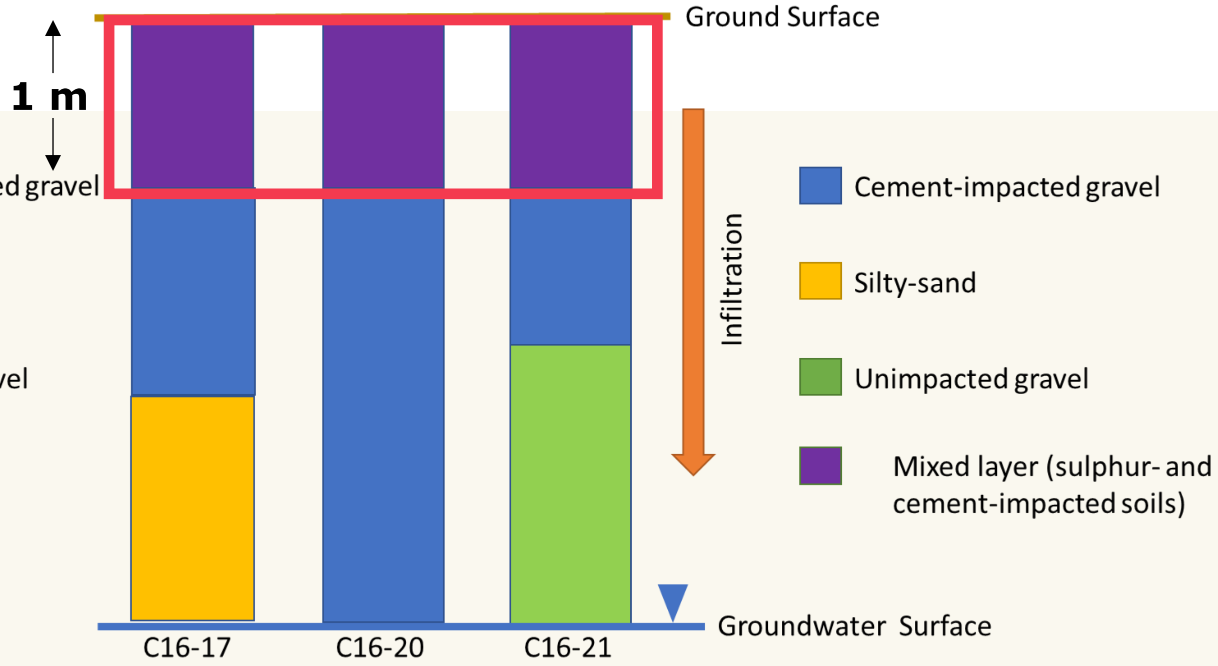
$$D_y = 0.01x$$

Conceptual Soil Profiles

Pre-Treatment

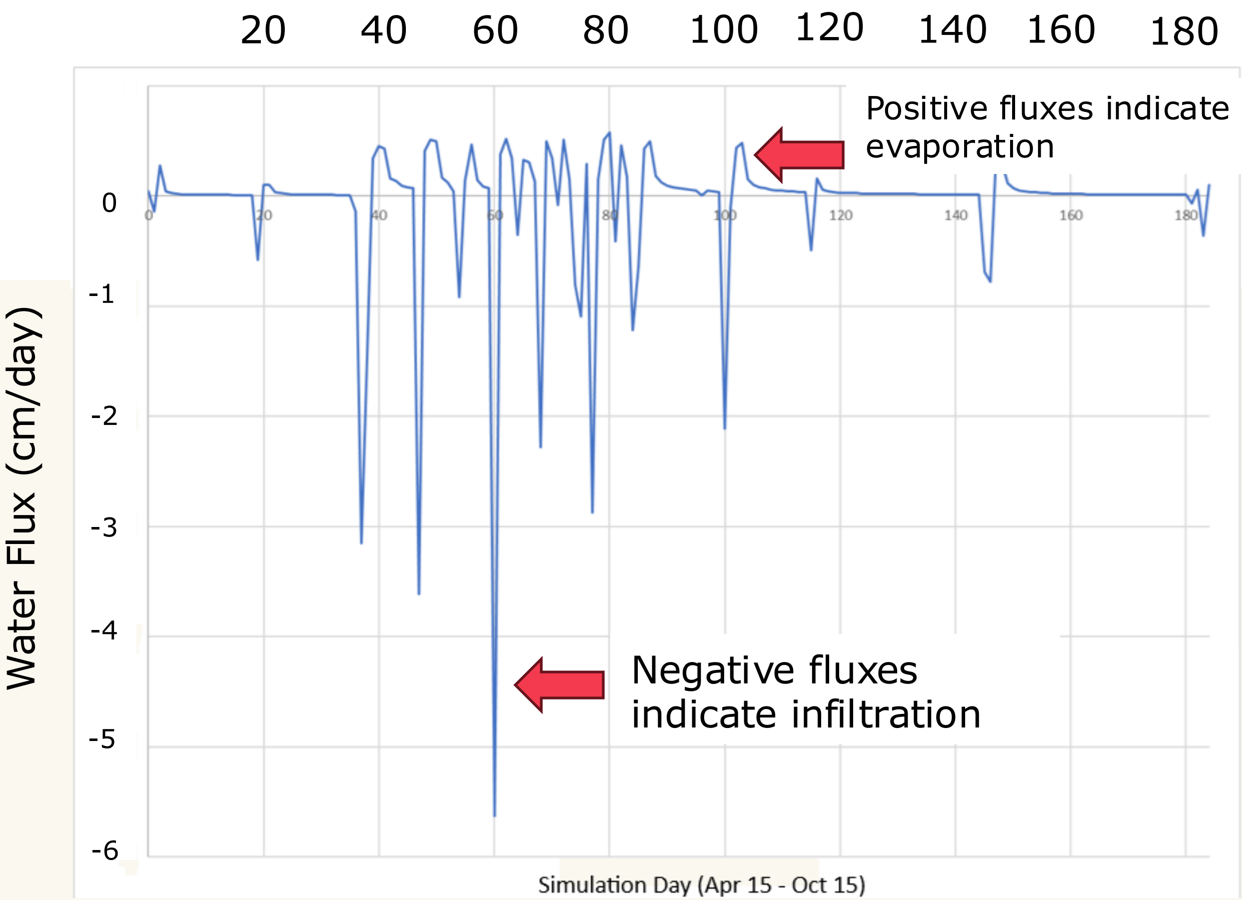


Post-Treatment

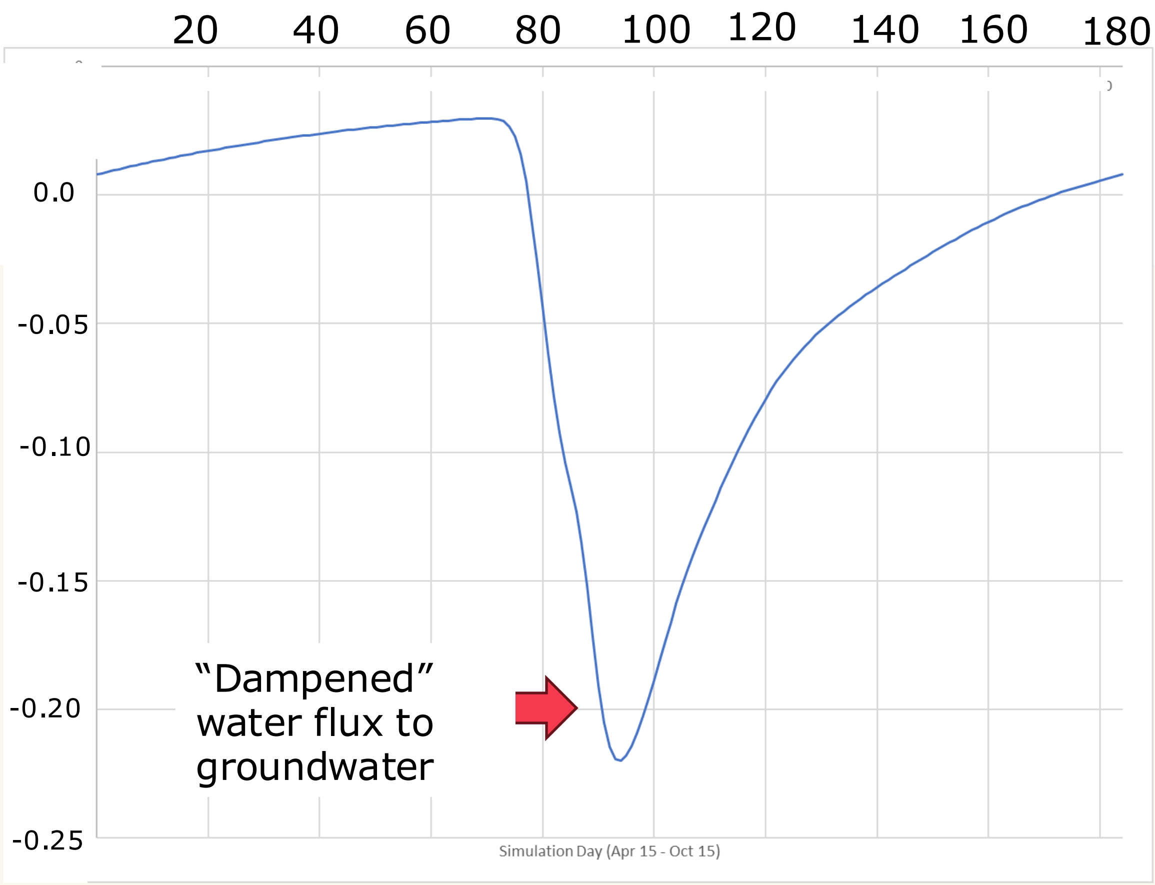


Hydrus 1-D Unsaturated Flow Model and FEFLOW

Modeled Surface Water Flux (cm/day)



Water Flux to Groundwater (cm/day)



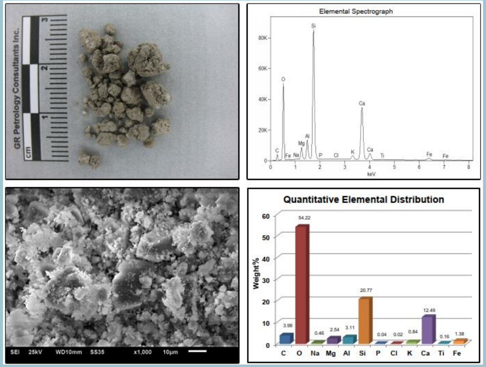
Hydrus 1-D Unsaturated Flow Model and FEFLOW

Monitoring Well		Profile 1	Profile 2	Profile 3
Water Flux (across water table) [cm/day]	Pre-treatment	0.020 - 0.27	0.007 - 0.45	0.017 – 0.30
	Post-treatment	0.025 - 0.37	0.13 – 0.64	0.021 – 0.39
Travel Time to Water Table (from 50 cm bgs) [days]	Pre-treatment	201 – 332	121 - 188	208 - 294
	Post-treatment	216 – 337	106 - 181	159 - 220

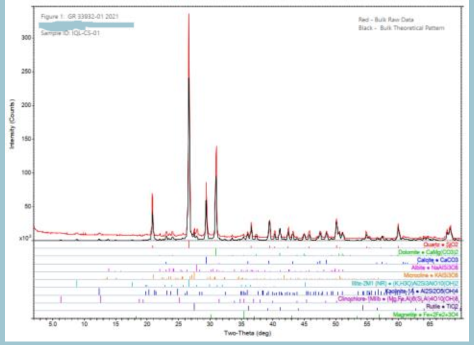
PhreeqC Geochemical Model

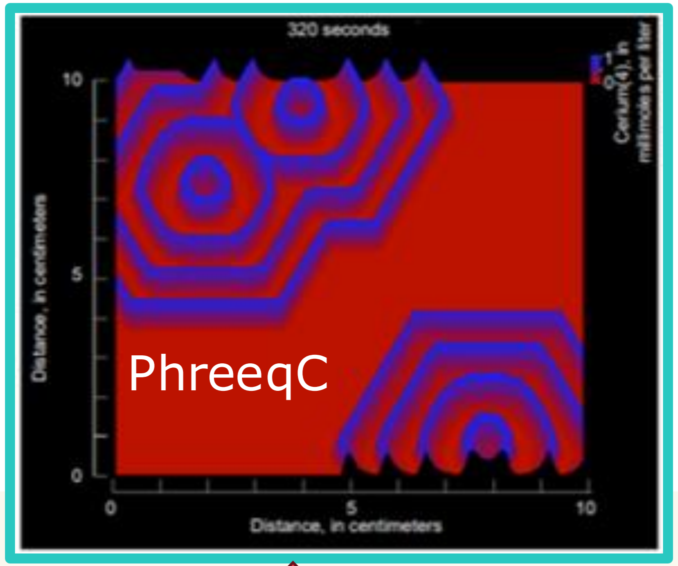
Mineral Phases

SEM and EDS

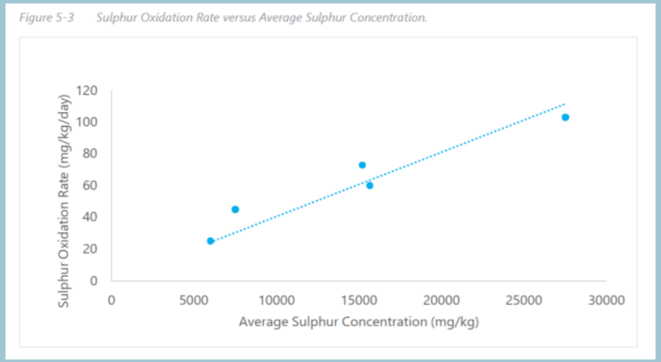


XRD





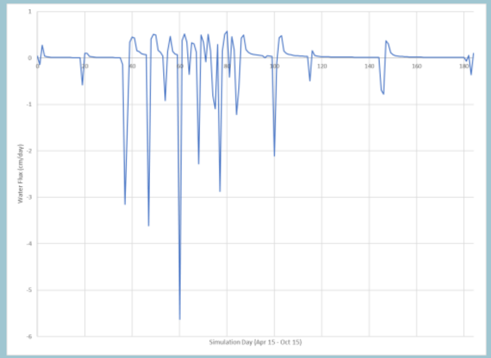
Sulphur Oxidation Kinetics from Microcosm Experiments



Shake Flask Tests

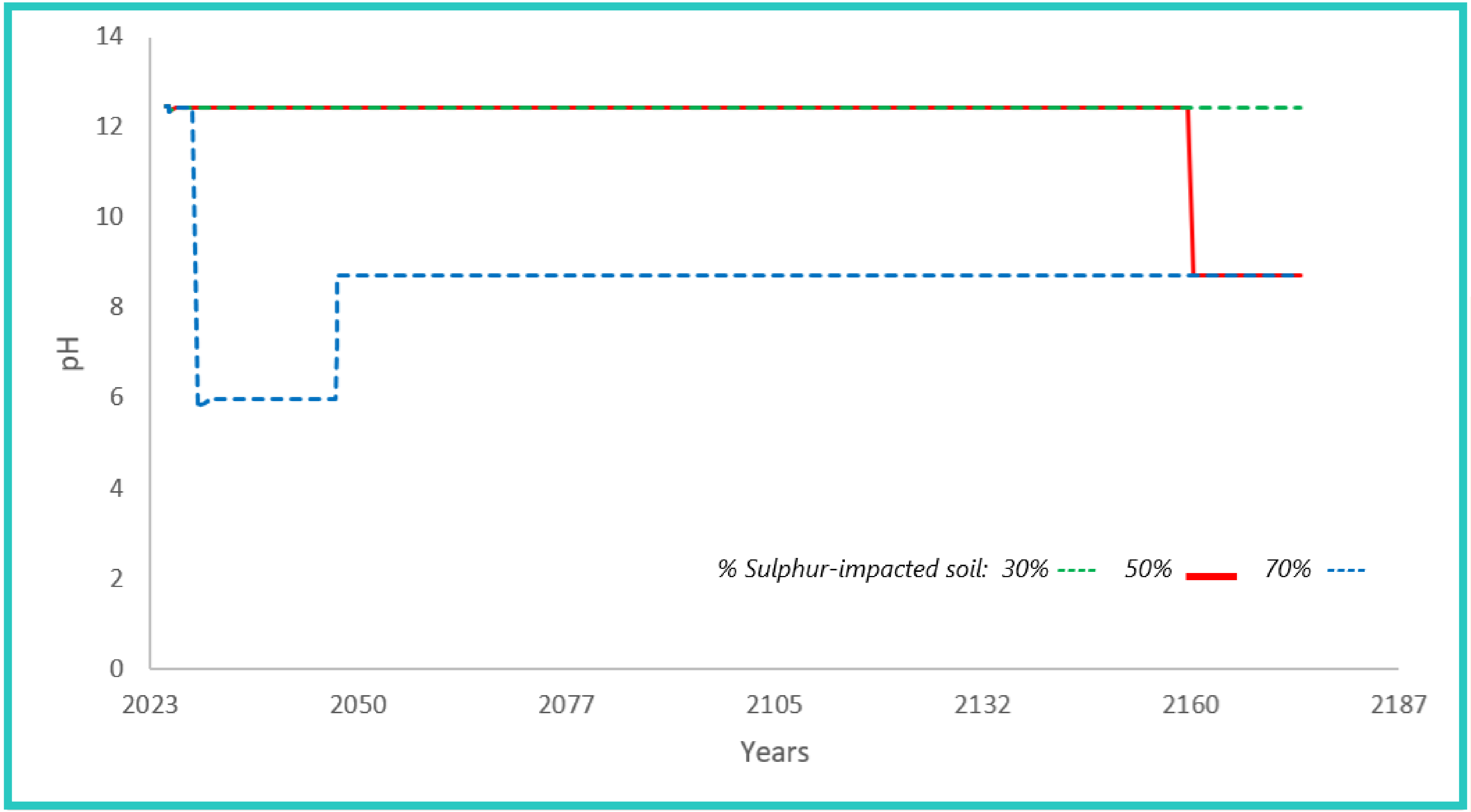
Initial porewater equilibrium compositions

Hydrus 1D Output



Modelled pH in Top (Mixed) Layer

Modelled pH in Bottom (Leachate) Layer



Geochemical Modelling Results

Sulphur Impacted Soil Proportion (%)	Lowest Mixed Layer pH (Cell 1)	Lowest Effluent pH	Highest Effluent Sulphate Conc. (mg/L)	Highest Effluent Sulphide Concentration (mg/L)	Time required for Neutralization of Portlandite in Effluent (Years)
70	~ 0.6	~5.8	~ 1,532	7.76	~ 4
50	~ 5.9	~8.8	~ 1,532	0	~ 136
30	~ 6.0	~12.4	~ 1,221	0	>150

Transport Modelling

- In applying the proposed remediation technique, it was necessary to ensure that the groundwater mixing with leachate generated at the Site meets guidelines at the location where it will discharge to a river.
- The same models used to calculate dilution factors for deriving the Alberta Tier 1 Remediation Guidelines were used to model the following two processes:
  1. Mixing of leachate with groundwater (Dilution Factor [DF] 3)
  2. Transport of mixed leachate downgradient to discharge point at the river (DF4)

Dilution Factor 3

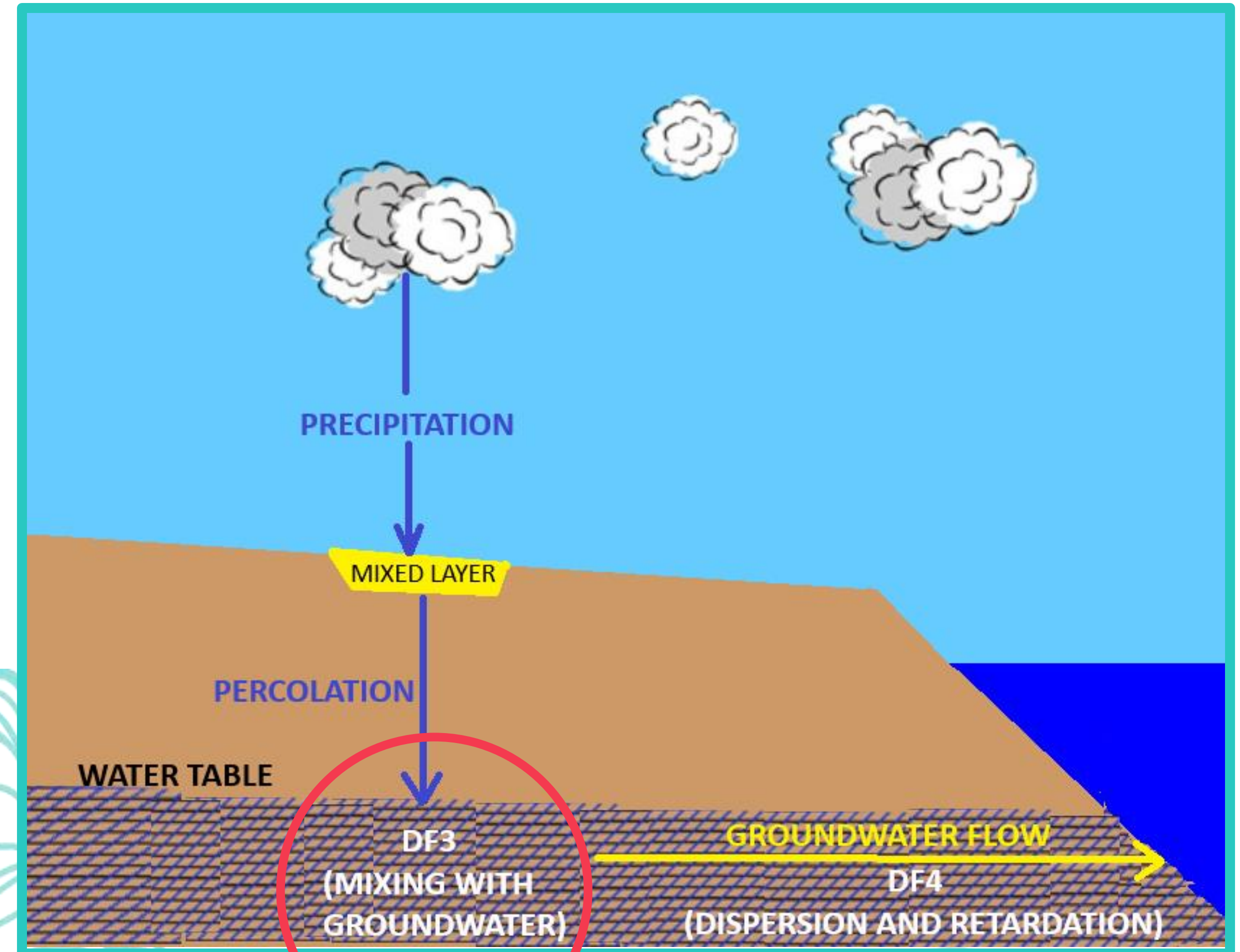
Dilution Factor 3 Calculator
AB Tier 1 Guidelines

Parameter	Symbol	Unit	Default Tier 1 Parameter Values	Model Value
Soil Guidelines				
TIER 1 SOIL REMEDIATION GUIDELINES	SQG_{AL}	*mg/kg*		-
Tier 2 Soil Quality Objectives	SQG_{AL}	*mg/kg*		-
Geometric Parameters				
source length (along groundwater flow)	X	*m*	*10*	90
thickness of unconfined aquifer	d_a	*m*	*0*	3
Flow Parameters				
saturated hydraulic conductivity	K	*m/year*	*320*	**3150**
lateral hydraulic gradient	i	-	*0.0280*	0.0022
infiltration (recharge) rate	I	*m/year*	*0.00*	0.000
darcy velocity	V	*m/year*		0.693
Mixing Zone Calculation				
mixing depth due to dispersion	r	*m*		0.90
mixing depth due to infiltration rate	s	*m*		2.990
overall mixing depth	Z_d	*m*		3.89
Calculation of Dilution Factors				
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		**3.82**

DF3 as function of Hydraulic Conductivity

	K		DF3
Lower	1.00E-05	m/s	1.5
Mid	1.00E-04	m/s	3.82
Upper	4.00E-04	m/s	7.65

Note: Hydraulic Conductivities are for Fluvial Sand and Gravel (Bow Valley) after model calibration
Source: Advisian (2016)

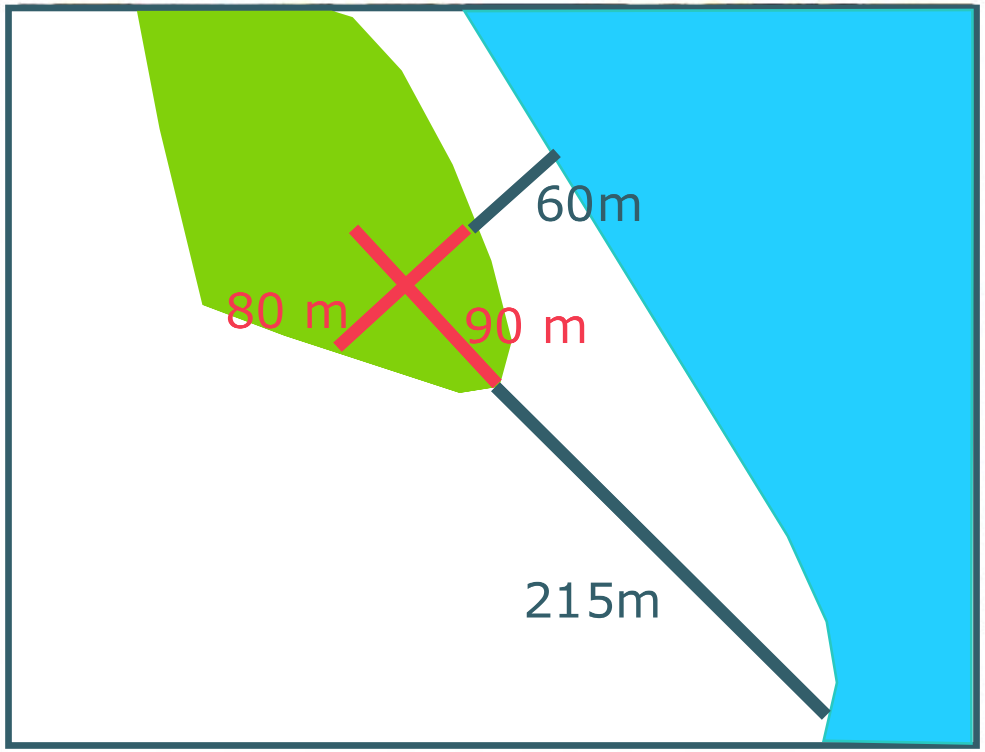


Dilution Factor 4

Parameter	Symbol	Unit	Default Tier 1 Parameter Values	Model Value
water - organic carbon partition coefficient	K_{oc}	*mL/g*		0
water - soil partition coefficient	K_d	*mL/g*		0
solubility	S	*mg/L*		2500
dimensionless Henry's law coefficient	H'	-		0
Proportion of Total Mass Fraction	F_i			
Soil Properties				
soil bulk density	ρ_b	*g/cm³*	**1.7**	1.7
total porosity	θ_t	*cm³/cm³*	**0.36**	0.36
fraction of organic carbon	f_{oc}	*mass/mass*	**0.005**	0.005
Geometric Parameters				
source width (perpendicular to gw flow)	Y	*m*	**10**	80
distance downgradient to water body	x	*m*	**10**	215
perpendicular distance to water body	y	*m*	**0**	60
thickness of unsaturated zone (depth to groundwater)	d	*m*	**3**	3
Flow Parameters				
aquifer hydraulic conductivity	K	*m/year*	**320**	3,150
lateral hydraulic gradient in aquifer	i	-	**0.028**	0.002
longitudinal dispersivity	D_x	*m*		22
transverse dispersivity	D_y	*m*		2.15
Darcy velocity in groundwater	V	*m/year*		6.93
retardation factor in saturated zone	R_s	-		1.0
contaminant velocity	v	*m/year*		19.3
Degradation Parameters				
contaminant half life (saturated)	$t_{1/2(s)}$	*year*		1,000,000
decay constant (saturated)	L_s	*1/year*		0.00
Calculation of Dilution Factors				
	DF4	-		**1.34**
	A	-		0.00
	C	-		2.33
	D	-		0.47

Key to Text Colours:

Red Text = Input Variables
Blue Text = Calculated Values



DF4 as function of Hydraulic Conductivity

	K		DF4
Lower	1.00E-04	m/s	1.34
Upper	4.00E-04	m/s	1.34

Transport Modelling Results

- Combined dilution factor = 5
- Would result in a modeled sulphate concentration of 300 mg/L at the point of compliance (guideline = 429 mg/L)
- For a sulphur-impacted soil mixing ratio of less than 50%, diluted leachate from the treatment area would not exceed the applicable guidelines at the surface water body.

Conclusions

- Based on the microcosm and modelling results, the approach appears to be sound
- Mixtures consisting of 50% sulphur-impacted soil (0.67 mol/kg S before mixing) resulted in rapid neutralization of portlandite present in the mixed layer (up to 0.5 mol/kg before mixing).
- Mixtures consisting of greater ratios of sulphur-impacted soil (e.g. 70%) would result in faster remediation times but could introduce new environmental risks, such as surface water sulphide exceedances.
- Pilot testing of the technique would be critical before applying it at full scale.
- Field trials will need to be carefully controlled, with sentinel wells and contingency plans for dealing with unacceptably high groundwater contaminant concentrations should they occur.

“Bonus Conclusion”

- The rate of carbonation of portlandite in the control microcosm (i.e., the microcosm without the addition of sulphur-impacted soil) was faster than expected. Introducing carbon dioxide into cement-impacted soil offers another remediation approach.

It Takes a Village.....

Marc Bowles – Concept and Client Representative

Worley Team
Dr. Kimberley McLeish – Project Management, Experimental Design and Data Analysis
Vincent Stein – Experimental Design, Data Management, Transport and Microbial Kinetics Modelling
Robert Newcomer – Geochemical Modelling
Kayode Famade – Geochemical and Unsaturated Flow Modelling
Dr. Andrew Hinnell - Unsaturated Flow Modelling

External
Equilibrium Environmental Inc – Tony Knafla and Viktoria Winter – Experimental Design and Laboratory Microcosms
Cirrus Environmental Services – Historical Site Data
Ecometrix – Dr. Elizabeth Haack – 3rd Party Geochemical Model Reviewer
University of Calgary – Dr. Jordan Hollman and Dr. Cathy Ryan