Passive treatment of ARD impacted waters using waste mussel shells

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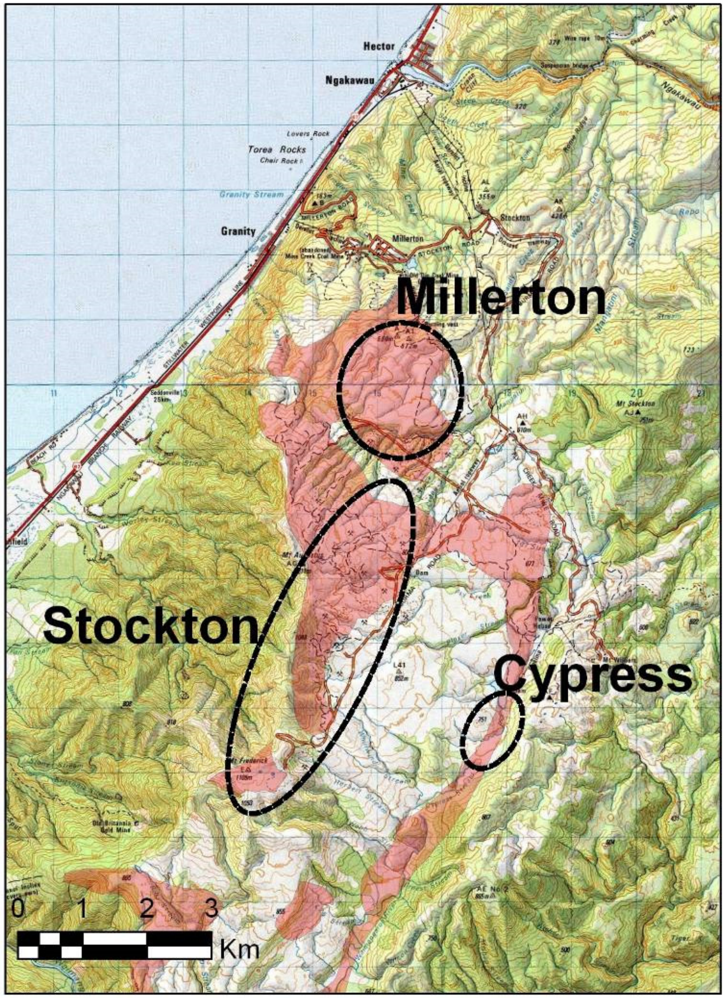
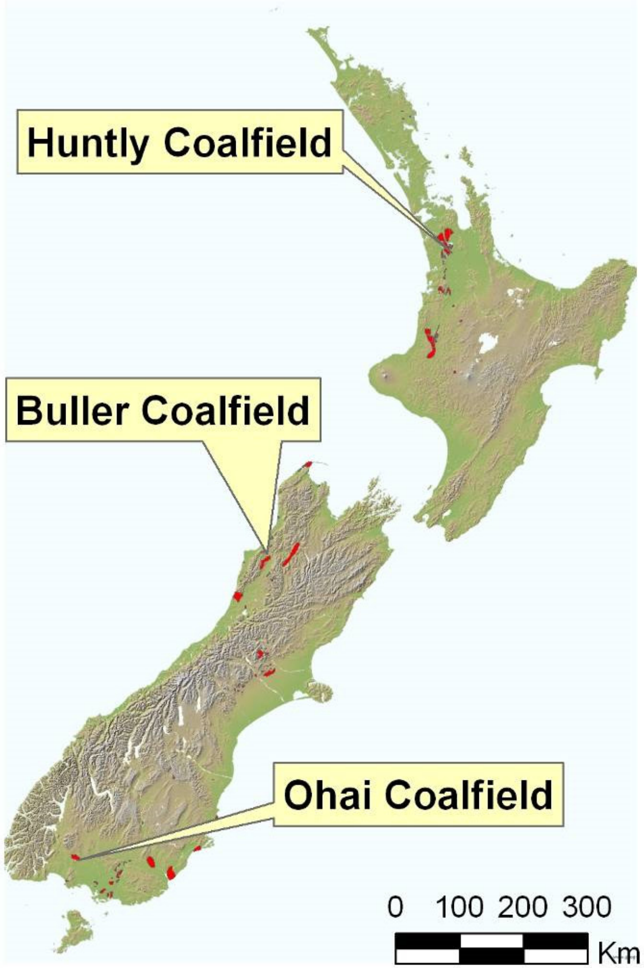
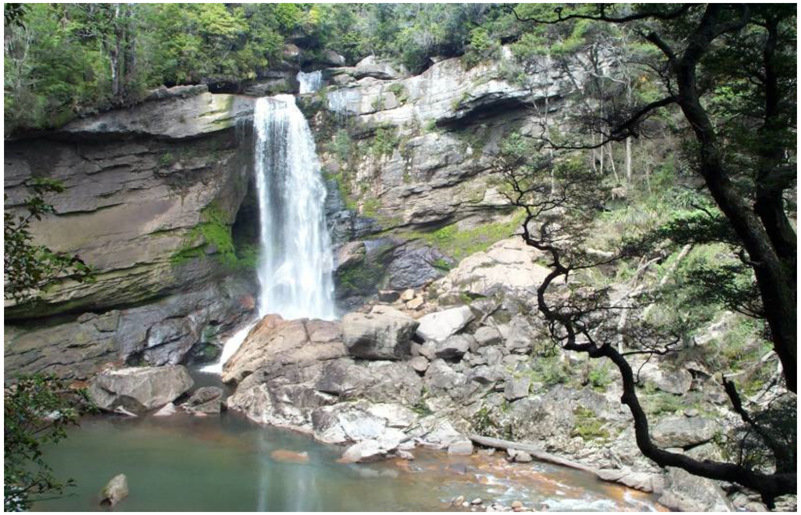
21st Annual British Columbia – MEND ML/ARD Workshop
3rd and 4th December 2014

Introduction





Stockton Coal Mine



Mangatini Waterfall

•Elevation: 1000 m asl and 2km from the coast

•Temperature: 9 ^{o}C (mean)

•Rainfall: 5000 – 7000 mm/year

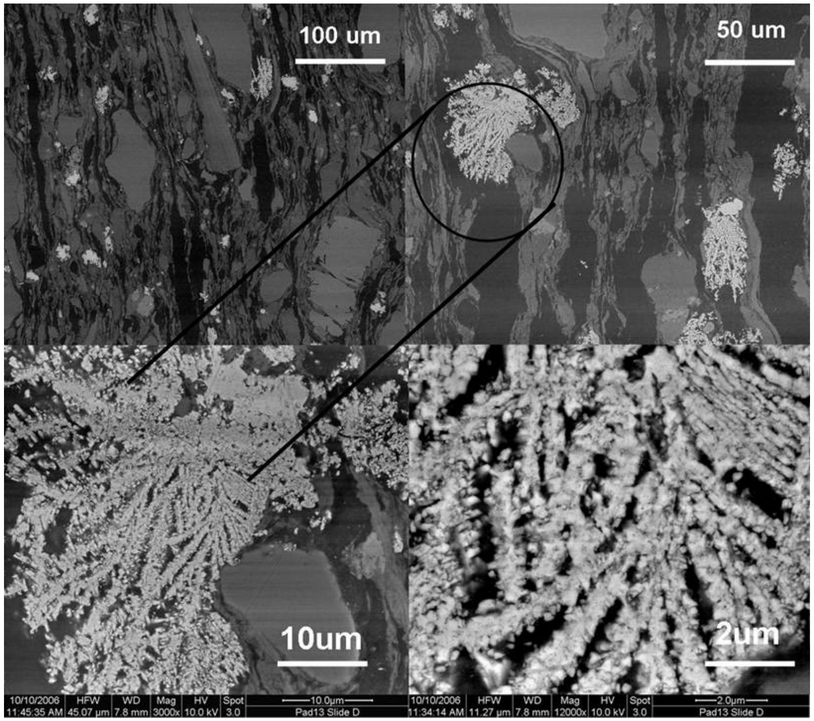
•1100 ha disturbed area (FY14)

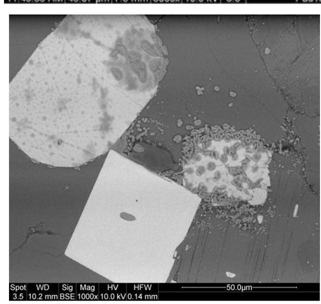
•250 Mt overburden disturbed

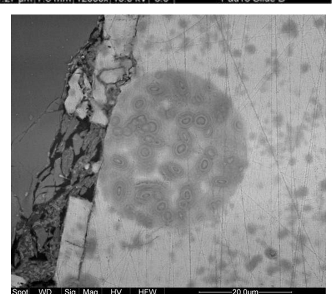
• ~0.7 wt% S as pyrite

Pyrite

- **Reactive pyrite morphologies are present in significant quantities**







Mangatini Stream

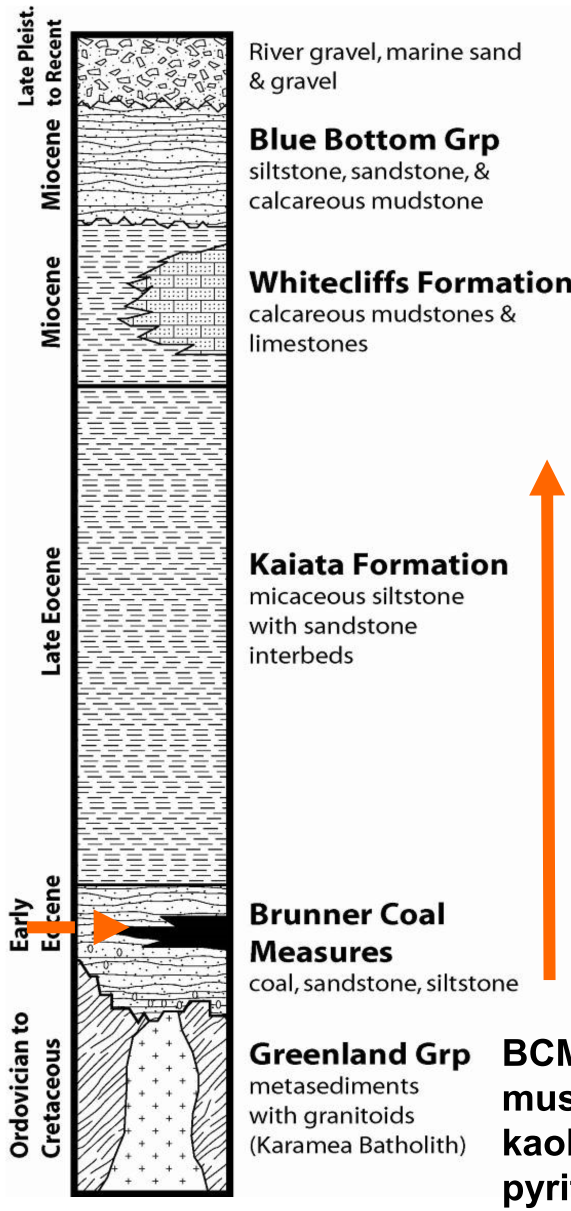
Weisener, C.G., Weber, P.A. (2010). Preferential oxidation of pyrite as a function of morphology and relict texture. New Zealand Journal of Geology and Geophysics Special Edition: Mine Drainage Vol 53 (2&3): 167 -176

Geology

Increasing carbonate content

Increasing Pyrite content

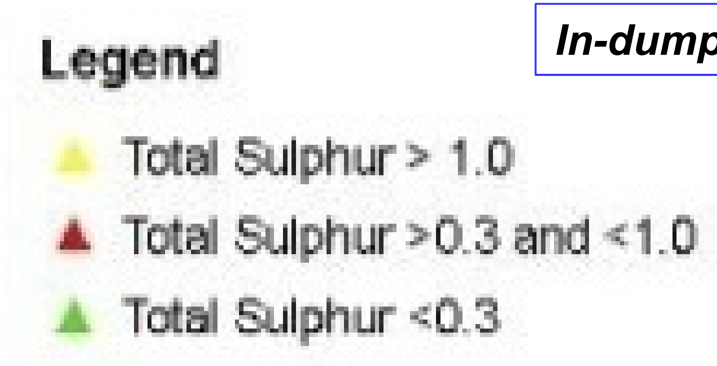
Coal Seams



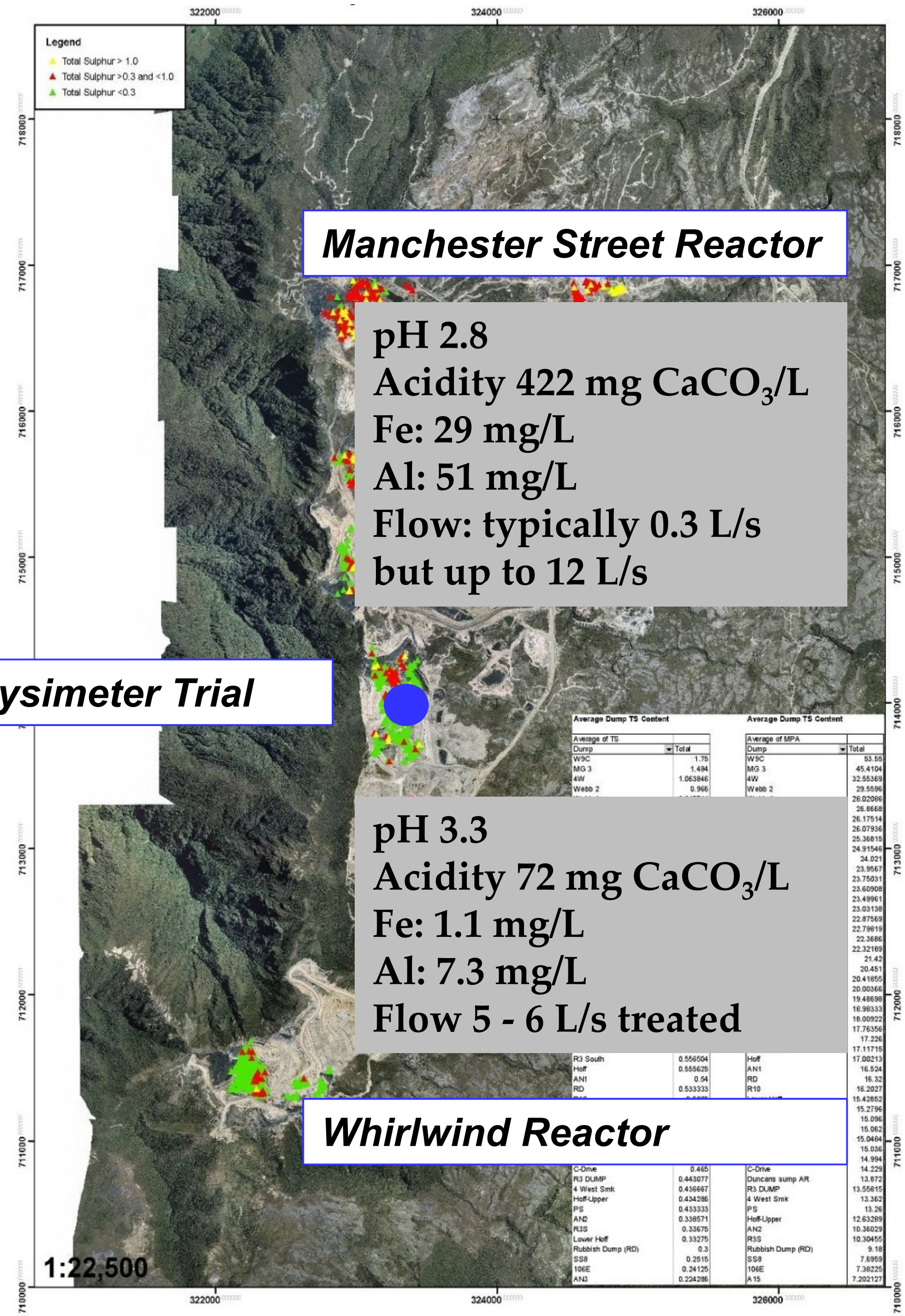
Transgression sequence

BCM – quartz, muscovite, K-feldspar, kaolinite, and minor pyrite

Sulfur (Pyrite) Distribution



In-dump Lysimeter Trial



Manchester Street Reactor

pH 2.8
Acidity 422 mg $CaCO_3$/L
Fe: 29 mg/L
Al: 51 mg/L
Flow: typically 0.3 L/s
but up to 12 L/s

pH 3.3
Acidity 72 mg $CaCO_3$/L
Fe: 1.1 mg/L
Al: 7.3 mg/L
Flow 5 - 6 L/s treated

Whirlwind Reactor

ANC Fresh (850 kg/tonne)
ANC Weathered (950 kg/tonne)

Fresh shell up to 10% organics (meat)

Samples are chipped by the manufacturer to reduce bulk for cartage

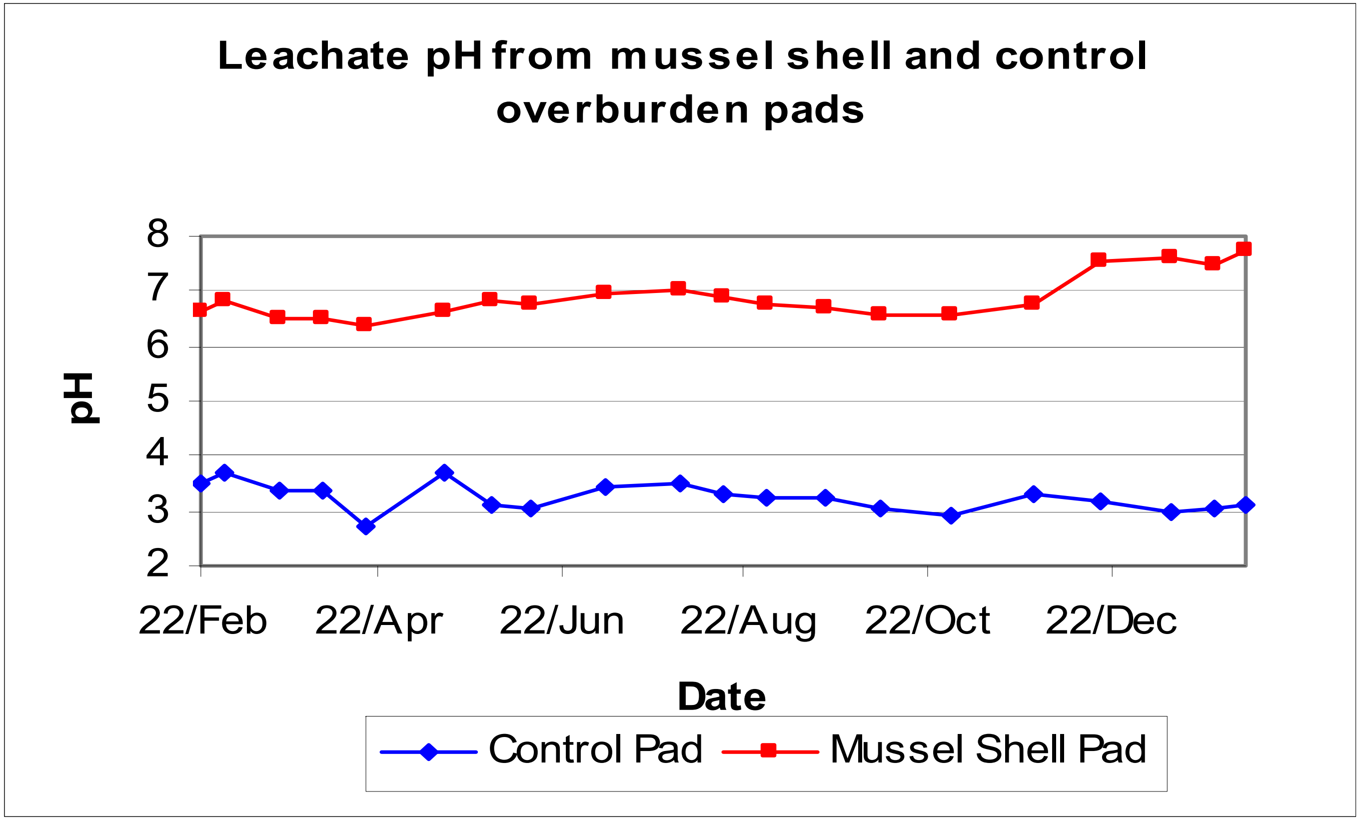
Hydraulic conductivities of 1 x 10^{-3} m/s

- 20,000 – 60,000 tpa of shell waste produced in New Zealand.
- Waste product: often free or negative value

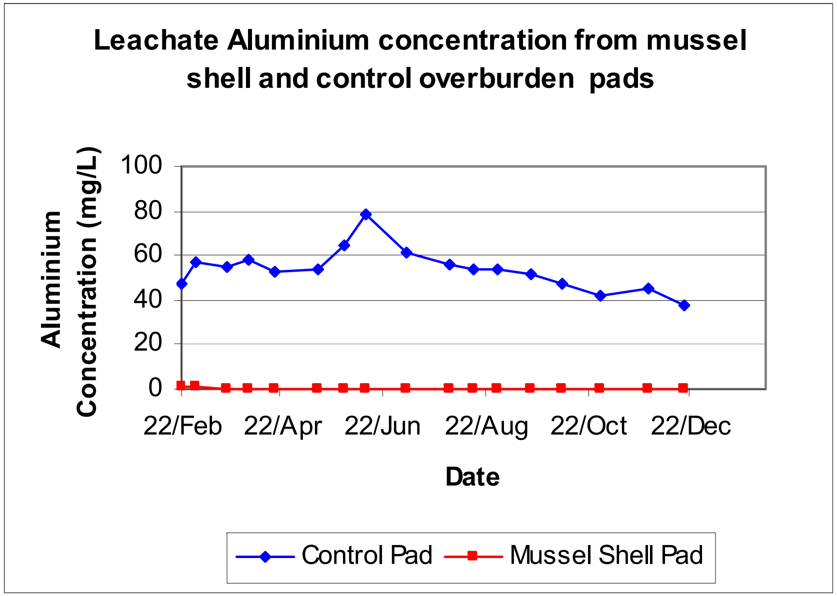
- The above is a 60,000 tonne stockpile 3 hrs drive from Stockton

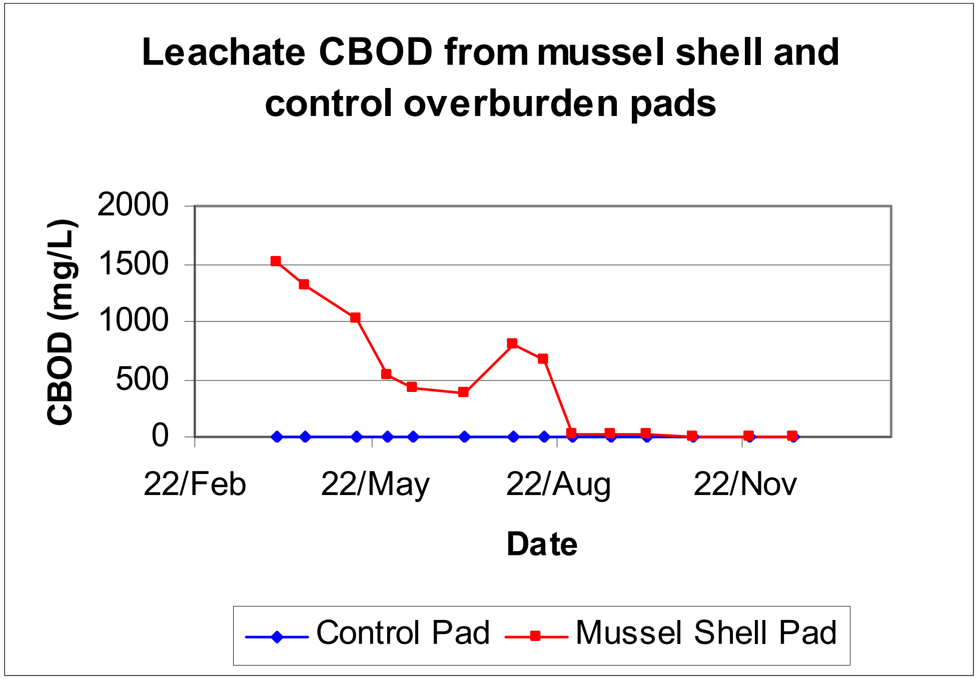
In-Dump ARD Treatment - Mussel Shells

- In-dump trial established using shells covered by 3m of PAF waste rock.
- 10 tonnes of mussel shells (300mm thick) in a 4 m by 10 m lysimeter.
- A control lysimeter with PAF waste rock was also established



In-Dump ARD Treatment -Mussel Shells





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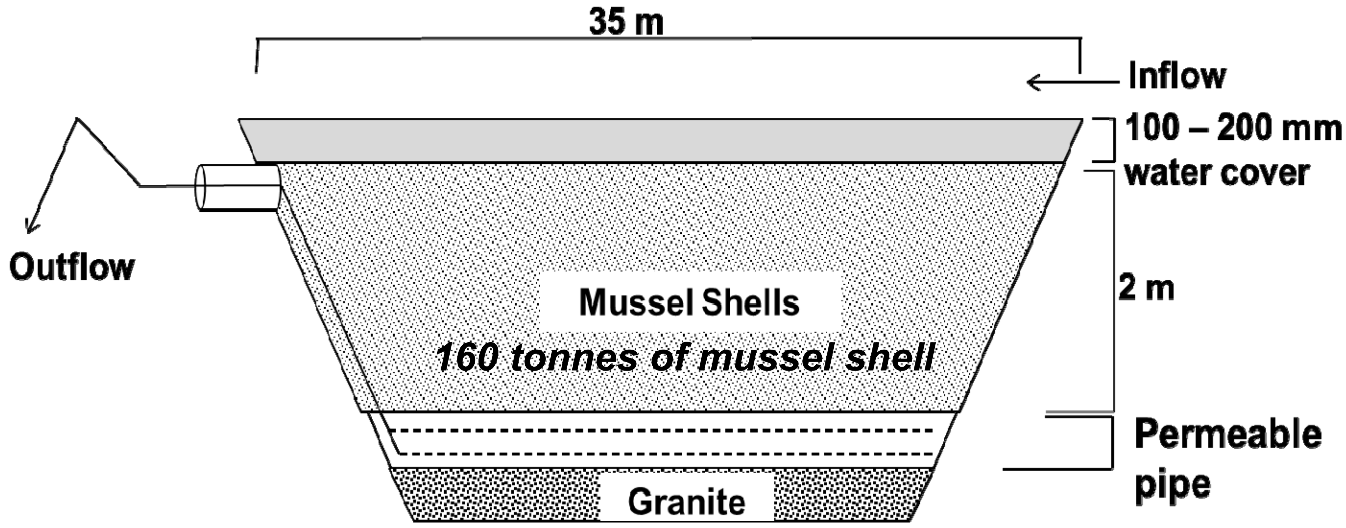
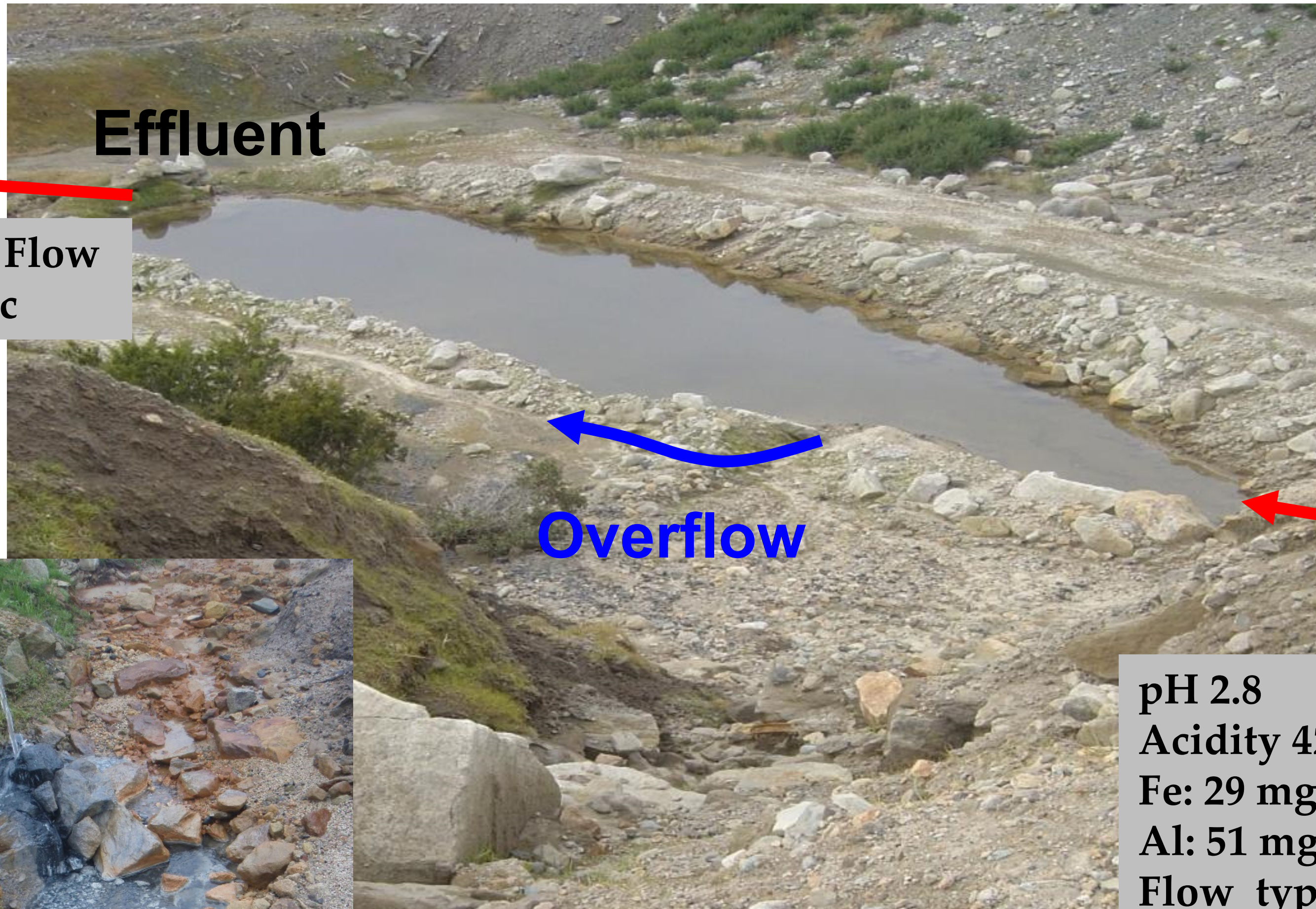
Manchester Street MS Reactor Proof of concept trials

- A simple design utilising an old sediment pond (no earthworks required)
- 50m of 50mm perforated "nova flow pipe" placed on the floor and connected to a riser
- Downflow design
- Designed for 6 days residence time




Fresh shell stockpiles:
Vectors (seagulls, rats)
Odour

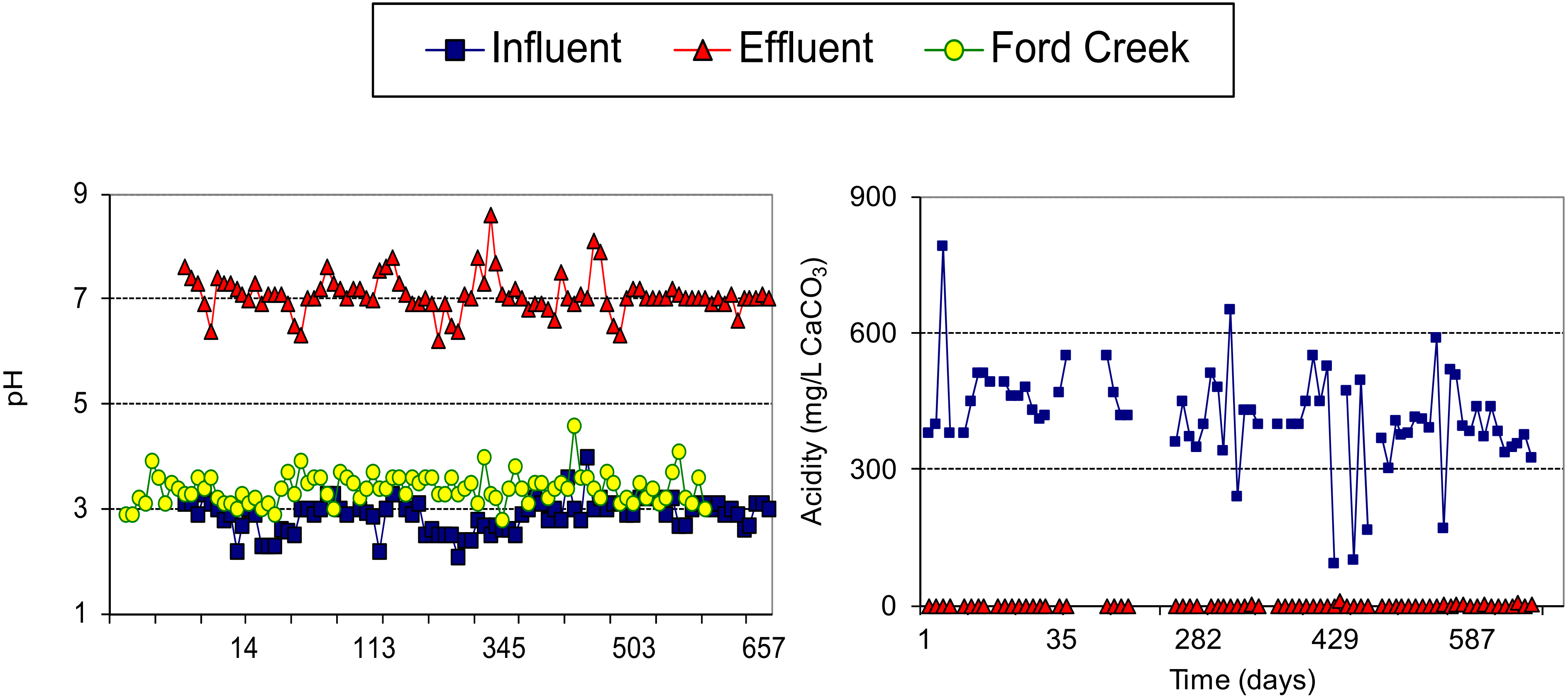
Manchester Street MS Reactor



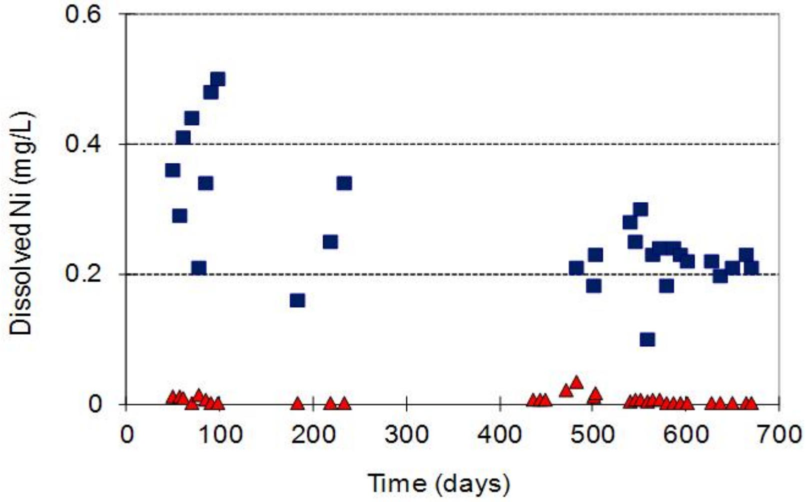
Treated Flow
~0.3L sec

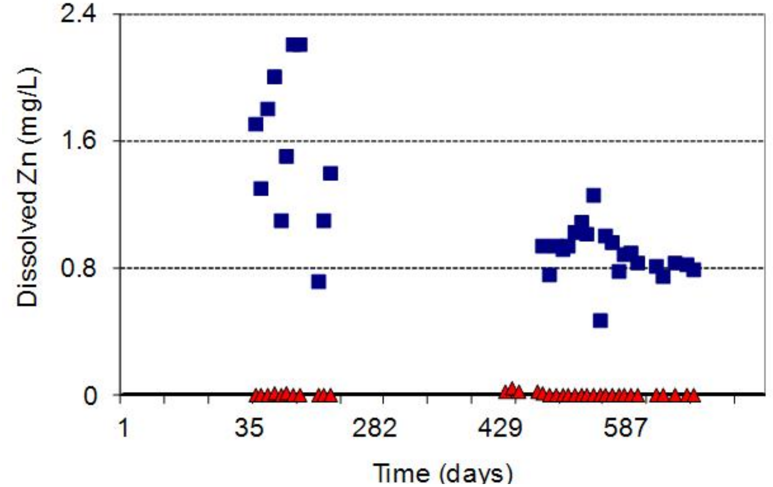
pH 2.8
Acidity 422 mg $CaCO_3$/L
Fe: 29 mg/L
Al: 51 mg/L
Flow typically 0.3L/s but up to 12 L/s

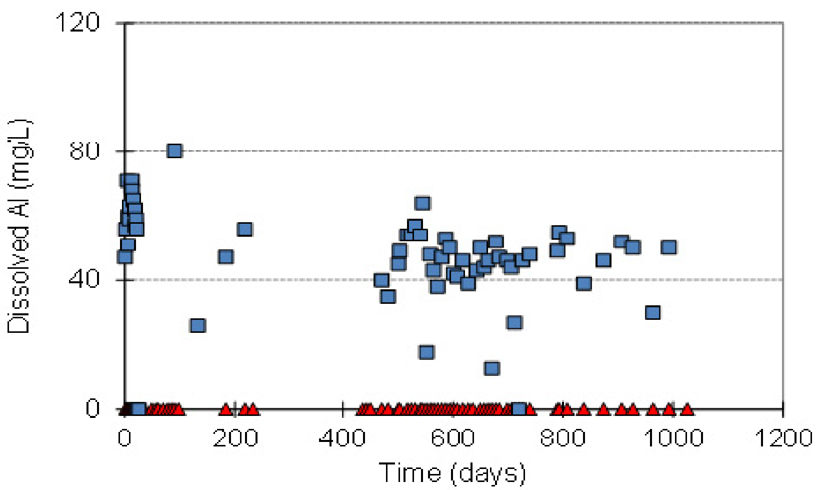
Manchester Street MS Reactor

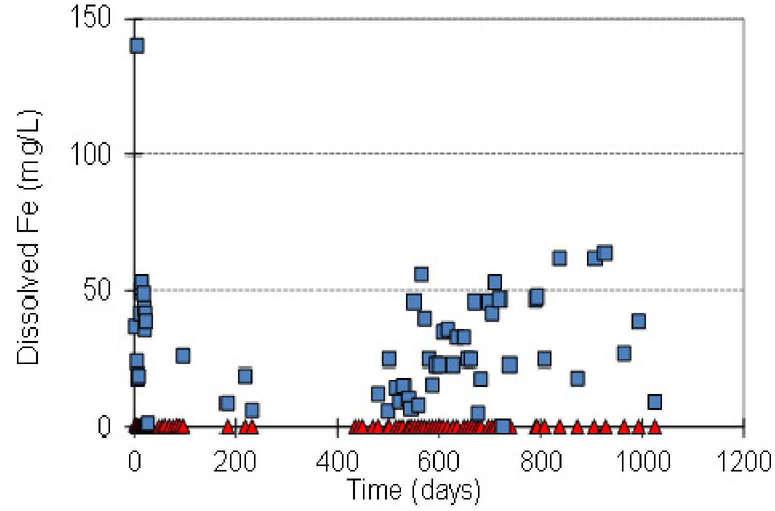


Manchester Street MS Reactor









Reactor Autopsy (2 years)

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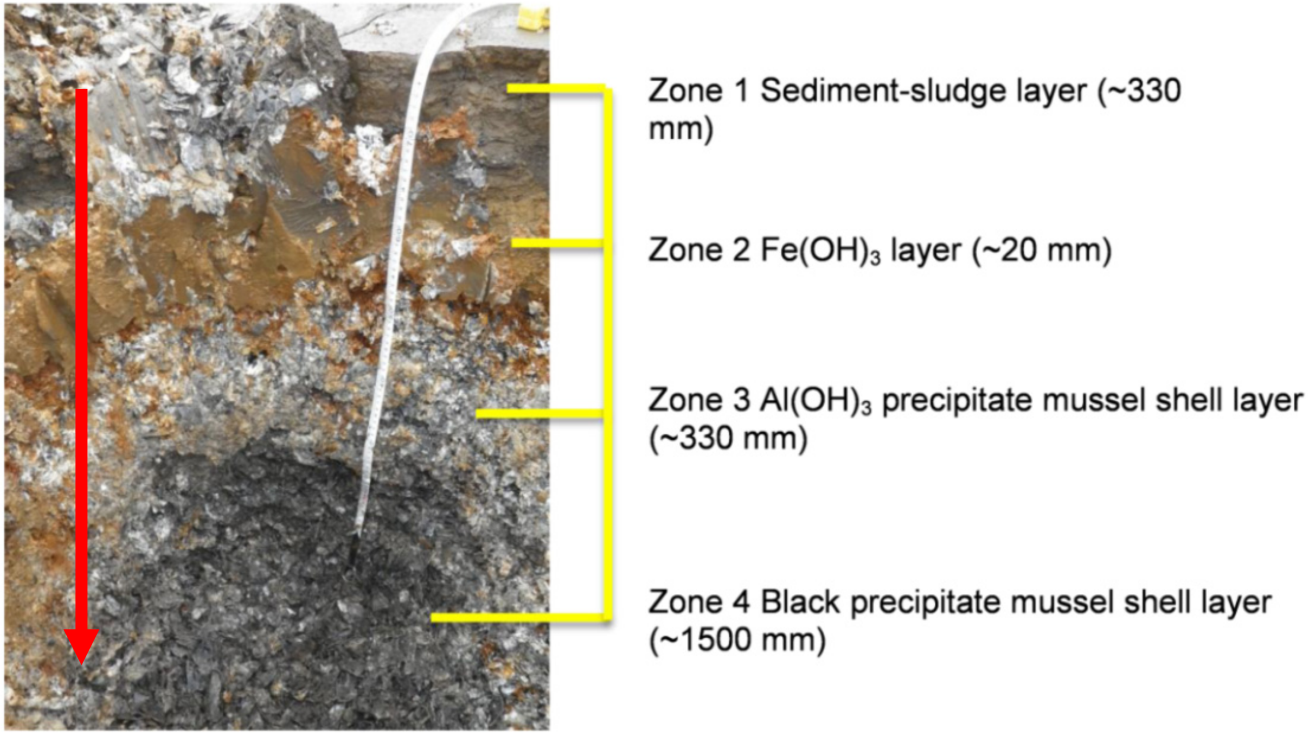
Mussel Shell Reactor –2 years on



pH increasing with depth

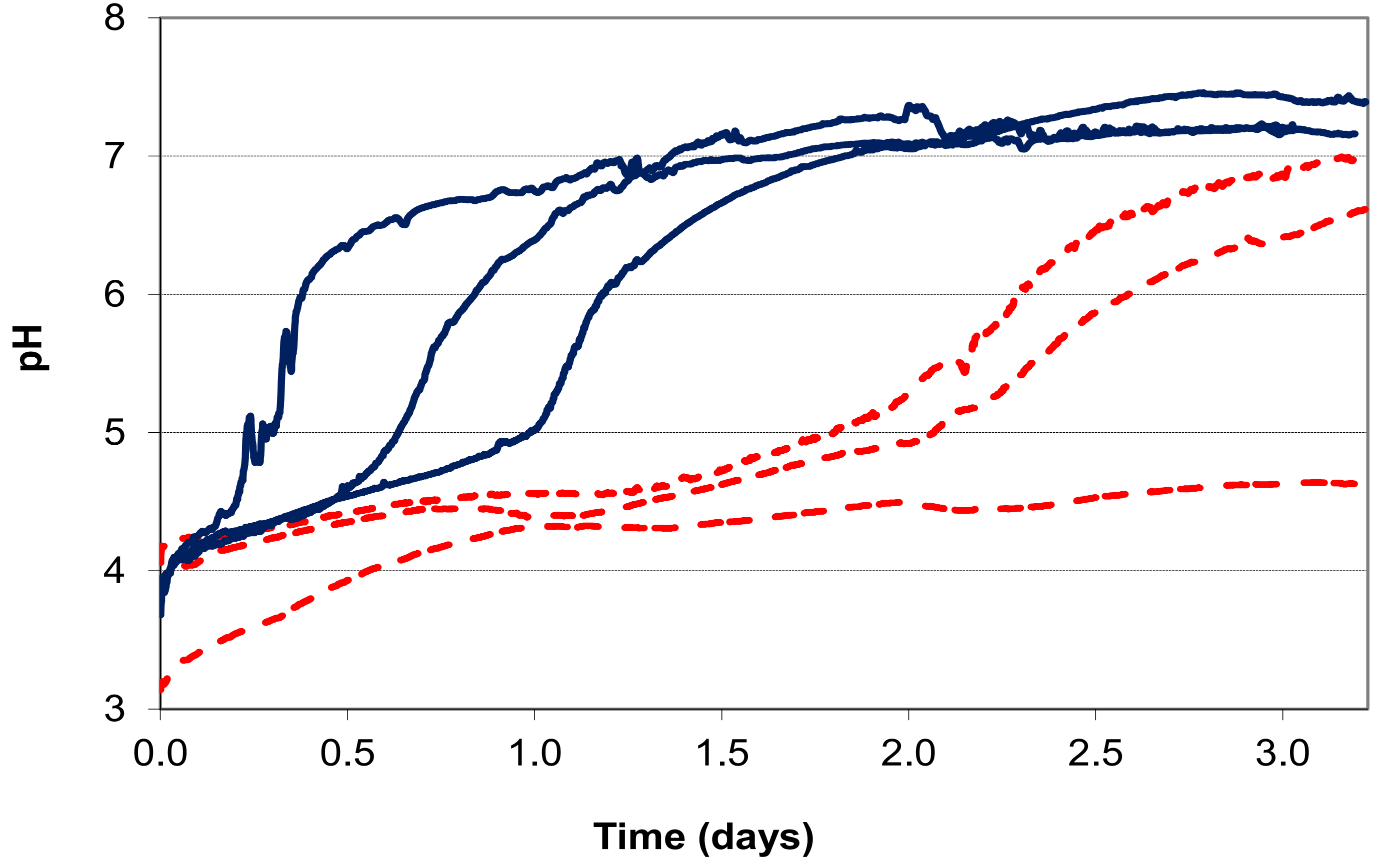
Layer	Mean Depth (mm)	ANC
Sediment Sludge Layer	160	8.76
Orange $Fe(OH)_3$ Layer	340	288
White $Al(OH)_3$ Layer (upper)	420	499
White $Al(OH)_3$ Layer (lower)	550	825
Black Shell Zone	1050	846

Leach test

1L jar filled with shell and then topped up with AMD

Zone 4 Shells - Unreacted

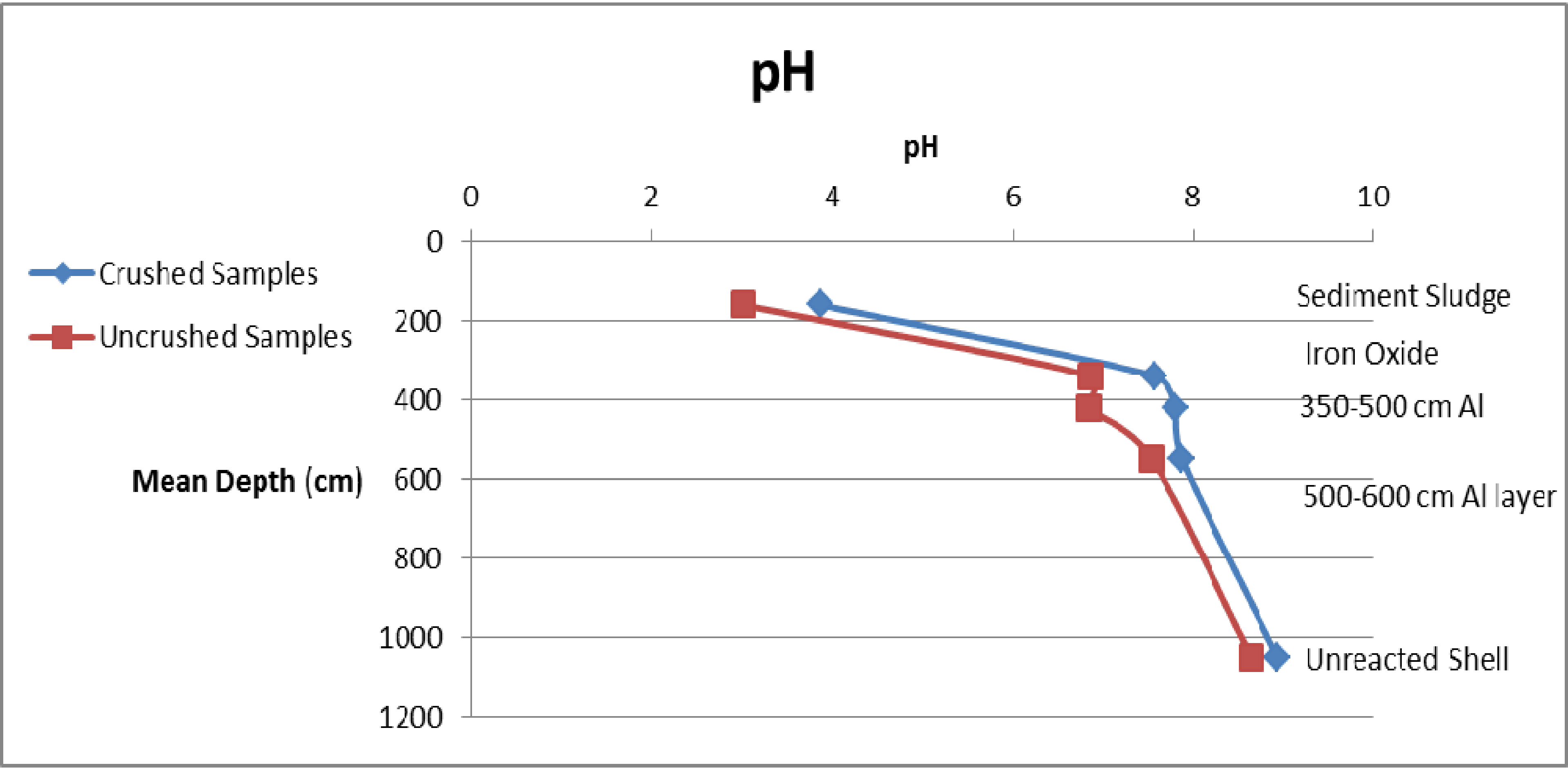
Zone 3 Shells – $Al(OH)_3$ layer (350-500mm)



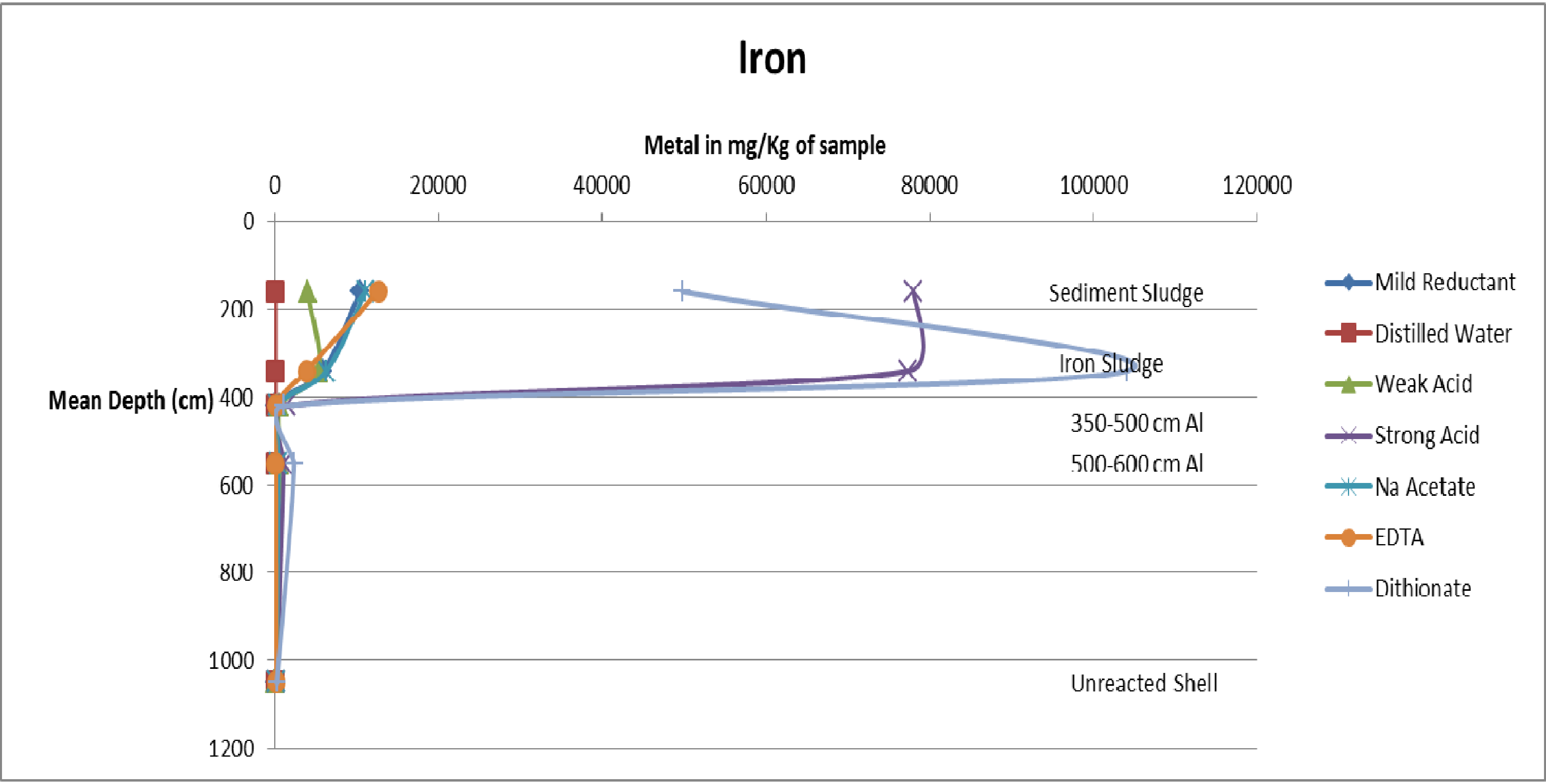
Extraction Type	Extractant	Environment targets
Distilled Water	Nitrogen purged Milli-Q® water	Water soluble phases, including salts
EDTA	0.05M EDTA adjusted to pH 6	Metals (Cd, Cu, Cr, Pb, Fe, Zn and Ni) as organically complexed and carbonate bound material
Mild reductant	57 g/L Sodium citrate dihydrate + 50 g/L sodium bicarbonate + 24 g/L L-ascorbic acid sodium salt	Poorly crystalline or amorphous oxyhydroxides
Sodium Acetate	1M sodium acetate solution adjusted to pH 4.5 using acetic acid.	Carbonate phases, siderite, ankerite, acid volatile sulfides, adsorbed material.
Sodium Dithionite	50g/L sodium dithionite solution adjusted to pH 4.8 with 0.35 M acetic acid/0.2M sodium citrate	Iron and Magnesium oxides/hydroxides, trace metals.
Strong acid extraction	5M HCl	All acid-extractable phases
Weak acid extraction	0.5M HCl	Poorly crystalline phases, surface complexes, adsorbed metals.

Rinse pH Profile

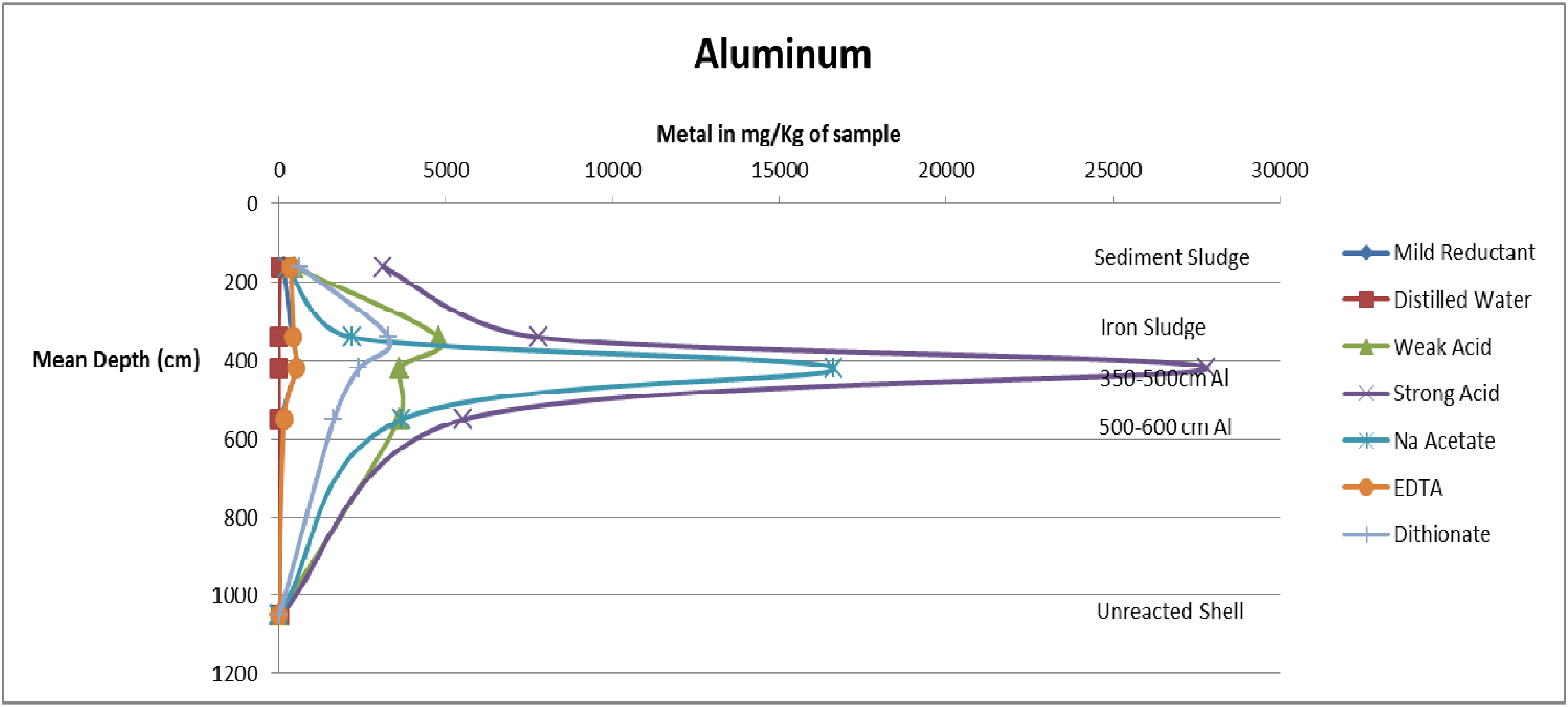
5g sample with 10 mL water (5 min gentle agitation)



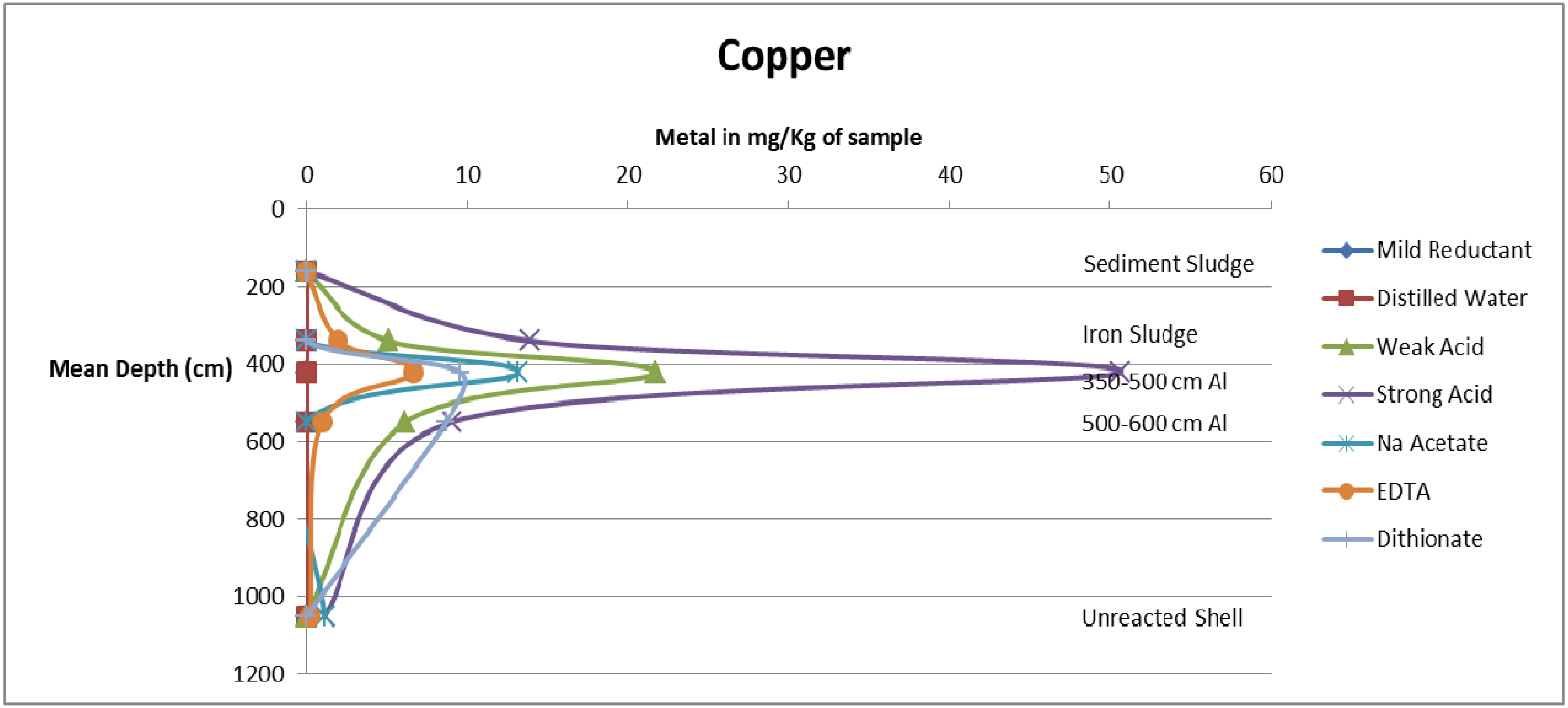
Iron Profile



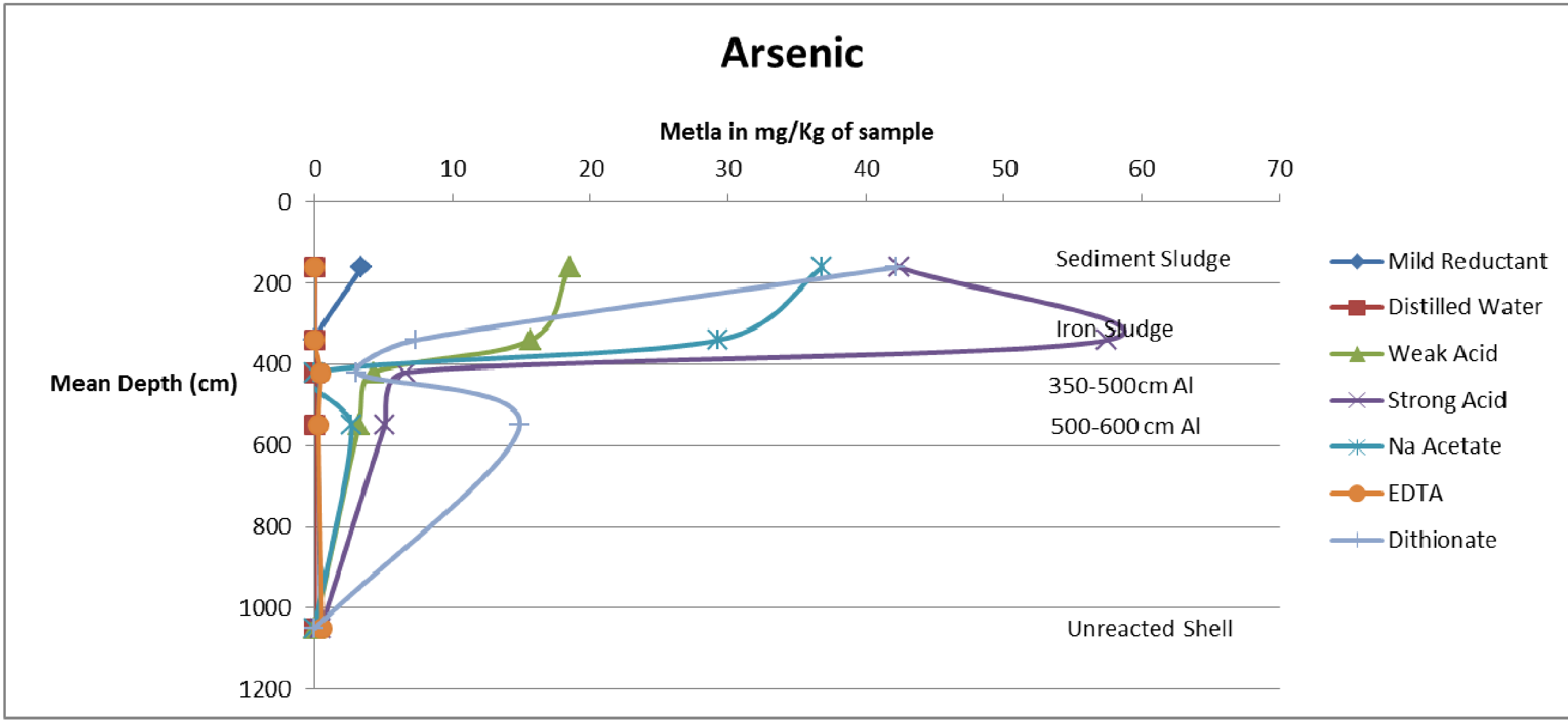
Aluminium Profile



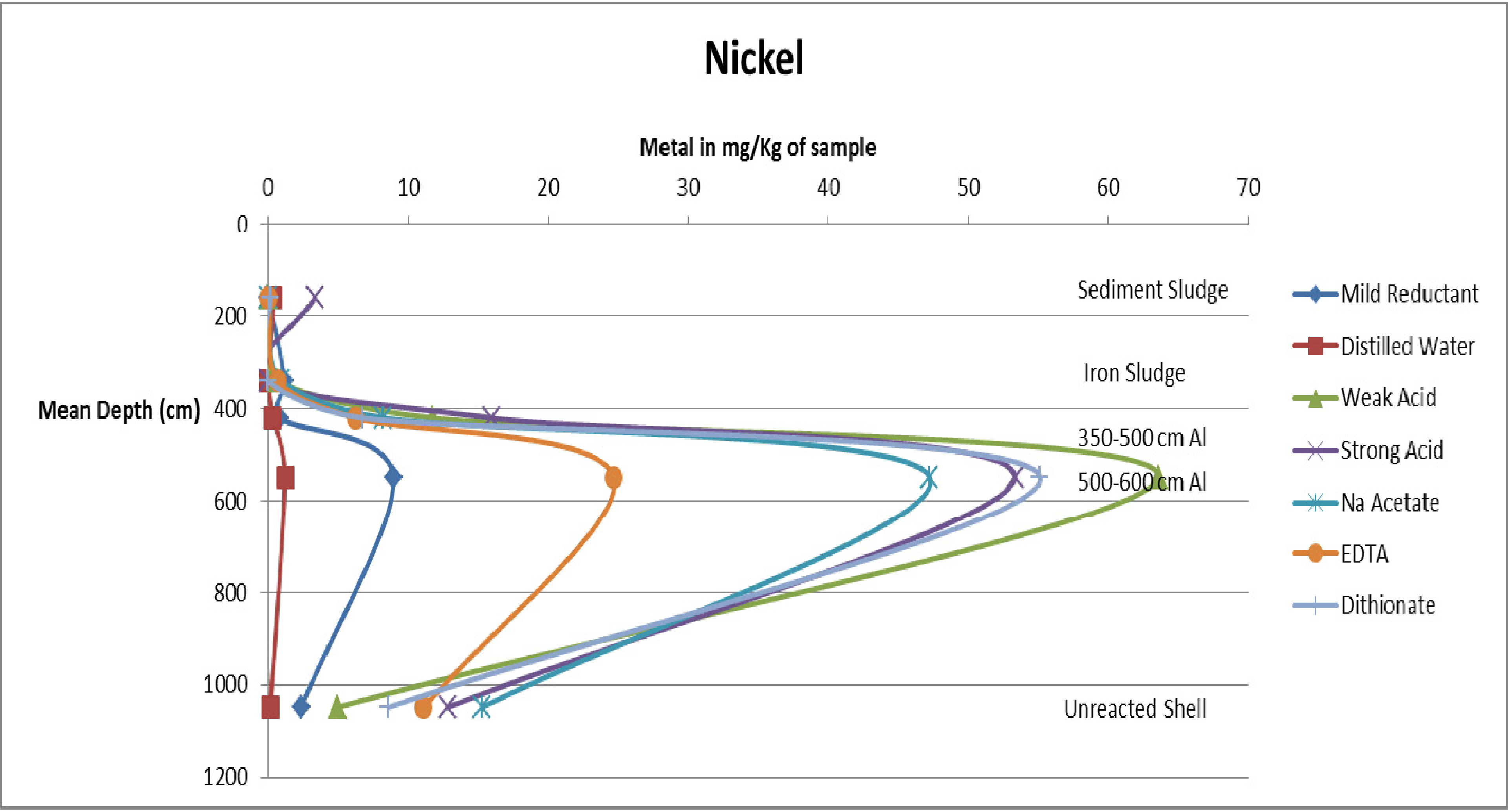
Copper Profile



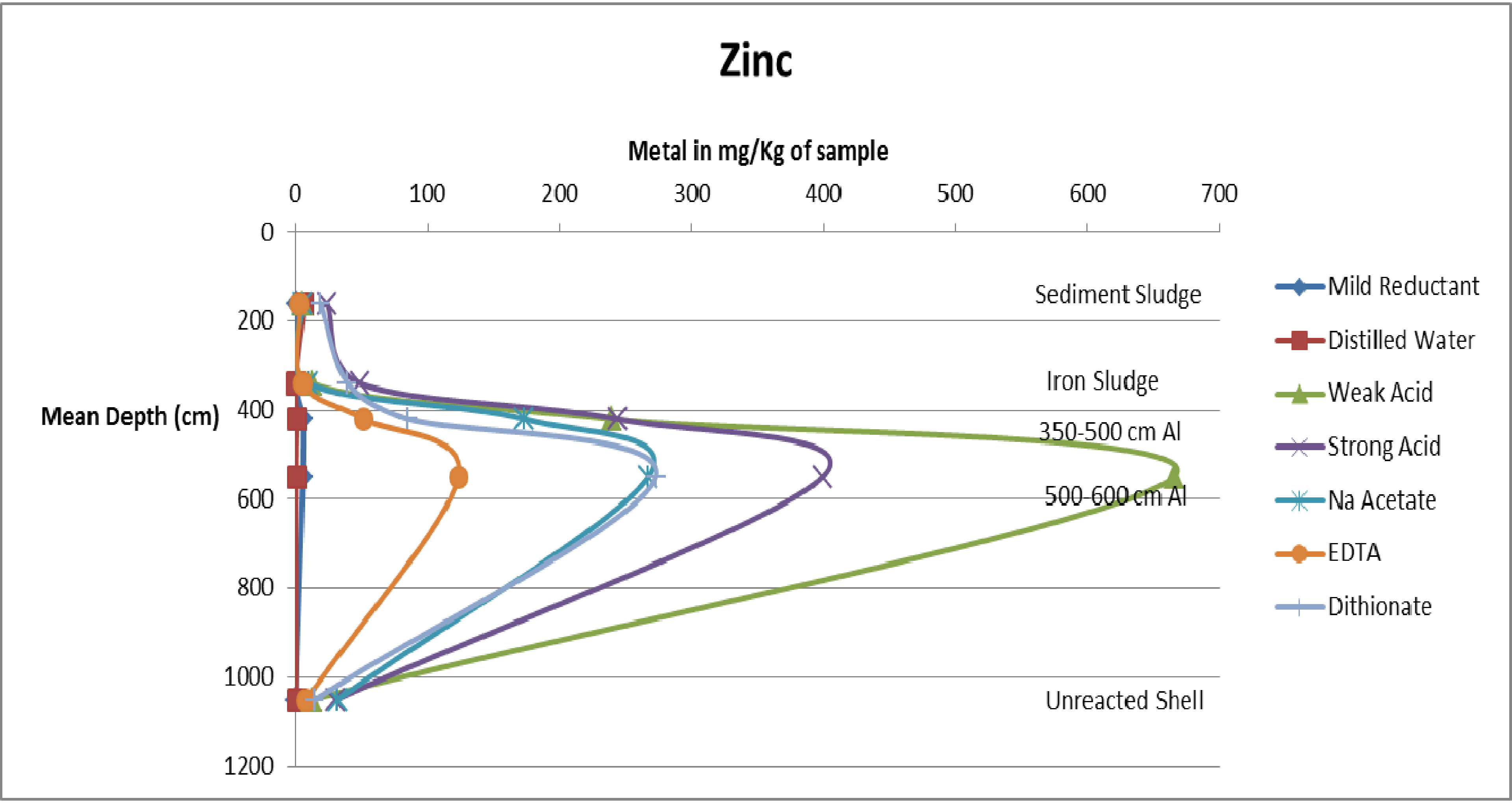
Arsenic Profile



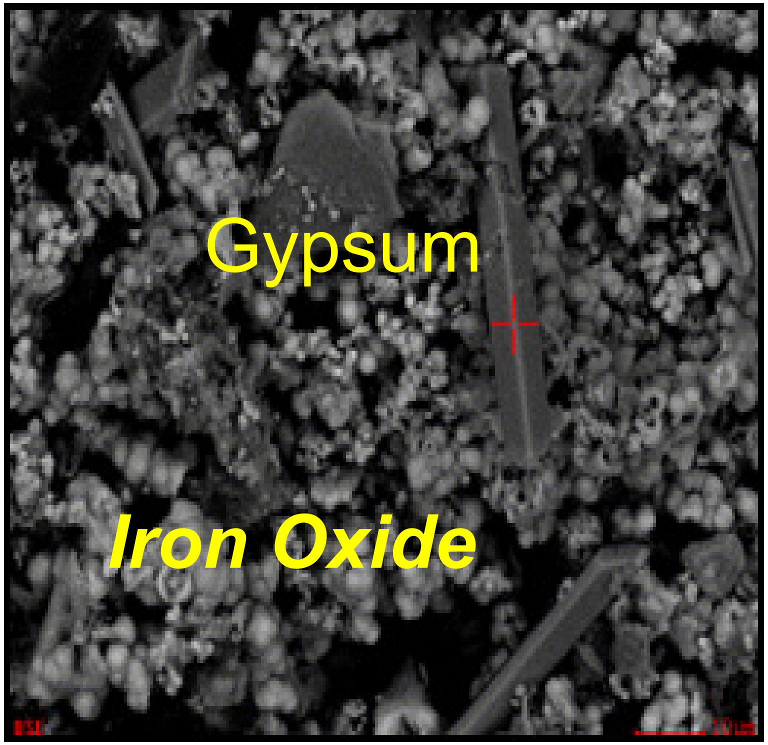
Nickel Profile



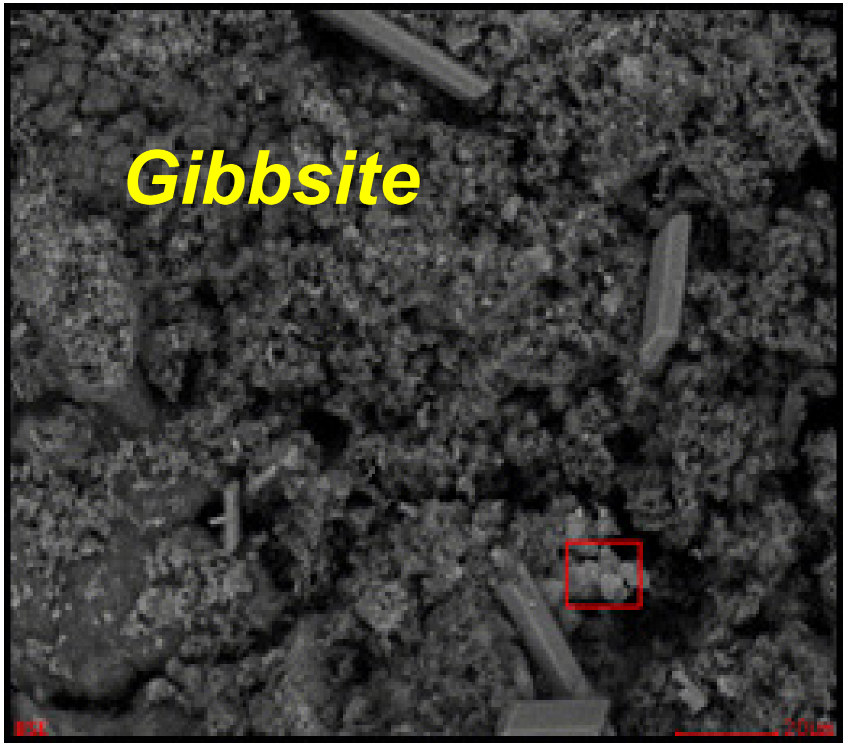
Zinc Profile



SEM Analysis

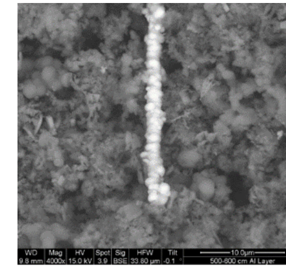


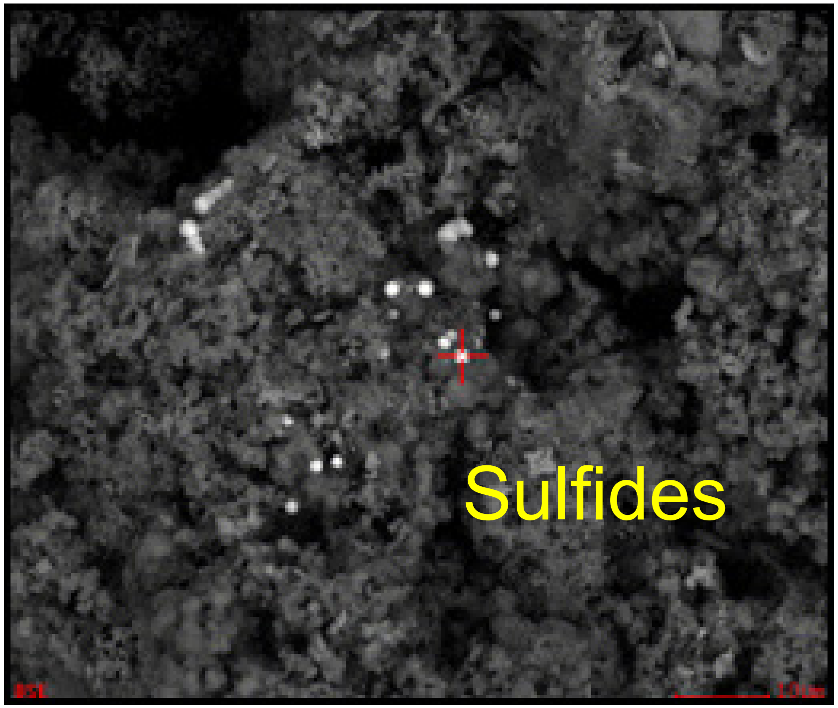
Fe(OH)$_3$ Layer

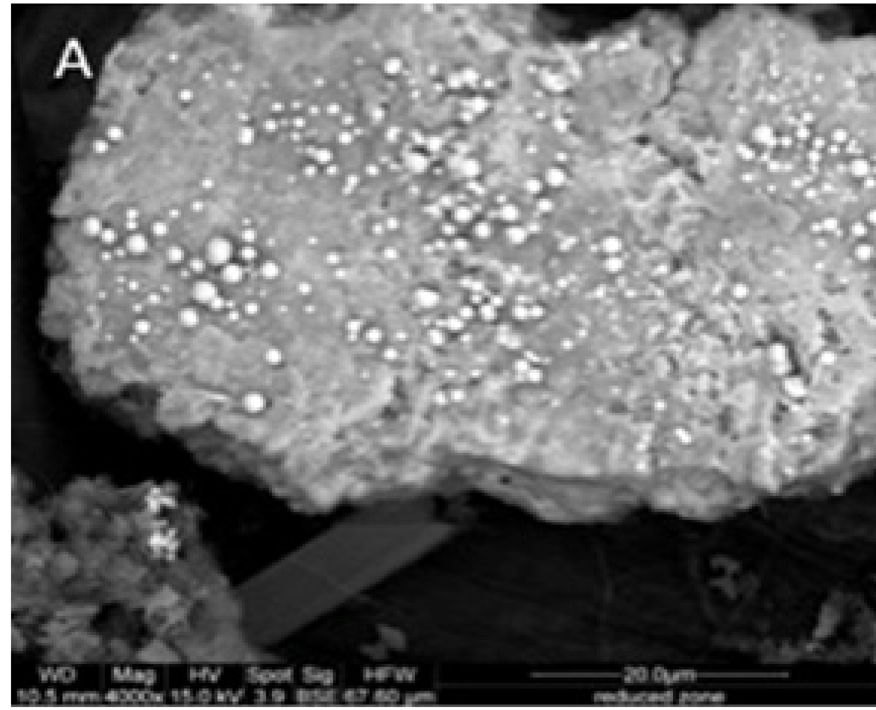


Al(OH)$_3$ Layer (350-500mm)

SEM Analysis







500-600 mm Al Layer anaerobic transition zone

Unreacted anaerobic zone

Manchester Street Summary

Layer	Mean Depth (mm)	ANC	Rinse pH	Dominant region of metal removal	Likely metal removal mechanism as determined by extract
Sediment Sludge Layer	160	8.76	3.01		
Orange Fe Layer	340	288	6.86	Fe, As, Cr	As – Adsorbed Cr- co-precipitated
White Al layer	420	499	6.84	Al (peak), Cu	Cu - sorbed
White Al Layer	550	825	7.54	Al, Zn, Ni	Ni- Co-precipitated with Al Zn - sulfides
Black Shell Zone	1050	846	8.64		Sulfides: wurtzite
Weathered shell from Stockpile	Stockpile	956	8.77	-	-

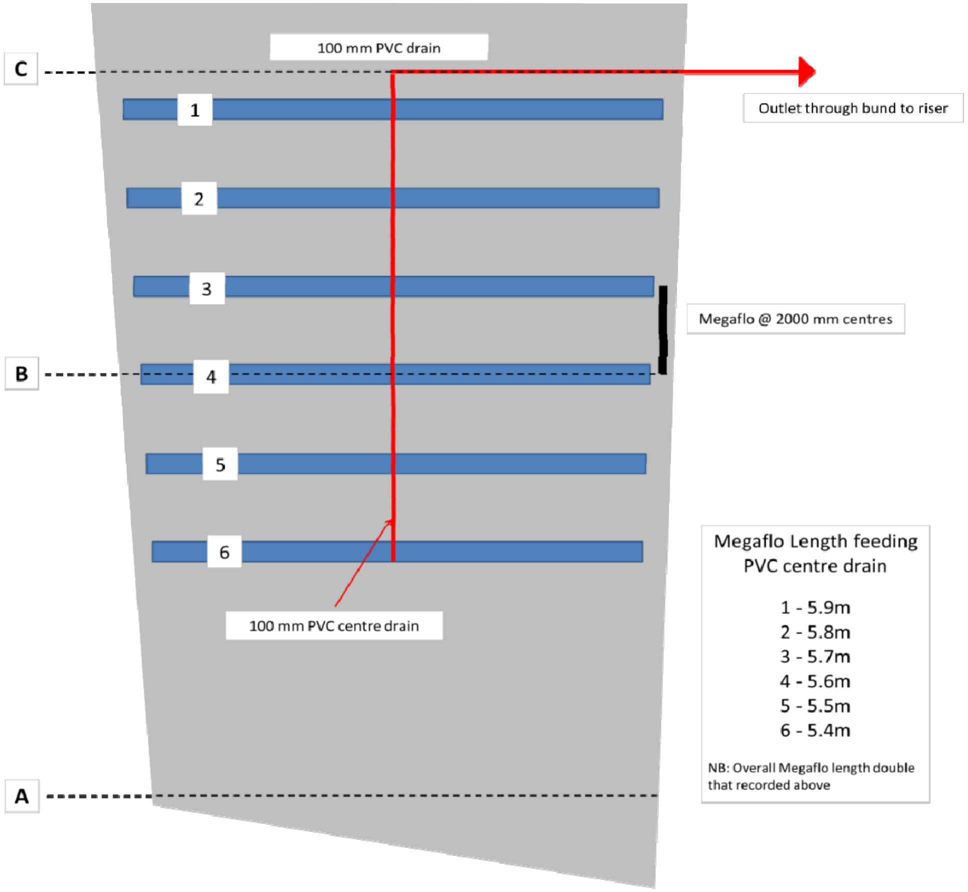
Whirlwind Mussel Shell Reactor
Constructed in 2012

pH*	EC (µS/cm)	Turbidity (NTU)	TSS (mg/L)	Dissolved Al (mg/L)	Dissolved Fe (mg/L)	Acidity** (mg $CaCO_3$ eq./L)
3.3	287	7.2	11.5	7.3	1.1	71.5

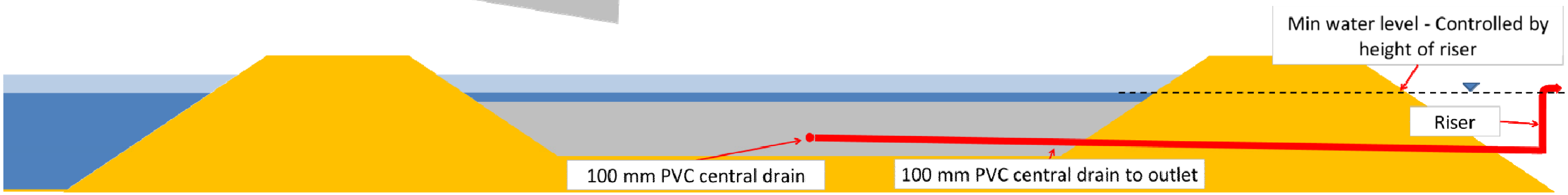
Mussel Shell Reactor

Upstream sediment pond

Drainage System



Herring-bone Drainage System to Riser.



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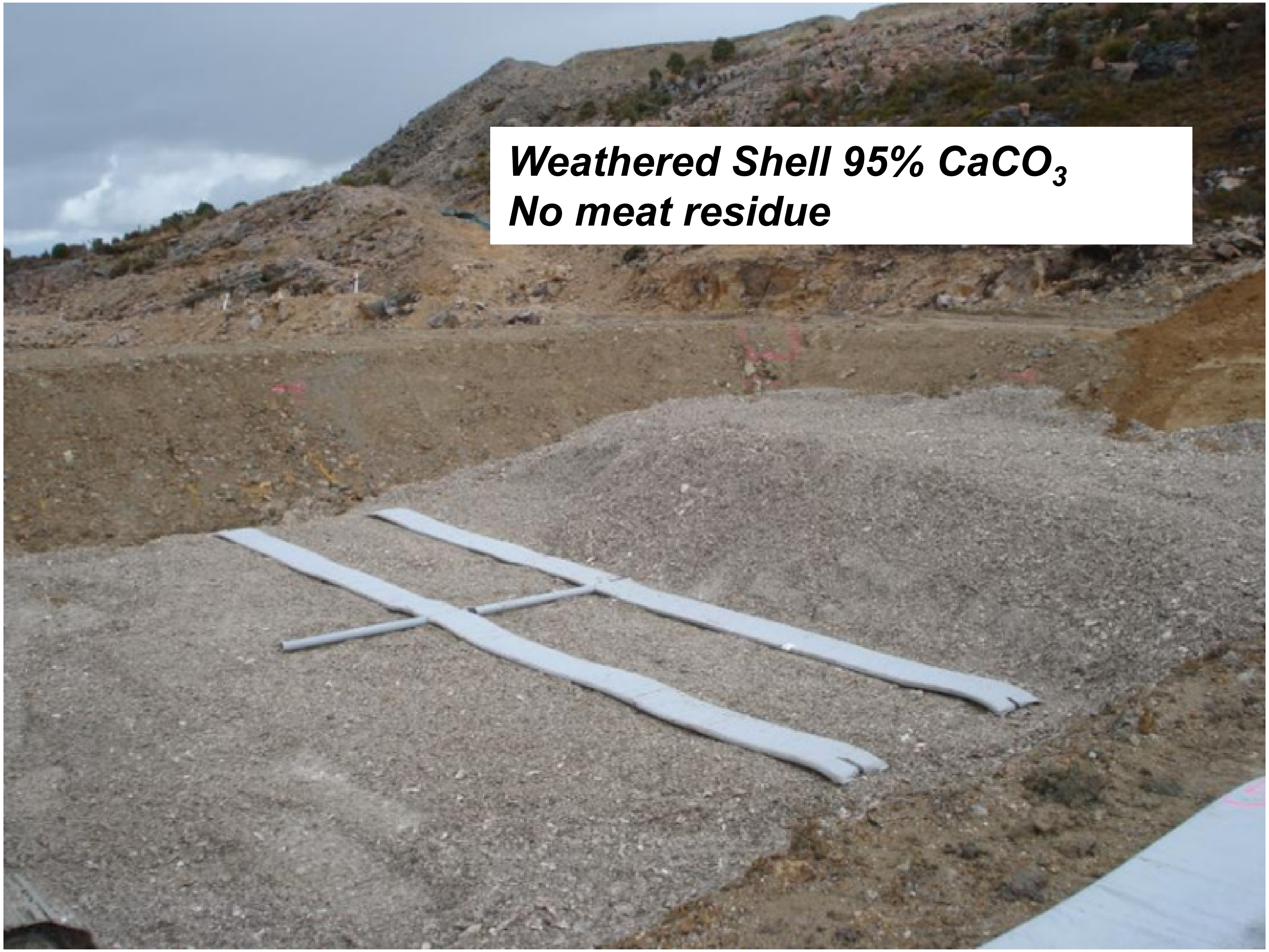
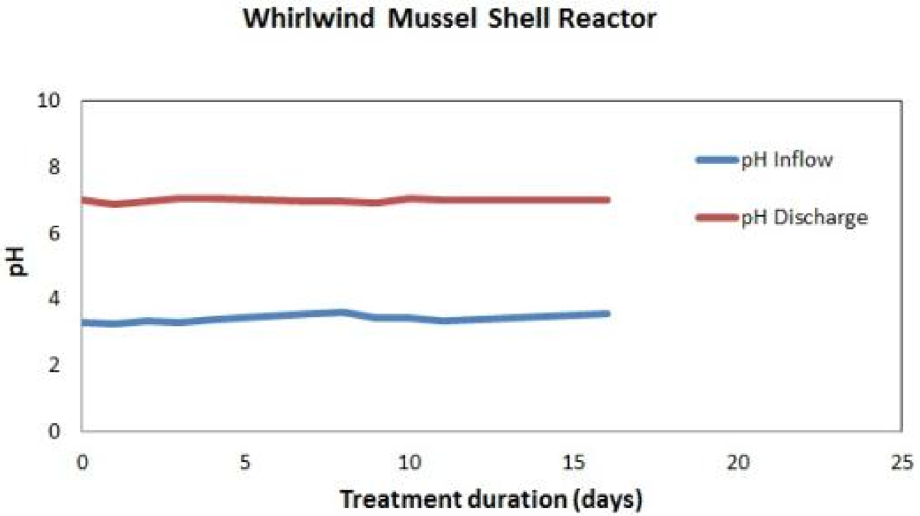
Construction Photos



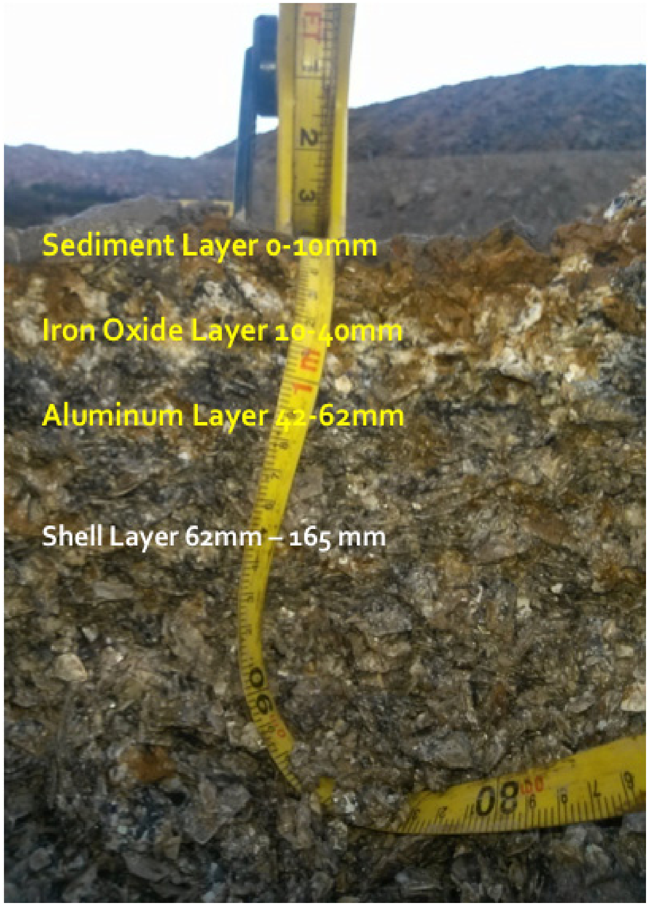
Whirlwind Mussel Shell Reactor

Parameter	Rough size
Average Plan Dimensions (m) (Shell layer)	14.0 x 21.5
Average Plan Area (m^2) (Shell layer)	302
Average Shell depth (m)	1.2
Ponding depth (m)	0.2 - 0.6
Freeboard (m)	0.8 - 0.4
Volume of shells (m^3)	366
Mass of Shells* (T)	362
Pore volume (m^3)	192
Residence time (days) (@ 1 - 6 L/s)	2.2 - 0.44
Total ANC** (T $CaCO_3$)	290

Whirlwind Mussel Shell Reactor



Whirlwind Reactor Shell Profiles



Year 1

Year 2

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Summary

- **Year 2 infiltration rate measured at 1.9 $\times 10^{-5}$ m/s**
- **Based on surface area this enables a flow rate of 5.6L/sec**

Layer	Manchestor Street Reactor	Whirlwind Reactor
Sludge (TSS) layer (mm)	330	22
$Fe(OH)_3$ layer (mm)	20	16.5
$Al(OH)_3$ layer (mm)	330	52.5

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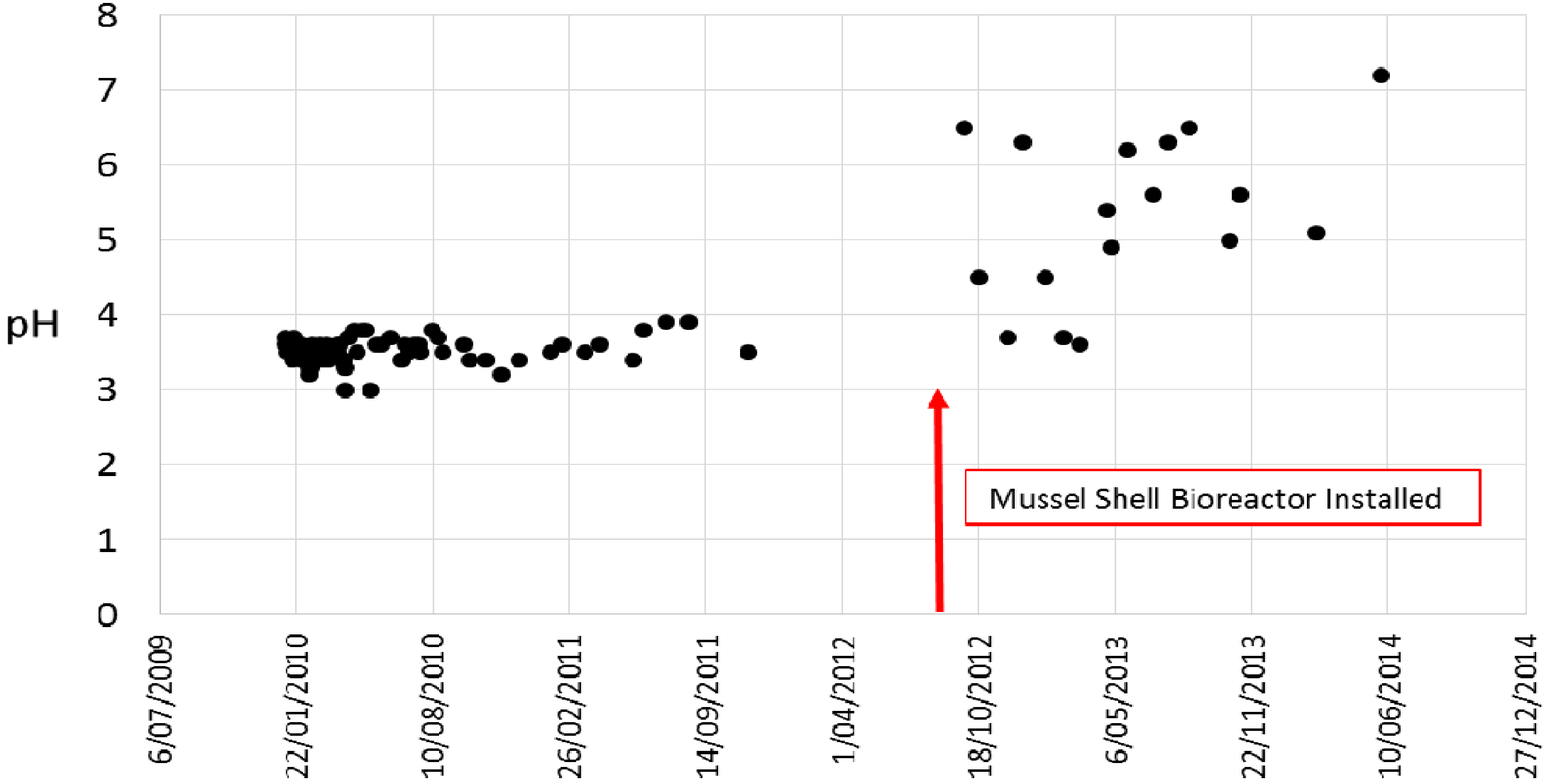
West Coast Drought (6 weeks)

Site S4 Monitoring



Whirlwind Reactor - Site S4

Installation costs and estimated maintenance

Component	Capex and installation costs	Annual Costs	Cost after 20 years	Comment
System design (capex)	5,000			
System construction (capex)	25,000			20 years replacement
Material Costs (Capex)[1]	15,000			20 year replacement
Exceptional design and construction costs	5,000			Endangered flora and fauna surveys and clearance
Repairs and Maintenance		800	16,000	2% pa of Capex per year
Labour		90	1,800	2hr per month to sample and inspect
Road Maintenance		1,000	20,000	
Sludge Disposal			5,000	$2.5k every 10 years to remove sludge and replace upper shells
Monitoring and analysis		1,200	24,000	Analysis costs
Reporting		135	2,700	3hr at $45/hr
Regulatory review costs		220	4,400	2hr at $110/hr
Decommissioning and closure	-	-	-	Treatment in perpetuity
Total	**50,000**	**3,445**	**123,900**	
Subsequent capex replacement	26,250			Every 20 years (matrix costs; 25% of construction costs; sludge management)

Analysis

Material Characteristics		
Supply	• Limited by location of shells and reasonable transport distance. • Other shells may also be suitable (e.g., oyster, zebra mussels).	
Cost	• Low- or no-cost dependant on transport distance and commercial negotiations.	
Preparation	• No preparation costs as suppliers generally chip shells to increase density for transport to landfill.	
Blending	• No blending of shell with other materials required as it is a stand-alone product.	
Carbonate Neutralisation	• ANC values of > 800 kg $CaCO_3$/tonne expected with high surface area. • Carbonate alkalinity better than limestone based products on a weight basis.	
Organic Matter	• Greater organic matter content in fresh shells; unweathered shells contain less. • Longevity of organic matter unknown, although bacterial recycling may provide additional carbon. **Further investigations are underway.**	
Porosity	• Measured hydraulic conductivities of 1×10^{-3} m/s for fresh shells. • Porosity better than limestone for the available surface area.	
Odour	• Can be a key issue for community and workforce. • Burial under a water cover removes the issue of odour; fine limestone application to the stockpile can also reduce the odour.	
Lifecycle Analysis	• Mussel shells are a waste stream and beneficial reuse of such materials provides a win-win for both the supplier and end-user. • $CaCO_3$ is not fossil CO_2 and can be considered renewable.	

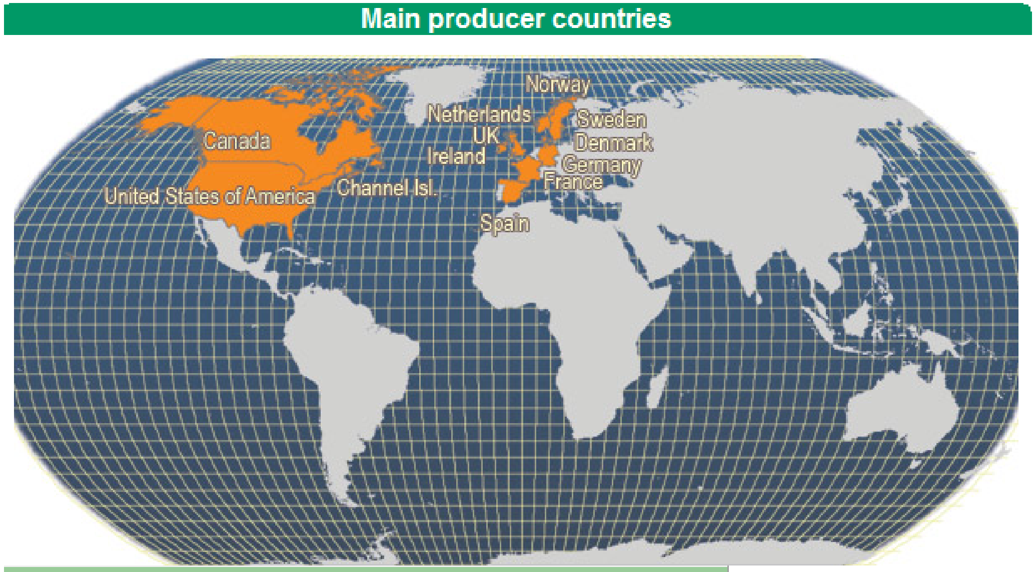
Analysis

Operational Performance		
Construction	• Shells can be placed directly into the reactor without further processing. • The system should be constructed such that excavators can access the site and remove any sludge as required.	
Start-up	• AMD impacted waters were fed in directly. • Sulfate reducing bacteria quickly populate the low DO high pH zones.	
Permeability	• Measured infiltration rates of 1.87 x 10^{-5} m/s determined; although this may decrease with time. **Further investigations are underway.**	
Longevity	• Such systems are expected to last 10-20 years and will be a function of cycling organic C, acidity and metal load. **Further investigations are underway.**	
Transitional pH, Eh profiles	• With maturity the defined geochemical layers may change resulting in the release of metals. Monitoring effluent discharge will provide early warning signs of such changes and system failure. **Further investigations are underway.**	
Maintenance	• It is expected regular maintenance is required to remove the formation of sludge on the surface of the reactor. Timeframes for this will be site specific. • Removal of the sediment sludge and Fe-oxide sludge in down-flow reactors could provide additional space in the reactor for upper shell layer replenishment.	
Sludge Disposal	• Oxidised materials from the upper layers can be disposed of in a "high and dry' environment.	

Future Opportunities

Mussel Shell Bioreactors are a new technology that requires further research

- Ongoing research into bio-geochem by Chris Weisener and Zach DiLoreto.
- Assessment of up-flow reactors (NZ CMER)
- New trial sites planned in New Zealand
- Global opportunities?



Main producer countries of Mytilus edulis (FAO Fishery Statistics, 2006)

Acknowledgements

- Solid Energy New Zealand Ltd

CMER

- Additional funding was provided by the Ministry for Business, Innovation and Employment, Contract CRL1202.

Papers:

Diloreto, Z.A., Weisener, C.G., Weber, P.A., (2014, in prep) Geochemical dynamics of a mussel shell bioreactor for the treatment of ARD, Stockton Coal Mine New Zealand. Applied Geochemistry.

Diloreto, Z.A., 2013. Characterization of a mussel shell bio-reactor for the treatment of mine waste: Stockton Coal Mine New Zealand. Hons Thesis, University of Windsor.

Crombie, F.M., Weber, P.A., Lindsay, P., Thomas, D.G., Rutter, G.A., Shi, P., Rossiter, P., and Pizey, M.H. (2011) Passive treatment of acid mine drainage using waste mussel shell, Stockton Coal Mine, New Zealand. In: Proceedings of the Seventh Australian Workshop on Acid and Metalliferous Drainage, pp. 393–405.

Weber, P.A., Lindsay, P., Hughes, J.B., Thomas, D.G., Rutter, G.A., Weisener, C.G., Pizey, M.H., 2008. ARD minimisation and treatment strategies at Stockton Coal Mine, New Zealand. In "Proceedings of the Sixth Australian Workshop on Acid and Metalliferous Drainage", Burnie, Tasmania. 15-18 April 2008. (Eds LC Bell, BMD Barrie, B Baddock, and RW MacLean) pp. 113 - 138 (ACMER: Brisbane).

Thank You!

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