P. mine waste and pyritic waste-rock: N.Quebec
P. mine waste and coarse coal waste: Devco
P. mine waste and concentrate spill: Newfoundland

Margarete Kalin
Boojum Research LTD

Presented in IMWA, 2010

Using phosphate in mining wastes is nothing new!
It worked ! Why didn’t the previous work take off ?

ECONOMICS
- **Refined, costly phosphate material**
- **Transportation cost**
- **Cost of application**

MODE OF APPLICATION
- **Mixing into tailings at about 5 %**
- **Coating surfaces with P**
- **Encapsulating with P**

Prevention of acid generation - Where does it need to take place?

- On the mineral surface, as a result of oxidation and microbial activity, metals are liberated such that they become water soluble
- This process is similar to corrosion
- Corrosion protection is achieved through phosphate coating

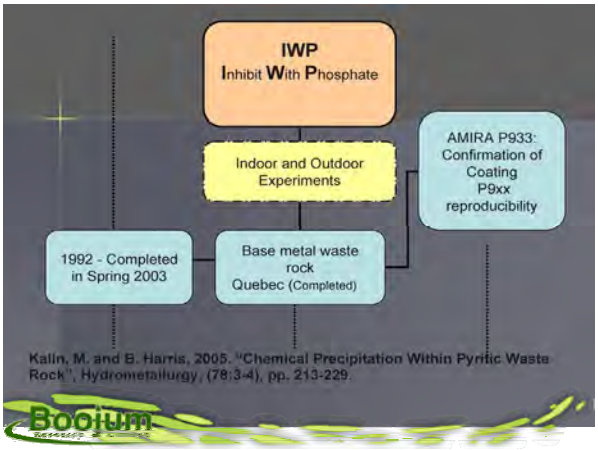
The different approach : Integrated into the mining waste generation process

Application of phosphate with focus on the contaminant generating process – work inside the wastes

- Test if it works in the field over a long time
- Test in “high quality” acid mine drainage
- Examine the causes of the improvement once it has practical results in the field

WHY so many sites the same thing ?

•Selbaie
pilot test system and lab tests
•Devco
•coal – field tests and coarse waste rock tests
•Buchans
• water reactions- solute phosphate (buffering) and solids reactions in neutral and acidic AMD
•Comparative leaching of other phosphate mine material
• South bay:
sequential extractions on tailings



Ecol engineering principle

Change the habitat conditions and thereby the forcing function is altered

This principle applied to the mineral surface oxidation – and with the assumption that Fe III and metals are indeed the main forcing function

It would follow that by:

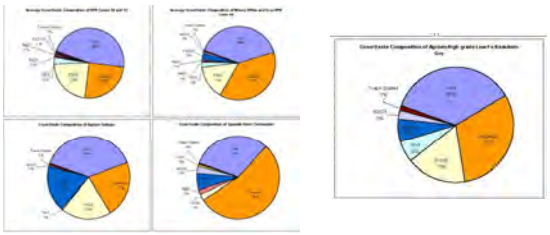
- adding a reactant (s) to the water which is then transported to the weathering site on the mineral surface – the forcing function would be changed.

-the reactant should contain essential elements to microbial growth, then the habitat would be altered – to allow other microbial groups to colonize.

Does the colonization step require the presence of some organic carbon in the form of dormant chemolithotrophs ?

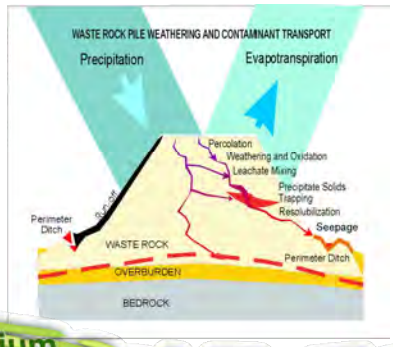
If this is roughly reasonable – then it would explain the effects of the NPR on the rocks and in the tailings ?

Composition of NPR – nutrients

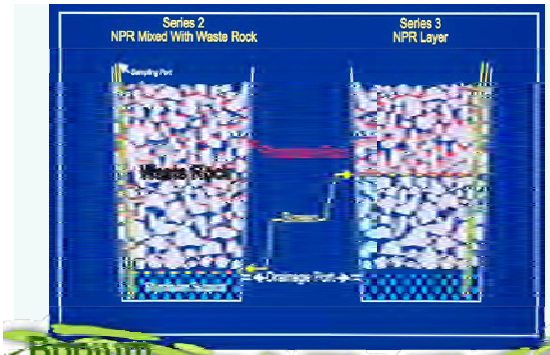


Why a waste product – large problem –economics
Why a secondary mineral of phosphate – weathering ability rain water
Why containing P – chemistry and nutrient supply is appropriate

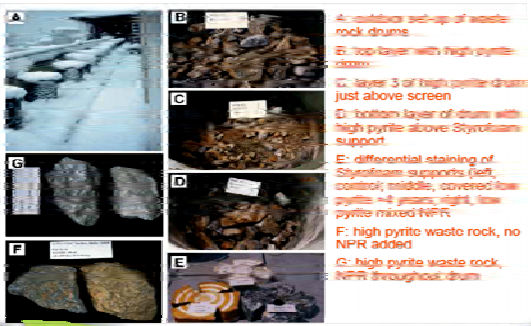
Waste rock piles- dissolve P in rainwater to react on rock surfaces inside pile



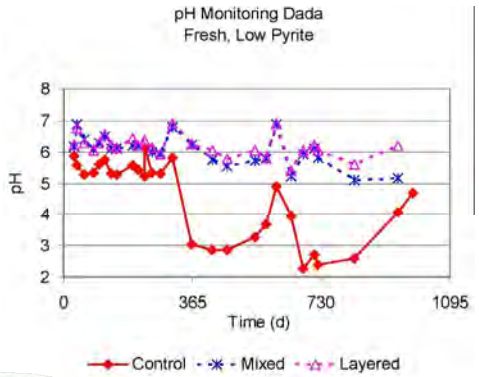
Waste Rock Drum Experimental Setup

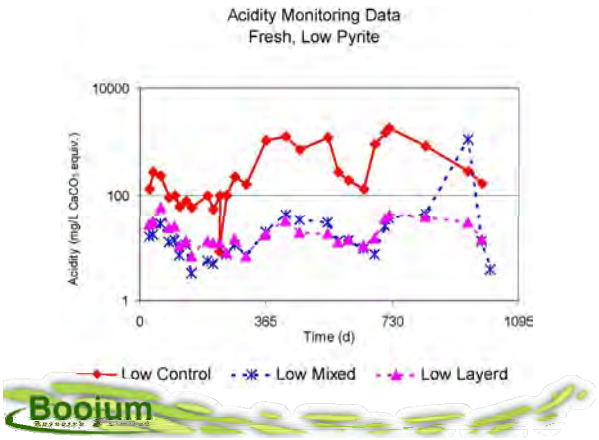


Waste Rock Drum

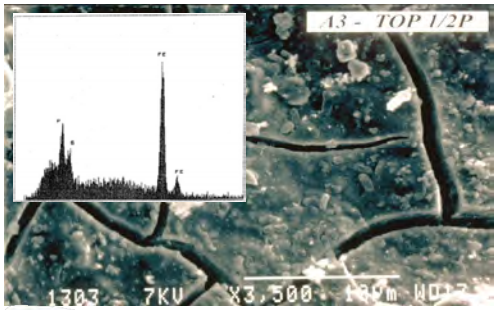


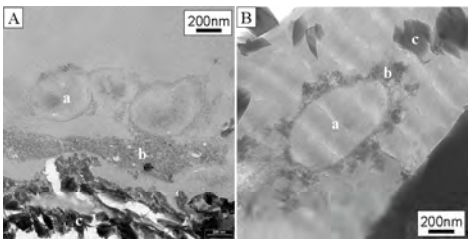
A: outdoor set-up of waste rock drums
B: top layer with high pyrite drums
C: layer 3 of high pyrite drum just above screen
D: bottom layer of drum with high pyrite above Styrofoam support
E: differential staining of Styrofoam supports (left, control; middle, covered low pyrite ~4 years; right, low pyrite mixed NPR
F: high pyrite waste rock, no NPR added
G: high pyrite waste rock, NPR throughout drum



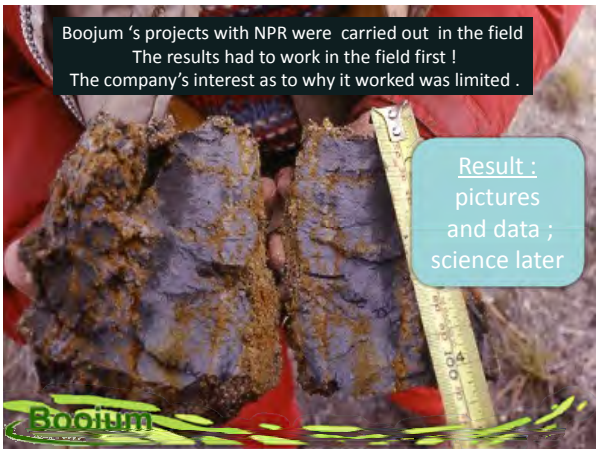


SEM and X-ray scan of surface of pyritic waste rock treated with phosphate rock





- **Figure 4.** Stained thin sections of the biofilms formed in the pH 2.2 and 7.2 system after 73 days (A and B, respectively). (A): The biofilm was composed of cells (a), very fine precipitates trapped in an exopolymer-like matrix (b) and detrital fragments from the rock surface (c). (B): cell (a) surrounded by secondary precipitates trapped in extracellular material (b) and detrital fragments from the rock surface (c).



Buchans Tailings Phosphate Rock Experiment

Buchans Tailings/concentrate

Elemental concentration of Phosphate Rock and Tailings

Element (µg/g)	Phosphate Rock Long Harbour Sand	Tailings/ concentrate	
		Control 1	Control 2
Al	7435	1900	12900
Cu	34	420	3800
Fe	5330	24500	24800
K	1201	360	3200
Mg	2736	1600	3800
Mn	59	46	90
Na	5136	100	270
P	135987	50	80
Pb	48	92	1100
S	6493	31700	45700
Si	104	NM	NM
Sr	933	270	140
Zn	95	1600	31400

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Methods

- Set up in open buckets (top and bottom) with different phosphate:tailings ratios. Exposure in the field started in June 1999
- 3 buckets (2,3 and 7) remained exposed in field until 2002
- After 10 days settling in field, shipped to laboratory for measurements
- Buckets 1,4, 5 and 6 to laboratory
- Exposure in fridge - saturated 40 g of phosphate tailings and 200 ml of distilled water
- Comparison of field exposed and fridge saturated samples

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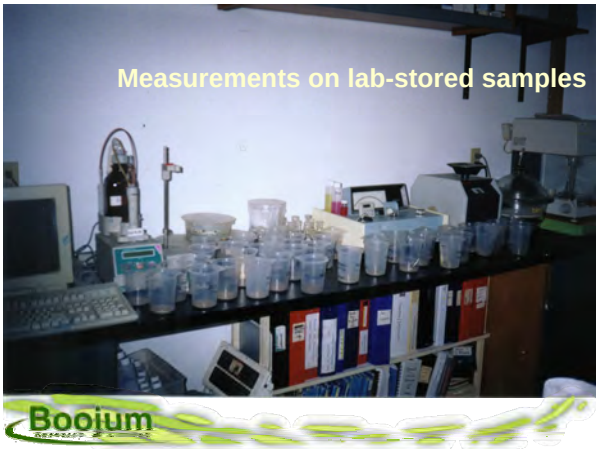

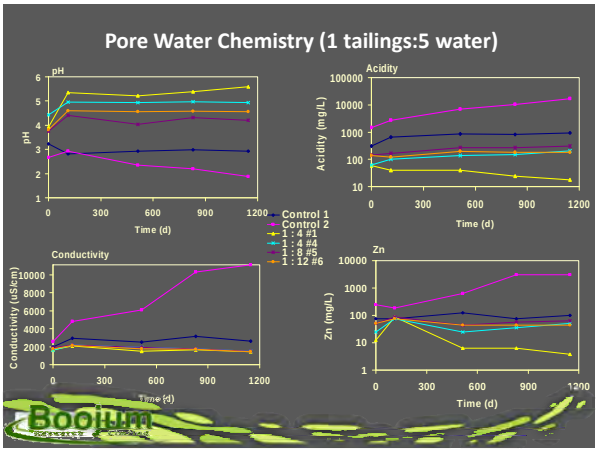

Acidity Generated over Time (mg/L/month) for Tailings/Phosphate Rock Mixes						
LAB						
Days	Control 1	Control 2	1:4 #1	1:4 #4	1:8 #5	1:12 #6
0-112	95.4	345	-4.9	9.8	6.2	-5.0
112-514	13.6	320	-0.03	3.0	7.2	5.4
514-830	-4.0	309	-1.4	1.0	0.2	-1.2
830-1147	10.9	655	-0.6	5.4	3.3	0.2
FIELD STORAGE						
Days	1:8 #2	1:12 #3	1:20 #7			
0-27	124	61.3	-15.3			
27-67	-27.0	24.0	0.4			

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Elemental concentration of pore water after phosphate mixed into tailings (1147 d)						
PO_4:Tailings ratio	Control		1 to 4		1 to 8	1 to 12
Element (mg/L)	1	2	#1	#4	#5	#6
Al	64	140	0.17	9.6	24	11
Cu	12	160	0.022	0.15	0.51	0.15
Fe	4.2	2920	0.052	0.19	0.14	0.09
Mg	43	120	61	33	41	31
Na	13	290	9	51	28	25
P	<0.05	1.3	<0.05	0.07	0.37	0.16
S	670	5860	480	510	510	480
Si	35	74	11	38	47	39
Zn	200	4320	3.5	72	74	52

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View of drainage ditch toward Buchans River constructed with a phosphate waste drainge barrier in 2009 on the left .

View of same ditch toward mill building on the right – (oposite view compared to left) in 1994.

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Coarse coal waste : lime compacted etc . and NPR

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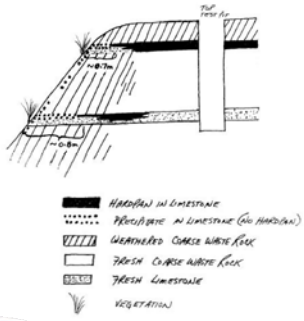
Coarse Coal Waste Pile



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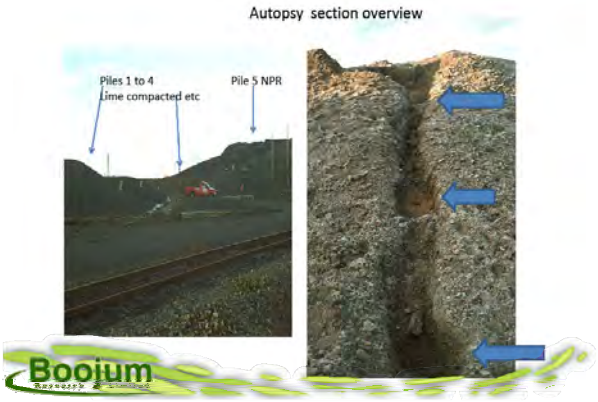
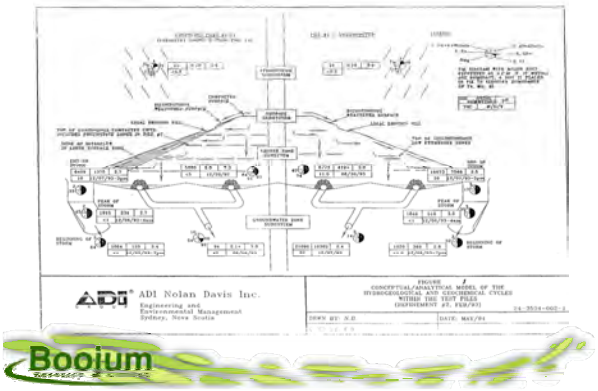
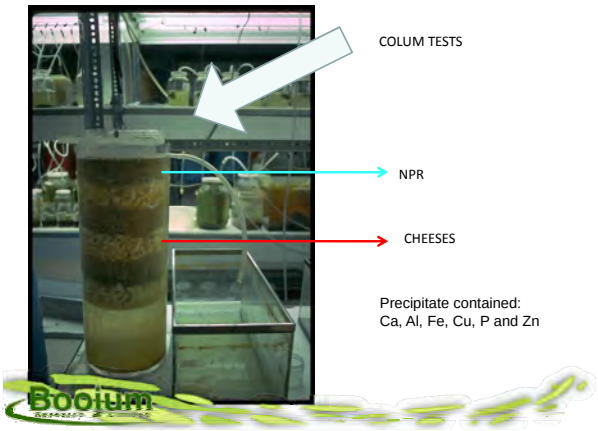
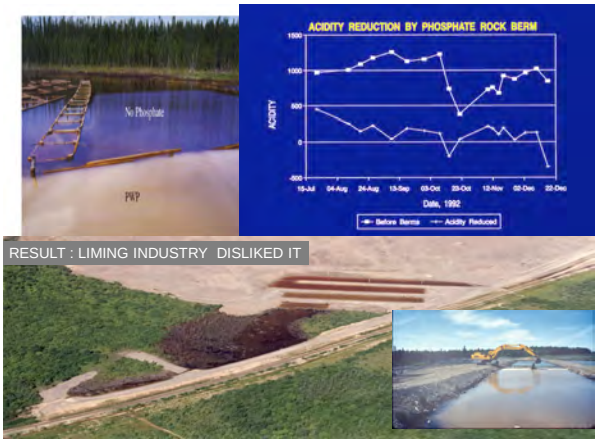


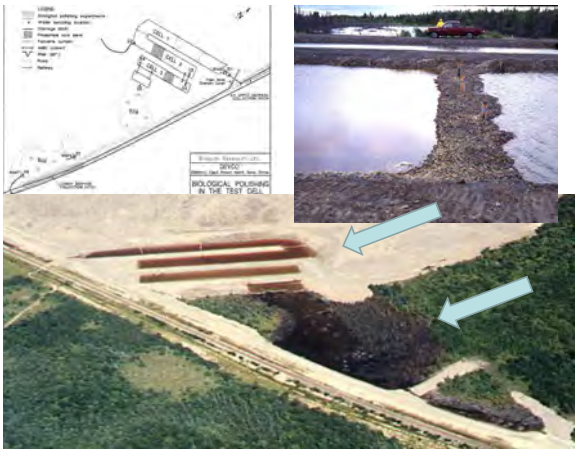
Hard pan top view

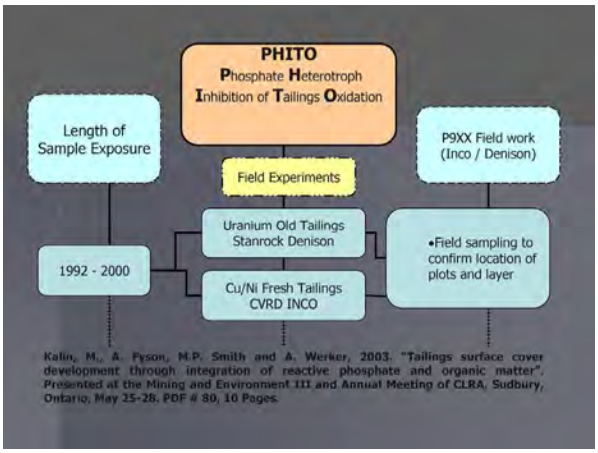
Pile instrumentation



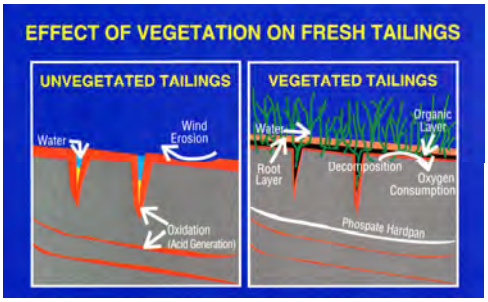


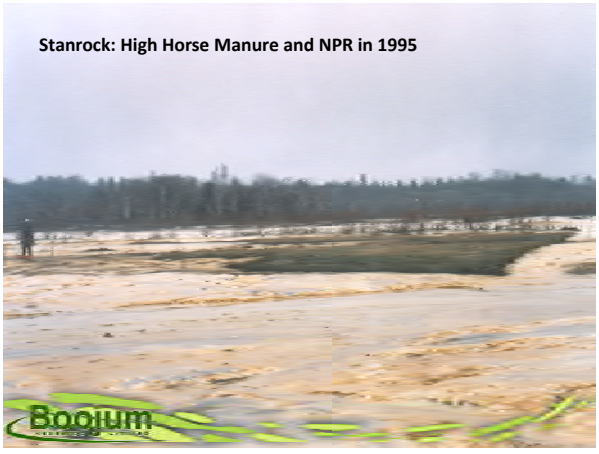


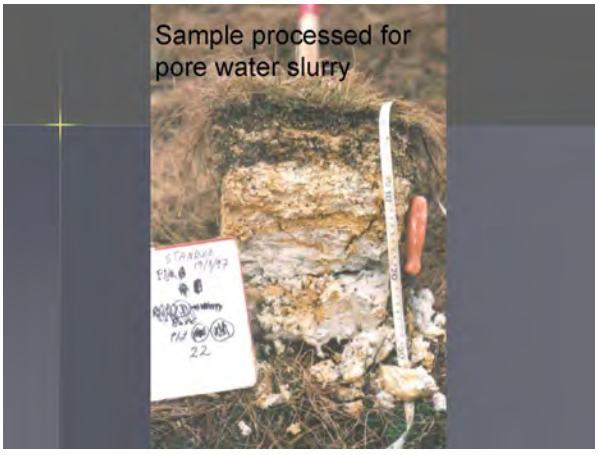


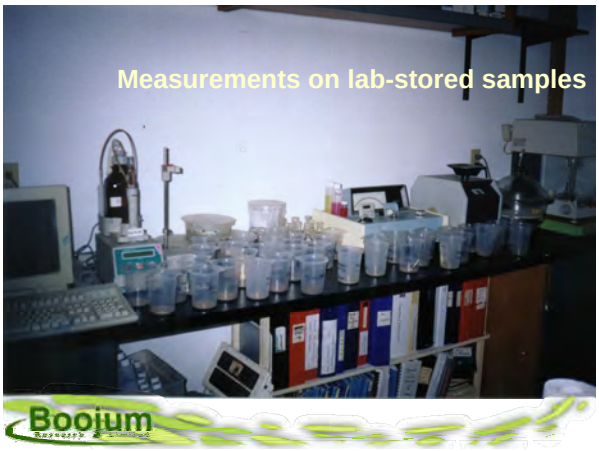


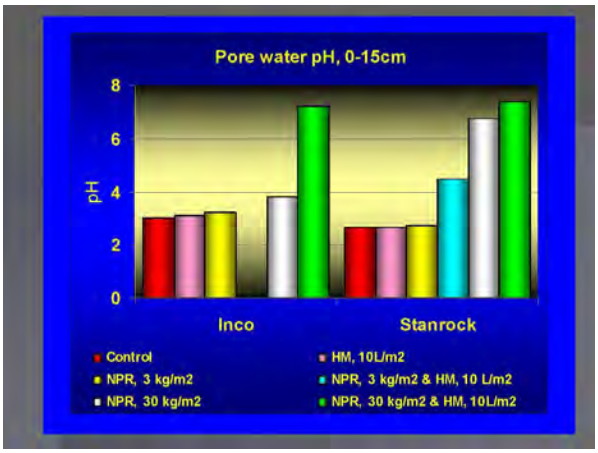
Tailings Surface Cover Development through
Integration of Reactive Phosphate and Organic Matter

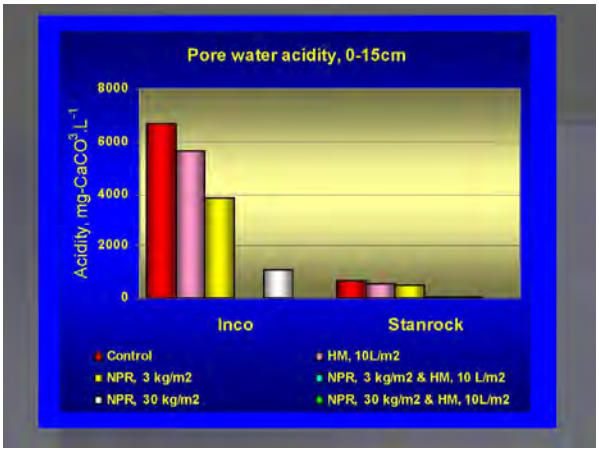












Publications

Boojum

Precipitate with phosphate

PHITO:Phosphate heterotroph Inhibition of Tailings Oxidation

2003 Kalin, M., A. Fyson, M.P. Smith and A. Werker, “ **Tailings surface cover development through integration of reactive phosphate and organic matter” Proceedings of the Mining and Environment III** and Annual Meeting of CLRA, Sudbury, Ontario, May 25-28,PDF#80, 10 pages.

2004 Kalin, M. **“Improving pore water quality in reactive tailings with phosphate mining wastes”** Proceedings of the “The Conference of Metallurgists”, COM 2004, Materials: The Future of Manufacturing in a Sustainable Environment, August 22-25, Hamilton, Ontario, pp. 427- 437.

2006 Kalin, M., W.N. Wheeler and M. Olaveson**, “Response of phytoplankton to the long-term remediation of a Canadian Shield Lake affected by acid mine drainage”,** Ecological Engineering. (28) pp. 296-310

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Publications

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Inhibition with phosphate

1997 Kalin, M., M.P. Smith and A. Fyson **"The Use of Natural Phosphate Rock to Reduce Acidic Drainage from Pyritic Waste Rock"** Poster Presented at the WISMUT Conference/Workshop on "Water Treatment and Residues Management - Conventional and Innovative Solutions", Chemnitz, Germany, September 24-26, 13 pages.

1998 Kalin, M., M.P. Smith and A. Fyson, **"The Role of Phosphate in Applied Biotechnology in Mine Waste Management: Reduction in AMD from Pyritic Waste Rock"** Proceedings of the Metallurgical Society of Canadian Institute for Mining, Calgary, Alberta, August 16-19, pp. 15-31.

2003 Ueshima, M., M. Kalin and D. Fortin, **“Microbial Effects of Natural Phosphate Rock (NPR) Addition to Mining Wastes”** Proceedings of the Joint Conference of the 9th Billings Land Reclamation Symposium and the 20th Annual Meeting of the American Society of Mining and Reclamation,Billings, MT, USA, June 3-6, pp. 1294-1303.

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Publications

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Inhibition with phosphate

2004 Kalin, M. and B. Harris, “Chemical precipitation within pyritic Waste Rock”, Hydrometallurgy, (78:3-4), pp. 209-225.

2005 Ueshima, M., D. Fortin and M. Kalin, **“Development of iron-phosphate biofilms on pyritic mine waste rock surfaces previously treated with natural phosphate rocks”,** Geomicrobiology Journal (ISEB 16 presentation), (21:5) pp. 313-323

Assumptions made for the field work

The corrosion process on metal is the same or similar to that on the rocks or on mineral surfaces Reasonable ?

The first weathering step acidifies the mineral surface colonization by Chemolithotrophs takes place Why do they not form biofilms?

Release of iron- in contact with oxygen – change in redox – induction of microbial Starvation-Survival mode – drying leads to changing conditions on the mineral surface and revival of microbial activity, so moisture further leaching

results in ARD or AM Does this make sense?

AMIRA project – 1st Progress report

AMIRA P933 Process oriented investigation on passive treatment systems

Objectives

I) critical assessment of currently available passivation technologies → inhibit or slow sulfide oxidation in mine waste rock and tailings for management of acid rock drainage (ARD).

II) short term effectiveness evaluation with a complete understanding of the reaction mechanisms and stability of the products

Program 5: Ecological Engineering (Biological Remediation) with Both Organic Waste and Phosphate Additions
(in Collaboration with Boojum Research, Canada)

Boojum send NPR Rocks to Australia

First Findings P933 AMIRA

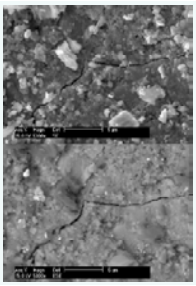


Figure 5.4.3.2 SEM images of pyrite surface in A3 Bottom.

XRD patterns of control (not shown)

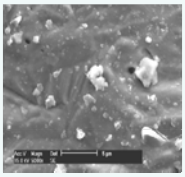
Table 5.4.3.1 EDS atomic concentration of pyrite surfaces in NPR rocks (1

Element	A3 Bottom	A3 Bottom	A3 Top	A3 Top	A3 Top
C K	DNA	28.5	DNA	DNA	20.0
O K	11.8	21.7	44.7	42.0	51.1
Zn L	-	0.8	-	-	-
Mg K	-	-	0.8	-	-
Al K	-	-	1.9	0.9	2.1
Si K	0.6	1.1	1.8	0.7	1.7
S K	58.0	29.9	30.0	35.0	9.7
K K	-	-	0.4	-	-
Fe K	29.5	18.1	20.0	21.6	15.5
Zn K	-	-	0.4	-	-
	Fig. 5.4.3.1	Fig. 5.4.3.2	Fig. 5.4.3.3	Fig. 5.4.3.3	Fig. 5.4.3.4

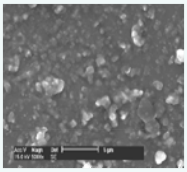
Fig. 5.4.3.3[1]: The rumplos in the coating.
Fig. 5.4.3.3*: The rumplec area in the coating.
DNA: Did not analyse due to C concentraton contributed from carbon coating.

AMIRA project – 2nd Progress report

Control Samples

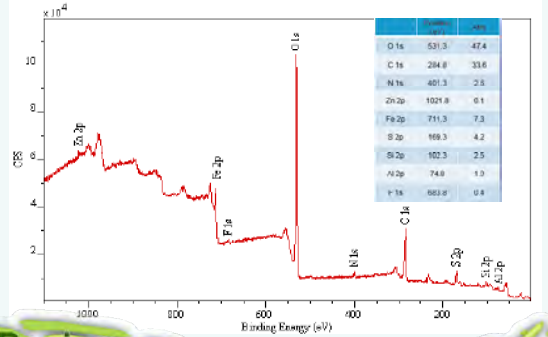


Low pyrite



High pyrite

Second Findings P933 AMIRA



AMIRA project – P933 and P933A

Toward understanding biofilm initiating factors

What are the conditions needed to give the stimulus for the start of growth?
Where does the process start on the mineral surface?
What was it what started the biofilm?
Did the biofilm originate from NPR particles, which fell or were transported with the first years fall rains throughout the drum?
Can one of these particles fall into a corrosion pit and start the biofilm?
Are the metabolic products of the “phosphate mining“microbes the nutrient source of the oxidation reduction biofilm?
How does rain water to path through a waste rock pile?

WHY so many sites the same thing ?

•Selbaie

pilot test system and lab tests

•Devco

•coal – field tests and coarse waste rock tests

•Buchans

• water reactions- solute phosphate (buffering) and solids reactions in neutral and acidic AMD

•Comparative leaching of other phosphate mine material

• South bay:

sequential extractions on tailings

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I believe focused field work is needed

Concurrent process understanding site specific

Suppresion of Sulphide Mineral Oxidation in waste Rock and Tailings – anyone has a waste rock pile ?

1. Scoping the sulphate challenge
2.Consolidate existing Boojum data and new literature – ongoing
3.Assess the durability of the sulphides inhibition technique – IMWA paper
4.Establish the universality and optimize the process – ICARD - paper

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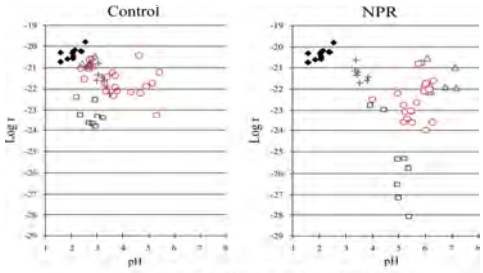
OXIDATION RATES – log r – drastic diff.

Williamson and Rimstidt , 1994

$r = 10^{-19.71\ (\pm 0.86)}.\ Eh^{12.93(\pm 1.04)}.\ pH^{1.0(\pm 0.29)}$ (1)

$\log r = -19.71(\pm 0.86) + 12.93(\pm 1.04)\log(Eh)$



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