# *Pro-active Prevention of Acid Generation:*

## *Reduction/Inhibition of Sulphide Oxidation*

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## Mineral Surfaces: The Site of the Problem and the Solution

Oxidation of sulphide particles in tailings, waste-rock piles, underground mine workings and open pit walls

➢Limited by the transport of oxygen

➢Convection, advection or diffusion to the mineral surface

➢Bacterial biofilm activity

**We need a reactant which is low cost , readely available** Wastes such as Natural Phosphate Rock or tailings

- Un-economic for fertilizer production
- this was a sedimentary deposit N. Carolina – Sea shells –Shark teeth
- biologically produced phosphate – expected slow weathering
- grain size 4cm to < 0.04 mm, 8-12 % P and 20-35 % Ca (as $CaCO_3$)
- Solubility in 0.1 N sulphuric acid:

**Table 2 Release of macronutrients from NPR after Decant Cycles 0 to 8 (g per 10gr of NPR)**

| NPR Composition | | Sulphuric Acid | | Distilled water | |
|---|---|---|---|---|---|
| g per 10g of NPR rock | | Decant Cycles 0 - 8 | 1L | Decant cycle 10 | 1L |
| | | stirred | Non stirred | stirred | Non stirred |
| | | Grams released from NPR | | | |
| P | 0.840 | 0.451 | 0.490 | 0.010 | 0.011 |
| K | 0.015 | 0.011 | 0.009 | 0.001 | 0.001 |
| Ca | 2,788 | 0.731 | 0.680 | 0.510 | 0.450 |
| Mg | 0.033 | 0.033 | 0.031 | 0.001 | 0.001 |


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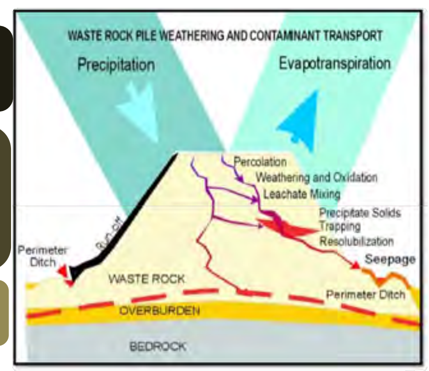
The location where the reactant has to be is in the seepage pathway.

The reactant needs to be transported by atmospheric precipitation in particulate form solutes get easily washed out.

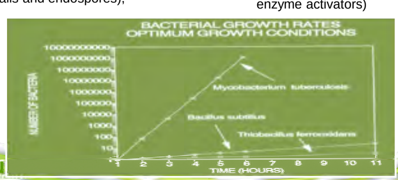
Particles get stuck on the surface – and have to react in acid




1. Find a waste product which would be suited – acid solubility and providing nutrients – a sedimentary phosphate deposit – North Carolina Aurora mine
2. **FRANCIS CHAPELLE 1993** - review of the needed nutrients in the ground water for microbial growth *1993 "Ground-Water Microbiology & Geochemistry" John Wiley & Sons, Inc*
3. Nutrient requirements **NOT** *in water* **BUT** on rock surfaces*:* **NPR releases all needed macronutrients for microbial growth**

**MACRONUTRIENTS**
P (nucleic acids synthesis, ATP),
K (enzymes activation),
Ca (cells walls and endospores),

**MICRONUTRIENTS**
Fe (electron transport systems),
Mn, Cu, Ni, Mo, Co and Zn
(components of protein complexes and enzyme activators)




**THIS PAPER IS NOTHING NEW!**

**It is a summary of work started in 1992**
**many publications**
**this paper is about 17 years of perseverance**

### What was done ?

•Natural Phosphate Mining Wastes (NPR) was added to different types of tailings and waste rock in the field or outdoors**.**

• Effluent from the waste rock experiment and from tailings slurries were monitored for 2 to 4 years in ideal conditions to oxidize.

•Commonality in all the experiments – all are acid generating and to all the same NPR was added

•Application rates – no science at all - determined by $$ haulage costs
•I

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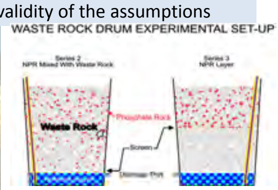
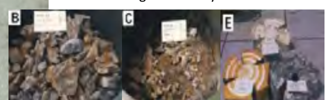
**Only practical long term tests** in mining wastes in the field can provide evidence of the validity of the assumptions




- Tests NPR additions to tailings and conc. spill
- 2- 85 % sulphide
- left in field 3.2-3.7 years
- monitor the pore water metal acidity
- TAILINGS AREA –
  Inco: 2700m²;
  Stanrock:432 m²

- Test NPR additions to waste rock
- 4-15 % sulphide
- left outdoors 2.7 years
- monitor the effluent metal acidity
- Monitoring 1.8 to 2.7 years

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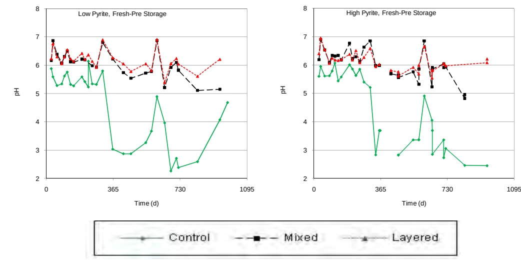



**If sulphide oxidation can be reduced - the process has to be similar in a large variety of mining wastes:**

| Elements (mg.L$^{-1}$) | Uranium | | Pyhrrotite | | Polymetalic | | *Waste rock* | |
|---|---|---|---|---|---|---|---|---|
| | Control | NPR | Control | NPR | Control | NPR | Control | NPR |
| | N=1 | N=1 | N=1 | N=1 | N=2 | N=2 | N=3 | N=6 |
| Fe | 18 | 0.01 | 43 | 0.1 | 1053 | 0.02 | 3.77 | 0.32 |
| P | 0.03 | 0.05 | 0.22 | 6.9 | 0.16 | 0.04 | 0.20 | 0.13 |
| S | 630 | 510 | 4460 | 1060 | 3020 | 500 | 126 | 123 |
| pH | 2.67 | 6.75 | 3.06 | 3.84 | 2.59 | 5.40 | 4.06 | 6.09 |
| Acidity (mgCaCO$_3$.L$^{-1}$) | 656 | 39 | 6715 | 1090 | 5544 | 87 | 257 | 76 |

Pore water results : Control NO NPR and NPR additions

**The path of Destruction ended at of U of T after :**

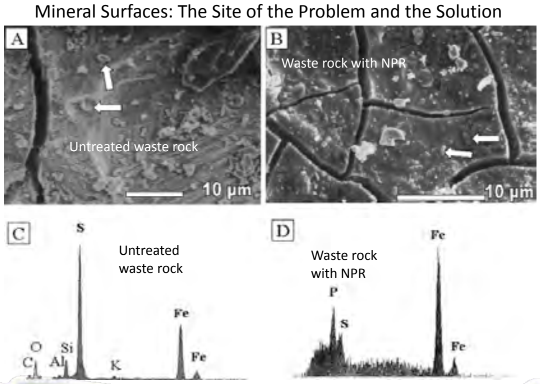
**2.7 years outdoors- but sheltered sort of**

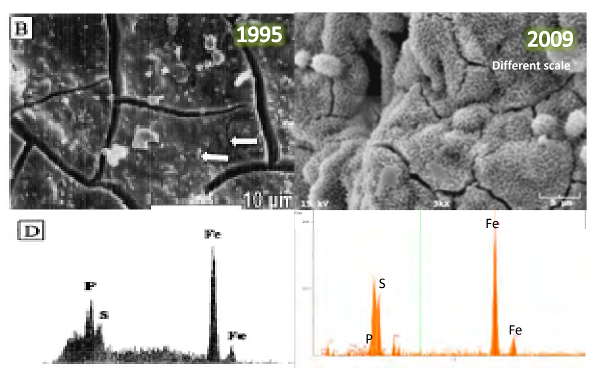
**4.5 years in storage in industrial basement in open drums**

**1.1 year re- outdoor exposure to generate acid**

**8 years in buckets exposed to temp of freezing to up 50 °C**

Mineral Surfaces: The Site of the Problem and the Solution



## IIRA project P933 and ongoing

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)**

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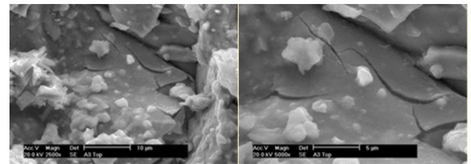

SEM images of pyrite surface in A3 Top.

Gel layers >1 µm thick
Exfoliation
Embedded secondary sulfate/hydroxide
Gypsum fine particles

ACeSSS, Applied Centre for Structural and Synchrotron Studies
EGi, Environmental Geochemistry International
Levay & Co. Environmental Services
Boojum Research

UNIVERSITY OF SOUTH AUSTRALIA

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**Thank you for listening…**
**Questions.**

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## Next steps – from Boojum’s perspective

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?

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## Many Questions remain open !

Does the colonization step require the presence of some organic/inorganic carbon in the form of dormant chemo-lithotrophs or will it be started by microbes which fix atmospheric carbon ?

- Transport mechanism – solute or particle ?
- Dosage needed – about 50 % of NPR was not used.?
- Organic or inorganic phosphorus – is NPR –P or NPR microbes ?

**Go in the field – test different local P-sources - as decant experiments**

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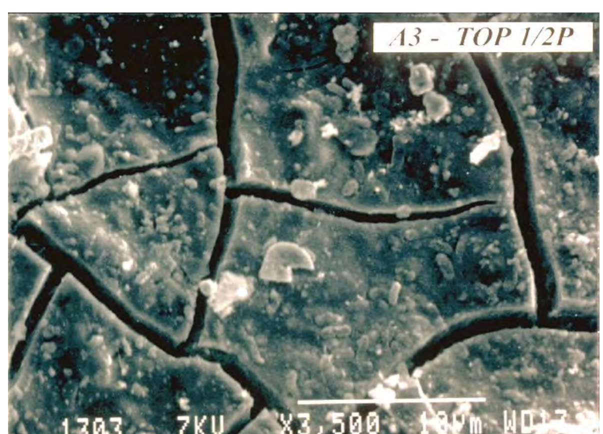
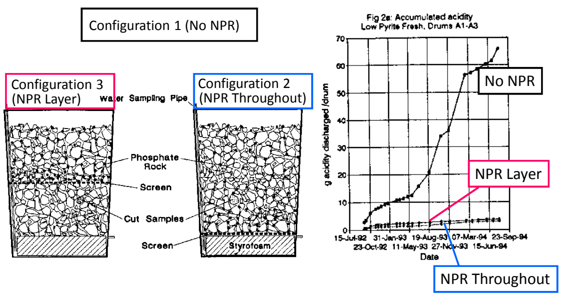


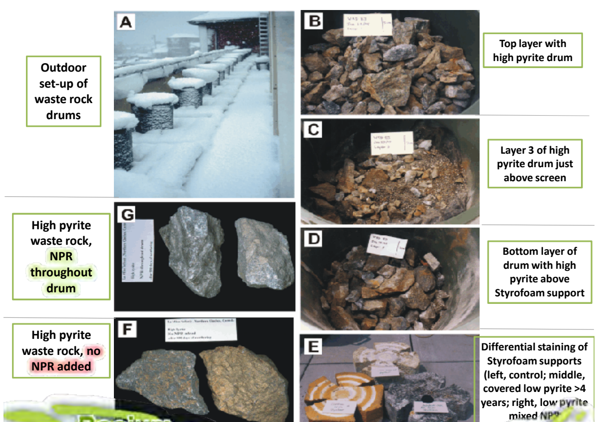
## Acid Mine drainage treatment: Phosphate Technology

- P and Fe cycling are closely linked
- P concentrations (e.g. for organisms) are generally very low
- P is sequestered as co-precipitates with Fe hydroxides (oxic conditions)
- P forms metal salts (anoxic conditions)
- P is bound by organics (e.g. humic substances in muskeg)
- P may absorb to pyrite (source of AMD) surfaces and inhibit acid generation

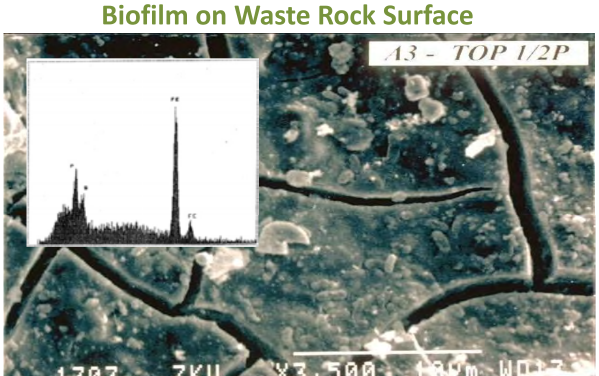
## Waste Rock Drum Experiment

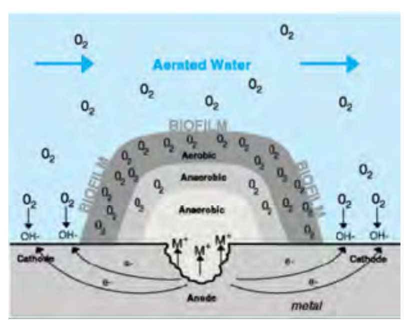
(15 Jul. 92 – 23 Sep. 94)




## Biofilm on Waste Rock Surface




From: Borenstein. S.B.. *Microbiologically Influenced Corrosion Handbook. Industrial* Press Inc.. New York (1994).

### Pore-water characteristics tested in oxidizing condition

| | Uranium | | Pyhrrotite | | Polymetalic | | *Waste rock* | |
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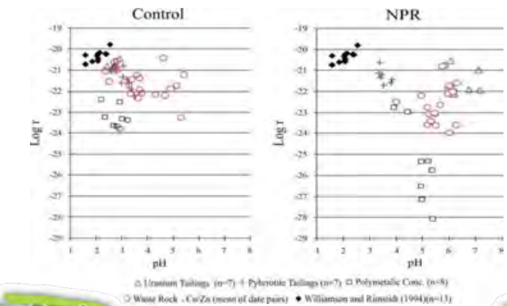
*n.a. - Not available*

## OXIDATION RATES

Williamson and Rumstidt . 1994

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

$\log r = -19.71(\pm 0.86) + 12.93(\pm 1.04)\log(Eh) + 1.0(\pm 0.29)\log(pH)$




## Conclusions

**Future RESEARCH**

NPR fate in sediments ?
Biomineralisation ?
Phosphate cycling water/biota/sediment ?

**DID WE NEED 160 TONNES ?**

**FUTURE APPLICATION**

Find alternative slow release finely ground phosphate source useful e.g. phosphate mine tailings - slurried

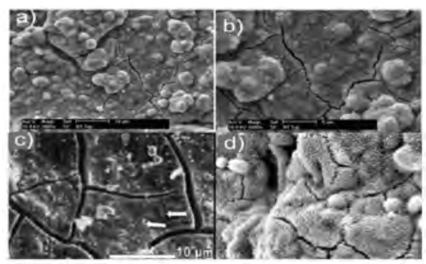



*Figure 1 Low pyrite < 1y after 1st exposure with NPR: (a, b) AMIRA P933 observed in 2006 after 11 years in storage at mag. (10 and 5 µm); (c) Kalin et al. 1997 observed in 1996 after 1 year of storage at g. (10 µm); (d) observed in 2009 after 14 years of storage at mag. (5µm)*

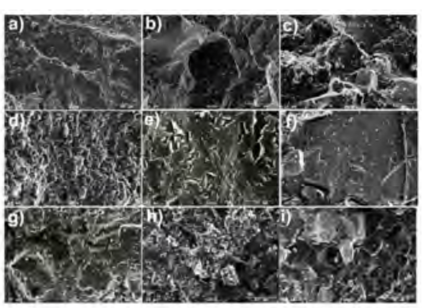
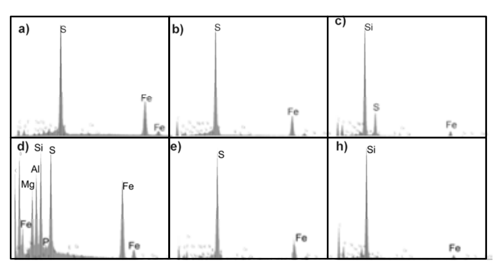
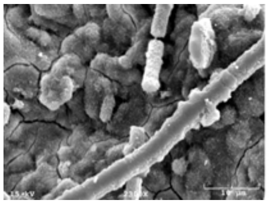
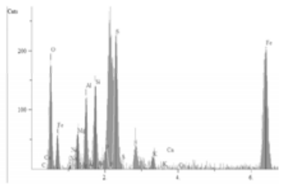


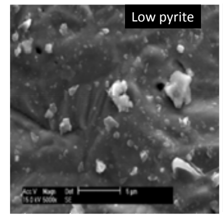

*Figure 2 All observations in 2009 at magnification of 50 µm (a) never exposed outdoors stored for 17 years (b,c) No NPR added 2nd exposure stored for 8 years after 2nd exposure. Fig 2 d,e,f,h,i are NPR added in 1st exposure only; exposed in 2nd outdoor exposure with no NPR and stored for 8 years.*

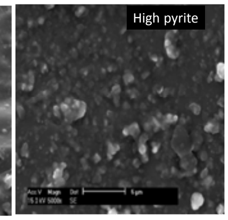






## P933 AMIRA ; No NPR March 2008




## Coating verified on rock from NPR experiment

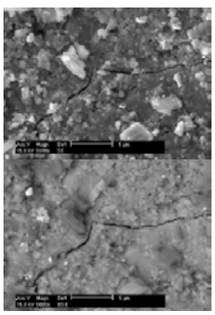


Figure 5.4.3.2 SEM images of pyrite surface in A3 Bottom.

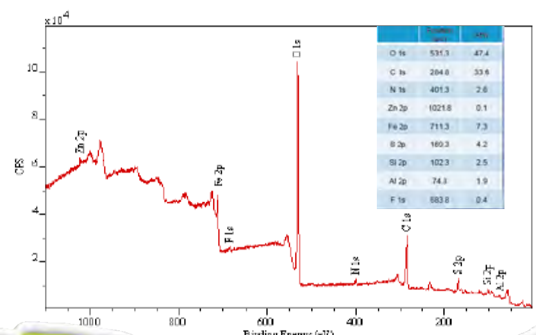
XRD patterns of control (not shown)

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 | 11.3 | 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 [1] | Fig. 5.4.3.3 [2] | Fig. 5.4.3.4 |

Fig. 5.4.3.3[1]: The rumples in the coating.
Fig. 5.4.3.3[2]: The rumpled area in the coating.
DNA: Did not analyse due to C concentration contributed from carbon coating.

## P933 AMIRA March 2008 – no P found

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