ACID BASE
ACCOUNTING OF
MINING ORE AND
WASTE

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Waterlab (Pty) Ltd and NLA-SA

SANAS Accredited Laboratory No T0391

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Acid Rock Drainage (ARD) is caused by the exposure of rock containing certain sulphide minerals, most commonly pyrite (FeS$_2$), to air and water, resulting in the production of acidity and elevated concentrations of sulphate and metals into the aquatic and terrestrial environment (SRK, 1988).
“The high liability costs of ARD carried by many mining companies and governments are a clear indication of the gravity of the problem of older, primarily closed mines.

At the end of the 1990’s, the estimated financial liability at mining sites was estimated to be:

Australia : A$ 1 billion
Canada : C$ 3 to 5 billion
USA : US$ 5 to 72 billion

With the increased level of mining and the greater societal expectation that mining companies leave a positive legacy at their closed mines, these costs have significantly increased during the past decade.

Statement by IM-Mining, 2010
“De re Metallica”
Georgius Agricola (1494-1555)
**Typical relation to drainage pH:**

- **Saline Drainage**
- **Neutral Mine Drainage**
- **Acid Rock Drainage**

**pH**

<table>
<thead>
<tr>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
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</tbody>
</table>

**Typical drainage characteristics:**

<table>
<thead>
<tr>
<th>Acid Rock Drainage:</th>
<th>Neutral Mine Drainage:</th>
<th>Saline Drainage:</th>
</tr>
</thead>
<tbody>
<tr>
<td>• acidic pH</td>
<td>• near neutral to alkaline pH</td>
<td>• neutral to alkaline pH</td>
</tr>
<tr>
<td>• moderate to elevated metals</td>
<td>• low to moderate metals. May have elevated zinc, cadmium, manganese, antimony, arsenic or selenium.</td>
<td>• low metals. May have moderate iron.</td>
</tr>
<tr>
<td>• elevated sulphate</td>
<td></td>
<td>• moderate sulphate, magnesium and calcium</td>
</tr>
<tr>
<td>• treat for acid neutralization and metal and sulphate removal</td>
<td></td>
<td>• treat for sulphate and sometimes metal removal</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Acid Rock Drainage Generation
The first important ARD reaction is the oxidation of pyrite (or sulphide mineral) into dissolved iron, sulphate, and hydrogen (H⁺):

\[
\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad [1]
\]

The dissolved Fe\(^{2+}\), SO\(_4^{2-}\) and H\(^+\) represent an increase in the TDS and Acidity of the seepage water, as well as a decrease in pH. If the surrounding environment is sufficiently oxidizing, much of the ferrous iron will oxidize to ferric iron:

\[
\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \leftrightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \quad [2]
\]
At pH values above 2.3 to 3.5, the ferric iron precipitates as Fe(OH)$_3$, leaving little Fe$^{3+}$ in solution while lowering the pH simultaneously:

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \quad [3]$$

Any Fe$^{3+}$ from reaction [2] that does not precipitate from solution through reaction [3] may be used to oxidize additional pyrite:

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad [4]$$

From these simplified reactions [1-3] it is clear that the overall reaction liberates 4 moles of protons for each mole of pyrite. Iron is produced and precipitated as Fe(OH)$_3$ (Yellow Boy):

$$\text{FeS}_2 + 15/4\text{O}_2 + 7/2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad [5]$$

These reactions show that for this process to occur, the vital components pyrite, air and water is required

SRK, 1988 ; Usher et al., 2003
Examples of Acid Rock Drainage
Comstock Creek, Tasmania
Blue Dam: JHB, 1993
Copper Sulphate crystals, Kalgoorlie, Western Australia
Simmer & Jack: Germiston, 1991
Grootvlei Mine: Springs, 1994
Blesbokspruit 1996. Iron contaminated discharge from Grootvlei 3 Shaft
Mine builds wall

Pumping to continue

Report by CHRIS FEY and KATY O’DONOVAN

On Thursday morning, workers and earth moving machinery were at work erecting a wall of large concrete blocks to completely obscure the pipes, which used to be visible when Grootvlei Mine was pumping water into the Blesbokspruit.

This follows a decision on Wednesday afternoon, by Professor Kader Asmal, Minister of Water Affairs and Forestry - and ratified by Cabinet - to withdraw the mine’s permit, which allowed it to discharge underground water into the spruit.

A spokesman for the mine confirmed that they intend to continue pumping.

Asked about the mine’s sudden burst of activity on Thursday morning, Alan Maddon, a committee member of the Springs and Nigel Wild Life society, who has been very involved in the wetlands in our area said: “If they have closed it off, it only means one thing, they are involved in dirty business.”

His father, Stan Maddon, was unavailable for comment at the time of going to press.

Members of the Wildlife Society and residents who live along the banks of the Blesbok were involved in a rescue mission over the weekend, trying to relocate fish which are suffocating in the polluted water of the spruit.

Professor Asmal said that over past months, the Department of Water Affairs and Forestry persistently tried to get the mine to comply with the permit conditions, but had been unsuccessful.

However, the permit could be reviewed - should the department and the mining industry take immediate, concrete steps to bring the quality of any discharged water within the tolerable level set by the Department of Water Affairs and Forestry.

Race against time

On Wednesday afternoon, Trevor Welbourne, chief geologist at Grootvlei, said the mine will be forced to close permanently if the present position is not altered within two months.

“It’s basically a race against time,” says Mr Welbourne.

It is estimated that if the mine stops pumping, it will be able to continue operating for approximately 30 days before the escape routes are blocked off. After 60 days, the pump station will be flooded and the mine lost forever.

Within two years, mines from Benoni to Nigel, which are dependent on Grootvlei for pumping 100 mega litres of water a day, will also be forced to close as a result of flooding.

If Grootvlei does not come up with an alternative in the next 60 days, 2 200 people will lose their jobs. Once the remaining mines flood, 6 000 workers in total, will have lost their jobs.

When we attempted to speak to Mr Welbourne again as we went to press, and to mine manager, Peter Nobel, we were told the mine would not comment at that stage.

But Dirk van Eeden, spokesperson for Grootvlei Mine at Randgold,
Environmentalists at odds with mine

By KATY O’DONOVAN and EUGENE GODDARD

Angry environmentalists believe that the water flowing from the settling facility at Grootvlei Mine into the Blesbokspruit is not of a satisfactory standard.

Last week this newspaper was told by a resident close the Blesbokspruit that polluted water was leaking into the spruit.

However, Anthony Courinho, sectional engineer at Grootvlei Mine, said what environmentalists believe is leakage, is actually the flow of clear water from the third and last settling dam into the spruit.

He said that a problem had been experienced when the plastic lining of one of the spillover dams was ripped and had to be repaired.

On Friday, sediment at the bottom of the spillover dam was seen being pumped directly into the Blesbokspruit.

General manager of the mine, Peter Noble, denied that any sludge from the spillover dam was being pumped into the Blesbokspruit.

"It wasn't sludge that was pumped into the Blesbokspruit, it was reddish water which is nothing really," he said.

Mr Noble added that it wasn't the mine that was pumping the substance into the spruit, but one of the contractors.

Attempts to determine whether it was Envirotech, Sear, Aquaton or United Linings - the four contractors working on the settling site - who were pumping the sediment straight into the spruit have been unsuccessful.

Expert on the Blesbokspruit, Stan Madden, said that the water flowing into the spruit is worse than before the settlers were constructed.

He says that a group of Wits students were taken on a tour of the Blesbokspruit on Wednesday, when he noticed that there was something wrong.

Mr Madden believes that one of the settlers is out of operation, which results in the iron oxide not having enough time to settle (settle) before entering the spruit.

"Now, not only sediment is flowing into the spruit, but also chemicals," says Mr Madden.

"It is obvious that the contractors are not doing their jobs properly," he added.

Phillip de Jager, a concerned resident living on the banks of the Blesbokspruit, says that if anything goes wrong with the water treatment facilities, pumping should cease.

It was initially believed that the wall of this spillover dam had cracked, but this week officials from Grootvlei Mine set the record straight when they explained it was the plastic coating that had torn.
### Acid Generating Minerals

<table>
<thead>
<tr>
<th>Mineral Type</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite &amp; Marcasite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Chalcopyrite; Chalcocite; Bornite</td>
<td>CuFeS₂; Cu₂S; Cu₅FeS₄</td>
</tr>
<tr>
<td>Arsenopyrite; Realgar; Orpiment</td>
<td>FeAsS; AsS; As₂S₃</td>
</tr>
<tr>
<td>Tetrahedrite &amp; Tennenite</td>
<td>Cu₁₂(Sb,As)₄S₁₃</td>
</tr>
<tr>
<td>Molybdenite</td>
<td>MoS₂</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
</tr>
<tr>
<td>Cinnabar</td>
<td>HgS</td>
</tr>
<tr>
<td>Niccolite</td>
<td>NiAs</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>(Fe,Ni)₉S₈</td>
</tr>
</tbody>
</table>

Aqueous end products include metal ions, sulphate and hydrogen ions.

Possible secondary minerals formed at neutral pH after complete oxidation and neutralization include metal hydroxides, -carbonates and –sulphates and gypsum.

SRK, 1988
## Acid Consuming Minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
<th>[1] Acid Consuming Potential</th>
<th>Buffer pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>CaCO$_3$</td>
<td>100</td>
<td>5.5 – 6.9</td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO$_3$</td>
<td>116</td>
<td>5.1 – 6.0</td>
</tr>
<tr>
<td>Magnesite</td>
<td>MgCO$_3$</td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>MnCO$_3$</td>
<td>115</td>
<td>-</td>
</tr>
<tr>
<td>Witherite</td>
<td>BaCO$_3$</td>
<td>196</td>
<td>-</td>
</tr>
<tr>
<td>Ankerite</td>
<td>CaFe(CO$_3)_2$</td>
<td>108</td>
<td>-</td>
</tr>
<tr>
<td>Dolomite</td>
<td>MgCa(CO$_3)_2$</td>
<td>92</td>
<td>-</td>
</tr>
<tr>
<td>Malachite</td>
<td>Cu$_2$CO$_3$(OH)$_2$</td>
<td>74</td>
<td>5.1 – 6.0</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>Al(OH)$_3$</td>
<td>26</td>
<td>4.3 – 3.7</td>
</tr>
<tr>
<td>Limonite/Goethite</td>
<td>FeOOH</td>
<td>89</td>
<td>3.0 – 3.7</td>
</tr>
<tr>
<td>Manganite</td>
<td>MnOOH</td>
<td>88</td>
<td>-</td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(OH)$_2$</td>
<td>29</td>
<td>-</td>
</tr>
</tbody>
</table>

[1] Acid consuming potential is given as the weight (g) of the mineral to have the same neutralizing effect as 100g of calcite.

SRK, 1988
Test Methods
The Prediction Wheel for Mine Drainage Chemistry and the part of ABA (Morin & Hutt, 1999; Usher et al., 2003)
Field Test Methods
Test Cells for waste rock:
Grasberg Mine, Indonesia

Humidity Cells

Test Plot for paste tailings:
Somincor Neves Corvo Mine, Portugal

Wall Washing

Ref: INAP
Static Test Methods
Water : ARD, Seepage, Effluent

- Major Cations & Anions

- Metals (ICP-OES, ICP-MS) (Fe, Mn, Al, U, Hg and others)

- Toxicity (*Daphnia* & Fish)
Solids: Rock, Coal, Spoil

- **Static**: ABA, NAG, BCIR, S(%)  
- **Dynamic**: Leach Column, Humidity Cells  
- **Other (Solids)**: XRD, XRF  
- **Other (Extracts)**: Shakeflask, Acid Rain
Acid – Base Accounting

First-order classification, determining the Acid-Neutralizing and Acid-Generation potentials of rock, and the difference or Nett Neutralizing Potential is calculated.

\[ \text{NP} \quad \text{AP} \]

\[ \text{NNP} = \text{NP} - \text{AP} \]
## Short history of ABA

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABA Method</td>
<td>Sobek <em>et al.</em>, EPA-600/2-78-054, 1978</td>
</tr>
</tbody>
</table>
Acid – Base Accounting Terminology

**AP** (Acid Potential) = S(%) \times 31.25 \text{ (Eltra)}

**NP** (Neutralization Potential) is the capacity to consume (acid) (Base Potential)

**NNP** (Nett Neutralizing Potential) = NP – AP

**NPR** (Neutralizing Potential Ratio) = NP:AP

Results reported as kg of CaCO_3 equivalent of NNP per ton of rock
Representative samples should be quartered, recombined and re-sampled. Select a portion for crushing.

Crush samples individually in a jaw crusher.

Pulverize samples in a disk mill to <325 mesh.

Conduct quartering and sub-sampling again of pulverized material and select portions for ABA testing.
A distinction is made between “paste pH” measured in the field, and “initial pH” measured in the laboratory.

A 1:10 (1g Sample : 10ml de-ionized water) ratio is used, and pH measured after 24 hours.
Acid Potential (AP)

**Leco**: \( \text{AP} = \text{Total S(\%)} \times 31.25 \text{ (kg CaCO}_3\text{/t equivalent)} \)

**Peroxide**: To 1-4g of sample, 80–120 ml peroxide is added incrementally.

Complete oxidation is achieved after sample stops “boiling” or effervescing ceases.

Determine final pH (NAG pH).

Analyze supernatant for \( \text{SO}_4 \) and total S by ICP. Calculate Total S (\%) and AP.
### NAG pH Results

<table>
<thead>
<tr>
<th>Final pH in NAG Test</th>
<th>Acid Generating Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 5.5</td>
<td>Non-Acid Generating</td>
</tr>
<tr>
<td>3.5 – 5.5</td>
<td>Low Risk Acid Generating</td>
</tr>
<tr>
<td>&lt; 3.5</td>
<td>High Risk Acid Generating</td>
</tr>
</tbody>
</table>

Pure de-ionized water in equilibrium with CO₂ has a pH of 5.69, therefore the pH value of 5.5. Any pH above this should be non-acid generating.
## ABA Results

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Acid Generating Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>If NNP=NP-AP &lt; 0</td>
<td>Sample is potentially Acid Generating</td>
</tr>
<tr>
<td>If NNP=NP-AP &gt; 0</td>
<td>Sample is potentially Acid Neutralizing</td>
</tr>
</tbody>
</table>

There is a range for NNP from -20 to +20 kg/t CaCO₃ where the system or sample can either become acidic or remain neutral.

Any sample with NNP < 20 is potentially acid generating, while any sample with NNP > -20 might not generate acid.
Interpretation of NNP values for Acid Base Accounting

- **TYPE III ROCK**
  - NON ACID FORMING
  - NNP: +200
  - STRONG ALKALINE GENERATING

- **TYPE II ROCK**
  - INTERMEDIATE
  - S: <0.25%
  - NNP: +20
  - MILD ALKALINE GENERATING

- **TYPE I ROCK**
  - ACID FORMING
  - S: >0.25%
  - NNP: -20
  - MILD ACID GENERATING

- **TYPE III ROCK**
  - NON ACID FORMING
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  - S: >0.25%
  - NNP: -20
  - MILD ACID GENERATING
### Neutralizing Potential Ratio (NPR)

<table>
<thead>
<tr>
<th>Potential for ARD</th>
<th>Initial Screening Criteria</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Likely</td>
<td>&lt; 1:1</td>
<td>Likely ARD generation</td>
</tr>
<tr>
<td>Possibly</td>
<td>1:1 – 2:1</td>
<td>Possible ARD generation if NP is insufficiently reactive or is depleted at a faster rate than sulphides</td>
</tr>
<tr>
<td>Low</td>
<td>2:1 – 4:1</td>
<td>Possible ARD generation unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficiently reactive NP</td>
</tr>
<tr>
<td>None</td>
<td>&gt; 4:1</td>
<td>No further ARD testing required unless materials are to be used as a source of alkalinity</td>
</tr>
</tbody>
</table>

**NPR = NP : AP**

*Price et al., 1997*
ARD rock type classification based on ABA (NPR) and NAG test

Ref: INAP
ARD rock type classification based on NPR (NP:AP) Ratios

Ref: INAP
### Examples of ABA Results

<table>
<thead>
<tr>
<th>Acid – Base Accounting Modified Sobek (EPA-600)</th>
<th>Sample Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste pH</td>
<td>A</td>
</tr>
<tr>
<td>Past pH</td>
<td>7.0</td>
</tr>
<tr>
<td>Total Sulphur (%) (LECO)</td>
<td>0.763</td>
</tr>
<tr>
<td>Acid Potential (AP) (kg/t)</td>
<td>24</td>
</tr>
<tr>
<td>Neutralization Potential (NP)</td>
<td>8.75</td>
</tr>
<tr>
<td>Nett Neutralization Potential (NNP)</td>
<td>-15</td>
</tr>
<tr>
<td>NP : AP Ratio</td>
<td>0.367</td>
</tr>
<tr>
<td>Rock Type</td>
<td>I</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acid – Base Accounting Modified Sobek (EPA-600)</th>
<th>Sample Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste pH</td>
<td>F</td>
</tr>
<tr>
<td>Past pH</td>
<td>9.6</td>
</tr>
<tr>
<td>Total Sulphur (%) (LECO)</td>
<td>0.015</td>
</tr>
<tr>
<td>Acid Potential (AP) (kg/t)</td>
<td>0.47</td>
</tr>
<tr>
<td>Neutralization Potential (NP)</td>
<td>12.25</td>
</tr>
<tr>
<td>Nett Neutralization Potential (NNP)</td>
<td>11.78</td>
</tr>
<tr>
<td>Neutralising Potential Ratio (NPR) (NP : AP)</td>
<td>26.13</td>
</tr>
<tr>
<td>Rock Type</td>
<td>III</td>
</tr>
</tbody>
</table>
In Conclusion

Acid Base Accounting is a low-cost analysis, requiring relatively simple analytical procedures at a low cost and short turn-around time for sample processing and analyses.

The development of ABA and interpretation of results are based on many years (decades) of international research and experience.

- ABA only provides a possibility of occurrence
- Reaction rates are ignored
- Assumes instant availability of reactive species
- Simple reaction stoichiometry is assumed
- Sampling is critical and often not correctly practiced
Thank You


Infomine: www.infomine.com

IMWA: International Mine Water Association: www.imwa.info/