ABSTRACT

The formation of acidic effluents from mining waste materials is discussed and the chemistry involved explained. The bacterium *Thiobacillus ferrooxidans* plays an important role in acid production due to its ability to rapidly oxidize reduced forms of iron and sulphur which can result in the generation of H₂SO₄. The sulphide mineral pyrite (FeS₂), often present in waste materials, is generally recognized as the chief source of acid mine drainage.

A small-scale test procedure has been developed which rapidly evaluates a waste material's capability to produce an acidic effluent. If the material is assessed as a potential acid producer, then scale-up testing procedures are available which can be used to simulate the characteristics of the effluents produced from a commercial-size waste dump.

During periods of little rainfall, localized biological activity may occur in wet areas of a waste dump, resulting in possible accumulation of soluble pollutants. The length of these dry periods greatly affects effluent characteristics during subsequent rainfalls.

BACKGROUND AND THEORY

The production of acid waters arises from the oxidation of metallic sulphide minerals, particularly those containing iron. In theory, this oxidation can occur either chemically or biologically, but in practice the bacterium *T. ferrooxidans* is always present in acid mine waters, suggesting that the organism plays a major role in the formation of acid mine waters.

*T. ferrooxidans* is a unique bacterium; its energy for growth is obtained from the oxidation of reduced sulphur compounds, e.g. sulphides, and ferrous iron. It is the only organism known that has the capability of oxidizing the sulphide portion of insoluble metallic sulphides. The bacterium requires an aquatic environment but air is the source of the oxygen and carbon dioxide required. The bacterium also required a source of ammonia nitrogen as well as small amounts of phosphate, calcium and magnesium, which are usually present in natural waters.

Much evidence exists that suggest that *T. ferrooxidans* can attack sulphide minerals by direct oxidation of the sulphide moiety. An enzyme containing a sulphhydryl group is postulated to attack the sulphide ion, and a polysulphide chain is built up. The sulphur atoms on this chain are ultimately oxidized through to the sulphate ion form which is released into solution. Ferrous iron, if present, is oxidized simultaneously to the ferric form by a different enzyme system.

Microbiological acid production from sulphide minerals can be illustrated using pyrite as an example:

\[
4\text{FeS}_2 + 15\text{O}_2 + 14\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 8\text{H}_2\text{SO}_4 \quad (1)
\]

This equation represents the complete hydrolysis of all the ferric iron and the production of two moles of sulphuric acid per mole of pyrite. In practice, we find that in an acidic environment, the iron does not precipitate as ferric hydroxide, but rather as a basic ferric sulphate or jarosite type mineral, represented by the formula:

\[
\text{AFe}_3(\text{SO}_4)_2(\text{OH})_6 \quad (\text{A can be } \text{H}_3\text{O}^+, \text{NH}_4^+, \text{K}^+, \text{Na}^+, \text{etc.})
\]

Assuming all the iron precipitates as hydronium-jarosite, the following equation explains the oxidation of pyrite:

\[
12\text{FeS}_2 + 45\text{O}_2 + 34\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6 + 16\text{H}_2\text{SO}_4 \quad (2)
\]

In this case, 1.33 moles of sulphuric acid are produced per mole of pyrite. In practice, neither reaction (1) nor reaction (2) applies completely and the actual amount of sulphuric acid produced in a natural situation will depend...
upon a combination of reactions (1) and (2) and does vary
between 0.67 and 1 mole of acid per mole of sulphide
present.

If the mineralization contains a copper sulphide such as
chalcopyrite, acid can be produced according to either
reactions (3) or (4), thus producing 0.5 moles or 0.17
moles of acid per mole of sulphide:  

\[
\begin{align*}
4\text{CuFeS}_2 &+ 17\text{O}_2 + 10\text{H}_2\text{O} \\
- 4\text{CuSO}_4 + 4\text{Fe(OH)}_3 + 4\text{H}_2\text{SO}_4 \\
12\text{CuFeS}_2 &+ 5\text{O}_2 + 22\text{H}_2\text{O} \\
- 12\text{CuSO}_4 + 4\text{H}_2\text{OFe}_2(\text{SO}_4)_2(\text{OH})_6 + 4\text{H}_2\text{SO}_4
\end{align*}
\]

(3) (4)

However, some sulphides such as bornite (Cu$_2$FeS$_4$) will
be net acid consumers when oxidized, as shown by the
following reaction.  

\[
12\text{Cu}_2\text{Fe}_4 + 111\text{O}_2 + 20\text{H}_2\text{SO}_4 \\
- 60\text{CuSO}_4 + 4\text{H}_2\text{OFe}_2(\text{SO}_4)_2(\text{OH})_6 + 2\text{H}_2\text{O}
\]

(5)

Other non-ferrous sulphides such as millerite (NiS) and
spalerite (ZnS) also undergo direct biochemical
oxidation, which can be represented as follows:

\[
\text{MS} + 2\text{O}_2 \rightarrow \text{MSO}_4
\]

(6)

where M = Zn, Ni, Pb, Co, etc. Acid is neither consumed
nor produced in this sulfubilization reaction; however
these sulphate salts do have an acidic pH which mobilizes
the metals they contain.

From the foregoing discussion, it is evident that pyrite
is the major contributor to acid production, and that
the maximum possible amount of acid generation is one mole
per mole of sulphide present. In practice, the amount of
free acid is usually considerably less due to incomplete
sulphur oxidation. If one assumes a one-to-one ratio, a
safety factor will ensue.

\[ \text{T. ferrooxidans} \] is also capable of producing acid by the
oxidation of dissolved components in waters emanating
from mining and milling operations. In this paper we will
center ourselves only with the formation of strong acid,
that is, sulphuric acid, and not with the formation of weak
organic acids resulting from heterotrophic growth on
available organic matter.

Two possible sources of strong acid arise from soluble
components: the oxidation of ferrous iron and the
oxidation of reduced sulphur compounds such as thiosulphate or polythionates. If ferrous iron is present, it
produces is less soluble than the ferrous iron and it tends
to hydrolyze, releasing its acid content:

\[
2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H} \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}
\]

(7)

However, if \text{T. ferrooxidans} is present, the rate of this
reaction can be increased by a factor of 500,000 times.\text{12}
Although reaction (7) consumes acid, the ferric iron
produced is less soluble than the ferrous iron and it tends
to hydrolyze, releasing its acid content:

\[
2\text{Fe}^{3+} + 6\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 + 6\text{H}^+
\]

(8)

Thus, a net gain of 2 moles of hydrogen ions per mole of
ferrous iron is obtained if the hydroxide product is
formed.

With reduced sulphur compounds, either chemical or
biological oxidation can take place, depending on
conditions. The amount of acid released would depend on
the ionic species present, the nature of the associated
cations and the mode of oxidation. Three possible

\[
\begin{align*}
\text{S}_2\text{O}_3^{2-} + 2\text{O}_2 + \text{H}_2\text{O} &\rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\text{SO}_3^{2-} + 2\text{O}_2 + 2\text{H}_2\text{O} &\rightarrow 3\text{SO}_4^{2-} + 4\text{H}^+ \\
\text{SO}_4^{2-} + 7/2\text{O}_2 + 3\text{H}_2\text{O} &\rightarrow 4\text{SO}_4^{2-} + 6\text{H}^+
\end{align*}
\]

(9) (10) (11)

These three equations assume complete oxidation of all
the reduced sulphur compounds, a result normally
occurring only in the presence of sulphur oxidising
bacteria. Chemical oxidation in the acidic environment is
usually incomplete.

**PRINCIPLE OF ACID PRODUCTION POTENTIAL**

**TEST PROCEDURE**

A small-scale test procedure has been developed to
determine whether a waste material may become acid
producing.\text{13} For the purpose of this paper, we will briefly
discuss the principle of the method.

To determine whether a waste material has the
potential to become acid producing, the acid consuming
capability of the material, expressed as kilograms of
H$_2$SO$_4$ per tonne waste, is determined by chemical
titration of a finely ballmilled sample (~400 mesh). This
number is compared with the maximum theoretical
amount of sulphuric acid which could be produced,
calculated stoichiometrically from the sample's total
sulphur content. If the alkaline content of the sample
consumes more acid than could theoretically be
produced, there is no danger that the waste, in run-of-
mine size, will become a source of acidic effluents. The
sample is classified as a non-acid producer.

However, if the opposite is true, i.e. the waste material
could theoretically produce more acid than it can
consume, a biological leach test must be performed to
determine how much of the contained sulphur can be
converted into sulphuric acid. This biological test consists of
mixing into a 250 ml baffle-bottom Erlenmeyer flask,
15-30 g of ~400 mesh sample with 70 ml of a nutrient
medium.\text{14} The test pH is stabilized at 2.2-2.5 over a
period of a few days, followed by inoculation with an
active culture of \text{T. ferrooxidans}. The flask is loosely
stopped and put onto a gyratory shaker in an
incubation room, which has a CO$_2$-enriched atmosphere
and is temperature controlled at 35°C. This procedure
ensures conditions ideal for bacterial growth. An active
bacterial population will be indicated by a steadily
decreasing sample pH as biochemical sulphide oxidation
occurs. At this point, the flask receives further
incremental additions of sample and the effect on pH is
closely monitored. If the test pH rises and approaches the
sample's natural pH, then the waste material is confirmed
to be a non-acid producer, because any acid produced
biologically is consumed by alkaline components in the
material. However, if the test pH remains low, indicative
of a steady net acid production, then the waste material is
confirmed to be a potential acid producer.

**SCALE-UP TESTING PRINCIPLE AND
PROCEDURE**

Since the acid production potential tests are performed on
a small scale on finely ground material, under conditions
ideal for biological growth, scale-up effects must be
considered in order to realistically evaluate a waste