Acid mine drainage – the chemistry

Mining is one of South Africa's most important industries, but it comes with a cost. **Rebecca Garland** explains about acid mine drainage.

A sign warning people not to use the water in Carletonville on the Wonderfonteinspruit, close to Khutsong. They have had a history of poor water quality, linked in part to the gold mining activities in the area. Image: Rebecca Garland

Acid mine drainage (AMD), also called acid rock drainage (ARD) has recently attracted lots of attention in South Africa, both in parliament and in the media. In December, parliament released an Inter-ministerial Committee Report focusing on the AMD in the Witwatersrand gold fields. However, this is not the only area in South Africa that is at risk of AMD. In that report, the coal fields in KwaZulu-Natal and those in Mpumalanga, as well as the copper district in O'Kiep were some of the areas that were highlighted as areas with AMD. In order to understand why AMD is a problem in those areas, it is necessary to first understand the science of how AMD occurs.

How AMD happens

AMD usually enters the environment as polluted water. However, it is formed in the mine itself through a variety of chemical reaction pathways. The most common pathway starts with the mineral pyrite (FeS_2), which is also known as 'fool's gold'. However, many other reactive sulphur containing mineral have the ability to produce AMD. The following are the equations that show the generalised reaction pathway for pyrite to start to produce AMD:

(1) $2FeS_2\ (s) + 7O_2\ (g) + 2H_2O\ (l) \rightarrow 2Fe^{2+}\ (aq) + 4\ SO_4^{2-}\ (aq) + 4H^+\ (aq)$

(2) $4Fe^{2+}\ (aq) + O_2\ (g) + 4H^+\ (aq) \rightarrow 4\ Fe^{3+}(aq) + 2\ H_2O\ (l)$

(3) $4Fe^{3+}\ (aq) + 12H_2O\ (l) \rightarrow 4Fe(OH)_3\ (s) + 12\ H^+\ (aq)$

(4) $FeS_2\ (s) + 14\ Fe^{3+}\ (aq) + 8H_2O\ (l) \rightarrow 15Fe^{2+}\ (aq) + 2\ SO_4^{2-}\ (aq) + 16\ H^+(aq)$

In equation (1), the pyrite is exposed to air and water to produce the ferrous or iron (II) cation (Fe^{2+}), sulphate anion (SO_4^{2-}) and the aqueous hydrogen cation (H^+). Note that both SO_4^{2-} and H^+ are produced in this step, which is really just dissociated sulphuric acid. You can see from equation (1) that in order for these reactions to happen, the pyrite must be exposed to both air and water. Under normal circumstances the pyrite may well be exposed to both of these because it is on the surface. But the reactions proceed at a very slow rate because there is not much pyrite available to react with. However, once mining begins, rocks are split up into smaller fragments. These smaller fragments have a larger surface area so more of the pyrite is exposed at any one time to air and water. This is especially seen in the mine dumps such as gold tailing dumps, where rainwater can seep through the dump (which is made up of crushed up rock that contains pyrite) and these reactions can occur.

Tailings are the materials that are left over after the process of separating the valuable fraction of an ore from the uneconomic fraction. They are different from the waste rock, which is the material in which the ore is found and which is displaced during mining without being processed.

In addition, mining creates holes and tunnels and other areas where water may be able to collect. This water then has to be constantly pumped out of the mine in order to prevent the reactions shown in the equations from occurring.

In equation (2), the iron (II) cation goes on to further react with oxygen and some of the H^+ from equation (1). This then produces the ferric or iron (III) cation (Fe^{3+}) and water. Equation (2) is considered the 'rate determining step' of the four equations and is therefore the equation that limits the rate of the reaction. The rate of this reaction can be increased with the help of certain bacteria (e.g. *Thiobacillus ferrooxidans*) that also oxidise iron (II) to iron (III).

The iron (III) cation can then either react with water to produce iron (III) hydroxide ($Fe(OH)_3$) and more H^+ as in equation (3), or it can react with more pyrite and water to produce the iron (II) cation, the sulphate anion and H^+ as in equation (4). The resulting iron (II) cation from equation (4) can react further, as shown in equation (2), leading to a cyclic pathway where pyrite reacts to form Fe^{2+}, which can be oxidized to form Fe^{3+}, which can react with pyrite to form more Fe^{2+}, and so on – all the while producing more H^+ than is consumed.

Acid mine drainage. Image: Rebecca Garland

A generalised overall equation for this whole process is:

(5) $4FeS_2$ (s) + $15O_2$ (g) + $14H_2O$ (l) → $4Fe(OH)_3$ (s) + $8H_2SO_4$ (aq)

Where does acidity come from in these reactions?

All of the reactions, except that shown in equation (2), produce the aqueous hydrogen cation (H^+). A more common way to see this written is H_3O^+ which is called the hydronium ion. pH is calculated using the concentration of the hydronium ion. A high concentration of these ions will make a solution acidic. In this reaction pathway, the reactions are occurring in water and thus produce an aqueous solution that has a high concentration of acid (i.e., the aqueous hydrogen cation), sulphates and the iron (III) hydroxide.

Acidity not the only problem with AMD

In addition to producing acid, iron (III) hydroxide is formed. This solid has a yellow colour and the nickname 'yellow boy'. This solid can precipitate out of the aqueous solution when the pH is increased to above 3.5 and leads to yellow-orange coloured solid.

However, the chemical reactions do not stop with these four equations. The water that is produced from these reactions can be extremely acidic; under these acidic conditions, heavy metals that are in the surrounding rocks are more soluble and they can then leach out of the rocks into the water. Some of the heavy metals that can be present in AMD in South Africa are Al, As, Cr, Cu, Hg, Mn and U. Many of these heavy metals are toxic both to the ecosystem and humans. Thus in the end, the AMD is an aqueous solution that can have a low pH and a high concentration of sulphates, iron (III) hydroxide and heavy metals.

Natural neutralisation

However, not all acid mine drainage is actually acidic. One of the reasons is because there are natural pathways through which the solution can be neutralised. For example, calcium carbonate ($CaCO_3$), which is found in rocks such as limestone, can neutralise the acid through the following reactions. And in fact, limestone has been used to treat AMD water in treatment plants.

(6) $CaCO_3$ (s) + H^+ (aq) → HCO_3^- (aq) + Ca^{2+} (aq)

(7) $CaCO_3$ (s) + $2H^+$ (aq) → H_2CO_3 (aq) + Ca^{2+} (aq)

In both reaction pathways the acid (H^+ (aq)) is a reactant and is thus

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consumed. This decrease in the H^+ (aq) will lead to a decrease in acidity and an increase in pH. The reaction in equation (7) occurs at lower pH values than the reaction in equation (6) because more acid is needed; two moles of acid are required for the reaction in equation (7) while only one is required in the reaction in equation (6). Thus, if AMD occurs in an area where the rocks contain calcium carbonate, then the effluent that is released into the environment might not have a low pH at all. This may lead some of the pollutants (such as $Fe(OH)_3$) to precipitate out of the water, but others (such as the sulphates and some heavy metals) will stay in the water.

AMD variability

Just by looking at the chemistry of AMD, it becomes obvious that there are many factors that might have an impact on both the chance that AMD will be produced and what pollutants will be in the AMD. For example, in order to decrease the risk that AMD will be produced, active mines constantly pump water out of their mines to try to prevent the pyrite in equation (1) from being exposed to water and air. This constant pumping can also remove any AMD that is produced and not allow it to build up. In areas where there is high rainfall or where there are abandoned mines, it is more difficult to ensure that all mines do not flood with water. Also local geology and what heavy metals are present will determine which heavy metals are leached from the nearby rocks into the AMD. And of course, the geology will play a large part in possibly neutralising the AMD through the presence of neutralising compounds such as calcium carbonate. Thus, while the general chemistry is described above, the exact composition of the AMD can vary from site-to-site. This can then have implications for both managing the AMD and the impacts that the AMD can have on the ecosystem and human health. ❑

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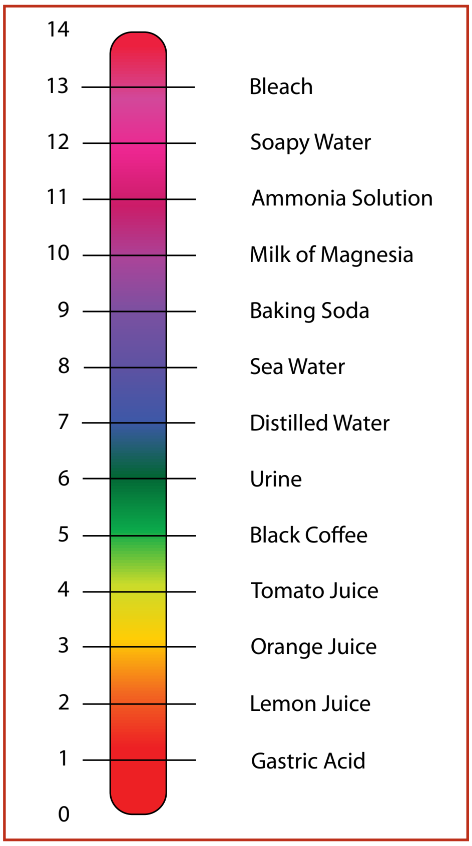
The solid precipitate that is called 'yellow boy'.

Image: Rebecca Garland

pH

pH is a measure of the acidity or alkalinity of an aqueous solution. Pure water is said to be neutral, with a pH close to 7.0. Solutions with a pH less than 7 are said to be acidic and solutions with a pH more than 7 are said to be alkaline or basic.



The pH of some common solutions.

Recommended reading on AMD in South Africa

McCarthy TC. The impact of acid mine drainage in South Africa. *South African Journal of Science* 2011; 107. (can be accessed online: http://www.sajs.co.za/index.php/SAJS/article/view/712)

Expert Team of the Inter-Ministerial Committee. Mine water management in the Witwatersrand Gold Fields with special emphasis on acid mine drainage. *Report to the Inter-ministerial Committee on Acid Mine Drainage, Pretoria: Department of Water Affairs.* 2010. (can be accessed online: http://www.dwaf.gov.za/Documents/ACIDReport.pdf)