

Tutor instructions: Course split into three 1.5 hour sessions. Each involves a lecture follow by a practical session.

Structure and rough timings for part 3. Lecture (slides 1 to 26): 30-40minutes Break: 5minutes Introduce practical (slides 27 to 29): 5-10minutes Production of posters by participants: 30minutes Group poster presentations: 20 minutes

For the practical session you will need flip chart paper (x3) and marker pens of different colors (enough for 3 groups). You will also need print outs of the following paper: Johnson and Hallberg, 2005, Acid mine drainage remediation options: a review, Science of the Total Environment, 338, pages 3-14 (provided as a pdf as part of the course materials)

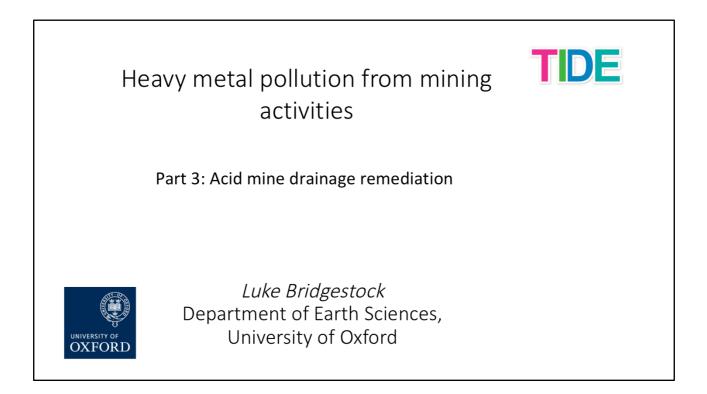
Tutor introduction

Dr. Luke Bridgestock

- MSci Geology and PhD Isotope Geochemistry, Imperial College London
- Postdoctoral Research Associate, University of Oxford (2015 to 2020)
- Leverhulme Early Career Research Fellow, University of Cambridge (May, 2020 to present)
- Research interests in metal cycling in the environment
- More details at <u>https://www.earth.ox.ac.uk/people/luke-bridgestock/</u>



TIDE



In this final part of the course we are going to learn about remediation options for acid mine drainage

Activity Outline



This activity will focus on the exposure of local populations to heavy metal pollution from mining operations

Part 1; the impact of heavy metal pollution from mines on water quality and the health of local populations

Part 2; the release of heavy metals to surface waters (rivers and lakes) from mining activities

Part 3; remediation techniques for acid mine drainage

Practical; a case study to assess the exposure routes of local people to heavy metals and the sources of heavy metals to a river system impacted by mine pollution.

As a reminder of the course overview;

We have learnt how humans are exposed to metals and how to assess chronic toxicity risks due to metal exposure, how mining processes release metals into the environment, and in particular have learnt that acid mine drainage represents the dominant mining process for generating metal pollution

We will now focus in more detail on the issue of acid mine drainage, and some of the options available to address this problem.

Similar to the first 2 parts of this course, this section is split into a short lecture followed by a practical session. In this practical session you will work in 3 groups to produce posters covering different acid mine drainage remediation options, and at the end of the session each group will present their poster to the rest of the class.

Introduction



Acid mine drainage is a globally major source of heavy metal pollution

Minimizing the environmental impacts of acid mine drainage is very challenging, due to;

- 1. The extremely large volume of mine materials involved
- 2. The persistence of acid mine drainage generation for decades to centuries

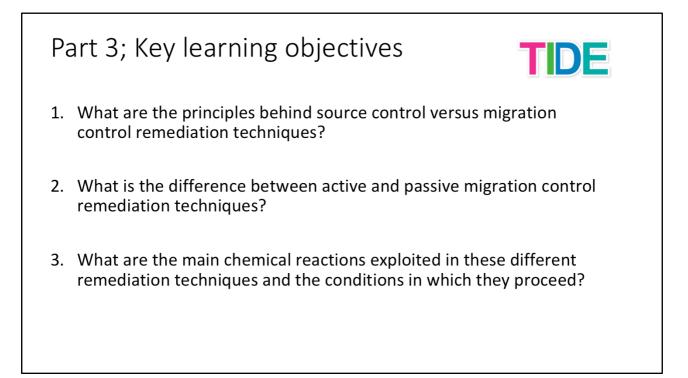
Solutions to acid mine drainage therefore need to be applied at a large scale and sustained over long time periods (much longer than the operational timescale of the mine)

Addressing the impacts of acid mine drainage are challenging due to the extremely large volume of mine materials involved, and the fact that acid mine drainage is continued to be generated from this material for many decades to centuries.

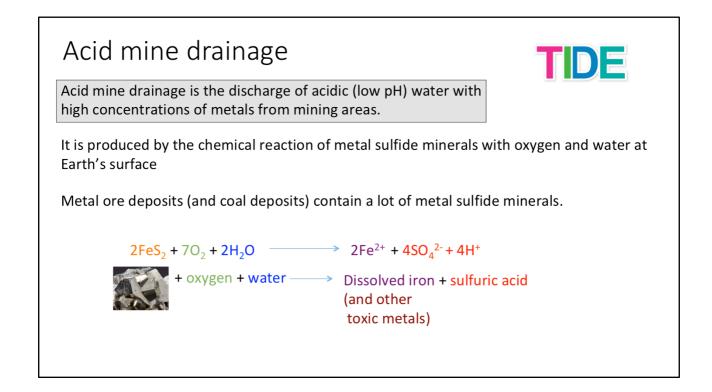
Solutions to this environmental issue therefore need to be applied at a large scale and to be able to be sustained over long time periods, much longer than the operational timescale of the mine.

This is a particular issue. For active mining operations there is a source of income and a mine company that can be held responsible by governing bodies to pay for and implement remediation techniques. However in areas with historic mining activities, conducted decades or even centuries ago, it is challenging to determine who is responsible for implementing and paying for remediation techniques. These problems of long-term sustainability will ultimately be faced by all active mining operations once they eventually close.

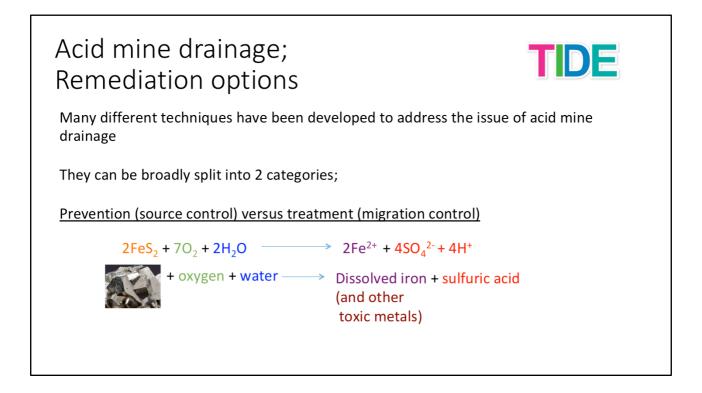
For this reason the 'ideal' solution are remediation techniques that remain effective for many centuries without continued effort to sustain. In reality this is difficult to achieve.



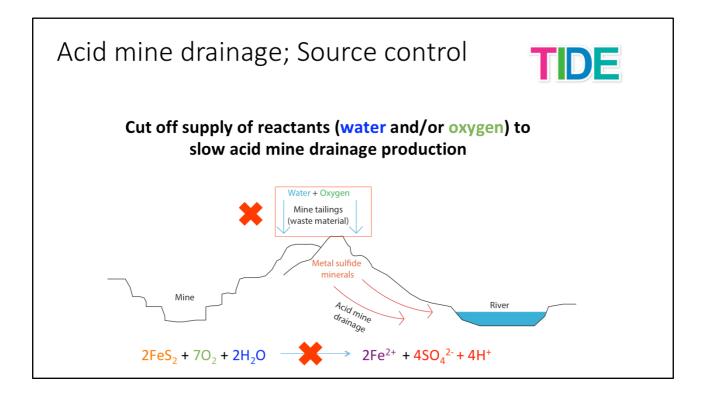
In this final part of the course the learning objectives are to understand the principles behind different categories of acid mine drainage remediation technique, including source control versus migration control techniques, and active and passive migration control techniques. By the end of this lecture hopefully you will understand the meaning of these terms. You will also hopefully understand the main chemical reactions exploited in these different techniques.



As a reminder, acid mine drainage is the discharge of acidic waters with high concentrations of metals from mining areas. It is generated by the chemical reaction between metal sulfide minerals with water and oxygen at the surface of the earth. Metal ore deposits (and coal deposits) contain high concentrations of metal sulfide minerals, so that extracting this material from the ground greatly increases the rate at which this reaction occurs.



Broadly there are 2 categories of acid mine drainage remediation technique, ones that try to prevent the generation of acid mine drainage in the first place, known as source control techniques, and ones that aim to treat waters impacted by acid mine drainage and prevent its dispersion into the wider environment, known as migration control techniques

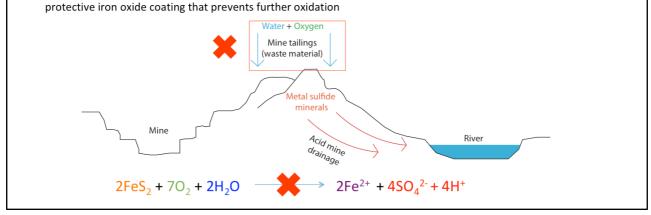


To prevent the generation of acid mine drainage source control techniques aim to prevent, or a least slow, the interaction of metal sulfides with water and/or oxygen, to stop, or at least slow the rate of this chemical reaction.

Acid mine drainage; Source control



- Divert water flow away from mine and mine tailings
- Seal up mine shafts slow supply of water and oxygen (for underground not open pit mines)
- Store mine tailings under stagnant water slows the supply of oxygen
- Cover mine tailings with various caps/seals slow supply of water and/or oxygen
- Use anionic surfactants to kill microbes that mediate important chemical reactions that produce acid mine drainage • Coat mine tailings with phosphate solutions containing H_2O_2 – oxidizes surfaces of sulfide minerals creating a



There are many different ways to try to achieve this, including;

diverting the flow of surface or groundwater away from exposed ore deposits and mine tailings,

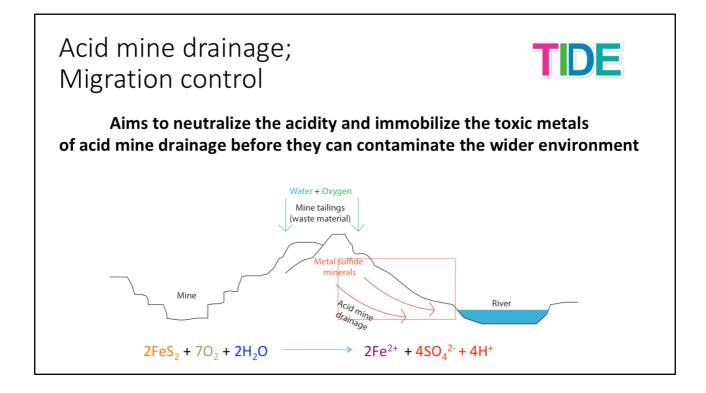
sealing up mine shafts to slow the supply of oxygenated waters,

storing mine tailings beneath a layer stagnant water, which slows the supply of oxygen,

covering mine tailings with various caps/seals to slow the supply of water and/or oxygen,

The kinetics (rate) of the chemical reactions that produce acid mine drainage are typically enhanced by microbial mediation. Using anionic surfactants to kill these microbes can slow the rate of acid mine drainage generation

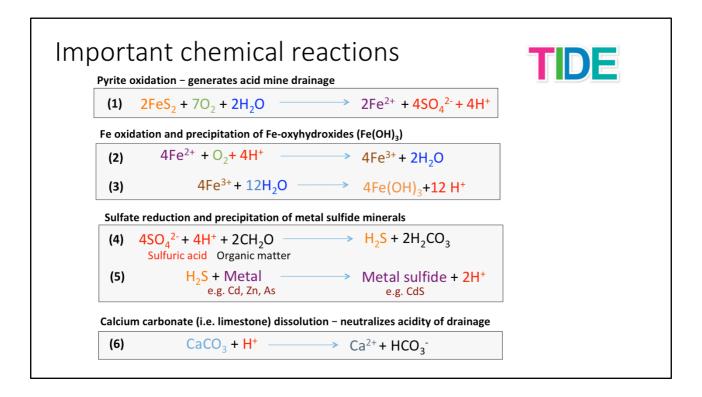
Can also coat the surfaces of sulfide minerals with a layer of iron oxide to prevent further reaction with water/oxygen –achieved using phosphate solutions containing hydrogen peroxide.



In practice stopping acid mine drainage completely is very difficult to achieve, and in most cases remediation efforts rely on migration control measures.

Migration control measures aid to neutralize the acidity of acid mine drainage (raise the pH) and trap the toxic metals in mineral form proximal to sites of acid mine drainage generation to prevent its dispersion into the wider environment.

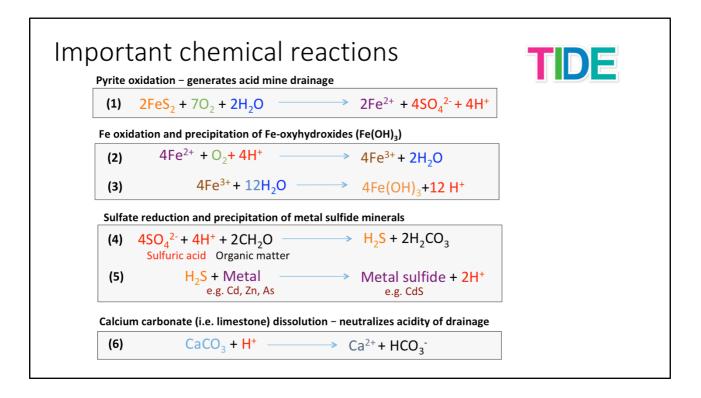
Essentially the aim to reverse this chemical reaction, rather than stop/slow it.



To do this migration control techniques exploit a range of secondary chemical reactions

These reactions are strongly controlled by the pH and redox (availability of electron acceptors such as oxygen)

Listed here are a some of the most important of these reactions.

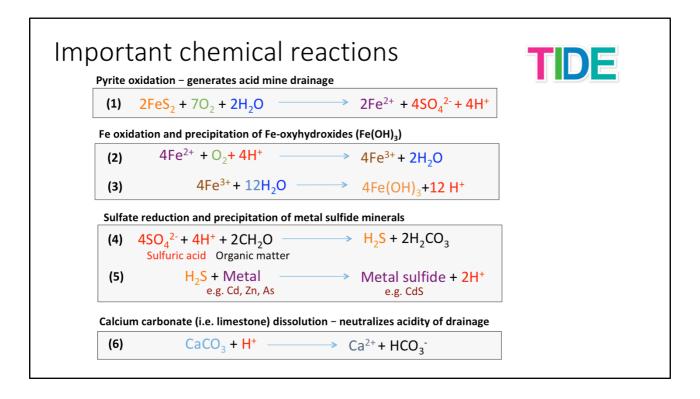


Reactions 2 and 3

In oxic environments (waters containing dissolved oxygen), Fe2+ released during acid mine drainage is oxidized to Fe3+ (reaction 2), which in turn reactions with water to precipitate as Fe-oxyhydroxide minerals (represented as Fe(OH)3) (reaction 3). These minerals colour the soils and waters around mining areas orange, a common visual characteristic of acid miner drainage impacted areas.

There is a production of H+ during these 2 reactions, meaning they decrease pH (increase acidity). These reactions (in particular reaction 3) are therefore favored at higher pH, and inhibited at lower pH (more acidic conditions).

These 2 reactions act to remove dissolved Fe form solution and fix it into mineral form. Fe-oxyhydroxide minerals have high sorption capacities, so that precipitation of these minerals results in the removal other toxic metals by adsorption to the surfaces of these mineral phases. Adsorption of metal cations to these mineral phases is also pH dependent, with stronger metal adsorption at higher pH



Reactions 4 and 5

These reactions occur in anoxic waters, where oxygen, and other electronic acceptors (nitrate, Fe3+ and Mn4+) have been completely consumed, in contrast to reactions 2 and 3 which occur in oxic conditions.

In the absence of other, more favorable, electron acceptors, microbes will use sulfate (SO42-) to respire organic molecules and drive their metabolisms. In doing so sulfuric acid is consumed, and hydrogen sulfide (H2S) and carbonate species are produced (reaction 4). This reaction consumes acidity (H+).

Many heavy metals will react with hydrogen sulfide to produce metal sulfide minerals (e.g. CdS, FeS2, ZnS) (reaction 5), immobilizing these metals in mineral form. Note that the combination of these 2 reactions are essentially the reverse of reaction 1 - the generation of acid mine drainage due to the oxidation of metal sulfide minerals – with sulfuric acid being consumed and dissolved metals converted back into metal sulfide minerals.

Reaction 6

Finally the dissolution of calcium carbonate, and other salts, can be used to neutralize the acidity of acid mine drainage impacted waters

Summary *True or false?*



- 1. Source control techniques aim to preventing acid mine drainage generation by isolating sulfide rich mine material from oxygen and/ or water
- 2. Migration control techniques aim to treat water impacted by acid mine drainage to minimize contamination of the wider environment
- 3. Remediation techniques only need to be applied to active mining areas to address acid mine drainage

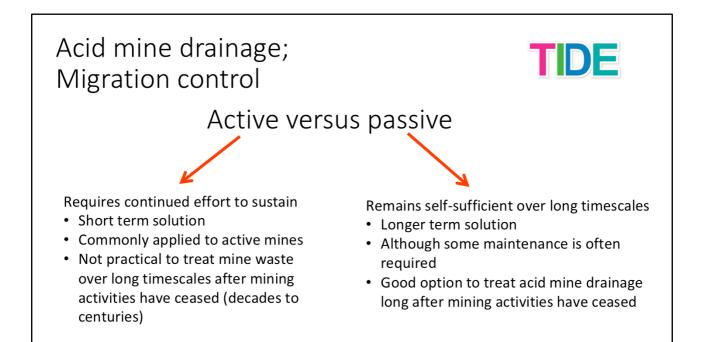
Tutor instruction: Ask them to read through these statements and decide, based on the material presented so far, if they think they are true or false. Give them 3-5mins to to this and discuss among themselves. Then ask them to shout out what they think, before revealing the answers on the next page.

Summary *True or false?*



- Source control techniques aim to preventing acid mine drainage generation by isolating sulfide rich mine material from oxygen and/or water TRUE
- 2. Migration control techniques aim to treat water impacted by acid mine drainage to minimize contamination of the wider environment **TRUE** ✓
- Remediation techniques only need to be applied to active mining areas to address acid mine drainage FALSE X Remediation needs to continue for many decades to centuries after mines have become inactive to address acid mine drainage – this is a major challenge

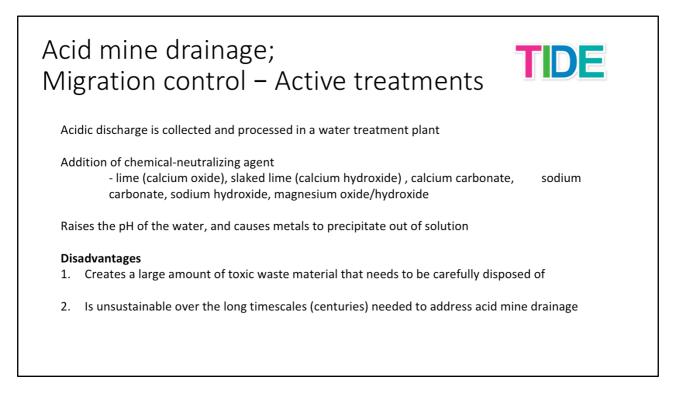
Tutor instruction: Spend a moment to briefly explain any incorrect answers.



Migration control techniques can be further subdivided into active and passive techniques, which refers to the long-term sustainability of the technique

Active techniques require continued effort and input of resources to sustain, and are only considered a short term solution. Applied to active mining operations where there is a source of income and a mining company to maintain these treatments. Active treatments however are not practical to apply over the long timescales (centuries) needed to address continued generation of acid mine drainage once mines are closed, and in areas impacted by historic mining activities.

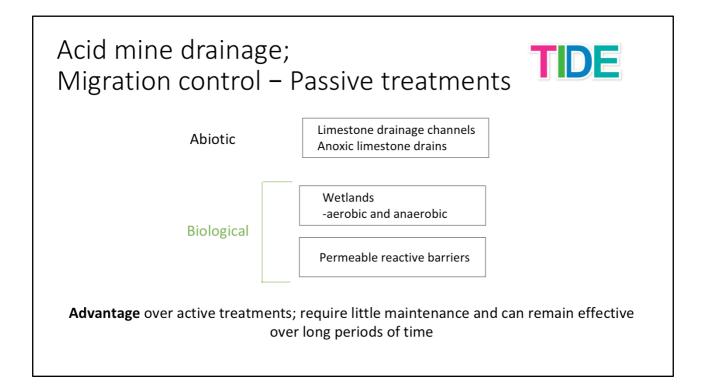
Passive techniques aim to be sustainable over long timescales, with minimal on-going input of resources. In reality some long-term maintenance is required to ensure these techniques remain effective, but they allow issues of acid mine drainage to be addressed over the longer timescales required after the closing of mining operations



Active techniques involve the collection of waters impacted by acid mine drainage and their treatment in a waste water plant to neutralize their acidity and remove toxic metals.

Typically achieved by the addition of neutralizing agent such as oxides, hydroxides and carbonates of Ca, Mg and Na. This raises the pH of the water and causes the metals to precipitate out of solution. This creates a slurry of containing high concentrations of toxic metals, which itself needs to be carefully stored/disposed of to prevent/minimize the release of these metals into water sources and the wider environment.

As previously mentioned these active treatments are not sustainable in the long term, and ultimately passive techniques will be required



Passive migration control techniques can be further catagorized into those that use biology to mediate the chemical reactions that neutralize acidity and convert dissolved metals into mineral form, and those that don't (abiotic)

In the following we will learn about some of these different passive migration control techniques in more detail, in particular limestone drainage channels (an abiotic technique), and wetlands and permeable reactive barriers (rely on microbes to drive key chemical reactions)

Acid mine drainage; Migration control – Passive treatments



Limestone drainage channels and anoxic limestone drains



Photo; open limestone drainage channel (France) (Luke Bridgestock)

Stream channel is constructed of limestone gravel

Limestone dissolution raises the pH of acid mine drainage prior to discharge into larger rivers (reaction 6; slide 12)

Precipitation of Fe-oxide coatings on limestone surfaces can reduce effectiveness (reaction 3; slide 12)

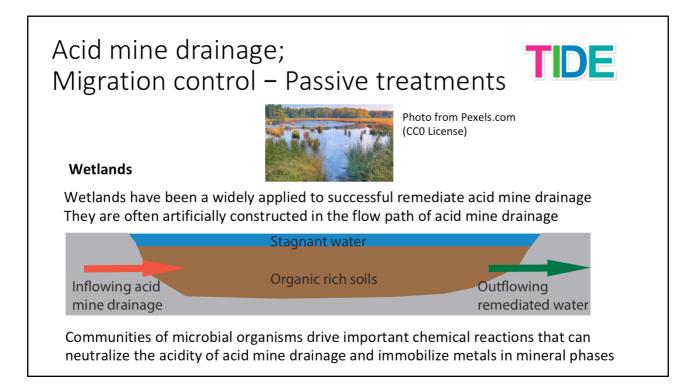
Isolating from oxygen, in sealed channels (anoxic limestone drains) can improve this by preventing Fe-oxide precipitation

Limestone drainage channels are commonly applied to areas impacted by acid mine drainage. They simply involve directing the flow of acid mine drainage impacted water through channels made of crushed limestone (rocks composed of the mineral calcium carbonate)

The calcium carbonate minerals are dissolved by the acidic waters, which acts to neutralize the acidity (see reaction 6 on slide 12)

This increase in pH causes the precipitation of Fe-oxyhydroxide minerals (see reaction 2 and 3 on slide 12), as can be seen here giving the orange colour to the stream. Over time this can reduce the effectiveness of this technique to neutralize acid mine drainage as limestone fragments become coated with these Fe precipitates which prevents further dissolution of calcium carbonate.

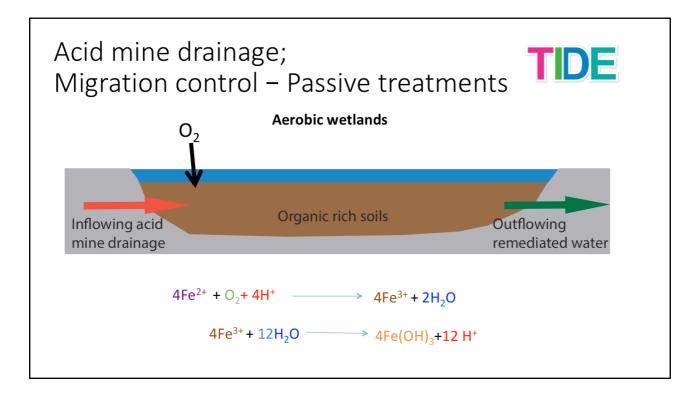
A modification to address this issue and help maintain the effectiveness of this technique for longer periods of time is to seal these channels underground. This reduces the supply of oxygen to these waters, and is known as an anoxic limestone drain. The effect is to reduce the oxidation of Fe2+ to Fe3+ (reaction 2 slide 2), which in turn reduces the precipitation of Fe-oxyhydroxides (reaction 3, slide 12)



Wetlands, often artificially constructed in the flow path of acid mine drainage have been commonly applied to treat acid mine drainage.

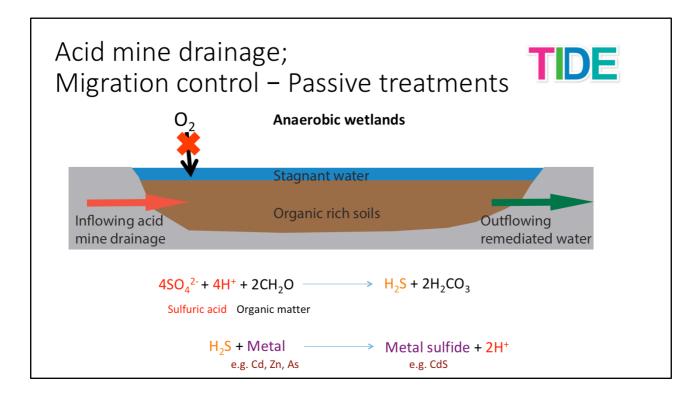
Communities of microbes drive important chemical reactions that can neutralize acidity and/or immobilize metals in mineral form.

There are 2 types – aerobic wetlands that have abundant oxygen, and anaerobic wetlands which are not oxygenated. They feature distinctly different chemical reactions (see slide 12 for reference) and suitability to treat acid mine drainage of different chemistries.



In aerobic wetlands, Fe2+ in the mine drainage reacts with oxygen to produce Fe3+. This Fe3+ in turn reacts with water to precipitate as Fe-oxyhyroxide minerals (reactions 2 and 3, slide 12). This reduces the high dissolved Fe concentrations of the mine drainage, and through adsorption of metals to the surfaces of these Feoxyhyroxide minerals can reduce dissolved concentrations of other toxic metals, improving the quality of the outflowing water.

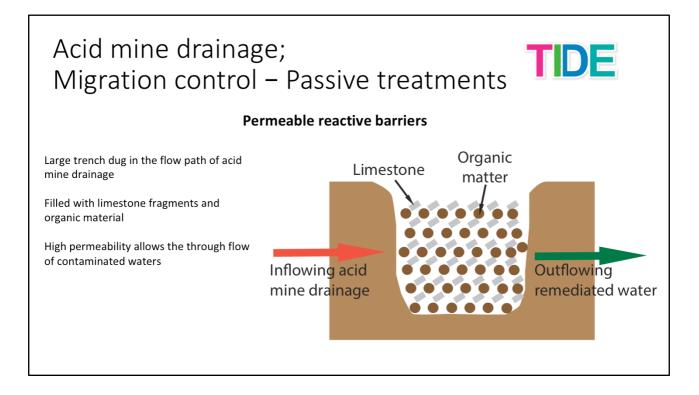
As mentioned previously these reactions generate acidity (H+) and only proceed at higher, near neutral pH. This technique is therefore only suitable for mine drainage that has had is acidity neutralized, either due to dissolution of carbonate minerals present in the mine waste/surrounding area, or due to the funneling of mine waste waters through limestone drainage channels prior to entering the wetland. It also requires that oxygen is readily supplied to the soil pore waters of the wetland. Growing plants in the wetlands can help with this, as their roots provide pathways for oxygen to migrate into the soil pore waters.



In contrast, anaerobic wetlands rely on a different set on chemical reactions that operate in environments completely devoid of oxygen.

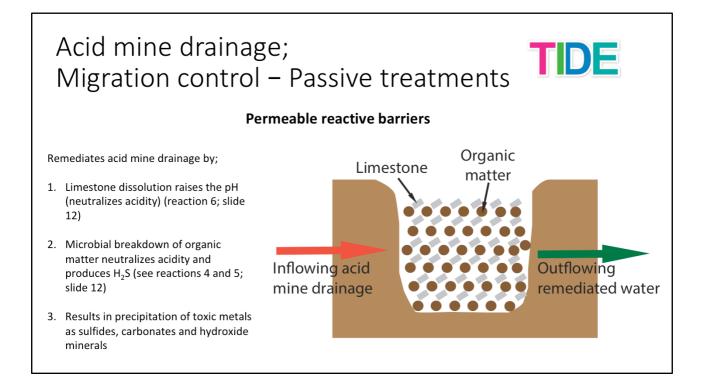
In the absence of oxygen and other more favorable electron acceptors (e.g. nitrate, Fe3+, Mn4+) microbes will use sulfate to respire organic matter. In the process sulfuric acid is consumed and hydrogen sulfide is produced.

Many dissolved metals react with hydrogen sulfide to form metal sulfide minerals. These 2 reactions result in the net consumption of acid and fix dissolved metals into mineral form (reactions 4 and 5, slide 12).



Permeable reactive barriers are another passive, migration control technique.

A trench is dug in the flow path of mine drainage and filled with a mixture of limestone fragments and organic material, that is designed to have a high permeability to allow the through flow of the mine drainage.



The dissolution of the limestone (calcium carbonate) raise the pH of the drainage (neutralizes the acidity) – reaction 6, slide 12. Increase in pH can result in the precipitation of carbonate and hydroxide minerals which remove toxic metals from solution.

Similar to anaerobic wetlands, microbial organisms decompose the organic matter using sulfate as an electron acceptor, consuming sulfuric acid and producing hydrogen sulfide. Metals then react with the hydrogen sulfide to for metal sulfide minerals.

Summary *True or false?*



- 1. Active treatment of acid mine drainage is a sustainable remediation option
- 2. All passive treatments of acid mine drainage require no maintenance and are guaranteed to remain effective over long time periods
- 3. The best remediation options for addressing acid mine drainage vary depending on numerous factors, including geology, costs, surrounding land use and legislation

Tutor instruction: Ask them to read through these statements and decide, based on the material presented so far, if they think they are true or false. Give them 3-5mins to to this and discuss among themselves. Then ask them to shout out what they think, before revealing the answers on the next page

Summary *True or false?*



- Active treatment of acid mine drainage is a sustainable remediation option FALSE X Active treatments require continued effort and financial support to sustain, and tend to produce additional waste streams that need to be carefully managed
- 2. All passive treatments of acid mine drainage require no maintenance and are guaranteed to remain effective over long time periods FALSE × All remediation techniques require some level of maintenance to remain effective over the long time periods (centuries) required to address acid mine drainage
- 3. The best remediation options for addressing acid mine drainage vary depending on numerous factors, including geology, costs, surrounding land use and legislation TRUE ✓

Tutor instruction: Spend a moment to briefly explain any incorrect answers.



1. What are the principles behind source control versus migration control remediation techniques?

Part 3; Key learning objectives

-Source control techniques aim the prevent the generation of acid mine drainage by limiting the exposure of metal sulfide rich mine material to oxygen and water. Migration control techniques aim to treat acid mine drainage, by raising its pH and immobilizing toxic metals in mineral form.

2. What is the difference between active and passive migration control remediation techniques?

-Active migration control techniques require continued effort to sustain and is generally only suitable for active mines. Passive control techniques require lower levels of maintenance and can operate over longer timescales

3. What are the main chemical reactions exploited in these different remediation techniques and the conditions in which they proceed?

-Include, dissolution of CaCO₃ (raise pH), precipitation of Fe-oxyhydroxides that can adsorb other toxic metals (proceed in oxygen rich conditions, at neutral pH), and microbial sulfate reduction/metal sulfide precipitation (proceeds in anoxic conditions)

This brings us to the end of the lecture.

Hopefully you have all now learnt the meaning of source control and migration control acid mine drainage remediation techniques. Source control techniques aim to prevent or at least slow the generation of acid mine drainage by isolating metal sulfide rich mine material from water and/or oxygen. Migration control techniques aim to treat acid mine drainage, by raising its pH and trapping toxic metals in dissolved form

Migration control techniques can be considered active or passive. Active techniques require the continued input of resources to sustain and are only suitable for active mining operations. Once mining operations have ceased, passive techniques that require minimal on-going maintenance are more suitable for addressing the continued generation of acid mine drainage for many decades to centuries.

Migration control techniques use secondary chemical reactions to treat acid mine drainage. Important ones are the dissolution of calcium carbonate minerals that increases pH (neutralizes acidity), the oxidation and precipitation of Fe as Fe-oxyhydroxide minerals that can adsorb other toxic metals, reactions which occur in oxygenated neutral pH conditions, and the microbial reduction of sulfate and metal precipitation as sulfide minerals, which proceed in anoxic conditions.



Tutor instruction: Depending on time availability it is good to pause for a 5 minute break at this point to give the participants to discuss the lecture materials among themselves. It is also a chance for participants to ask the tutor questions about the lecture material individually (i.e. not in front of the whole class), which they are often more confortable/willing to do.

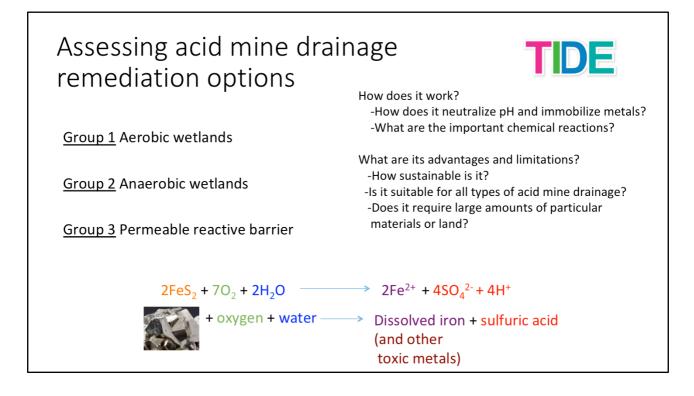
Assessing acid mine drainage remediation options There have been countless different remediation techniques developed to address acid mine drainage. Choice of optimal remediation techniques vary greatly between different mining sites To select the optimal remediation technique first requires an understanding of the underlying scientific principals (i.e. how does it work?) and its advantages and limitations

Split into 3 different groups

Each group will create a poster presentation of a different acid mine drainage remediation technique.

At the end of the practical sessions, the groups will present their posters to each other

In this final practical session you are going to split into 3 groups (of between 4 and 6 people per group, depending on the class size), and create poster presentations of different acid mine drainage techniques. At the end of this session, the groups will present their posters to the rest of the class.

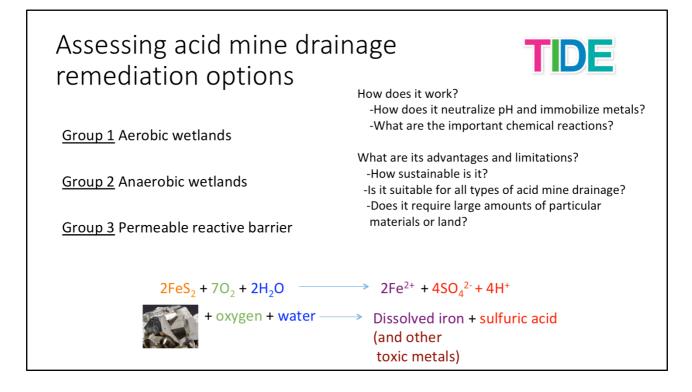


1 group will focus on aerobic wetlands, 1 group on anaerobic wetlands, and 1 group on permeable reactive barriers.

Focus on how these techniques work. Specifically the key chemical reactions involved and the conditions that control them. Also think about their advantages and disadvantages and suitability to acid mine drainage under different circumstances. To aid you with this task, each group will be given a printed copy of a review article on acid mine drainage remediation techniques

Tutor instruction: Hand out 1 piece of flip chart paper, different colour marker pens and printed copies of the paper by Johnson and Hallberg, 2005 to each group. Go around an point out the relevant section in the to each group, depending on the technique they are covering; section 4.2 for aerobic wetlands, section 4.3 for anaerobic wetlands section 4.5 for permeable reactive barriers. Recommend to all groups to read section 4.1.

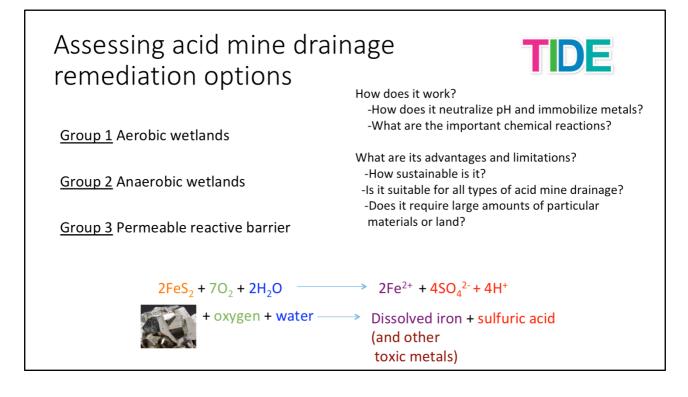
Allow ~ 30 minutes for the participants to make their posters and 15 to 20 minutes for presentations by the groups to the rest of the class. During the poster presentation stage interact with the different groups, and guide them with any questions they have. During the presentations encourage the other participants to ask questions to the presenting group so that the discussion is lead by the participants.



Key points for each poster presentation

Aerobic wetlands – recognize that Fe oxidation and Fe-oxyhyroxide precipitation are the key chemical reactions (mediated by microbes), and that they require oxygen rich and neutral pH conditions. Point out that this technique does not act to neutralize low pH drainage, and in fact is only effective for drainage with higher pH. This requires that the acid mine drainage is neutralized prior to entering the wetland, either due to dissolution of carbonate minerals in the rocks surrounding the site, or by construction of a limestone drainage channel. Wetlands – often require lots of land around mine area to construct.

Anaerobic wetlands – recognize that sulfate reduction and subsequent precipitation of metal sulfide minerals are the main chemical reactions, mediated by microbes. Requires very anoxic conditions with oxygen and other electron acceptors (nitrate, Fe3+, Mn4+) completely consumed, can be achieved by stagnant water layer (slows oxygen supply) overlying organic rich sediment (promotes consumption of electron acceptors). Reactions essentially reverse of acid mine drainage generation – sulfuric acid consumed (raises pH) and metals trapped as sulfide minerals. Wetlands – often require lots of land around mine area to construct.



Permeable reactive barriers – main chemical reactions are the dissolution of calcium carbonate minerals and the microbial decomposition of organic matter, using a variety of electron acceptors including sulfate. All these reactions act to neutral the pH of the mine drainage. In response this pH change causes the precipitation of dissolved metals into a variety of carbonate, hydroxide and sulfide minerals. Advantage over wetlands of requiring less land area. Challenge to remain sustainable over long time periods include the reduction of permeability due to mineral precipitation and the consumption of reactive material (carbonate minerals and organic matter) over time.