

# Acid and metalliferous drainage contaminant load prediction for operational or legacy mines at closure

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## Abstract

*Predicting the acid and metalliferous drainage (AMD) contribution from waste rock dumps (WRDs) containing potentially acid forming (PAF) material is a key step when planning for closure. For sites already demonstrating impacts from the generation and release of AMD, estimating final water quality and flow rates emanating from WRDs is key to quantifying the level of remediation and/or management required at closure. Predictions of final water quality need to be compared with regulatory limits for closure, stakeholder expectations and any anticipated treatment options (including treatment longevity and costs).*

*In the absence of WRD sample data collected from intrusive investigations, there are often numerous WRD seeps and impacted streams that can be used to determine typical water quality, solubility constraints, flow rates, contaminant loads and thus source terms for PAF WRD drainage. The preceding step critical to the determination of source terms is the development of a conceptual model that incorporates potential/stored acidity components, flow rates and water quality. The developed conceptual model can then be further refined and strengthened with geochemical modelling.*

*The potential acidity component, that is primarily associated with acid generating sulphides, is typically estimated from assay databases and materials placement records. Laboratory derived pyrite oxidation rates can be used to estimate the remaining potential acidity component as well as the formed stored acidity component. The mobilisation of stored acidity and other oxidation products is often constrained by solubility controls, particularly in older WRDs. These solubility controls are often associated with the formation and dissolution of melanterite-type soluble acidity, jarosite-type sparingly soluble acidity and other secondary phases such as gypsum. The determination of these mineral and/or the proportion of which they make up the estimated oxidised sulphur content allows for more accurate determination of the stored acidity component for source term derivation.*

*Geochemical testwork can then confirm the presence of such minerals, which is incorporated into an acid-base accounting modelling process and the determination of three key phases of closure water quality; (1) the draindown water quality phase; (2) the transition water quality phase; and, (3) the long-term water quality phase. During the WRD draindown phase, after cover system installation, the seepage quality can be assumed to be equal to the derived WRD source term with the duration of this phase determined by numerical modelling. Seepage quality for the transition phase is determined from the stored acidity (or metalliferous oxidation products), which also incorporates elemental loading. The long-term water quality can be determined by forward reaction path modelling or by using key mineral dissolution kinetics (first principal approach). Combining these three phases then produces a model for the prediction of long-term water quality after operations, which can be utilised for closure planning.*

*This paper presents a number of case studies that utilise the above methods for the prediction of site water quality at closure.*

# 1 Introduction

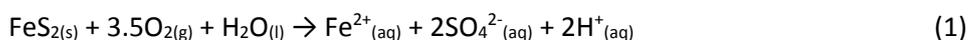
Acid and metalliferous drainage (AMD) is recognised internationally and within Australia as one of the most significant and difficult environmental issues facing mining operators and regulators (Egiebor & Oni 2007; Watkins 2007). A key reason for its importance is that AMD has the ability to cause significant ongoing pollution of the surrounding environment that could potentially persist for hundreds of years (Department of Mines and Petroleum & Environmental Protection Authority of Western Australia 2015). As such, AMD has been highlighted in recent mine closure guidelines by Western Australian regulators as one of the key environmental issues relevant to mine closure (Department of Mines and Petroleum & Environmental Protection Authority of Western Australia 2015).

Therefore, predicting AMD contaminant loads from existing waste rock dumps (WRDs) and tailings storage facilities (TSFs) containing potentially acid forming (PAF) material is a key step when planning for closure. In order to estimate potential AMD contaminant loads, it is important to first develop a conceptual model that describes how contaminant sources (potential/stored acidity), flow rates and drainage quality interact. The potential acidity component, that is primarily associated with acid generating sulphides, can be estimated from geochemical/assay databases and materials placements records. Laboratory derived pyrite oxidation rates can then be used to estimate the remaining potential acidity component as well as the formed stored acidity component. The mobilisation of stored acidity and other oxidation products is often constrained by solubility controls, particularly in older WRDs. These solubility controls are often associated with the formation and dissolution of melanterite-type soluble acidity, jarosite-type sparingly soluble acidity and other secondary phases such as gypsum (Weber et al. 2015). The determination of these mineral and/or the proportion of which they make up the estimated oxidised sulphur content allows for more accurate determination of the stored acidity component for source term derivation.

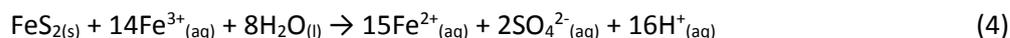
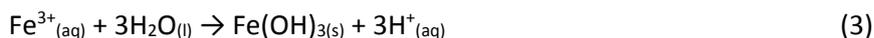
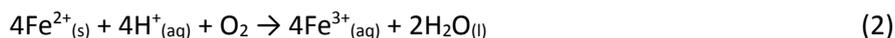
For sites already demonstrating impacts from the generation and release of AMD, estimating final water quality and flow rates emanating from WRDs is key to quantifying the level of remediation and/or management required at closure. Predictions of final water quality needs to be compared with regulatory limits for closure, stakeholder expectations and any anticipated treatment options (including treatment longevity and costs).

## 1.1 AMD fundamentals

Generally, acidic drainage is initially generated when pyrite ( $\text{FeS}_2$ ) (or other acid generating sulphides) is exposed to oxygen and water and becomes oxidised (Watkins 2007). Oxidation of pyrite produces sulphuric acid and ferrous iron ( $\text{Fe}^{2+}$ ) via Equation (1) (Sracek et al. 2004). Once the process begins, further acid can be generated via a number of alternative reaction mechanisms.



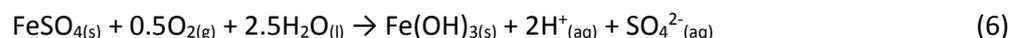
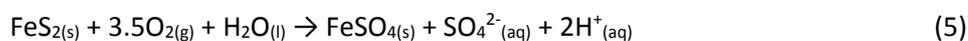
Ferrous iron can be oxidised to ferric iron ( $\text{Fe}^{3+}$ ) via Equation (2) which will produce acidity when ferric hydroxide is precipitated via Equation (3) (Egiebor & Oni 2007). If conditions exist for significant quantities of ferric iron to remain in solution, such as low pH and low oxygen, then ferric iron can oxidise pyrite as per Equation (4). Reactions 2 to 3 are highly dependent on environmental conditions such as pH, dissolved oxygen concentration, biological activity and solution chemistry (Lottermoser 2010).



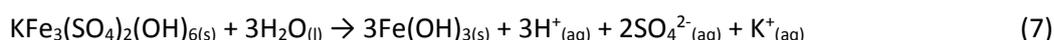
The oxidation of ferrous iron to ferric iron is important because ferric iron, as shown in Equation (4), in substitution for oxygen can act as the oxidising agent in the oxidation of pyrite (Lottermoser 2010). This substitution of oxygen for ferric iron not only indicates that the reaction can continue should conditions become anoxic, but significantly more acidity is generated per mole of pyrite (Lottermoser 2010). However, it should be noted that if there is no oxygen, then the  $\text{Fe}^{2+}$  cannot be oxidised to  $\text{Fe}^{3+}$  and the process is not

cyclic. As the rate of ferric iron production is mediated by acidophilic bacteria such as *Thiobacillus ferrooxidans*, the growth of these bacteria can significantly influence the severity of AMD effects observed at a mine site (Nordstrom & Southam 1997; Pugh et al. 1982).

If there is incomplete oxidation of the ferrous ( $\text{Fe}^{2+}$ ) iron to ferric ( $\text{Fe}^{3+}$ ) iron, ferrous salts such as melanterite ( $\text{FeSO}_4$ ) can form, which, following any subsequent wetting, can release the stored ferrous acidity (Equation (5) and Equation (6) respectively).

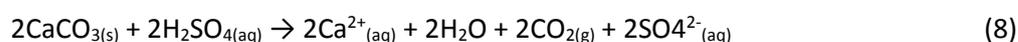


However, if oxidation to ferric ( $\text{Fe}^{3+}$ ) iron is complete yet the hydrolysis is incomplete, jarosite type secondary minerals can form. The dissolution of jarosite then releases the acidity, Equation (7).



Melanterite- and jarosite-type acidity can be referred to as the stored acidity component of a WRD or TSF.

The acidity generated by pyrite oxidation and acidic oxidation products can be neutralised by materials such as limestone ( $\text{CaCO}_3$ ), as shown in Equation (8).



Although AMD has traditionally been referred to as acid rock or acid mine drainage, it is now ever more recognised internationally, and in particular within Australia, that not all problematic drainage is associated with acidic drainage (Department of Industry Tourism and Resources 2007). Near-neutral but metalliferous drainage, as well as saline drainage, can be as complex to manage as acidic drainage (Department of Industry Tourism and Resources 2007).

Non-acidic metalliferous drainage can be generated if amphoteric metals such as aluminium, arsenic or zinc are released from geological materials as a result of the generation of acidic drainage. Amphoteric metals, which can have an increased mobility at higher pH levels, may remain in solution following the neutralisation of acidic drainage (Cheng et al. 2009). Saline drainage can also be generated from the neutralisation of acidic drainage resulting in a sulphate salinity issue (Department of Industry Tourism and Resources 2007). If magnesium carbonates are responsible for the neutralisation of acidic drainage then high salinity may result due to the high solubility of magnesium sulphate (Egiebor & Oni 2007).

## 1.2 Geochemical conceptual models

For many operational mine sites a key objective for closure planning is determination of water quality at closure and over the longer term associated with geochemical maturity of the site. WRDs and TSFs are typically important components to consider. These data need to be compared with regulatory limits for closure; stakeholder expectations; and be considered in regards to anticipated treatment options, treatment longevity, and treatment costs. Even for greenfield sites, given the nature of the resources industry, it is likely that mine plans will change during the operational phase from those originally permitted, resulting in modifications to the closure plan. Analysis of site-based empirical data (such as water quality monitoring databases) to derive water quality models for closure and beyond can assist in developing closure plans and management strategies.

For operational sites with AMD issues there are often numerous seeps and streams impacted by AMD, which can be used to determine typical water quality, solubility constraints, flow rates, and contaminant loads from their parent structures (e.g. the WRD, TSF etc.). This generally requires the development of a conceptual model for the catchment to determine source terms (water quality) from the various site components (WRD, TSF etc.), which are based on flow rates and water quality. Geochemical processes can then be incorporated into the model to determine long-term water quality trends.

This paper presents an approach that firstly defines and quantifies AMD sources and then outlines three general phases of closure water quality including the draindown water quality phase; the transition water

quality phase; and the long-term water quality phase. The process for estimating post-closure water quality is site specific. The quantity of flow rate and water quality data collected across a site also affects modelling methodologies.

## 2 AMD source definition and quantification

To predict final water quality for closure planning, a robust understanding of the contaminant sources identified by the geochemical conceptual model is required, such as potentially acid forming (PAF) materials within WRDs and TSFs. Although water quality of site seepages offer the best indication of current conditions, quantifying the stored and potential contaminant sources will allow validation of the developed conceptual model as well as enabling forward predictions (longevity) of site water quality for closure planning.

### 2.1 Potential and stored contaminants

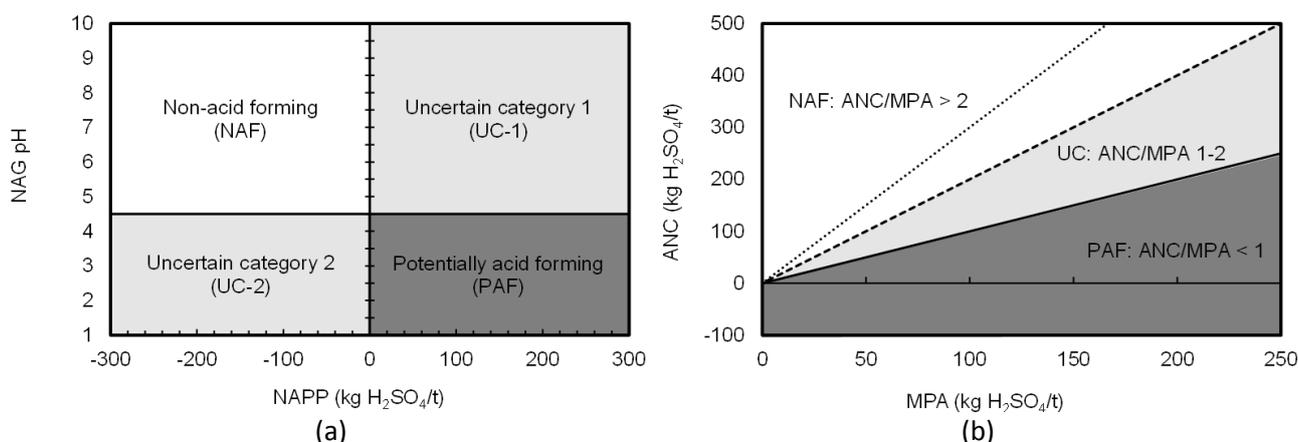
If accurate materials movement records have been maintained, the resource assay database can often be used to estimate the maximum potential acidity (MPA) of a WRD; should sulphur be contained in the database. The MPA is a measure of acid production and is a function of the sulphide content, making the assumption that the maximum acidity produced by a sample containing 1% sulphur, as pyrite, is 30.6 kg H<sub>2</sub>SO<sub>4</sub>/tonne. MPA can be calculated using sulphide data via Equation (9) (Price 2009), however, it is common for total sulphur to be used as a conservative alternative. Total sulphur is considered a conservative substitution in the absence of sulphide data due to the assumption that all sulphur measured is present as pyrite. This will over-estimate the potential acidity should non-acid generating sulphides and/or sulphates be present in the waste materials.

$$\text{MPA} = \text{sulphide sulphur (wt\%)} \times 30.6 \tag{9}$$

Acid neutralising capacity (ANC) determined by titration (Sobek 1978) can be determined in conjunction with MPA to determine the net acid production potential (NAPP) of a sample (AMIRA 2002). The NAPP is the difference between the ANC and the MPA, expressed in kg H<sub>2</sub>SO<sub>4</sub>/t equivalent (Equation (10)).

$$\text{NAPP} = \text{ANC} - \text{MPA} \tag{10}$$

The established approach to classifying mine waste rock is to use a simple combination of acid-base accounting (ABA) tests, such as ANC/MPA ratios or NAPP versus net acid generation (NAG) testing (Price 2009; AMIRA 2002). Depending on the classification system used (Figure 1), generally material is classified as either non-acid forming (NAF), PAF or Uncertain (e.g. Olds et al. 2015). These tests focus on the potential acidity component, which is often associated with unoxidised sulphides.



**Figure 1** The modified (a) AMIRA (2002) NAPP and NAG pH and (b) Price (2009) MPA and ANC (taken from Olds et al. 2015). (a) Classification as UC-1 is generally due to non-acid forming sulphur, iron carbonates, or insufficient hydrogen peroxide used in NAG testing. Classification as UC-2 is generally due to inorganic acid interference during NAG testing

As outlined above, estimations of NAPP is a routine process undertaken by industry. However, deriving the stored acidity component requires knowledge of oxidation rates (pyrite oxidation rate) or undertaking sampling and analysis of WRD materials, due to the oxidation of sulphide minerals.

Laboratory derived pyrite oxidation rates (PORs) can be applied to the known sulphur grades and PAF volume of the WRD being investigated to estimate the stored acidity component. This approach results in the WRD sulphur volume being assumed to be either present as pyrite (potential acidity) or present as acidic oxidation products (stored acidity). This method does not allow the distinction between non-acid generating sulphides, non-acid generating sulphates (e.g. gypsum), readily soluble acid generating sulphates (e.g. melanterite) or slightly soluble acid generating sulphates (e.g. jarosite).

Depending on the age of the WRD, an assumption on the quantity of oxidation products released as toe or basal seepage needs to be subtracted from the total stored component calculated. An allowance for acidity neutralisation could also be incorporated at this point depending on available ANC.

If WRD materials have been sampled, the opportunity to undertake a series of detailed testing to better characterise the stored acidity component, as well as clarifying the estimated potential acidity component by identifying non-acid generating sulphides is possible. Such tests include mineralogical assessments, NAG testing, and acidic salts analysis. NAG testing can refine the potential component through comparison of the NAG acidity and the NAPP (NAG/NAPP ratio). Assuming sufficient oxidant had been added during the NAG test to completely oxidise the sample, low  $NAG_{4.5}/NAPP$  ratios (0.1–0.8) typically indicate the presence of non-acidic sulphur minerals or the presence of other acid generating sulphur minerals that do not produce the acid quantity equivalent to pyrite oxidation (e.g. jarosite) (Weber 2003).

Understanding the proportion of stored and potential contaminants, as presented in Figure 2, is a key aspect of understanding the longevity of AMD impacted waters at closure, in the longer term, and also for treatment of AMD. Exclusion of oxygen ingress will mostly prevent the ongoing oxidation of sulphide minerals (potential contaminants) and therefore reduce the production of acid and metalliferous oxidation products. Stored acidity and metalliferous oxidation products create the reservoir of contaminants that lead to poor water quality. Exclusion of water, the transport medium, will prevent the dissolution, mobilisation and subsequent release of these stored contaminants as toe or basal seepage.

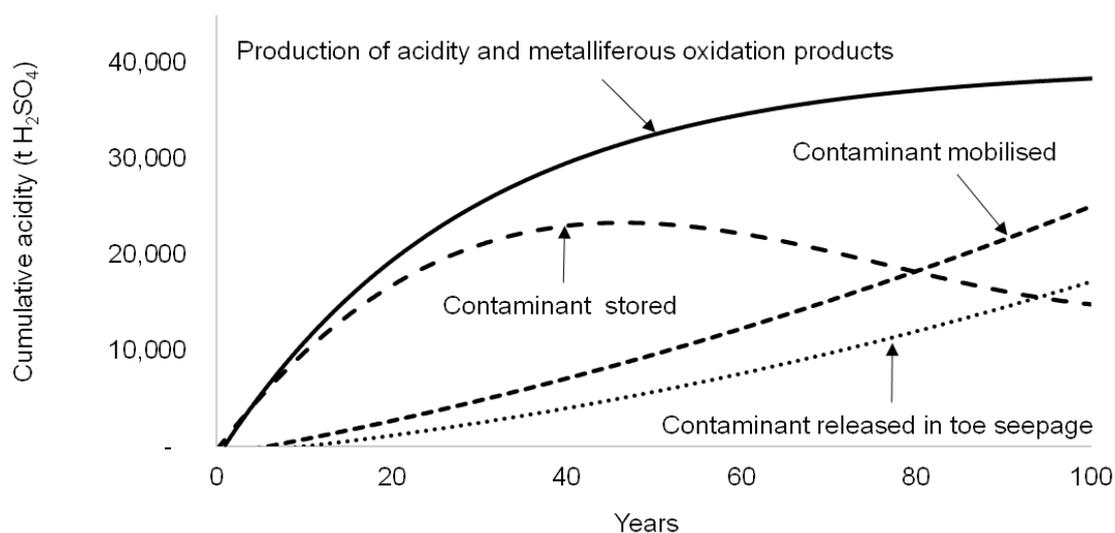


Figure 2 Predicted contaminant generation, storage and mobilisation based on detailed waste rock characterisation, seepage modelling and measured toe seepage quality

## 2.2 Refining stored contaminant component

For operating mine sites, legacy sites, or sites with substantial oxidised/weathered overburden, additional tests that target stored acidic/metalliferous oxidation products should be undertaken (Weber et al. 2015).

These tests include quantification of the soluble stored acidity/metals and sparingly soluble acidity/metals (e.g. Ahern et al. 2004). Quantitative mineralogical assessments can provide valuable information on both stored and potential acidity components of samples tested. Key geochemical indicators of stored acidity from conventional ABA testing is low paste pH values < 5.5, negative ANC values, high salinity (e.g. as measured by EC), and the observation of secondary minerals in laboratory tests.

### 2.2.1 Acid salt analysis

Titrateable actual acidity (TAA) data are derived from titration of the 1M KCl digest and represents the readily soluble (available) acidity that can be flushed out as a function of net percolation (Ahern et al. 2004). Readily available soluble acidity includes acidity contributed from free H<sup>+</sup> ions, exchangeable H<sup>+</sup> ions and acidity from soluble acidic sulphate salts such as melanterite (FeSO<sub>4</sub>.7H<sub>2</sub>O). The sulphur data obtained from the 1M KCl extraction (S<sub>KCl</sub>) may not all be acid forming salts and may include gypsum, epsomite, barite etc. and thus it is better to use the TAA data to determine readily soluble acidity. Comparison with x-ray diffraction (XRD) data can then provide clarification to the proportion of acid and non-acid generating sulphates.

The acid soluble acidity is the retained acidity that is sparingly soluble and its dissolution is kinetically controlled. Acidity generated from the dissolution of minerals such as jarosite and alunite contribute to the acid soluble acidity fraction. Therefore, stored acidity is equal to the sum of readily soluble acidity (TAA) and acid soluble acidity determined from sulphate analysis (S<sub>HCl</sub> - S<sub>KCl</sub>).

### 2.2.2 Mineralogy

Detailed mineralogical analysis can help further partition the various sulphur phases that are key to defining potential and stored contaminant sources. Sulphur minerals can be separated into five key groups: (1) acid generating sulphides (e.g. pyrite); (2) non-acid generating sulphides, yet acidity and metal generating (e.g. sphalerite); (3) readily soluble acid generating sulphates (e.g. melanterite); (4) slightly soluble acid generating sulphates (e.g. jarosite); and (5) non-acid generating sulphates (e.g. gypsum). Figure 3 incorporates measured non-acid generating gypsum and anhydrite for stored acidity estimations resulting in an overall reduction in the size of the reservoir when compared to estimations from the simplistic assay/POR method.

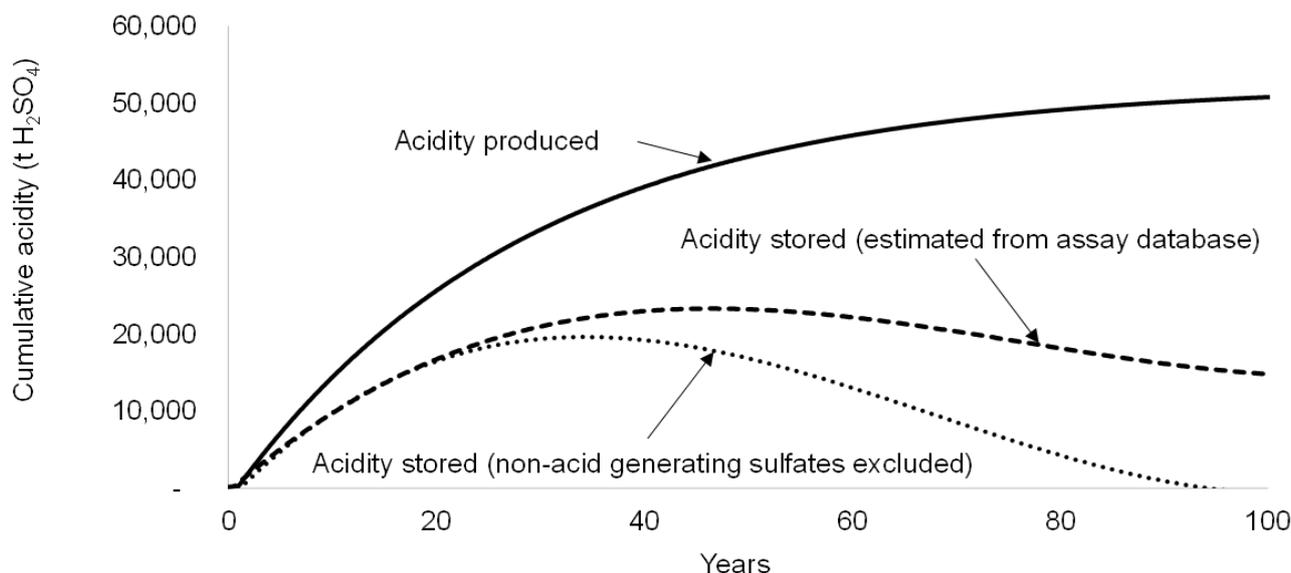


Figure 3 Application of mineralogy results, specifically non-acid generating sulphates, to the stored acidity estimations reduces the stored contaminant reservoir

### 3 Closure water quality phases

Quantified contaminant sources need to be coupled with seepage rates for each of the waste landforms investigated for water quality predictions to be made. In addition to solid phase analyses, water quality from WRD seeps and/or impacted streams can be incorporated into the modelling process to define the three key phases of closure water quality (Figure 4) (Weber et al. 2015):

1. Draindown water quality phase.
2. Transition water quality phase.
3. Long-term water quality phase.

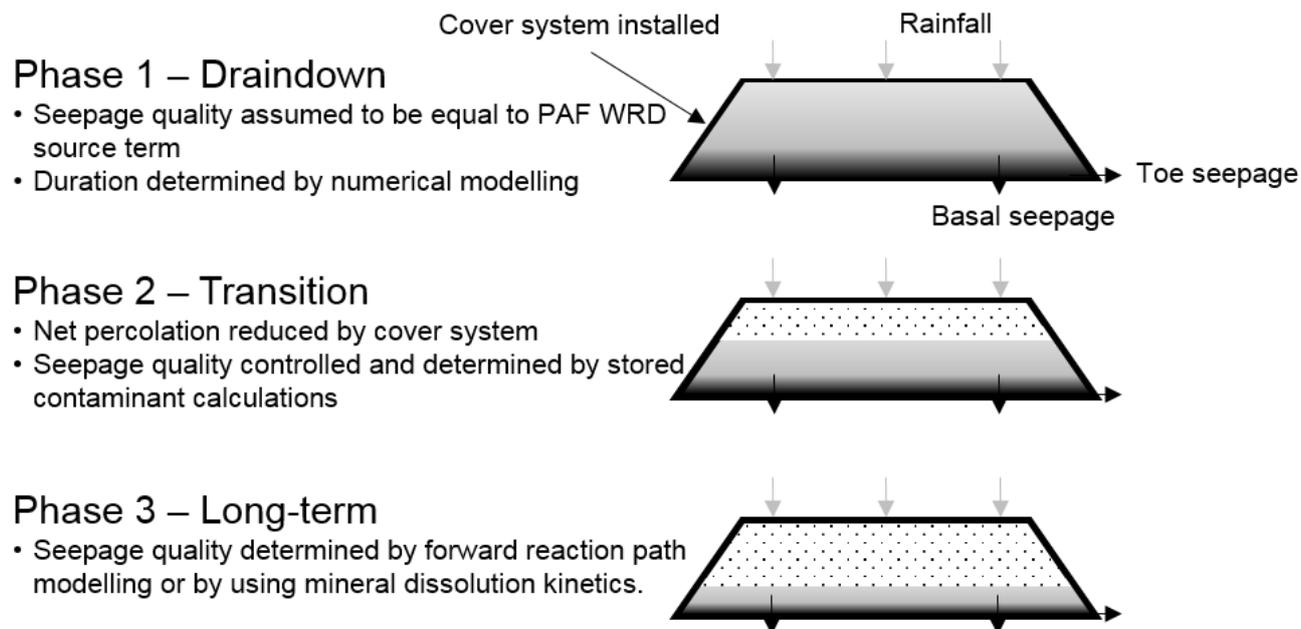


Figure 4 The three key phases of closure water quality

#### 3.1 Phase 1: Draindown

Draindown occurs as a function of a change from a higher permeability dump surface to a lower permeability surface after cover installation as the system equilibrates to the new net percolation rate. Water quality measured at mine closure is expected to represent this first draindown phase, although there may be small changes in flow regimes. Therefore, site flow rates and water quality monitoring databases in the years preceding closure are used to derive source terms for modelling the draindown period. In many instances, a waterway, or seep, will be the product of a number of water source types such as groundwater, clean surface waters, and AMD point sources (underground workings, TSFs and WRDs). To determine the water quality from a discrete component of a mixed water system (that cannot be measured directly) requires inverse geochemical modelling using the conceptual model as the blue print.

##### 3.1.1 Draindown analysis

Numerical modelling programs (e.g. SEEP/W) are used to determine the duration of the draindown phase and net percolation rates. Draindown duration may be affected by changes in the water table, for instance, due to restoration of streams or pit lake flooding. The modelled flow regimes at the end of the draindown period are generally expected to remain constant over the long term, i.e. the site is hydrologically stable at the end of the draindown period.

### 3.1.2 Inverse geochemical modelling

Inverse geochemical modelling is completed in a systematic process and aims to provide the water quality (source term) for the component of interest (e.g. the WRD) that was identified as missing from a geochemical conceptual model. This process essentially fills data gaps in site monitoring databases or models that would otherwise be managed using assumptions or simplification. The steps involved with inverse geochemical modelling are presented in Table 1.

Often the derived source terms are considered constant for modelling purposes during the draindown phase. A constant concentration assumption can be validated by analysis of flow rate variability from the component (WRD or TSF) and water quality.

**Table 1** Inverse geochemical modelling steps

Step	Description
1	<i>Flow rates</i> : Based on measured or calculated values, assign flows to all components of the conceptual model based on measured or calculated values.
2	<i>Water quality</i> : Based on measured or calculated values, allocate water quality to all components of the conceptual model based on measured or calculated values.
3	<i>Loads</i> : Calculate contaminant loads for each component and then allocate remaining load to missing component by inverse calculation. Produce water quality.
4	<i>Geochemical modelling</i> : Complete geochemical modelling of the derived water quality to estimate likely solubility constraints and create a balanced water type. Validate model outputs by comparing to available mineralogical data and determine the final source term for the WRD.

## 3.2 Phase 2: Transition

The transition period is defined as the time it takes for the waste landform (WRD/TSF) to reach geochemical maturity. The stored contaminant reservoir and the mobilisation of its acidity and metalliferous oxidation products controls the contaminant loads observed during this phase. Understanding the proportions of stored versus potential contaminants, as detailed in Section 2, is critical for the prediction of the persistence of AMD impacted waters in the medium and longer term. Should oxygen ingress not be effectively mitigated by the implementation of a cover system prior to mine closure, the reservoir of stored acidity can continue to be replenished as acid generating sulphides oxidise. Therefore, both potential and stored components require consideration in modelling for this phase.

The stored and potential contaminant distribution will dictate closure AMD management strategies. For instance, components with significant concentrations of soluble stored oxidation products, such as melanterite etc., would be best managed by limiting net percolation to reduce loads to the receiving environment.

### 3.2.2 Flow dominated contaminant loads

Often WRD or TSF drainage water quality is solubility controlled, particularly for an older WRD or TSF where water quality is associated with the formation of stored oxidation products including melanterite-type soluble acidity; jarosite-type sparingly soluble acidity; and other secondary phases such as gypsum and metal salts. The solubility limits control the rate that stored acidity, and metalliferous oxidation products are mobilised from the waste landform, the solubility limits therefore define the duration of the transition water quality phase, thus increasing flow through these systems increases contaminant loads.

Solubility controlled systems are easily identified by assessment of flow rate versus contaminant load. A solubility controlled system will typically have an increasing contaminant load with increasing flow rate, which means that with more flow (i.e. net percolation) there are more stored oxidation products flushed

from the system. Solubility controlled systems are observed at both acid-forming sites and non-acid forming metalliferous drainage sites.

Figure 5 (taken from Weber et al. 2015) presents examples of solubility controlled systems. Fanny Creek (Figures 5 (a) and (b) from Mackenzie 2010) drains a side-cast open coal operation (Island Block Coal Mine). There is generally a constant acidity concentration with increasing flow, which equates to an increasing acidity load with flow rate. This confirms that the acidity load to the receiving environment is constrained by net percolation through the waste rock dump. Acidity load could therefore be reduced by minimising net percolation.

Figures 5 (c) and (d) present data collected for the St Patrick's Stream, Stockton Coal Mine. The dataset also demonstrates an increasing acidity load with increasing flow rate (Figure 5 (d)). It is interesting to note the logarithmic nature of concentration (mg/L) in the stream (Figure 5 (c)), with the acidity concentration decreasing with increasing flow rate. This is likely to be a function of increasing uncontaminated surface runoff associated with increasing rainfall during any storm event (Weber et al. 2015). Inverse geochemical modelling of components upstream of the St Patrick's Stream may identify the source of the contaminant load. If the source is a seep it is likely to have a linear acidity load to flow rate correlation.

Underdrains were installed to collect toe and basal seepage that has passed through the Devil's WRD and the Fossickers TSF at the Globe-Progress Gold Mine. Results presented in Figure 5 (f) present a strong correlation between contaminant load and flow rate. In this example, sulphate concentrations are reasonably constant for each component (Figure 5 (e)) and each site appears to have a relatively constant flow rate, although the Devils WRD has the greatest range in flow (2–3 orders of magnitude). Analysis of flow rate versus sulphate load for all these structures provides a robust correlation, which becomes an excellent tool for subsequent analysis and closure planning.

Evidence of a solubility controlled systems is supported by the strong correlations presented in Figure 5, which also provide confidence in the data for each component. The results indicate contaminant loading is a function of net percolation, which is likely to persist until the stored acid and metalliferous oxidation products have been flushed from the system. The datasets presented in Figure 5 also support the derivation of source terms from seepage water quality and flow monitoring data using inverse geochemical modelling. For example, concentration data shown for Globe Progress Mine underdrains can be used to provide a robust source term based on median or average data for WRD and TSF seepage water quality.

The longevity of poor water quality in the transition phase is often unknown unless the mine site has completed the initial conceptual geochemical modelling and AMD source quantification steps, equating to a detailed understanding of the site hydrology, mineralogy and waste rock bulk characteristics. By adopting the derived source term for WRD or TSF seepage water quality (as validated by assessment of load versus flow rates) and then forecasting future flow rates through the structure (using modelled or measured net percolation rates), a transition phase water quality model can be created.

As the system approaches completion of the transition phase and achievement of the long-term quality, the solubility controlled water quality condition will likely change to a more geochemically stable water quality condition. This will likely coincide at the time that contaminant generation equals contaminant release, that is, when the stored contaminant reservoir is depleted. For this to occur the concentration of contaminants in seepage must decrease as the waste landform achieves geochemical maturity.

In theory, the transition phase may be by-passed if there is minimal accumulation of stored contaminants. This scenario is likely to eventuate if at the end of the draindown period the contaminant load is controlled by oxygen flux and, therefore, oxidation of acid generating sulphides. For that reason, the site may proceed straight to the long-term water quality phase associated with geochemical maturity of the site.

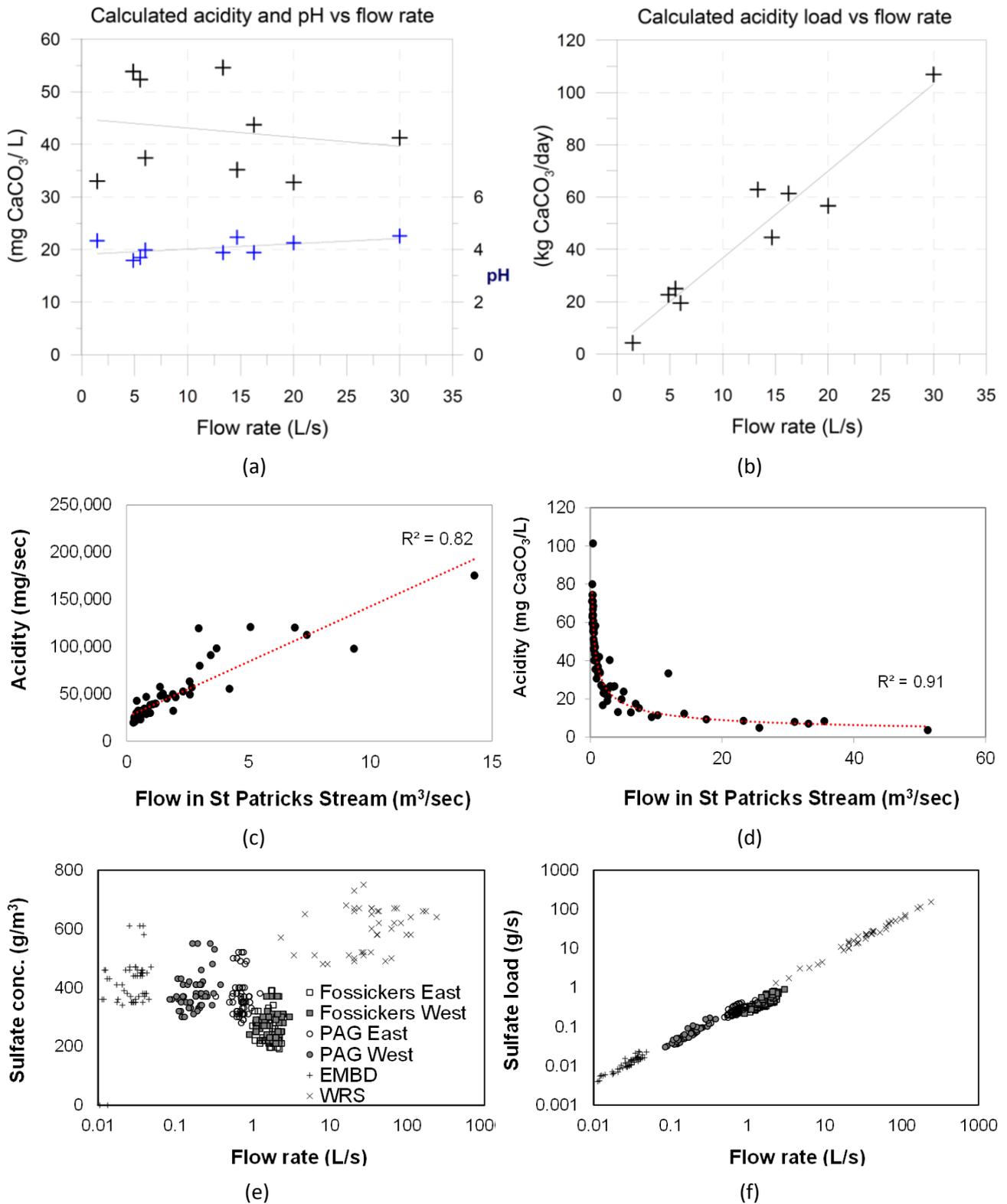


Figure 5 Examples of solubility controlled systems (taken from Weber et al. 2015). (a) and (b) are data sets from Fanny Creek, Island Block Coal Mine, Stockton: (a) acidity concentration and (b) acidity load versus flow (Mackenzie 2010). (c) and (d) are data sets from St Patrick's Stream, Stockton: (c) acidity concentrations and (d) acidity loads versus flow. (e) and (f) are data sets from the Globe Progress Gold Mine: (e) sulphate concentration and (f) sulphate load versus flow

### 3.3 Phase 3: Long-term

For the purposes of this paper the long-term water quality is defined as the point in time when the system achieves geochemical maturity. This is characterised by stabilised oxygen ingress rates and with the production of contaminant almost equalling contaminants released, that is, depletion of the contaminant reservoir. Long-term water quality can be determined by forward reaction path modelling or by a first-principles approach using key mineral dissolution kinetics.

Geochemical modelling software can be used where key reactive mineralogy is included in the model with dissolution and/or oxidation rates allocated from peer reviewed literature. Geochemical modelling should consider aspects such as oxygen flux, net percolation, all the findings from the AMD source definition and quantification stage, carbonate minerals, and reactive silicate minerals.

A first principles approach can also be undertaken to estimate long-term water quality. For AMD sites where the oxygen flux is the key driver to poor water quality, a numerical calculation can be undertaken to determine oxygen flux. This allows assessment of pyrite oxidation rates and subsequent contaminant generation. Contaminant loads can then be compared against the environmental geochemical database (mineralogy, ABA data etc.) to estimate key water quality parameters.

These modelling processes also allow the quantification of minerals that can be difficult analytically to determine (e.g. soluble secondary oxidation products). These problematic minerals can be managed by simple numerical analysis as part of the long-term water model (e.g. Ahern et al. 2004). Sparingly-soluble minerals such as alunite and jarosite can also be included in the geochemical model to determine effects on the long-term water quality.

## 4 Simplistic long-term water quality model example

The following section provides an example for how a simplistic long-term water quality model can be developed, based on an understanding of the potential and stored acidity load; drainage water quality and flow rates, and long-term water quality forecasts after geochemical maturity.

For the purpose of providing a simplistic example, the water quality only considers Fe, Al, and pH, which are considered, in this example, as the main constituents of acidity load. Trace metals and other dissolved contaminants have not been considered, but could be incorporated in a similar manner. The same process can be applied to a metalliferous drainage site.

### 4.1 Model inputs

Site A has a 5 Mt WRD with a mean MPA value of 30 kg H<sub>2</sub>SO<sub>4</sub>/t based on total sulphur content (Equation (9)). Potential acidity is represented by MPA and is based on a sulphide sulphur content of 24 kg H<sub>2</sub>SO<sub>4</sub>/t. Soluble stored acidity (melanterite-type acidity) is represented by the difference between the total sulphur and sulphide sulphur derived MPA values (6 kg H<sub>2</sub>SO<sub>4</sub>/t). This means that there are 120,000 tonnes of potential acidity (as H<sub>2</sub>SO<sub>4</sub> equivalent) and 30,000 tonnes of stored acidity (as H<sub>2</sub>SO<sub>4</sub> equivalent) within the WRD. Such data would be reasonable for a waste rock having fine grained reactive pyrite and no ANC. Table 2 presents key summary data.

This example WRD has a significant quantity of unreacted potential acidity, therefore the site should plan to restrict oxygen ingress to prevent ongoing pyrite oxidation. In the absence of reconstruction of the WRD and applying tight waste placement controls, limiting oxygen ingress to reduce acidity generation in the longer term can be achieved by installing a cover system. However, acidity will continue to report to the receiving environment as a function of net percolation as the stored contaminant reservoir is depleted. For this example, following installation of the cover system, it is expected that the net percolation will reduce from 40 L/s to 30 L/s. It is also assumed that the installation of the cover system will reduce oxygen ingress to an insignificant flux rate ( $\approx 0$  kg O<sub>2</sub>/m<sup>2</sup>/sec).

Table 2 Acid base accounting data for the Site A WRD

Parameter	Units	Quantity
Waste rock	tonnes	5,000,000
Total sulphur	wt%	1
MPA (based on total sulphur)	kg H <sub>2</sub> SO <sub>4</sub> /t	30
MPA (based on sulphide sulphur)	kg H <sub>2</sub> SO <sub>4</sub> /t	24
ANC	kg H <sub>2</sub> SO <sub>4</sub> /t	0
Stored soluble acidity	kg H <sub>2</sub> SO <sub>4</sub> /t	6
Total potential acidity	tonnes	120,000
Total stored acidity	tonnes	30,000

#### 4.1.1 Draindown phase

Numerical modelling programs (e.g. SEEP/W) are typically used to determine the duration of the draindown phase and net percolation rates. For this example a draindown period of 20 years was modelled. At mine closure water quality is poor with the following water quality parameters; Fe = 50 mg/L, Al = 25 mg/L, pH = 2.5, and acidity = 430 mg/L H<sub>2</sub>SO<sub>4</sub>. Based on a flow rate of 40 L/s, this equates to an annual acidity load of ≈ 550 t H<sub>2</sub>SO<sub>4</sub>/yr. For modelling purposes it is assumed that this acidity load will remain for almost the entire draindown phase. The cover system was assumed to completely eliminate oxygen flux meaning no additional acidity is generated, therefore the entire acidity load represents depletion of the stored contaminant reservoir.

#### 4.1.2 Long-term water quality phase

The long-term water quality is assumed to have a pH of 5.5 and an acidity < 1 mg H<sub>2</sub>SO<sub>4</sub>/L. Thus, the concentration of Lewis acids (Fe and Al) will be low. In practise, geochemical modelling to derive actual long-term water quality would use calculated oxygen flux rates, mineralogy etc., but has not been done for this example.

#### 4.1.3 Transition phase

No model can remove more contaminant load than is present within the WRD or TSF contaminant reservoir (acid and metalliferous oxidation products). Such oxidation products have to be present to be mobilised and transported by net percolation. Furthermore, it is generally expected that not all these oxidation products will be removed from the WRD or TSF due to the solubility and heterogeneous flow effects through the landform. Generally 20–40% of contaminants might not report in the transition phase but rather be released within toe and basal seepage over the very long term such that their contribution to seepage quality is negligible.

In this example there are 30,000 tonnes of stored acidity (as H<sub>2</sub>SO<sub>4</sub> equivalent); of this only 23,000 tonnes (as H<sub>2</sub>SO<sub>4</sub>) will be removed by net percolation during the transition phase (≈ 75%). This means approximately 25% of the stored contaminants are considered immobile. The model is thus constrained to a reservoir of 23,000 tonnes of contaminant (as H<sub>2</sub>SO<sub>4</sub> equivalent). Furthermore, the maximum annual acid load the model can remove is 550 t H<sub>2</sub>SO<sub>4</sub>/yr, due to the closure acidity concentration of 430 mg H<sub>2</sub>SO<sub>4</sub>/L equivalent.

Artificial modelling effects need to be considered when applying constant concentrations for contaminant load release. Forecasting a model using a constant acidity yield of 550 t H<sub>2</sub>SO<sub>4</sub>/yr would see a step-change in acidity load at approximately 40 years after closure and a step-change in concentration from 430 to 0 mg H<sub>2</sub>SO<sub>4</sub>/L following total depletion of the stored contaminant reservoir. Such dramatic changes are not natural, and thus this is not a reasonable model. However, it does provide a minimum time frame for the model.

A gradual improvement rather than step-change in water quality during the transition phase is more realistic. This will be a function of flow path variability, flow path flushing, and a decreasing quantity of acidic salts

being dissolved during the transition phase. Decreases in acidity have been reported as being up to 3.3% per year over a 30+ year period for underground coal mines (Mack et al. 2010) and such models could be applied to WRDs and TSFs. However, for this example, this would also result in a step-change in acidity load at approximately 60 years from  $\approx 130$  to 0 mg  $\text{H}_2\text{SO}_4/\text{L}$  as the contaminant reservoir is depleted. This is also not indicative of a natural system.

## 4.2 Example summary

A simple model was created using the data from Table 2 to provide a graphical summary for the Site A example using a reasonable decrease in acidity and consideration of basic geochemical principles, such as hydrolysis reactions. Figure 6 shows the three key phases of long-term water quality after closure. The draindown phase lasts for 20 years, which is followed by a transition phase of 70 years. The long-term phase commences when pH reaches 5.5 and acidity of less than 1 mg  $\text{CaCO}_3/\text{L}$  is achieved.

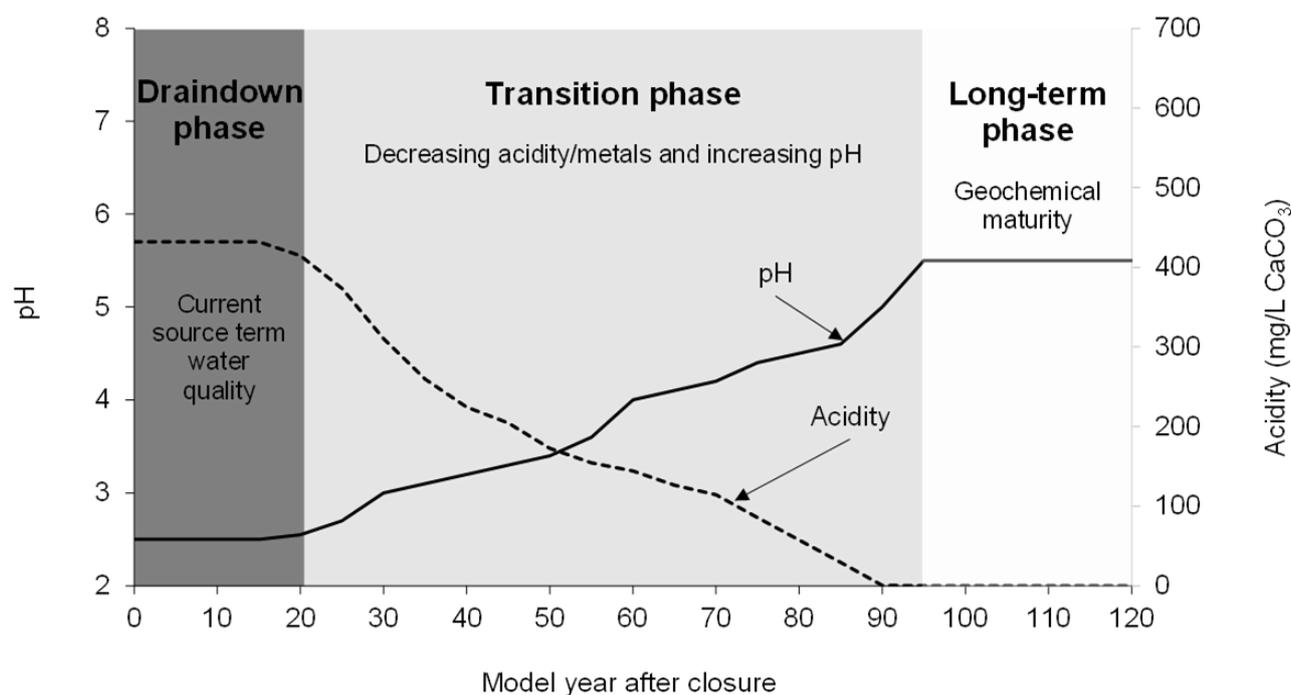


Figure 6 Example long-term water quality model. Model commences at closure after cover installation (taken from Weber et al. 2015)

## 5 Conclusion

This paper has presented a stepwise method to quantify and predict water quality at closure based on acid-base accounting principles used to determine potential and stored acidity. Initially a conceptual geochemical model is developed to determine source terms (water quality) from the various site components (WRD, TSF etc.). The second step is to define and quantify contaminant sources, such as WRDs containing PAF materials. Finally, water quality modelling can be undertaken to assess the three stages of closure water quality; the draindown, transition and long-term water quality phases.

There are many industry accepted geochemical modelling methods to predict long-term water quality. The method presented in this paper provides a simple approach that is reasonable given the many uncertainties in forecasting long-term water trends for mine sites after closure.

As shown by examples presented in this paper, the mobilisation and release of stored contaminants (acid and metalliferous oxidation products) from the landform to the surrounding environment are often a function of flow rate (net percolation). In a solubility controlled system it is reasonable to assume that current water quality will persist until the end of the draindown phase. Following that a dilution effect will occur as

the remaining stored contaminant reservoir is depleted and clean water pathways increase in proportion. At the end of this transition phase, contaminant loads will have stabilised and remain constant over the long term water quality phase. Commencement of the long-term water quality phase represents the depletion of the contaminant reservoir with contaminant generation equalling contaminant release from the landform.

Model predictions assist mining operators to determine if, and what, water treatment options are required at closure and for how long. This allows the operator to forecast contaminant loads post-closure and estimates the time to transition from an active to passive treatment system. Such data is invaluable for net present analysis of closure options.

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