



# Guidance for the Integrated Use of Hydrological, Geochemical, and Isotopic Tools in Mining Operations

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## Abstract

This paper summarizes international state-of-the-art applications and opportunities for employing and deploying hydrological, geochemical, and isotopic tools in an integrated manner for investigations of mining operations. It is intended to aid formulation of more integrated approaches for evaluating the overall sustainability of mining projects. The focus is particularly on mine waters, including: environmental water sources, mine water dynamics, and as a source and vector for pollution in the wider environment. The guidance is generic to mining projects and not just reflective of a particular extraction (e.g. coal, metalliferous, uranium) industry. A mine life cycle perspective has been adopted to highlight the potential for more integrated investigations at each stage of a mining operation. Three types of mines have been considered: new (i.e. those in the planning stage), active (i.e. working mines), and historical mines (i.e. inactive and abandoned mines). The practical usage of geochemical analyses and isotopic studies described here emphasise characterisation, dynamics, and process understanding for water quality considerations in tandem with water resource and environmental impact implications. Both environmental (i.e. ambient) and applied (i.e. injected) tracers are considered. This guide is written for scientists (including isotope specialists) who have limited or no mine water experience, environmental managers, planners, consultants, and regulators with key interests in planned, active, and legacy mining projects.

**Keywords** Mine water management · Isotope studies · Site investigation

## Introduction

Our primary objective with this paper is to provide relevant information on integrating hydrological/hydraulic, hydro-geochemical, and isotopic tools regarding characterization, monitoring, and remediation of metal and coal mine sites. This paper was initiated by the IAEA Vienna based on a need by member states to understand ground- and mine water issues and the use of isotope tools for the identification of environmental problems related to mine sites. It is not meant for an experienced mine water researcher, but for someone who needs to know the basics of mine water

so that they can then employ the appropriate specialists. It is, therefore, written for scientists, environmental managers on mine sites, consultants, and regulators who wish to answer questions with tools other than mine water statistics, thermodynamics, and numerical modelling. Given that it is intended for such a broad audience with various areas of expertise, we anticipate that some sections, though needed by some readers, will be too basic for others; feel free to skip over such sections. For example, based on our experience, not all isotope specialists know the basics of mine water genesis; therefore, this guide gives a short summary introduction to the topic, which we will refer to as mine water, ARD (acid rock drainage), AMD (acid mine drainage), or mine leachate—depending on the context.

Some sections of this paper have been adapted from previous publications of the authors with the permission of the copyright holders. As this paper briefly summarizes mine water geochemistry, mine water sampling, and the interpretation of the results in conjunction with isotope studies, and

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since this information has not been placed before in this strategic integrated context, the authors thought that readers might benefit from this compilation. Thus, this section is based on a publication by Wolkersdorfer (2008) where more detailed references can be found. The first four paragraphs of the Water Treatment section are based on CSIRO and Prosser (2011). The Natural and Artificial Mine Water Tracer Tests section is largely based on Wolkersdorfer (2006) where specific additional details can be found. Using quotation marks would possibly have distracted from reading these sections.

Using the ‘mine life cycle’ as an overarching concept, we have attempted to integrate environmental planning considerations with mine planning, operation, closure, remediation, and post-closure monitoring (Fig. 1). For each stage, it is important to know how the tools have been employed or potentially might be deployed to enhance knowledge and understanding of system processes and effects. Three types of mines are addressed: new mines (in the planning stage), active (i.e. working) mines, and historical (not currently active or abandoned) mines. Although new mines are generally larger and more complex than older or historical mines, the effluent quality from old mines is often much worse and of greater environmental concern than that from new ones.

Major environmental concerns at mine sites include effects on terrestrial and aquatic ecosystems as well as human health; however, this guide particularly emphasises the aquatic environments because of the importance of water as a resource both to stakeholders directly and in terms of ecosystem services, as well as its role as a vector for pollutant transport. Mine water should be recycled as much as possible on site and then treated before discharging offsite. Related concerns, which are however not covered in this

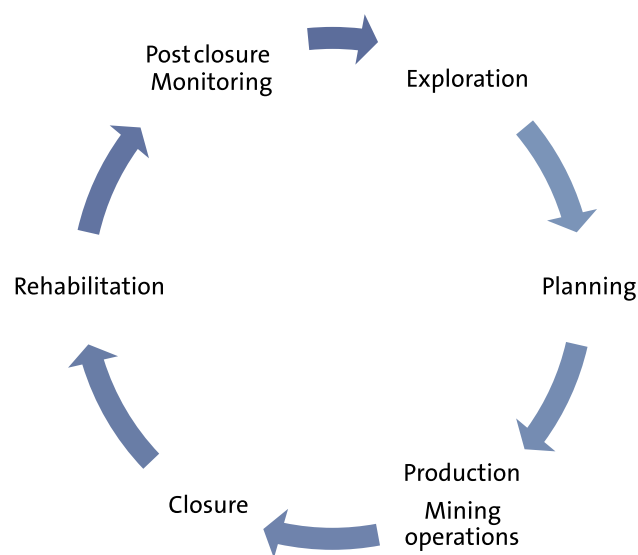


Fig. 1 The mine life cycle

guide, are the socio-economic interactions with local communities and stakeholders.

We structured and compiled this guidance paper around the mine life cycle and the natural and built environment composing the mine site (Fig. 2 represents this guide’s structure). This resulted in the chapters spatially belonging to either the natural or built environment or to both and temporarily to one of the six mine life cycle states we used.

### How to Consult the Literature

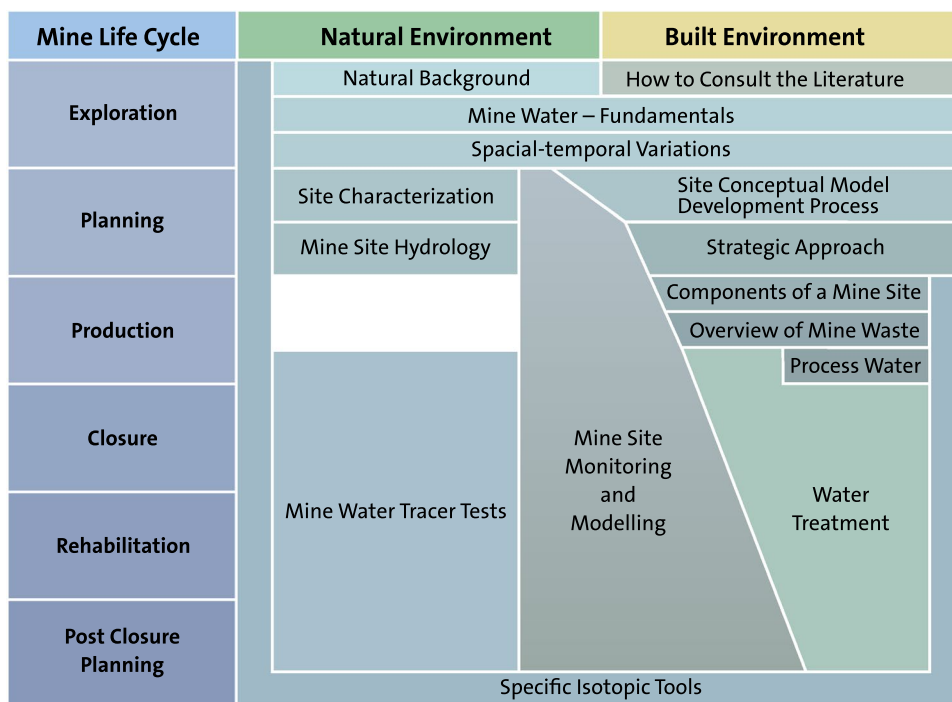
The sustainability of a mining project, especially prefeasibility and feasibility studies, but also for closure or remediation projects, should be supported by an extensive and detailed literature survey that provides different types and levels of information. Such a survey should identify relevant environmental compartments and their interactions, as well as potential harmful effects, human health, and ecological risks, and ensure legal compliance. A synthesis of the collected information will support the design of a conceptual model for the site.

A baseline situation regarding previous activities, mining, and environmental contexts should be established. More specifically, the literature survey must comprise studies about the type of mineral deposit and its main characteristics because these are the source material for potential contamination by mine wastes and mine water. Hence, the structure, paragenesis, geochemistry, mineralogy, and permeability of the ore deposit are critical aspects to be compiled and summarized. Similarly, compiling information at local and regional levels is necessary, covering:

1. Geological setting, including structural aspects, geomorphology, lithology, and mineralogy
2. Hydrology, including surface (type, flow and configuration of river network) and subsurface water, and hydrogeology (static and dynamic studies)
3. Hydrochemistry, comprising water type or chemical facies (major ions), potentially toxic minor and trace element concentration, and general water quality (set against local or international regulations or stakeholders)
4. Climate and meteorology, mainly precipitation (annual average, frequency, and intensity), temperature, evaporation, winds (direction, intensity, frequency) and solar irradiation.

This survey should address the water balance and other topics that will allow a more complete characterization of the area that will be influenced by the project, namely: soil, with respect to genesis and evolution, physical and chemical properties, ecology, soil fitness, air quality, biodiversity,

**Fig. 2** Structure of this paper and its relationship to the mine life cycle as well as the natural and built environment



biomes, and ecosystems. In addition, the problem definition should consider stakeholders, including socio-economic and cultural aspects in the global characterization of the site. For instance, from a holistic perspective, remediation and monitoring procedures and the value of water depend on its potential for consumption.

The above information can be obtained from geological, thematic maps and photo-geology or satellite databases as well as land-use plans and air and water quality surveys. In addition, the following sources should be considered:

1. Laws and regulatory frameworks
2. Technical reports
3. Historical mine records in geological services or mine administration
4. Review of historical aerial photographs and maps
5. Academic studies: thesis, papers, books
6. International guidelines and recommendations (institutions or agencies, organizations related to water management in mining activities).

### Mine water relevant, non-crawling-based databases (📖) and literature repositories (📚) that should be used are

- 📖 Web of Science: [WebOfKnowledge.com](http://WebOfKnowledge.com) (Clarivate 'Science Citation Index')
- 📚 Proquest: [www.Proquest.com](http://www.Proquest.com)

- 📖 SciFinder: [SciFinder.cas.org](http://SciFinder.cas.org) (CAS, Chemical Abstracts Service)
- 📖 EBSCOhost: [www.EBSCOhost.com](http://www.EBSCOhost.com)
- 📖 GeoRef: [www.americangeosciences.org/georef](http://www.americangeosciences.org/georef)
- 📖 ScienceDirect: [www.sciencedirect.com](http://www.sciencedirect.com) (Elsevier)
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- 📖 TandFOnline: [www.tandfonline.com](http://www.tandfonline.com) (Taylor & Francis)
- 📖 ACS Publications: [pubs.acs.org](http://pubs.acs.org) (American Chemical Society)

### Natural Background

Although 'natural background' is a concept generally understood and widely used, it is also misunderstood as pristine, natural conditions before humanity disturbed it. Strictly speaking, no such conditions exist, because, since civilizations began, anthropogenic contamination, at some level, occurs everywhere. Hence, alternate words are used. 'Baseline' is not natural background, but rather conditions that existed at the time of sampling, whether pre-, during, or post-mining. 'Pre-mining' is the preferred term for conditions that existed before mining. It should also be noted that 'background' conditions reflect scale and methodology (Reimann and Garrett 2005), and depending on what the objective is, their evaluation can be very challenging (Matschullat et al. 2000). However, in the case of mining, the difference between pre- and post-mining geochemical conditions can be orders of magnitude (Helgen and Moore 1996).

When setting remediation goals for water quality at mine sites, several choices are possible. Although existing water quality standards or guidelines can often be used for health or fitness criteria, the goal that is most generally justifiable is the pre-mining condition. For new mines, conducting a baseline, pre-mining study is strongly recommended. A proper baseline study before mining for a large, complex site includes ecosystem information, soils and geological setting, other resource concerns, social and local community concerns, and land usage in addition to the quantity and quality of water resources. Such a study can take two to more than five years, based on the proposed Pebble Mine (Alaska) and the Prosperity (Canada) experience (Einbinder and Nolin 2012; Zamzow and Chambers 2017).

It is more challenging to determine pre-mining conditions for an active or historical mine. Pre-mining conditions should be inferred from whatever information can be obtained and can range from crudely qualitative to semi-quantitative. Runnells et al. (1992) describe three general approaches: historical records and anecdotal information, natural analogue sites, and equilibrium geochemical modelling. Historical records and anecdotes may have large uncertainties associated with them as well as serious data gaps. Similarly, equilibrium geochemical modelling may have large uncertainties because of numerous assumptions embodied in the model and uncertainties in the database. Natural analogues should provide better inferences, but only if the site conditions are well understood and reasonably analogous. The recommended inference is a proximal natural analogue site, one with the same or similar geology, hydrology, geochemistry, and ecosystem as the mine site, but without any mining activities and, preferably, minimal human disturbance. A good example of this approach is the Questa project in New Mexico (USA), where molybdenum was actively mined at the time of the study (Nordstrom 2008). This site hosted natural acidic drainage, which would have naturally existed at the mine site because of the mineralized rock and sediment within the oxidising weathering zone.

Both Runnells et al. (1992) and the update by Nordstrom (2015) compile and describe several studies around the world where mineralized terrain has caused acid waters to form NARD (natural acid rock drainage). It is important to understand that natural processes can lead to acid water formation with high concentrations of potentially toxic metals (Eppinger and Fuge 2009). These sites would constitute distal analogues, often from different geologic, hydrologic, and lithologic settings. The more of these sites that can be documented, the more likely a distal natural analogue might be available to compare with any specific site under investigation. The important question is how much does mining change those natural conditions? A comparison of natural weathering rates with those from mine effluents indicates that mining increases the weathering rates (and AMD

production) by 2–3 orders of magnitude (Alpers et al. 2007; Nordstrom 2011).

The concept of identifying baseline conditions for surface water (e.g. Schneider et al. 2017) and groundwater (e.g. Edmunds and Shand 2008), including strategic environmental isotopes, has become an important baseline reference that can be useful if future water quality changes. Similar work is continuing because of EU Directives and NAWQA (National Water Quality Assessment) studies by the US Geological Survey.

### Mine Water: Fundamentals of Mine Drainage Quality

Problems with mine drainage arise when ground and surface water interact with mine sites and contact primary and secondary minerals under oxic conditions. During contact with those minerals, water becomes enriched in elements from the ore and rock-forming minerals. Water contaminants are dissolved particularly by acidic mine water. There are three important acid-producing sulfides: pyrite (FeS<sub>2</sub>), marcasite (FeS<sub>2</sub>), and pyrrhotite (Fe<sub>1-x</sub>S). Because metal or coal deposits differ in their geological, mineralogical, and hydrological settings, the metals and mine water composition are often unique to each mine site. Furthermore, the methods of mineral extraction and processing also affect the chemical composition of mine water.

#### The Process Starts: Abiotic Sulfide Weathering

It is commonly accepted that (di-)sulfide weathering, and especially pyrite oxidation, are the initial reactions in the formation of AMD/metal leachate (Fig. 3):

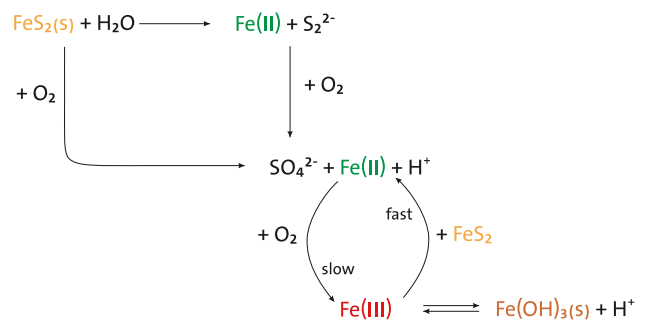
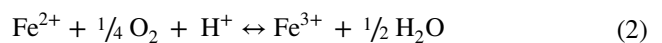
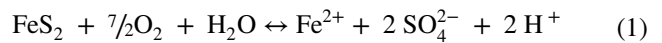
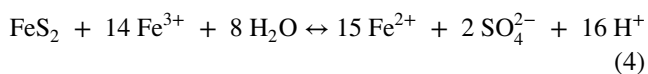
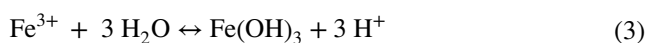


Fig. 3 Diagrammatic representation of the pathways during abiotic pyrite/marcasite oxidation (based on information in Kester et al. 1975; Singer and Stumm 1970; Stumm and Morgan 1996, after an idea in Banks (2004)

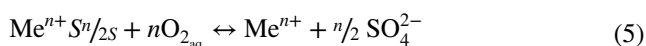


The overall reaction produces a large number of protons and releases acidity into the mine water. Consequently, pyrite weathering is the strongest acid-producing process of all oxidation processes known (Stumm and Morgan 1996) and can produce solutions with extremely low pH, with values of  $-3.6$  having been observed (Nordstrom and Alpers 1995, 1999). While reactions 1 and 2 can be catalysed by bacterial activity, reaction 3 is abiotic. When the pyrite grains are small, reactions 1 and 2 can be quite rapid, while the reaction rate of reaction 3 is slow at low pH values and fast at higher ones. However, once  $\text{Fe}^{3+}$  has formed, it rapidly reacts abiotically and more rapidly with pyrite to continue forming acid (reaction 4). As this reaction is exothermic, the mine air and mine water can reach temperatures up to  $47^\circ\text{C}$  (Nordstrom and Alpers 1995). Indeed, temperatures of  $221^\circ\text{C}$  have been reported on ore surfaces during mining of the Iron Mountain massive sulfide deposit (Wright 1906). Consequently, heat flux can be a driving force for underground mine water transport in addition to hydraulic pressure heads and gradients.

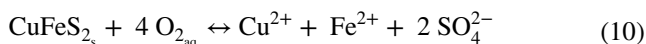
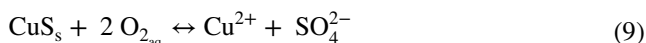
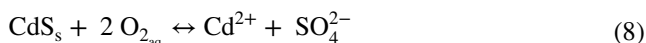
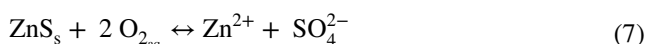
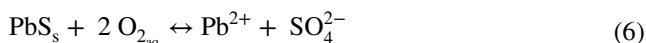
The above weathering reactions thus involve just four ingredients: a (di-)sulfide mineral (pyrite/marcasite/pyrrhotite), oxygen, water, as well as iron-and sulfur-oxidizing microbes. Because these four components can be found in most surface and underground mines, and because just 1–2% of pyrite exposed to the mine air is enough to keep the process going, this acid-generating process has worldwide importance.

## The Process Goes on: How the Metals Dissolve

Because pyrite always occurs in paragenesis with other minerals, mine water is commonly enriched in several elements. Their concentrations depend mainly on the mine water pH, with maximum concentrations at the lowest pH (Table 1). Like pyrite, most of these minerals are stable under the circumneutral anoxic conditions of the groundwater under pre-mining conditions. When oxygen enters the ore veins or rock matrix, the conditions become unstable, and those mineral phases start to oxidize to more mobile species, which are then transported with the water in the direction of lower hydraulic head, which is usually the open space of the underground mine or the mine sump. The simplified reaction, without including water, looks like:

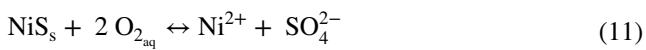


Some examples of primary minerals commonly found in underground mines include:

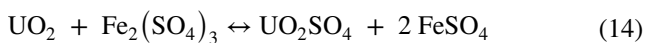
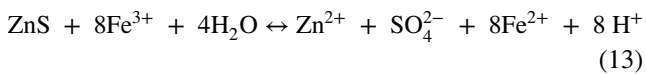
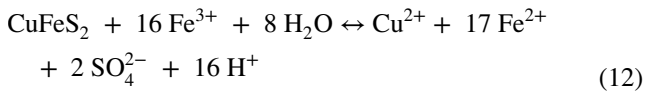


**Table 1** Composition of different mine waters with the most predominant mine water constituents sources: Banks 1996; Banks 2004; Banks et al. 1997; Hasche and Wolkersdorfer 2004; Johnson and Younger 2002; Nordstrom and Alpers 1999; Rüterkamp and Meßer 2000; Wolkersdorfer 1996; Yelpatyevsky 1995 (according to a pers. comm. by Vera Pavlovna Elpatyevskaya, the values in Yelpatyevsky's publication are incorrect in  $\text{mg L}^{-1}$  instead of  $\mu\text{g L}^{-1}$ ); unpublished data from Ch. Wolkersdorfer<sup>a</sup> and T. Valente<sup>b</sup>, concentrations in  $\text{mg L}^{-1}$

Locality	pH	$\text{SO}_4^{2-}$	$\text{Fe}_{\text{tot}}$	Al	Mn	Zn	Cu
Iron mountain California (copper) <sup>N99</sup>	0.5	118,000	20,300	2210	17	2010	290
Iberian Pyrite Belt <sup>b</sup>	1.4	157,229	52,767	7072	155	1885	2243
Cae Coch (pyrite) <sup>B97</sup>	2.5	5110	1460	84	3	1	0.2
Smirnovsky mine Sichote Alin (tin) <sup>Y95</sup>	3.2	–	132	–	14	25	5
R. Hipper discharge (coal) <sup>B97</sup>	3.6	1044	101	17	4	0.2	0.007
Ynysarwed Wales (coal) <sup>B96</sup>	4.2	1554	180	<0.5	6	0.06	–
Oatlands waste rock dump (coal) <sup>B96</sup>	5.5	146	287	1	5	0.05	<0.007
Gernrode Harz mountains (fluorite) <sup>H04</sup>	5.7	86	16	–	–	0.36	0.05
Straßberg Harz mountains (fluorite) <sup>R00</sup>	6.3	359	31	–	6	0.9	0.08
Dunston Chesterfield (coal) <sup>B96</sup>	6.3	210	11	<0.05	1.3	<0.007	–
Duke's level Buxton (coal) <sup>B96</sup>	6.3	83	5	0.08	0.4	0.05	0.005
Allen Hill Spaw (metal) <sup>B96</sup>	6.5	124	15	0.1	2	0.003	–
Niederschlema Erzgebirge (uranium) <sup>W96</sup>	7.1	1138	3	0.4	3	0.1	0.03
Frazer's Grove Yorkshire (fluorite) <sup>J02</sup>	7.6	76	0.4	–	0.8	0.2	–
Mine № 3 Svalbard (coal) <sup>B04</sup>	8.2	7	<0.01	<0.02	0.004	0.055	<0.005
Schwarz Austria (dolomite, fahlore) <sup>a</sup>	8.4	13	<0.01	–	0.002	0.022	0.04



Subsequently, a secondary process is induced by (di-) sulfide oxidation and the release of protons, lowering the pH and allowing Fe<sup>3+</sup> to become the predominant oxidant of pyrite (Nordstrom 1977, 1982):



### The Process Speeds Up: The Role of Microorganisms

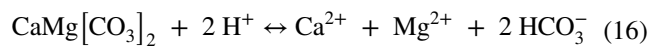
Microorganisms (mainly bacteria and archaea, but also eukaryotes such as fungi, *Euglenophyta*, *Chlorophyta*, and diatoms) play an important role in natural and anthropogenic processes in the environment. The most relevant are *Ferropasma* spp., *Leptospirillum ferrooxidans*, *Acidithiobacillus thiooxidans*, and *A. ferrooxidans* (Baker and Banfield 2003; Johnson and Hallberg 2003; Kelly and Wood 2000; Quatrini and Johnson 2016). From a mine water point of view, the role of microorganisms is twofold: they catalyse the formation of acidity and the dissolution of metals, and they can be used to remediate the polluted mine water. Compared to abiotic pyrite oxidation, the biotic pyrite oxidation occurs at a rate which is 10<sup>2</sup> to 10<sup>6</sup> times faster (Singer and Stumm 1970).

All these microbes need reduced sulfur (*A. thiooxidans*) or iron (*A. ferrooxidans*), and carbon dioxide, nitrogen, and oxygen to produce energy and to maintain their metabolism. Other important reactions catalysed by bacteria are sulfate

and iron reduction, especially useful in engineered passive treatment systems.

### The Process Slows Down: Buffering of the Acidity

Besides the minerals and microorganisms that are responsible for acid production, there are also minerals in the gangue or in the host rock of the raw material deposit that consume the protons produced by the described processes, buffering the acidity and preventing the mine water from becoming too acidic or acidic at all (Table 2). The most common group of buffer minerals are the carbonates, such as calcite, dolomite, or rhodochrosite. Oxyhydroxide minerals and silicates can also buffer acidity, but their rates and capacities are much less than the carbonates. Acid neutralization by carbonates proceeds according to Eqs. 15 and 16:



Other mechanisms that might consume acidity are ion exchange and surface protonation, but compared to mineral dissolution, they are comparatively slow and of limited capacity. It must be made clear that buffering minerals do not prevent pyrite oxidation. Even in the presence of buffering minerals, reactions 1–4 will not be stopped, but the protons produced are consumed by the buffering reactions, and therefore, the pH is buffered within a limited range. Thus, circumneutral mine waters can be as enriched in sulfate as acid mine waters (Table 1).

Usually, the buffering ranges can be attributed to particular minerals and sequence; this is referred to as sequential pH buffering. Once calcite and dolomite are consumed, the pH rapidly drops to the next occurring mineral phase buffer in the system. If all of the buffering minerals are consumed, the pH can drop below 1 and even reach extremely negative

**Table 2** Minerals which buffer the protons produced during sulfide weathering (Blowes et al. 1994; goethite, K-jarosite, and aluminosilicates from Jurjovec et al. 1995)

Mineral	Formula	Buffering stage	pH-buffer range
Calcite	CaCO <sub>3</sub>	Early	6.5–7.5
Dolomite	CaMg[CO <sub>3</sub> ] <sub>2</sub>	Early	6.5–7.5
Siderite	FeCO <sub>3</sub>	Early	4.8–6.3
Mixed carbonates	(Ca, Mg, Fe, Mn)CO <sub>3</sub>	Early	4.8–6.3
Gibbsite	Al(OH) <sub>3</sub>	Intermediate	4.0–4.3
Ferrihydrite	Fe(OH) <sub>3</sub>	Late	< 3.5
Goethite	α-FeOOH	Late	1.3–1.8
K-jarosite	KFe <sub>3</sub> [(OH) <sub>6</sub> ](SO <sub>4</sub> ) <sub>2</sub> ]	Late	1–2 (experimental)
Aluminosilicates		Late	1–2 (experimental)

Buffering ranges of K-jarosite and aluminosilicates deduced from column experiments (pers. comm. J. Jurjovec (1995))

pH values. Another factor in buffering the acidity are the different kinetic processes involved. Carbonate weathering rates, compared to pyrite, biotite, feldspar or chlorite, are comparably high and therefore, as long as carbonates are present, the acidity is quickly buffered. After the carbonates are consumed, the pyrite weathering rate is 2–3 orders of magnitude higher than that of silicates, and therefore buffering is slower (Reimann and Garrett 2005).

### The Process Ends: Mineral Precipitates in the Mining Environment

One of the predominant features of mine water is precipitation of mineral phases or amorphous substances when the relevant solubility products of the species in solution are exceeded (Alpers et al. 1994). Most of the secondary minerals in underground mines are iron minerals, as iron is usually the predominant ion in the water around a mine.

Two different groups of precipitates can be distinguished: minerals often referred to as ‘ochre’, which are mostly insoluble, and water-soluble minerals formed through evaporation and often referred to as efflorescent salts. Because many of the efflorescent salts can easily be dissolved when the water table in an abandoned mine rises, they become mobile again. The properties of both the insoluble iron and aluminium hydroxysulfates and the soluble metal-sulfate salts have been reviewed by Bigham and Nordstrom (2000) and Jambor et al. (2000) respectively.

As indicated above, the most common precipitates associated with mine water are called ochre, yellow boy, or hydrous ferric oxides, because they are a mixture of crystallized and amorphous substances with a yellowish to red colour (Jambor et al. 2003; Nordstrom 1982). Ochre mainly consists of the following mineral species: goethite (yellowish brown to brownish black), lepidocrocite (orange), ferrihydrite (reddish brown), schwertmannite (yellow), jarosite (sulfur yellow), and in some cases, the corresponding Mn species. Commonly, (semi-)metals co-precipitate with the ochre, such as Pb, Cu, As, Mo, U, Sb, Mn, and Se. Whereas As, Sb, and Se tend to co-precipitate or sorb at acidic conditions, the other elements precipitate or sorb in alkaline conditions (Alpers et al. 1994).

Additional mineral phases are formed when water enters a mine and oxidizes primary minerals within the ore veins or the host rock. Most of these minerals are fairly water soluble: goslarite, melanterite, rozenite, szomolnokite, epsomite, jurbanite, and coquimbite (Alpers et al. 1994; Younger et al. 2002). These minerals are formed because mining lowers the groundwater table, allowing oxygen as well as water to contact the primary ore minerals. Those minerals will oxidize or dissolve with or without the acid produced by sulfide weathering. Because the hydroxylated metal ions forming those minerals are proton acceptors,

they “store” the protons and consequently the acidity, mainly coming from sulfuric or carbonic acid. As long as those minerals are in the mine air and the overall situation does not change substantially, this acidity will be stored as minerals ad infinitum. Yet, after mining ceases and the mine is abandoned or flooded (if under the water table), then the easily water-soluble carbonates, hydroxycarbonates, sulfates, and hydroxysulfates are dissolved by the mine water. Consequently, flooded mines can have substantially lower pH and higher dissolved metal concentrations than before flooding (e.g. Nordstrom and Alpers 1999, pp 3459–3460; Wolkersdorfer 2008). This process has been observed in flooded mines and is responsible for the ‘first flush’ in both underground mines and surface waters (Aldous 1987; Banks et al. 1997; Nordstrom 2009; Younger 1997).

### Spatial–Temporal Variations

Environmental systems affected by mine drainage have substantial spatial and temporal heterogeneity and generate samples with complex matrices. Characterizing the presence of several pollutants, colloids, and interactions with organic matter present methodological challenges and require implementation of diverse and adapted or modified analytical methods. Aspects that are directly or indirectly related to the spatial and temporal variations of AMD-affected systems include:

- Genesis and evolution of mine drainage are complex phenomena, controlled by numerous physical, chemical, biological, and mineralogical factors.
- The affected systems have great heterogeneity, related to the existence of chemical reaction microenvironments and a variety of chemical, hydrologic, and microbial interfaces.
- The scale at which these transformations occur, and their heterogeneity, make it difficult to obtain representative samples.
- Small variations in environmental conditions can propagate sequentially, causing substantial changes in hydrochemical, mineralogical, and ecological aspects.

Temporal variation related to seasons and climate, especially the intensity and frequency of precipitation, temperature, and insolation, affects aspects such as:

- Hydrology, which controls the availability of water, regulates the circulation of the effluents, the precipitation-redissolution cycles and natural attenuation, for example by dilution processes

- Mine water is highly dynamic, heterogeneous with turbulent and convective flow and susceptible to stratification of the mine pool,
- Kinetics of biogeochemical reactions,
- Photodynamic effects (Fe(II) reduction–oxidation, Hg reduction),
- Biological activity (bacteria, archaea, algae), creating local environments that lead to complex precipitation scenarios.

Thus, climate can cause a diversity of drainage chemistries, being a key factor in mineral–water interactions, and controlling the:

- Rates of mineral dissolution,
- Mobility of chemical elements and mechanisms of transport of dissolved and particulate matter, and
- Retention of metals and metalloids through solubility control.

Local hydro(geo)logical conditions, along with seasonal fluctuations, can cause complex precipitation scenarios, depending on biogeochemical activity and the saturation levels achieved for each mineral phases. In fact, as described above, the development of secondary minerals, namely soluble minerals and ochres, is one of the most important issues related with climate. Efflorescences of these minerals have a strong influence on water quality. They retain sulfate, acidity, and metals during the dry periods, but are metastable; dissolution occurs during and immediately after the first rains, promoting peaks of contamination (Supplemental Fig. S-1).

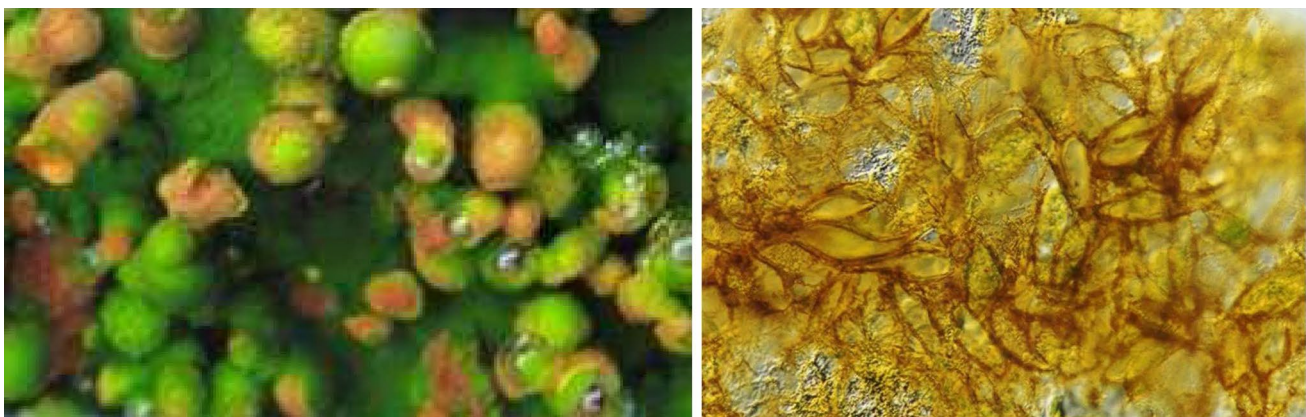
Also, photosynthetic activity (e.g. by acidophilic green algae) with its daily and seasonal variations, influences water properties. Oxygenated microenvironments can result from oxygen production via photosynthesis, promoting iron oxyhydroxide precipitation, as reported by Valente and Leal

Gomes (2007) and Rodrigues et al. (2012) in an AMD stream (Fig. 4). In sequence, this phenomenon can affect the concentrations of other metals and metalloids able to adsorb onto these iron-rich precipitates. Moreover, organic matter introduced by plant decomposition, secreted metabolites, or acidophilic algae degradation may contribute organic ligands that can influence component mobility.

Seasonal and diurnal light cycles are another focus of variability due to speciation of iron through photochemical responses. These cycles control the oxidation–reduction reactions that can cause the reduction of dissolved Fe(III) and dissolution of iron-oxyhydroxysulfates and iron-oxyhydroxides, such as schwertmannite and goethite, which are able to sorb metals and metalloids (Fig. 5). Thus, short-term variations in concentrations of Fe and potentially toxic elements, especially As, may occur in mine drainage due to photo-reduction of iron-rich phases.

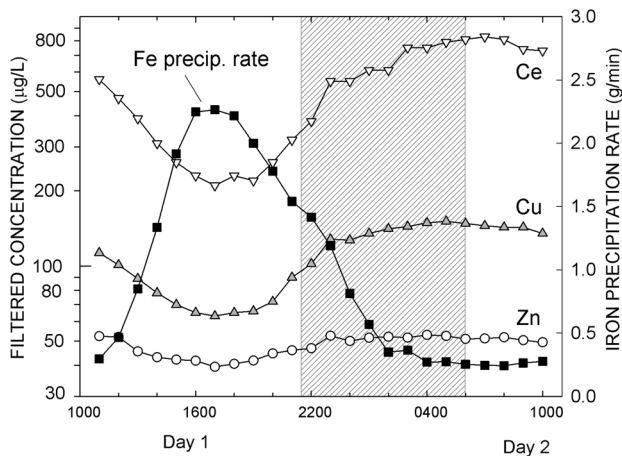
Changes in stream water chemistry at mine sites and in mineralized areas often occur due to inflow of waters from contamination point sources and dispersed geogenic sources. To capture the response of water chemistry to rainfall (dilution effects), continuous automated monitoring of flow, pH, redox potential, and electrical conductivity (EC) is suggested (please see [www.wolkersdorfer.info/orp](http://www.wolkersdorfer.info/orp) about correct redox measurement and conversion). EC is often strongly correlated with sulfate concentrations, and though there is a relationship between EC and TDS, it cannot readily be used to calculate TDS (total dissolved solids) concentrations (Hubert and Wolkersdorfer 2015) unless all the samples contain the same dominant anion and are of similar composition (Hem 1985).

For example, in pit lakes, sampling should account for changes of chemistry with depth as well as potential seasonal overturn of the pit lake water (Gammons et al. 2000). There is usually a change of water chemistry with the depth of pit lakes due to temperature and oxygen gradients that cause



**Fig. 4** In-situ images of iron-rich macro-accretions (left) and deposit of ochres at the extra-cellular polymers produced by the algae *Euglena mutabilis* (right)





**Fig. 5** Example of iron oxidation during the day promoting precipitation and sorption of trace metals from solution and iron reduction at night with consequent increase in dissolved Cu, Zn, and Ce (from Gammons et al. 2015). Shaded area marks the night time

stratification of the pit water (Geller et al. 2013). Extreme evaporation from the surface can increase the mineralisation and density of pit lake water.

The groundwater chemistry of a mine site can change over a short distance due to the presence of fracture zones and reactive veins or coal seams. Often waters from various sources on site may mix during rainfall events; for example, acid seepages from Waste rock dumps (WRDs) may mix with alkaline seepages from tailings storage facilities (TSFs). Some water chemistry differences on a mine site are due to changes in ore type and mineral processing, pumping of water between locations (e.g. collecting seepage from WRD and transferring to the open pit), as well as rate and location of dewatering. Large variations in water quality can occur from storm events, including:

- Effect of evaporation on water balance, deep infiltration into WRDs due to high intensity rainfall events, dust storms and increase in the number of airborne particles (e.g. from the surface of tailings).
- ‘First flush’ effects, i.e. dissolution of oxidation products (efflorescence salts/secondary minerals).

Long-term effects due to changing climatic conditions include effects of prolonged droughts and floods:

- Change in oxidation rates due to the availability of optimum moisture for reactions.
- Cracking of compacted clays used to construct covers on waste rocks or tailings, due to evaporation.
- Substantial increase in the contaminant loads transported downstream from mine sites.

- Substantial increase in contaminant concentrations from mine sites because of decreased meteoric dilution, even though loading from a mine site is constant (Nordstrom 2009).
- Greater build-up of soluble minerals during dry periods, with greater short-term pulses of contaminant wash-out from intense precipitation (Nordstrom 2009).

## Mine-Site Characterization

Environmental impacts such as AMD and metal leaching can be estimated based on mineralogy, and mining and mineral processing methods. Decommissioning options are also related to the composition and setting of an ore body (Plumlee and Nash 1995; Plumlee et al. 1999). Based on the data obtained during exploration, an initial estimate can be made of the potential for AMD formation. The essential characteristics of the water’s metal concentrations also allow a simplified prediction of the AMD potential. A general, simple classification of mineral deposits includes massive sulfides, vein deposits, disseminated deposits (porphyries), skarns, and placers (Pohl 2011). Economic geologists have also classified hydrothermal deposits based on temperature of formation: epithermal (low temperature), mesothermal (moderate temperature), and hypothermal (high temperature). Most mining deposits are formed by hydrothermal activity, with exceptions being except for some sedimentary deposits such as coal, placer deposits, salt and some phosphate mines. Coal deposits can also produce AMD from pyrite and marcasite oxidation, though generally with lesser concentrations of many trace metals and metalloids. However, if a coal deposit has undergone metamorphism, then it may contain elevated levels of these contaminants.

Usually, massive sulfide deposits form relatively large groups of mining districts (Eilu 2012). Their potential for generating acid lixiviates is important for most Ni-Cu deposits, as they usually contain iron sulfides such as pyrrhotite that may produce ARD, and very low for carbonatite deposits due to their high carbonate content.

Magmatic-related hydrothermal deposits, such as porphyry, epithermal, Sn-W-veins, or skarns, usually contain pyrrhotite or pyrite that can produce ARD. In the case of porphyry deposits, mineral treatment processes can affect the tailings ARD capacity because flotation is often under alkaline conditions, which prevents acid generation in the short term.

In epithermal deposits, and specifically in high sulfidation types, the acidic hydrothermal alteration inhibits rock buffering capacity. It is also important to note that jarosite-alunite dissolution from acidic hydrothermal alteration produces ARD.

In porphyry and epithermal deposits, where sulfur can be from both sulfides and sulfate mineral (e.g. anhydrite, gypsum, jarosite, alunite) dissolution, sulfur, and oxygen isotopes from dissolved sulfate can be used to differentiate these two sources. These isotopes can be used to determine their relative contribution, confirm the hydrogeological conceptual model, and define the geochemical baseline for this type of ore deposit. In addition, oxygen isotopic composition from dissolved sulfate ( $\delta^{18}\text{O}_{\text{SO}_4}$ ) coming from sulfide oxidation can be useful to discriminate between tailings effluents from ARD or otherwise, based on the evaporation rate of the related water.

Spangenberg et al. (2007) recognized that the differences between the stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in tailings from different climatic regions of Chile allowed statements to be made on the mixing and phase separation processes of fluid-liquid and fluid-sediment. Since these processes change the isotopic composition of AMD, they are clearly different from unaffected freshwaters. In addition, Dold and Spangenberg (2005) as well as Nordstrom et al. (2007) found that oxygen and stable sulfur isotopes in water-soluble sulfates help in identifying the sulfur source and, consequently, distinguishing microbial oxidation of sulfides from dissolution of primary sulfate minerals such as anhydrite.

Skarn deposits usually do not produce AMD, because of their small size and their association with carbonate sediments. AMD generation might be relevant in only a few endoskarn deposits. Valente and Leal Gomes (2009) report strong AMD contamination associated with mine wastes from a skarn deposit with massive sulfides in northern Portugal.

Sediment-hosted deposits can be derived from volcanic, diagenetic, and sedimentary processes. Some of these deposits are related to carbonate host-rocks with their intrinsic buffering capacity that prevents or minimizes acid production. In contrast, volcanic-associated deposits (VMS: volcanic massive sulfide) or volcanogenic deposits are generally composed of large iron sulfide bodies (from 1 Mt up to 500 Mt, like Rio Tinto, Huelva, Spain) with high AMD capacity, and minor neutralization capacity. Among all deposit types, massive sulfide deposits are the most likely to develop environmental problems, particularly AMD and metal pollution.

In addition to ore mineralogy, other factors should be considered when assessing the likelihood of AMD pollution. One of these is hydrothermal alteration, as neatly illustrated by the El Indio and Los Pelambres districts in north-central Chile (Parra et al. 2011). Both areas are similar in their geological, hydrological, and climatic conditions as well as the amount of pyrite. However, while El Indio shows advanced argillic alterations with dominant quartz, sericite, and pyrite and virtually no buffering capacity, the mafic host rocks of Los Pelambres have been hydrothermally altered and contain pyroxenes and Ca-plagioclase that act as acid buffers. In

addition, propylitic (low-temperature) alteration of the mafic rocks has formed additional buffering carbonates. Tectonics also have influenced the dispersion of ARD, with less fracturing, as in Los Pelambres, reducing the spread of ARD. Furthermore, a wide consideration of issues beyond the geological setting should be considered, such as the hydrologic regime under which a mine has operated in the past, along with future conditions. This is especially important when determining remedial actions and the temporal extent of monitoring campaigns (e.g. for water quality) in the framework of closure plan definition and implementation. These issues could be especially important for mining operations carried out at the headwaters of steep terrain basins (such as those in the Peruvian/Chilean Andean cordillera in South America), as documented in Oyarzún et al. (2018), which describes the post-closure situation of an El Indio vein-type (Au–Cu–As) deposit in the headwaters of the north-central Chilean Elqui river basin. Advanced argillic alteration at this site, high As concentrations, and intense rock fracturing in a steep hydraulic gradient present problems that cannot be solved and can only be mitigated, at best.

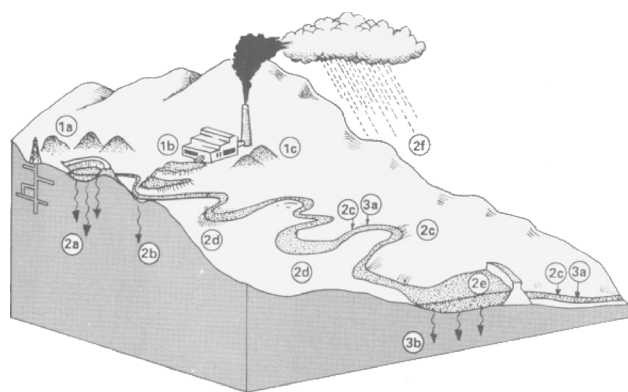
In addition to ‘normal’ seasonal variability of meteorological/hydrological processes (precipitation, surface discharges, groundwater levels), projected or expected climatic conditions should be considered when defining monitoring plans for compliance after closure. This precaution is necessary, because different parameters present different behaviours (in terms of concentrations) against discharge changes, as presented by Flores et al. (2017) for a sulfide mineral-rich arid zone in north central Chile. Another study pointing out the effects of seasonal and climatic variations on mine sites with acid drainage is described by Nordstrom (2009).

## Mine Site Hydrology

### Introduction

The site water balance characterizes the fluxes into and out of the system and the storage within the system. The objectives of the assessment, for example for a prefeasibility study or for a detailed design, determine the precision with which the components of the water balance and potential contamination sources should be characterized (Fig. 6). Important questions to be addressed in a mining context include:

- What water resources are available for mining operations and post-closure?
- What are the other uses of the water near the mine? Will mining affect other users and environmental flows?
- Will dewatering be required?



<b>Primary</b>	2d Floodplain sediment/soil
1a Waste rock	2e Reservoir sediment
1b Tailings	2f Soils from air pollution
1c Slag	
<b>Secondary</b>	<b>Tertiary</b>
2a Ground water at open pits	3a River sediment reworked from floodplain
2b Ground water beneath ponds	3b Groundwater from contaminated reservoir sediment
2c Sediment in river channels	

**Fig. 6** Block diagram with types of contamination resulting from large-scale mining extraction. Primary contamination is indicated by (1), secondary contamination by (2) and tertiary by (3) Adapted with permission from Moore and Luoma (1990). Copyright (1990) American Chemical Society

- Will dewatering adversely affect water levels and water availability to other users or the receiving water bodies?
- Where and how can the extracted water be discharged into receiving water bodies?

### Components of the Water Balance

**Precipitation** Mining projects are often located at remote locations without a record of local climate data. In mountainous terrain, orographic effects can result in substantial variations in rainfall at sub-kilometre scales.

**Rivers and streams** Typically, long-term average flow, flow variability, and instantaneous flows onto and from the site are required for mine monitoring and mine planning. Chemical constituents and isotopes can be used to determine whether a surface water body is gaining or in the case of a mine with active dewatering, losing water to the subsurface. Discharge of surface water should always be measured where possible when collecting water samples for chemical analysis (Wolkersdorfer 2008, pp. 142–169).

**Lakes, ponds, wetlands** Water levels (volume of water in storage), their seasonal and temporal variation, evaporation, fluxes into and out of the system via surface water, and subsurface pathways are needed to characterize local water balances. Subsurface groundwater fluxes into or from surface water bodies can be assessed using Darcy's law (Ward and Trimble 2003) by characterizing gradients in hydraulic

heads and hydraulic conductivity, or by tracking the movement of natural or artificial tracers.

**Evaporation and recharge** Evaporation ( $E$ ) and recharge ( $R$ ) are the most challenging components to characterize in the water balance. Once one knows the local precipitation ( $P$ ) and runoff ( $Ro$ ; typically of minor importance), the net infiltration ( $R$ ) can be measured directly with a lysimeter (Bews et al. 1999) and the evaporation can be determined by using the difference of the components:  $E = P - Ro - R$ . It is necessary to know that recharge strongly depends on near-surface properties, such as the grain size, vegetation, wind, and solar insolation.

### Site Conceptual Model Development Process

A conceptual model of a site is a written or pictorial representation, or both, of an environmental system that describes and integrates the processes that determine the release of pollutants, their migration, and the exposure of receptors to them. It contributes to: (1) determining routes of potential exposure as well as possible effects on human health and the environment, (2) integrating all site information, and (3) identifying gaps of information and data. It is also an effective communication tool that facilitates decision making in a multidisciplinary work team, particularly in the selection of remediation alternatives, remediation actions, the development of an environmental monitoring plan and associated programs (surface water, groundwater, soil, air, noise, biota) and environmental communication actions (ASTM E1689-95 2014; Instituto Argentino de Normalización y Certificación – IRAM 2016). The development process of a site conceptual model includes:

- Assembling historical and current site-related regional and local information of the mining activities and environmental liabilities (i.e. geology/lithology/structure, hydrology, hydrochemistry, isotopic composition);
- Identifying contaminants (i.e. AMD, SPM, As, Sb);
- Establishing background concentrations of contaminants;
- Characterizing sources of contaminants (i.e. mine tailings, waste rock dumps, heap leach materials, slag);
- Identifying migration pathways for each source. It includes the mechanism of release of the contaminant from primary or secondary sources (i.e. blasting, excavation, grinding, infiltration, evaporation, volatilization, lixiviation), transport media or environmental factor (air, groundwater, surface water, soils, sediments and the biota), and the contact point of environmental receptors;
- Identifying environmental receptors (human and ecological).

Figures 7, S-3 and S-4 were developed using this approach. They are good examples of a simple representation of site conditions that integrated the source, fate, and transport of pollutants for understanding the site, interpreting data, and making decisions, in terms of environmental management.

## Strategic Approach

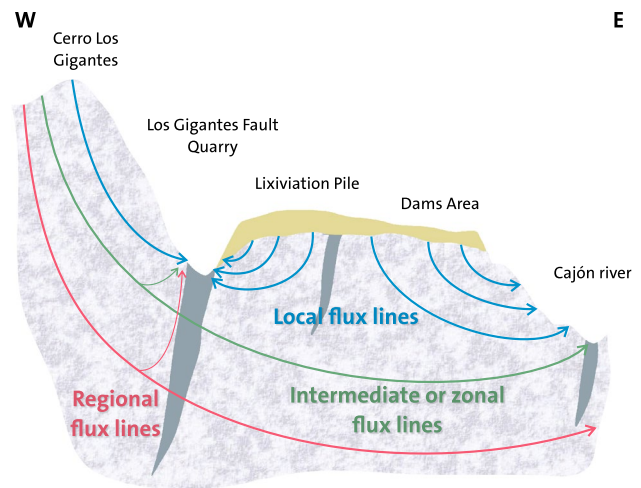
### Introduction

Screening and scoping processes are necessary to define and classify the main topics that should be addressed to characterize the interactions of the mine project (planning, ongoing, in operation, closure, rehabilitation, post closure monitoring) with the natural environment. It is an iterative process that receives inputs from the literature survey, exploratory studies (field and laboratory work), good professional judgement coming from the experts (independent review board or technical advisory committee), guidelines, recommendations as well as lessons learned from other projects (Supplemental Fig. S-2). Its output is the preliminary conceptual model of the site where the project could be implemented (sources, contaminants, environmental factors, receptors, major pathways of transport) (ASTM E1689-95 2014). Thus, it helps to define the problem, putting in perspective its complexity (legal framework, environmental aspects, stakeholders) and defining goals to achieve (specific objectives) to characterize mining sites (Supplemental Fig. S-3). This global conceptual model can even be refined, focusing on the water component and including sources, environmental factors, and interactions that can be integrated into a local or regional hydrogeological model (Fig. 7).

### Environmental Impact Assessments

Developing a new mine, or expanding or closing an existing one, requires that the owners submit environmental impact assessments to regulators. In some jurisdictions, these impact assessments are publicly available. The impact assessments contain detailed consulting reports that can be used as examples of the standard-of-practice methods to evaluate, for example, the mine's effects on water, air, or biota, including the use of isotopes for these assessments.

In Canada, for example, environmental impact assessments are submitted to both federal and provincial government regulators. Projects under review can be found on the Canadian Environmental Assessment Registry ([www.ceaa-acee.gc.ca](http://www.ceaa-acee.gc.ca)), and in the Province of British Columbia, projects are posted to the Environmental Assessment



**Fig. 7** Conceptual model of a mining site, focused on the water component at the Los Gigantes site, Córdoba, Argentina, incorporating the Tóth (1963) concept of groundwater flow (modified after Cane et al. 2018)

Office ([www.projects.eao.gov.bc.ca](http://www.projects.eao.gov.bc.ca)). Likewise, in Chile, the process is coordinated by the Environmental Assessment Service (SEA), and projects submitted for evaluation as well as the whole assessment process can be found at [www.sea.gob.cl](http://www.sea.gob.cl).

A good example of an industry assessment, where numerous entities were involved and an extensive interaction of the mining company and the stakeholders took place, is the ‘Prosperity Mine’, a copper–gold open pit mine that was first proposed in 2010 and rejected by regulators, claiming it would destroy a fish-bearing lake (Kunkel 2017). The owners redesigned the mine, renamed it the ‘New Prosperity Mine’ (Einbinder and Nolin 2012) and resubmitted a new assessment in 2012, which was also rejected by regulators. The assessment reports, public hearings, panel discussions, and expert testimonies can be found by searching for ‘Prosperity Gold-Copper’ at the above-mentioned web pages.

## Components of a Mine Site-Water Perspective

### Introduction

In active mines, the context is one of identifying and preventing or controlling seepage to operational areas. Sources of this water are direct precipitation and recharge, induced surface water inflow (including seawater intrusion in undersea operations) and groundwater seepage (Elliot and Younger 2007, 2014). Potentially catastrophic inrushes (inundation) can also occur in underground works (Gu et al. 2018; Li et al.

2014; Qian et al. 2016; Singh 1986; Vutukuri and Singh 1995; Wu et al. 2017). When active pumping of the mine is finally curtailed following closure, these same sources provide the natural water table rebound as recharge waters fill voids to form a ‘mine aquifer’ (Razowska 2001; Wolkersdorfer 1994, 2008; Younger 1997). The open conduit nature of mined systems means that the hydraulics of flow (either natural or forced, e.g. by pumping) in flooded mines is generally turbulent (Wolkersdorfer 2008). Additionally, a ‘vestigial’ component of water quality relates to the “geochemical trauma” which occurs while abandoned mine workings that were open to an oxygenated atmosphere for a long time are allowed to flood for the first time, dissolving efflorescent ferric and ferrous sulfates (Elliot and Younger 2007, 2014; Younger 1997). Potentially, a further ‘juvenile’ component arises e.g. from any pyrite-oxidation in the area of the mine pool and will only stop until all the pyrite is finally exhausted (Younger 1997). A key concern is then how and when poor quality mine water eventually may discharge at the surface.

Mine water quality usually starts to improve once the mine floods completely, and unpolluted groundwater replaces the water in the mine voids, resulting in a flushing of the mine workings. However, water quality stratification occurs in mine systems with a low flooding rate and a small number of inflow and outflow possibilities (Johnson and Younger 2002; Nuttall and Younger 2004; Wolkersdorfer 2008). Less mineralized groundwater percolates into the mine from shallower aquifers and fills the water column at the top, while more mineralized mine water usually can be found in deeper sections of the mine. Convective cells of different water qualities, driven for example by thermal gradients, may also build up in the subsurface controlled by the mine structure, such as developed roadways (Burnside et al. 2016a, b; Janson et al. 2016; Hünefeld-Mugova and Wolkersdorfer 2018). Disturbances of the system’s hydraulic equilibrium can result in a collapse of the water body’s stratification and the uncontrolled discharge of contaminated mine water. Such disturbances can be caused, for example, by pumping or raising the mine water reaching water paths via galleries or mine workings (Elliot and Younger 2007, 2014; Nuttall and Younger 2004; Wolkersdorfer et al. 2016b). Negative effects on water quality and their sources often can be traced and monitored using key hydrogeochemical parameters as well as environmental tracers (including isotopes) and are especially useful where multiple sources are involved or interact.

## Mine Tailings

Mine tailings are commonly layered due to variations in particle size, changes in ore mineralogy during mining, density segregation during deposition, oxidation of sulfides, climate cycles, and formation of hardpan-cemented layers after the

tailings surface begins to dry. Therefore, tailings are anisotropic with respect to hydraulic conductivity. In TSFs pore water chemistry changes with depth of tailings due to evaporation, oxidation of pyrite, dissolution of carbonate and silicate minerals, bacterial reduction of sulfate and attenuation of contaminants through surface-reactions, such as sorption by clay minerals and iron(III) oxide-hydroxides. Tailings can have a wide variety of chemical and mineralogical compositions controlled by supergenic evolution, depending on the original ore paragenesis, mineral processing techniques, and magnitude of weathering since the tailings were first deposited. The same is true for waste rock and heap leach piles.

## Waste Rock Dumps

Waste rock dumps are layered structures due to the segregation of heterogeneous coarse and fine rock fragments and formation of compacted surfaces by trafficking trucks at the time of disposal. With time, the preferential flow pathways may collapse or increase in size depending on the physical and geochemical nature of the rocks. This disturbance is likely to have discernible effect on the seepage volumes and water quality. Seepage from WRDs may originate from preferential flow pathways as well as matrix flow through finer particles.

## Heap Leach Materials

Heap leach materials (waste from leaching of ores) often have narrow ranges of particle size distribution with relatively large surface area for reactions. They contain secondary sulfate minerals that can flush out during precipitation events.

## Overview of Mine Waste

### Introduction

Mining can be considered a waste-management industry (Lottermoser 2010). Indeed, large volumes of material must be processed to extract a relatively small volume of the commodities of interest. The two principal solid wastes are waste rock and tailings, which together comprise the largest volume of materials handled in the world (Blowes et al. 2014). At large mines, tens to hundreds of millions of tons of waste rock can be produced. Waste rock and tailings can also produce low-quality drainage, which should be managed to protect the environment.

Waste rock is rock with sub-economic or no mineralization needing removal to gain access to the ore (Smith and Beckie 2003). Open-pit mines typically produce three to four volumes of waste rock for every volume of ore material,

while underground mines typically produce much less. The blasting methods used in modern open-pit mines produce waste rock with a wide range of grain sizes, from meter-size boulders to clay-sized fractions. This waste rock is disposed of near the mine site in waste-rock piles.

Tailings are by-products of the ore processing that concentrates the ore. The ore is typically crushed and the commodities of interest, often 1% or less of the total ore mass, is extracted by methods such as flotation, magnetic separation, and leaching. The remaining wastes from leaching are known as heap leach residues and are not necessarily transported to a tailings facility. The residual material from flotation or magnetic separation is tailings, which have a relatively uniform grain size, typically smaller than 1 mm (fine sand). Tailings are often conveyed as slurries and discharged into tailings management facilities, which are essentially reservoirs contained by a tailings dam. They contain reactive sulfide minerals, and processing reagents are often stored as slurries in tailings ponds. Management of seepage from tailings storage facilities to the environment is a major concern.

Minor wastes with the potential to contaminate water include slag (the residual wastes solidified from smelter furnaces), fly ash and flue dust (airborne particles and volatile gases from smelters), and eroded sediments from these sources. Flue dust is often enriched in As and Sb, and oxides of these elements can still be found in soil and sediments decades after smelting has stopped. Smelter-related wastes are not a focus of this paper.

### Drainage from Mine Workings

The disturbance of the natural ground by the creation of mine workings, and the blasting, excavation, and grinding of rock at mine sites increases the surface area and exposure of reactive minerals to oxygen and water. Consequently, it enhances the opportunity for the biogeochemical processes described earlier to produce poor quality drainage. Prediction and management of the drainage from mine workings and mine waste is a key environmental concern. The following are key issues related to drainage at mine sites.

- What are the reactive minerals in the tailings, waste rock, and mine workings and what might be the likely contaminants of concern?
- What quantity of drainage can be expected and how does it vary in time?
- What is the quality of drainage and how does it vary in time?
- What are the drainage flow paths?

The assessment and management of mine drainage is a well-developed subject with a rich literature, and several excellent guidance documents that describe prediction and management methods. A summary of this subject along with well-known guidance documents was described previously.

### Tailings

Tailings are often deposited as slurries into tailings ponds. The water quality within the tailings pond is often expected to be poor, particularly during operations, so management plans focus upon containment of the tailings and preventing uncontrolled releases to receiving water bodies, which are often the most important public concern (Walkey 2017). Subaqueous and submarine disposal of tailings inhibits contact with oxygen and limits oxidation of sulfide minerals (Dold 2014). Isotopes, hydrological and geochemical methods are important tools to detect and trace drainage from tailings management facilities.

### Waste Rock

Drainage water quality and quantity from waste rock is often controlled by coupled geochemical and physical processes (Amos et al. 2015; Smith and Beckie 2003). Waste rock is usually placed in waste-rock piles (WRPs) constructed by end dumping over a slope or push dumping on flatter terrain. The rate of mineral weathering and discharge into receiving water bodies depends upon geochemical conditions and fluid-flow patterns through the largely unsaturated piles. The wide range of grain sizes, and the distinct stratigraphic structures that result from end and push dumping give rise to a continuum of co-existing flow regimes during recharge events. Flow can be either rapid and channelized with relatively short water–rock contact times and relatively low concentrations, or slow and diffuse through the matrix, with long water–rock contact times and higher concentrations.

Evaporation and overall WRP water balance are controlled by climate and the grain-size distribution of the waste rock. Stable water isotopes can be used to assess flow and evaporation from near surface soils and waste rock (Barbour et al. 2016; Sprenger et al. 2016). At a study site in Peru, evaporation from a coarser-grained pile was  $\approx 60\%$  of the annual precipitation, whereas evaporation from a finer-grained pile was  $\approx 40\%$  of the annual precipitation. Seasonal variations in precipitation cause substantial variations in water quality, independent of the progressive weathering of waste rock. Concentrations peak at the onset of the wet season (first flush), whereas concentrations build over the dry season when flushing is weaker.

A detailed characterization of primary and secondary waste-rock mineralogy is an essential component of a predictive framework (Jamieson et al. 2015). Though leaching procedures

(i.e. humidity cells) and acid–base accounting usually provide valuable information, their representation of the large-scale chemical or physical processes often fails (Jambor 2003; Maest and Nordstrom 2017). These relatively rapid (weeks to months), small-scale assessment methods require sophisticated interpretation to be useful for predictions at field scales and over the decades to centuries time scales required for management decision making. The fundamental problem with applying lab-scale testing to field-scale processes is that there is no acceptable method for scaling, partly because lab conditions simply are not analogous to field conditions. Studies at different sites have shown that the chemical weathering rate in WRPs obtained from small-scale experiments often can be many times higher than shown by the discharge of large-scale piles. Gas- and heat-transport processes that are not represented in smaller-scale assessment methods, and unrepresented heterogeneity, largely explain the discrepancy (Malmström et al. 2000).

The spatial configuration of acid-producing and acid buffering waste rock within a WRP affects overall drainage quality (Pedretti et al. 2017). Relatively small pockets of reactive waste rock within composite heterogeneous waste rock can dominate the mixed drainage quality at the base of the pile, in part because the acidity of drainage produced by acid-generating materials can greatly exceed the alkalinity produced by acid-buffering materials. Reliable predictions of field-scale behaviour through small-scale assessments and modelling using physical parameters such as the general structure of the pile, its grain size distribution (end dumped or push dumped) and grain-size segregation, might be possible in the future without the need for large-scale experiments, but the uncertainties are substantial and quantitative predictions are not possible at this time (Nordstrom et al. 2017; Van der Sloot and Van Zomeren 2012). More research is required before these processes can be coupled together with confidence to make reliable predictions for decision making over long timescales. The heterogeneity and uncertainty of the geochemical composition and the internal structure of WRPs will hinder the application of detailed, high-resolution predictive models of drainage from WRPs. Simpler models that conform to geochemical principles and account for heterogeneity and uncertainty are promising alternatives.

## Process Water

Water is involved in every step of a mining and mineral processing operation (Supplemental Fig. S-4, IBRAM 2012). During operation, this water, which still has a substantial potential of usage reduction, is stored in process-related ponds, such as raw water, clarifier, and evaporation ponds (Gunson et al. 2012). Mining operations in remote areas are often self-supplying, generally using water extracted to dewater mines, mostly in the processing plant. The water can

also come from the ore concentrate dewatering processes and tailings dam; consequently, its characteristics and quality will depend on the nature of the adopted process.

Large mining companies require substantial amounts of water. Nevertheless, their share of total actual consumption is relatively low, when viewed at the national and international level. Water consumed by mining was just 4% in Canada (in 2005), 1% in the United States of America, and 2–3% in Australia (Miningfacts 2012). The amount of water required by a mine or mineral processing plant varies, depending on the mineral being extracted, the extraction process used, and the size of the mine and plant.

Chemicals are used in most mineral processing and metallurgical plants in flotation (mineral concentration), dewatering operations (particle aggregation to increase solid–liquid separation efficiency), leaching (metal extraction), and solvent extraction. The reagents range from bulk commodity inorganics to specialty synthetic polymers and extractants (Supplemental Table S-1). Pearse (2005) illustrates the diversity of these reagents used and gives a brief description of how and where they are used.

These reagents and ions can be classified as very toxic, such as thiol collectors, sulfonates, amines, and cyanides, and moderately toxic, such as alcohol-based frothers, such as polypropylene glycol. Some of these chemicals and ions (Supplemental Table S-1) might remain in the effluents and in the liquid phase of the tailings and can negatively affect direct water recycling or the ability to discharge. Therefore, the drive for new and improved mineral processing reagents is both technically and environmentally crucial and is one of the ever-evolving challenges of the industry.

Dewatering, to remove water contained in the slurry is an essential part of mineral processing, involving dewatering screens, thickening, and filtration (Galvez et al. 2014). It is done to enable ore and mineral concentrates to be more easily transported and allow further processing and gangue disposal. In addition, dewatering plays an important role in water recycling; the use of thickeners allows the partial recovery and recirculation of process water and chemicals at relatively low costs. Recycling also helps reduce fresh water abstraction, reducing operating costs and environmental impacts. Yet, as the particle size decreases, the difficulty and cost of dewatering increases.

Water is often reused and recycled in mining or mineral processing, especially in areas with arid climates. Several advanced water conservation practices and technologies have been developed and implemented. New processes allow the elimination of industrial contaminants (e.g. ions, chemical reagents, particles) and water reuse (Rubio et al. 2007). These efforts of mining companies to reuse and treat the process water and the generated effluents is a positive step in reducing their environmental impact and the risks to biota and human health. In addition, it ensures the stakeholders'

water quality and quantity, in view of availability problems and increased water demand. Yet, some treatment or management steps prior to application might be evaluated to ensure safety and efficiency in water recycling (Couto et al. 2014; França et al. 2017). For example, recirculating the water increases mineralization and, consequently, increases the solubility of minerals via the ionic strength effect. Similarly, the return of water flows from a circuit can introduce elevated concentrations of dissolved species from soluble mineral phases (e.g. some metal hydroxides, sulfates, and carbonates) that can have detrimental effects on the process, and may mandate additional treatment steps before recycling to remove these constituents (Chen et al. 2009; Harris et al. 2013; Levay et al. 2001; Manono et al. 2017; Polemio et al. 1980).

Many authors have reported their concerns regarding the reuse of process water within the minerals processing industry, specifically in some mineral concentration operations, such as flotation. Process water and fresh water differ in their chemical composition, which changes further during recycling. It is therefore essential to evaluate the effects of chemical parameters (e.g. ion type, ionic strength, pH value) on flotation efficiency (Levay et al. 2001; Manono et al. 2017; Rao and Finch 1989). Thus, responsible management of water quality is important during the entire mine life cycle.

## Water Treatment

Researchers conducting isotope studies should know how the polluted mine water is handled during the treatment process so that they select appropriate natural isotope or isotope tracers that won't be removed. Therefore, we provide a short overview of processes involved in mine water treatment.

Water from the extractive industry may be treated, reused, or discharged based on the relevant environmental regulations. Like any other polluted water from production processes, the treatment of the extracted water must ensure that its use or disposal will not cause any environmental harm. At mine sites, ground- and mine-water can have a wide range of mineralization, expressed in TDS (gravimetric method). A maximum of 10 g/L were analysed in an Australian mine, while up to 37 g/L were found at some sites in Germany, and 372 g/L in Poland (CSIRO and Prosser 2011; Rózkowski 2000; Rózkowski and Rudzinska-Zapasnik 1983; Wedewardt 1995). In addition, mine water may contain hydrocarbons, metals, or metalloids. As mineralized water can change the soil structure or cause accumulation of salts and other contaminants, it is rarely used in agriculture (Annandale et al. 2001). Discharging untreated water from the extractive industry into surface water bodies can similarly increase

mineralization and cause the accumulation of potential pollutants in aquatic organisms. In arid regions, mine water is often pumped into evaporation ponds, but there is a growing concern over the leakage of contaminants into soil, surface, and groundwater, which has ultimately led to treatment of many such discharges.

Though neutralization is the most commonly used mine water treatment process (Hatch 2014), membrane processes such as reverse osmosis (RO) are also very useful in removing water constituents and contaminants from mine or waste water. RO divides the waste stream into very pure water that can be used as drinking water or for industrial and agricultural purposes and highly concentrated brine for disposal ( $\approx 10\%$  of the original water volume). Although the water purified by RO is of high quality, its discharge into watercourses can be problematic, as it can cause "clean water pollution". Typically, aquatic organisms need nutrients in the form of dissolved salt or ions, which would no longer be available in appropriate quantities in RO treated water. When discharging this water into rivers is necessary, soluble minerals should be added to reach vital concentrations for aquatic life (CSIRO and Prosser 2011).

Process wastewater can be treated by various processes to produce clean water with the characteristics required for recycling or discharge. Some of the most common treatment processes are sedimentation, precipitation, filtration (including reverse osmosis), biosorption, and flotation (electroflotation, induced air flotation, dissolved air flotation, nanobubble flotation). Some innovative and/or restructured technologies, such as electrocoagulation, capacitive deionization, electroreduction, can also be used to improve sustainability of water use in mining processes (Wolkersdorfer et al. 2015).

However, chemicals added during mineral processing can complicate water treatment. For example, xanthates, which are used for flotation and treatment of sulfide and metallic ores, can be decomposed biologically or simply by increasing the pH, but is reported to generate  $\text{CS}_2$  that is even more toxic than the original compound (Shen et al. 2016). Oliveira and Rubio (2007) removed xanthate from mineral processing wastewater by adsorption on zeolite, followed by aggregation and dissolved air flotation.

Amines are extensively employed in silicate mineral flotation, due to their efficiency as a mineral collector. They are, however, highly toxic, and information on their rates of degradability, by-product formation, and residence time in tailing dams is generally lacking. Batisteli and Peres (2008) reported up to 95% recovery of amines from flotation wastewater by adsorption on natural zeolites, allowing the water to be reused in the flotation plant.

Combined treatment processes were tested by Amaral Filho et al. (2016) for sulfate removal by precipitation and



flocculation, followed by micro/nanobubbles flotation to treat a typical AMD generated in the coal mining region province of Santa Catarina, Brazil. The sulfate concentration was decreased below 500 mg/L, as recommended by the World Health Organization (WHO).

## Natural and Artificial Mine Water Tracer Tests

Understanding the hydraulic behaviour of mine water within an abandoned mine can substantially reduce the costs of mine closure and remediation (Wolkersdorfer 2008). Although few natural or artificial tracer tests in mines have been published to date, the difficulty of evaluating the hydrodynamics of flooded mines are well described (e.g. Hünefeld-Mugova and Wolkersdorfer 2018; Wolkersdorfer 2005, 2006; Wolkersdorfer et al. 2016a). A prerequisite for successful in situ treatment is a thorough understanding of the hydrodynamic conditions in a flooded underground mine. As has been shown by published in situ treatment projects, most failures have occurred because the mine water did not reach the point of alkalinity injection (as either fly ash, lime, or sodium hydroxide). Even where tracer tests were conducted prior to alkalinity injection, the results of the in situ treatment were not always satisfying on a long-term basis (Aljoe and Hawkins 1993). In fact, most tracer tests linked to mine water problems were related to either pollution of the aquifer or radioactive waste disposal, and not the mine water itself.

Artificial tracer tests are well established in groundwater studies where they are commonly used to investigate the hydraulic parameters or interconnections of groundwater flow (Käb 1998; Leibundgut et al. 2009). Most of the techniques used are well described and, depending on the aims of the tracer test and the hydrological situation, a range of tracers or methods can be chosen. Little has changed since Davis (1994) discussed the lack of published results of tracer tests in abandoned underground mines, due to the difficulties in conducting such tracer tests. Extensive underground workings can have numerous levels with substantial lengths largely sealed by collapse, allowing for groundwater transport to be stalled (and evaporating) in pools and shafts. This results in highly variable residence times, and it could take many years to many decades before the tracer is recovered (currently, the first author is conducting a mine water tracer test in Finland, which has already lasted four years). Thus, the results of a mine water tracer test can be inconclusive. Summarized, the aims of mine water tracer tests are:

- Testing the bulkheads' (dams') effectiveness
- Investigating the hydrodynamic conditions
- Tracing connections between mine and surface

- Clarifying water inundations
- Mass flow
- Estimating the decrease or increase of contaminants
- Attempting in situ treatment by injecting alkalinity and perhaps other reagents

Historically, the first tracer tests conducted in mines were simply to reveal connections between ground or surface waters and the mine (Skowronek and Žmija 1977). One of the first tracer tests in a deep flooded underground mine to investigate the more complex hydrodynamic conditions was conducted with the LydiA Technique in 1995 (Wolkersdorfer 1996) and since then, about 20 such tests have been successfully carried out in flooded mines (Wolkersdorfer and LeBlanc 2012).

An alternative technique to determine how strong the hydrologic connection is between different galleries is mass balance. This method was applied at the Iron Mountain site in California and after other methods failed, this one showed that only a small percentage of acid water from a higher gallery could be leaking into a lower gallery to account for the chemistry of the lower portal effluent (Alpers et al. 1992). The same approach was used by the first author at the Schwaz mine in Tyrol, Austria to determine flow from different locations within the mine (unpublished report to Montanwerke Brixlegg/Austria).

Tracer tests can also be used to assess mixing in pit lakes (von Rohden and Ilmberger 2001) and discharge mixing in streams and receiving waters. Several types of tracers have been used to investigate the mixing of density layers in lakes or the mixing of streams, including isotopes (Baskaran 2011; Harvey et al. 1996).

## Mine-Site Monitoring and Modelling

As addressed in Gammons et al. (2000), it is important to differentiate filtered (0.45 µm, 0.2 µm, 0.1 µm, or ultrafiltered [ $<0.1$  µm]) vs. unfiltered water samples in terms of the objective of the sampling campaign. Almost all environmental quality standards distinguish between 'total recoverable' or 'total metal' concentrations. It would therefore be easy to limit environmental monitoring of mines or treatment plants to filtered or unfiltered samples only. However, when geochemical models are used to address simple issues such as saturation indices or speciation determinations, as well as for more comprehensive applications such as the characterization of contamination problems, the prediction of environmental impacts or the study of the transport and fate of pollutants (e.g. Zhu and Anderson 2002), filtered concentrations are normally required. To determine toxicity, filtered samples are also required, sometimes even anoxic samples. Filtered samples are also necessary to predict the

transport or fate of potentially toxic elements. However, a comparison of filtered and unfiltered metal concentrations can provide information on whether possible exceedances of environmental quality standards are due to chemical or physical processes (e.g. Moreno et al. 2019). Furthermore, in the presence of high concentrations of iron, colloidal material can strongly influence the results obtained for dissolved matter. Fish mortalities are known to be caused by iron and aluminium colloids coagulating on gill surfaces (Duis and Oberemm 2000; Playle and Wood 1989; Stephens and Ingram 2006). Consequently, in these cases, other membrane sizes (0.20  $\mu\text{m}$ , 0.1  $\mu\text{m}$ , or even ultrafiltration) could be considered appropriate. In addition, although sampling should ideally be focused on water, other materials can be considered, such as secondary products, sediments, and even biological material, as they may give indication about the quality of the water system.

The heterogeneity and reactivity of mine waters impose a monitoring plan with a dense network of sampling points to cover spatial variability (ERMITE Consortium et al. 2004). In the same way, frequency must be representative of temporal variations as the reaction products are affected by climate and meteorological parameters. Therefore, whenever possible, the entire hydrological year, or at least a period long enough to reflect seasonal variations, should be considered.

The reactivity and instability of mine water makes it difficult to obtain representative samples. Moreover, chemical characteristics are affected by daily and seasonal cycles. Therefore, repeatability of procedures and monitoring for diel and seasonal cycles are critical issues. It is also important to record the exact time of sampling, weather conditions, on-site parameters (pH, temperature, EC, redox potential, oxygen saturation), and the flow (i.e. discharge).

Geochemical modelling can be useful in the characterization and remediation of mine sites if used judiciously by an experienced modeller (Nordstrom et al. 2017). It can be used to help interpret the source, fate, and transport of contaminants, identify potential toxins, identify mineral solubility controls, provide a QA/QC check on water analyses, assist in the conceptual model development for a site, and assist remedial planning of removing contaminant sources or estimating lime or limestone needs for a neutralization plant (for a general introduction, see Nordstrom and Campbell 2014).

## Specific Isotopic Tools

Stable isotope techniques have successfully been used at mine sites. Applications include identification of groundwater recharge, location of flow pathways, characterising and quantifying sources, and potential mixing and identification of source and fate of specific pollutants in contamination

studies. General information about isotopes and related studies can be found in Clark and Fritz (1999).

With respect to appropriate analytical techniques, the International Atomic Energy Agency (2009) has reported that laser instruments are capable of “providing accurate results with a precision of approximately 1 ‰ for  $\delta^2\text{H}$  and 0.2 ‰ for  $\delta^{18}\text{O}$  in liquid water samples of up to at least 1000 mg/L dissolved salt concentration. In addition, it has good linearity for running analyses of artificial isotope tracers which have values much heavier than natural samples”. Solutions of AMD often have high total dissolved solids concentrations (i.e. mineralisation). Therefore, the use of laser instruments for analysing these waters may require special attention because dissolved solids concentrations above 1000 mg/L are common and might confound analyses.

Practical results have been obtained at sites that present challenging water resource and usage issues (Araujo et al. 2010; Farid et al. 2014; Fernandes et al. 2006, 2008; Lamego et al. 2008; Otero and Soler 2002; Tsujimura et al. 2007). At a Brazilian uranium mine site, stable isotope ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) data were used to characterize the hydrogeology of the area and establish correlation between waste management and groundwater contamination (Araujo et al. 2010; Fernandes et al. 2008; Lamego et al. 2008). Management of the effluent produced by water draining from the mine pit and solid wastes (waste rock and processing waste) was not efficient enough to avoid contaminated water releases into receiving water bodies. The groundwater was characterized as a Na-HCO<sub>3</sub>-type water, with elevated concentrations of Cl observed in some samples. The results showed that groundwater uranium concentrations might result from their complexation by carbonates or other ions rather than contaminants in the open pit drainage water. In addition, it indicated that a shallow aquifer in this semi-arid region of Brazil might be better suited as a sustainable groundwater resource.

Lamego et al. (2008) and Fernandes et al. (2006) stressed the need for an integrated approach to environmental impact assessment and radiation protection. To achieve this, radiological and non-radiological aspects must be treated simultaneously and in an integrated manner. This ensures that all relevant processes during the mobilisation and transport of radionuclides from the source to the receptors are considered.

In addition to mine effluents, isotopes can be useful for assessing the potential negative effects of mineral processing plants effluents over water quality. A north-central Chilean example using sulfur isotopes is presented in Oyarzún et al. (2015). Their study allowed them to clearly distinguish between the natural sulfate concentration of the water in the semi-arid Limarí basin and the contamination effect of a Panulcillo metallurgical facility.

Stable isotopes provide a useful tool to assess water sources as well as mixing fractions in mine-related environments. For example, Walton-Day and Poeter (2009) used stable isotope ratios to investigate hydraulic connections between the Dinero mine tunnel and the nearby Turquoise reservoir in the Sugar Loaf mining district in Colorado (USA). These served to substantiate results obtained from on-site parameters studies, hydrographs, and water analyses.

Environmental isotopes ( $^2\text{H}$ ,  $^{18}\text{O}$ ,  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{13}\text{C}$ ), geo-physical, and hydrological measurements as well as water chemistry were used to identify the recharge source (local rainwater), residence time (3–4 years), origin (heap leach piles, tailings dump area), fate, and transport of contaminants (AMD) in the fractured granite of La Mesada, Los Gigantes, Córdoba, Argentina. This approach was chosen to support an engineering approach for remediation of the former mining site (Walton-Day and Poeter 2009). Elliot and Younger (2007, 2014) also used key environmental tracers (including sulfur isotopes) to identify mixing components during active pumping of mine waters to control unregulated discharges into two abandoned coal mine systems in the UK.

Along with water chemistry, isotopes are useful in characterizing AMD processes. For instance, Lepitre et al. (2003) used Pb isotopes in ARD to differentiate the origin of dissolved Pb in water in the Sullivan Mine, South British Columbia (Canada). They showed that specific isotopic compositions were typical for a given source region and could be used as ‘fingerprints’ to differentiate between various ore deposits and further sources. In addition, they developed a detailed sampling and analysis method for dissolved Pb in mine water. Coetzee and Rademeyer (2005) also used Pb isotopes as a tracer for contaminated waters from a uranium mine, and Yin et al. (2016) looked at Hg isotopes in sphalerites. Viers et al. (2018) used Cu isotopes in a small river system in the Iberian pyrite belt (Cobica River, Spain) to reveal sources and transport pathways. In addition, they assessed the potential of using Cu isotope signatures as a tracer.

Sulfur isotopic data of dissolved sulfate can also be used to elucidate the source of mine water mineralization. As dilution does not affect the sulfur isotopic composition substantially, the analysis of  $\delta^{34}\text{S}$  of dissolved sulfate provides an excellent tool for quantifying the environmental impact caused by potash mining in the Upper Eocene south Pyrenean Catalan evaporite basin (Otero and Soler 2002). The  $\delta^{34}\text{S}$  values of dissolved sulfate ranged from +18‰ to +20‰ (VCDT, Vienna-Canyon Diablo troilite) for mining effluents and from +10‰ to +14‰ (VCDT) for natural saline springs. The latter values are in accordance with the sulfur isotopic composition of sulfates from the evaporites of this area and allowed to determine the origin of mineralization where the chemical characteristics were not conclusive (Otero and Soler 2002, 2003).

Isotopes have also been used to investigate the effects of mining activities on biota (Bowen et al. 2005). For instance, Søndergaard et al. (2010) used Pb isotopes to assess Pb biota (i.e. lichens, seaweed, and mussels) contamination near west Greenland’s abandoned ‘Black Angel Mine’.

Ratié et al. (2016) used Ni isotope ratios in ores, fly ash, slags, and Fe–Ni samples from two metallurgical plants located in the Goiás State, Brazil (Barro Alto, Niquelândia) to characterize possible soil contamination from smelter emissions. They conclude that “tracing environmental contamination ‘remains challenging’”, though the slags showed Ni-enrichments and fractionation compared to soil samples. Skierszkan et al. (2016) looked at both Mo and Zn isotopes in mining waste rock and drainage in Peru.

Wiederhold (2015) comprehensively reviewed the use of metal (stable) isotope fractionation in natural systems. In processes such as redox reactions, complexation, organic material binding, mineral precipitation and dissolution, evaporation, condensation, diffusion, and biological cycling, he addressed their usefulness and limitations. Mohalik et al. (2017), Sloss (2013), Wu et al. (2012), and Yang et al. (2017) used environmental tracers and stable isotopes to identify the susceptibility of coal mines to the phenomenon of ‘spontaneous combustion’. In addition, N and O isotopes have been investigated particularly to trace the environmental impact of explosives used in mining and construction (Degnan et al. 2016; Hendry et al. 2018; Nilsson 2013).

Isotopes can also be used to constrain the source of air pollution resulting from mining activities. For instance, Félix et al. (2015) used  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$  isotope ratios, along with chemical and scanning electron microscopy analysis, for source apportionment of metal and metalloid contaminants transported by atmospheric particulates from an active copper mine site in Hayden-Winkelman, Arizona (USA).

Wetlands, either natural or artificial, are commonly considered for ARD remediation (Johnson and Hallberg 2005). Isotopes can be used to assess the performance of such systems. For instance Hsu and Maynard (1999) used sulfur isotopes to evaluate the effectiveness of constructed wetlands (Wills Creek) for AMD from underground abandoned coal mines in the Muskingum River watershed, Ohio (USA).

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## References

- Aldous PJ (1987) The groundwater hydrology of an abandoned coal mined aquifer—a case study from the Forest of Dean Coalfield. PhD, Univ. of Bristol
- Aljoe WW, Hawkins JW (1993) Neutralization of acidic discharges from abandoned underground coal mines by alkaline injection. *Bur Mines Rept Invest* 9468:1–37
- Alpers CN, Nordstrom DK, Burchard JM (1992) Compilation and interpretation of water-quality and discharge data for acidic mine waters at Iron Mountain, Shasta County, California, 1940–91. *Water Resour Investig Rep C* 91–4160:1–173
- Alpers CN, Blowes DW, Nordstrom DK, Jambor JL (1994) Secondary minerals and acid mine-water chemistry. In: Jambor JL, Blowes DW (eds) *Short course handbook on environmental geochemistry of sulfide mine-wastes*, vol 22. Mineralogical Assoc of Canada, Waterloo, Ontario, p 247–270
- Alpers C, Nordstrom D, Verosub K, Helm-Clark C (2007) Paleomagnetic determination of pre-mining metal flux rates at the Iron Mountain Superfund site, northern California (Abstract). In: Presented at the American Geophysical Union Spring Meeting, Acapulco, Guerrero, Mexico, Session GP41B-04
- Amaral Filho J, Azevedo A, Etchepare R, Rubio J (2016) Removal of sulfate ions by dissolved air flotation (DAF) following precipitation and flocculation. *Int J Miner Process* 149:1–8. <https://doi.org/10.1016/j.minpro.2016.01.012>
- Amos RT, Blowes DW, Bailey BL, Segó DC, Smith L, Ritchie AIM (2015) Waste-rock hydrogeology and geochemistry. *Appl Geochem* 57:140–156. <https://doi.org/10.1016/j.apgeochem.2014.06.020>
- Annandale JG, Jovanovic NZ, Pretorius JJB, Lorentz SA, Rethman NFG, Tanner PD (2001) Gypsiferous mine water use in irrigation on rehabilitated open-cast mine land: crop production, soil water and salt balance. *Ecol Eng* 17(2–3):153–164. [https://doi.org/10.1016/S0925-8574\(00\)00155-5](https://doi.org/10.1016/S0925-8574(00)00155-5)
- Araujo DM, Yoshida MI, Takahashi JA, Carvalho CF, Stapelfeldt F (2010) Biodegradation studies on fatty amines used for reverse flotation of iron ore. *Int Biodeterior Biodegrad* 64(2):151–155. <https://doi.org/10.1016/j.ibiod.2010.01.004>
- ASTM E1689-95 (2014) *Standard Guide for Developing Conceptual Site Models for Contaminated Sites*. ASTM International (ed), West Conshohocken
- Baker BJ, Banfield JF (2003) Microbial communities in acid mine drainage. *FEMS Microbiol Ecol* 44(2):139–152. [https://doi.org/10.1016/s0168-6496\(03\)00028-x](https://doi.org/10.1016/s0168-6496(03)00028-x)
- Banks D (1996) The hydrochemistry of selected coal mine drainage and spoil-tip run-off water, Longyearbyen, Svalbard. *NGU-rapport* 96(141):1–22
- Banks D (2004) Geochemical processes controlling minewater pollution. In: *Conference papers*, vol 35. Umweltbundesamt, Wien, pp 17–44
- Banks D, Younger PL, Arnesen RT, Iversen ER, Banks SB (1997) Mine-water chemistry: the good, the bad and the ugly. *Environ Geol* 32(3):157–174. <https://doi.org/10.1007/s002540050204>
- Barbour SL, Hendry MJ, Carey SK (2016) High-resolution profiling of the stable isotopes of water in unsaturated coal waste rock. *J Hydrol* 534:616–629. <https://doi.org/10.1016/j.jhydrol.2016.01.053>
- Baskaran M (2011) *Handbook of environmental isotope geochemistry*. Advances in isotope geochemistry. Springer, Berlin
- Batisteli GMB, Peres AEC (2008) Residual amine in iron ore flotation. *Miner Eng* 21(12–14):873–876. <https://doi.org/10.1016/j.mineng.2008.04.002>
- Bews BE, Barbour SL, Wickland B (1999) Lysimeter design in theory and practice. In: *Paper presented at the tailings and mine waste '99*, Fort Collins, pp 13–21
- Bigham JM, Nordstrom DK (2000) Iron and aluminum hydroxysulfates from acid sulfate waters. *Rev Mineral Geochem* 40:351–403. <https://doi.org/10.2138/rmg.2000.40.7>
- Blowes DW, Ptacek CL, Frind EO, Johnson RH, Robertson WD, Molson JW (1994) Acid-Neutralization reactions in inactive mine tailings impoundments and their effect on the transport of dissolved metals. In: *Presented at the International Land Reclamation and Mine Drainage Conf*, Pittsburgh, vol 1, pp 429–438
- Blowes DW, Ptacek CJ, Jambor JL, Weisener CG, Paktunc D, Gould WD, Johnson DB (2014) The geochemistry of acid mine drainage. In: Turekian HD, Holland KK (eds) *Treatise on geochemistry*, 2nd edn. Elsevier, Oxford, p 131–190. <https://doi.org/10.1016/B978-0-08-095975-7.00905-0>
- Bowen GJ, Wassenaar LI, Hobson KA (2005) Global application of stable hydrogen and oxygen isotopes to wildlife forensics. *Oecologia* 143(3):337–348. <https://doi.org/10.1007/s00442-004-1813-y>
- Burnside NM, Banks D, Boyce AJ (2016a) Sustainability of thermal energy production at the flooded mine workings of the former Caphouse Colliery, Yorkshire, United Kingdom. *Int J Coal Geol* 164:85–91. <https://doi.org/10.1016/j.coal.2016.03.006>
- Burnside NM, Banks D, Boyce AJ, Athresh A (2016b) Hydrochemistry and stable isotopes as tools for understanding the sustainability of minewater geothermal energy production from a 'standing column' heat pump system: Markham Colliery, Bolsover, Derbyshire, UK. *Int J Coal Geol* 165:223–230. <https://doi.org/10.1016/j.coal.2016.08.021>
- Cane A, Nader G, Folguera L, Sanchez Proaño P, Davite G, Silva A, Cicerone D (2018) *Modelo Conceptual Hidrogeológico Mejorado—Sitio Los Gigantes* [Hydrogeological aspects of Los Gigantes site], Report N° ARG/7/008. Comisión Nacional de Energía Atómica—CNEA, Buenos Aires, Argentina, 191 p
- Chen JM, Liu RQ, Sun W, Qiu GZ (2009) Effect of mineral processing wastewater on flotation of sulfide minerals. *Trans Nonferrous Met Soc China* 19(2):454–457. [https://doi.org/10.1016/S1003-6326\(08\)60294-0](https://doi.org/10.1016/S1003-6326(08)60294-0)
- Clark ID, Fritz P (1999) *Environmental isotopes in hydrogeology*, 2nd edn. Lewis, Boca Raton
- Coetzee H, Rademeyer M (2005) Lead isotope ratios as a tracer for contaminated waters from uranium mining and milling. In: Merkel BJ, Hascheberger A (eds) *Uranium in the environment—UMHIV*. Springer, Heidelberg, p 663–670. [https://doi.org/10.1007/3-540-28367-6\\_67](https://doi.org/10.1007/3-540-28367-6_67)
- Couto HJB, França SCA, Barbosa RKC (2014) The use of DAF (dissolved air flotation) as an alternative treatment for red mud wastewater. In: *Presented at the XXVII international mineral processing congress (IMPC 2014)*:CAC00160014
- CSIRO, Prosser IP (2011) *Water—science and solutions for Australia*. CSIRO Publishing, Collingwood
- Davis MW (1994) The use of tracer dyes for the identification of a mine flooding problem, Rico, Dolores County, Colorado. *Colorado Geol Surv Open-File Rep* 91–2:1–20
- Degnan JR, Bohlke JK, Pelham K, Langlais DM, Walsh GJ (2016) Identification of groundwater nitrate contamination from explosives used in road construction: isotopic, chemical, and

- hydrologic evidence. *Environ Sci Technol* 50(2):593–603. <https://doi.org/10.1021/acs.est.5b03671>
- Dold B (2014) Submarine tailings disposal (STD) – a review. *Minerals* 4(3):642–666. <https://doi.org/10.3390/min4030642>
- Dold B, Spangenberg JE (2005) Sulfur speciation and stable isotope trends of water-soluble sulfates in mine tailings profiles. *Environ Sci Technol* 39(15):5650–5656. <https://doi.org/10.1021/es04093a>
- Duis K, Oberemm A (2000) Sensitivity of early life stages of vendace, *Coregonus albula*, to acid pH in postmining lakes: an experimental approach. *Environ Toxicol* 15(3):214–224
- Edmunds WM, Shand P (2008) Natural groundwater quality. Wiley, Blackwell
- Eilu P (2012) Mineral deposits and metallogeny of Fennoscandia. *Special Pap Geol Surv Finland* 53:1–401
- Einbinder N, Nolin C (2012) No Means NO. *Altern J* 38(6):52–57
- Elliot T, Younger PL (2007) Hydrochemical and isotopic tracing of mixing dynamics and water quality evolution under pumping conditions in the mine shaft of the abandoned Frances Colliery, Scotland. *Appl Geochem* 22(12):2834–2860. <https://doi.org/10.1016/j.apgeochem.2007.07.007>
- Elliot T, Younger PL (2014) Detection of mixing dynamics during pumping of a flooded coal mine. *Groundwater* 52(2):251–263. <https://doi.org/10.1111/gwat.12057>
- Eppinger RG, Fuge R (2009) Natural low-pH environments unaffected by human activity. *Preface Appl Geochem* 24(2):189–190. <https://doi.org/10.1016/j.apgeochem.2008.11.020>
- ERMITE Consortium, Younger PL, Wolkersdorfer C (2004) Mining impacts on the fresh water environment: technical and managerial guidelines for catchment scale management. *Mine Water Environ* 23(Supplement 1):S2–S80. <https://doi.org/10.1007/s10230-004-0028-0>
- Farid I, Zouari K, Trabelsi R, Kallali AR (2014) Application of environmental tracers to study groundwater recharge in a semi-arid area of Central Tunisia. *Hydrol Sci J J Sci Hydrol* 59(11):2072–2085. <https://doi.org/10.1080/02626667.2013.863424>
- Félix OI, Csavina J, Field J, Rine KP, Sáez AE, Betterton EA (2015) Use of lead isotopes to identify sources of metal and metalloid contaminants in atmospheric aerosol from mining operations. *Chemosphere* 122:219–226. <https://doi.org/10.1016/j.chemosphere.2014.11.057>
- Fernandes HM, Lamego Simoes Filho FF, Perez V, Franklin MR, Gomiero LA (2006) Radioecological characterization of a uranium mining site located in a semi-arid region in Brazil. *J Environ Radioact* 88(2):140–157. <https://doi.org/10.1016/j.jenvrad.2006.01.006>
- Fernandes HM, Gomiero LA, Peres V, Franklin MR, Simoes Filho FF (2008) Critical analysis of the waste management performance of two uranium production units in Brazil—part II: caetite production center. *J Environ Manage* 88(4):914–925. <https://doi.org/10.1016/j.jenvman.2007.04.022>
- Flores M, Nunez J, Oyarzún J, Freixas G, Maturana H, Oyarzún R (2017) Surface water quality in a sulfide mineral-rich arid zone in north-central Chile: learning from a complex past, addressing an uncertain future. *Hydrol Process* 31(3):498–513. <https://doi.org/10.1002/hyp.11086>
- França SCA, Andrade LS, Loayza PEV, Trampus BC (2017) Water in mining—challenges for reuse. In: Wolkersdorfer C, Sartz L, Sillanpää M, Häkkinen A (eds) *IMWA 2017—mine water & circular economy*, vol I. Lappeenranta Univ of Technology, Lappeenranta, pp 445–452
- Galvez ED, Cruz R, Robles PA, Cisternas LA (2014) Optimization of dewatering systems for mineral processing. *Miner Eng* 63:110–117. <https://doi.org/10.1016/j.mineng.2014.01.026>
- Gammons CH, Mulholland TP, Frandsen AK (2000) A comparison of filtered vs unfiltered metal concentrations in treatment wetlands. *Mine Water Environ* 19(2):111–123. <https://doi.org/10.1007/BF02687259>
- Gammons CH, Nimick DA, Parker SR (2015) Diel cycling of trace elements in streams draining mineralized areas—a review. *Appl Geochem* 57:35–44. <https://doi.org/10.1016/j.apgeochem.2014.05.008>
- Geller W, Schultze M, Kleinmann R, Wolkersdorfer C (2013) Acidic Pit Lakes—the legacy of coal and metal surface mines. *Environmental science and engineering*. Springer, Heidelberg
- Gu H, Ma F, Guo J, Li K, Lu R (2018) Assessment of water sources and mixing of groundwater in a coastal mine: the Sanshandao Gold Mine, China. *Mine Water Environ* 37(2):351–365. <https://doi.org/10.1007/s10230-017-0458-0>
- Gunson AJ, Klein B, Veiga M, Dunbar S (2012) Reducing mine water requirements. *J Cleaner Prod* 21(1):71–82. <https://doi.org/10.1016/j.jclepro.2011.08.020>
- Harris A, Venkatesan L, Greyling M (2013) A practical approach to plant-scale flotation optimization. *J S Afr Inst Min Metall* 113(3):263–272
- Harvey JW, Wagner BJ, Bencala KE (1996) Evaluating the reliability of the stream tracer approach to characterize stream-subsurface water exchange. *Water Resour Res* 32(8):2441–2451. <https://doi.org/10.1029/96WR01268>
- Hasche A, Wolkersdorfer C (2004) Mine water treatment with a pilot scale RAPS-system. *Wiss Mitt Inst Geol* 25:93–99
- Hatch (2014) Study to identify BATEA for the management and control of effluent quality from mines. MEND Report, vol 3.50.1. The mine environment neutral drainage [MEND] Program, Ottawa
- Helgen SO, Moore JN (1996) Natural background determination and impact quantification in trace metal-contaminated river sediments. *Environ Sci Technol* 30(1):129–135. <https://doi.org/10.1021/es950192b>
- Hem JD (1985) Study and interpretation of the chemical characteristics of natural water. *US Geol Surv Water Suppl Pap* 2254:263. <https://doi.org/10.3133/wsp2254>
- Hendry MJ, Wassenaar LI, Barbour SL, Schabert MS, Birkham TK, Fedec T, Schmeling EE (2018) Assessing the fate of explosives derived nitrate in mine waste rock dumps using the stable isotopes of oxygen and nitrogen. *Sci Total Environ* 640–641:127–137. <https://doi.org/10.1016/j.scitotenv.2018.05.275>
- Hsu SC, Maynard JB (1999) The use of sulfur isotopes to monitor the effectiveness of constructed wetlands in controlling acid mine drainage. *Environ Engg Policy* 1:223–233. <https://doi.org/10.1007/s100220050026>
- Hubert E, Wolkersdorfer C (2015) Establishing a conversion factor between electrical conductivity and total dissolved solids in South African mine waters. *Water SA* 41(4):490–500. <https://doi.org/10.4314/wsa.v41i4.08>
- Hünefeld-Mugova E, Wolkersdorfer C (2018) A review of mine water stratification. In: Meier G et al (eds) *Altbergbau-Kolloquium—Tagungsband*, vol 18. Wagner, Nossen, pp 125–132
- Instituto Argentino de Normalización y Certificación—IRAM (2016) IRAM 29598—Calidad ambiental—Desarrollo de modelos conceptuales para sitios contouredados [Environmental quality—Development of conceptual models for contaminated sites]. Instituto Argentino de Normalización y Certificación, Buenos Aires
- Instituto Brasileiro de Mineração—IBRAM (2012) Gestão para a sustentabilidade na mineração—20 anos de história [Management for sustainability in mining—20 years of history]. Instituto Brasileiro de Mineração, Brazil
- International Atomic Energy Agency (2009) Laser spectroscopic analysis of liquid water samples for stable hydrogen and oxygen isotopes. IAEA Training Course Series IAEA-TCS-35

- Jambor JL (2003) Mine-waste mineralogy and mineralogical perspectives of acid-base accounting. In: Jambor JL, Blowes DW, Ritchie AIM (eds) Environmental aspects of mine wastes, vol 31. Mineralogical Association of Canada, Waterloo, Ontario, p 117–146
- Jambor JL, Nordstrom DK, Alpers CN (2000) Metal-sulfate salts from sulfide mineral oxidation. *Rev Mineral Geochem* 40(1):303–350. <https://doi.org/10.2138/rmg.2000.40.6>
- Jambor JL, Blowes DW, Ritchie AIM (2003) Environmental aspects of mine wastes. Short course series volume, vol 31. Mineralogical Assoc of Canada, Waterloo
- Jamieson HE, Walker SR, Parsons MB (2015) Mineralogical characterization of mine waste. *Appl Geochem* 57:85–105. <https://doi.org/10.1016/j.apgeochem.2014.12.014>
- Janson E, Boyce AJ, Burnside N, Gzyl G (2016) Preliminary investigation on temperature, chemistry and isotopes of mine water pumped in Bytom geological basin (USCB Poland) as a potential geothermal energy source. *Int J Coal Geol* 164:104–114. <https://doi.org/10.1016/j.coal.2016.06.007>
- Johnson DB, Hallberg KB (2003) The microbiology of acidic mine waters. *Res Microbiol* 154(7):466–473. [https://doi.org/10.1016/S0923-2508\(03\)00114-1](https://doi.org/10.1016/S0923-2508(03)00114-1)
- Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options—a review. *Sci Total Environ* 338:3–14. <https://doi.org/10.1016/j.scitotenv.2004.09.002>
- Johnson KL, Younger PL (2002) Hydrogeological and geochemical consequences of the abandonment of Frazer's Grove carbonate hosted Pb/Zn fluorspar mine, North Pennines, UK. *Spec Publ Geol Soc London* 198:347–363
- Jurjovec J, Blowes DW, Ptacek CJ (1995) Acid neutralization in mill tailings and the effect of natrojarosite addition. In: Proc, Sudbury '95—mining and the environment, vol I, pp 29–38
- Käb W (1998) Tracing technique in geohydrology. Balkema, Rotterdam
- Kelly DP, Wood AP (2000) Reclassification of some species of *Thiobacillus* to the newly designated genera *Acidithiobacillus* gen. nov., *Haloithiobacillus* gen. nov. and *Thermithiobacillus* gen. nov. *Int J Syst Evol Microbiol* 50:511–516. <https://doi.org/10.1099/00207173-50-2-511>
- Kester DR, Byrne RH, Liang Y-J (1975) Redox reactions and solution complexes of iron in marine systems. *ACS Symp Ser* 18:56–79. <https://doi.org/10.1021/bk-1975-0018.ch003>
- Kunkel T (2017) Aboriginal values and resource development in native space: lessons from British Columbia. *Extr Ind Soc* 4(1):6–14. <https://doi.org/10.1016/j.exis.2017.01.001>
- Lamego F, Santos RR, Ferreira da Silva L, Monken Fernandes H (2008) Water management of the uranium production facility in Brazil (Caetité, BA)—potential impacts over groundwater quality. In: Presented at the 12th international congress of the international radiation protection assoc (IRPA): strengthening radiation protection worldwide, Buenos Aires
- Leibundgut C, Małozzewski P, Külls C (2009) Tracers in hydrology. Wiley-Blackwell, Oxford
- Lepitre ME, Allen DM, Mortensen JK, Gabites JE (2003) Differentiating sources of dissolved lead in mine waters using lead isotope techniques, Sullivan Mine. British Columbia. *Water Resour Res* 39(1):HWC1-1–HWC1-13. <https://doi.org/10.1029/2001WR000606>
- Levy G, Smart RS, Skinner WM (2001) The impact of water quality on flotation performance. *J S Afr Inst Min Metall* 101(2):69–75
- Li GQ, Wang XQ, Meng ZP, Zhao HJ (2014) Seawater intrusion assessment based on hydrochemical analysis enhanced by hierarchy clustering in an undersea goldmine pit, China. *Environ Earth Sci* 71(12):4977–4987. <https://doi.org/10.1007/s12665-013-2888-8>
- Lottermoser B (2010) Mine wastes—characterization, treatment and environmental impacts, 3rd edn. Springer, Heidelberg
- Maest AS, Nordstrom DK (2017) A geochemical examination of humidity cell tests. *Appl Geochem* 81:109–131. <https://doi.org/10.1016/j.apgeochem.2017.03.016>
- Malmström ME, Destouni G, Banwart SA, Strömberg BHE (2000) Resolving the scale-dependence of mineral weathering rates. *Environ Sci Technol* 34(7):1375–1378. <https://doi.org/10.1021/es990682u>
- Manono MS, Matibidi K, Thubakgale CK, Corin KC, Wiese JG (2017) Water quality in PGM ore flotation: the effect of ionic strength and pH. In: Wolkersdorfer C, Sartz L, Sillanpää M, Häkkinen A (eds) IMWA 2017—mine water & circular economy, vol II. Lappeenranta Unive of Technology, Lappeenranta, pp 777–784
- Matschullat J, Ottenstein R, Reimann C (2000) Geochemical background—can we calculate it? *Environ Geol* 39(9):990–1000. <https://doi.org/10.1007/s002549900084>
- Mohalik NK, Lester E, Lowndes IS (2017) Review of experimental methods to determine spontaneous combustion susceptibility of coal—Indian context. *Int J Min Reclam Environ* 31(5):301–332. <https://doi.org/10.1080/17480930.2016.1232334>
- Moore JN, Luoma SN (1990) Hazardous wastes from large-scale metal extraction—a case study. *Environ Sci Technol* 24(9):1278–1285. <https://doi.org/10.1021/es00079a001>
- Moreno F, Valente TM, Gomes P, Fonseca R, Costa MR, Costa A (2019) Partitioning of potentially toxic elements among two colloidal fractions and relevance for their mobility in different water types. In: Presented at the E3S web of conferences, vol 98. <https://doi.org/10.1051/e3sconf/20199809020>
- Nilsson L (2013) Nitrogen transformations at the Kiruna Mine—the use of stable nitrogen isotopes to trace nitrogen-transforming processes. *Examensarbete* 30:1–39
- Nordstrom DK (1977) Hydrogeochemical and microbiological factors affecting the heavy metal chemistry of an acid mine drainage system. PhD Diss, Stanford
- Nordstrom DK (1982) Aqueous pyrite oxidation and the consequent formation of secondary minerals. In: Kittrick JA, Fanning DS, Hossner LR (eds) Acid sulfate weathering. SSSA Spec. Publ. Soil Science Soc. of America, Madison, p 37–56. <https://doi.org/10.12136/sssaspepub10.c3>
- Nordstrom DK (2008) Questa Baseline and Pre-Mining Ground-Water Quality Investigation. 25. Summary of Results and Baseline and Pre-Mining Ground-Water Geochemistry, Red River Valley, Taos County, New Mexico, 2001–2005. *US Geol Surv Prof Pap* 1728:1–111
- Nordstrom DK (2009) Acid rock drainage and climate change. *J Geochem Expl* 100(2):97–104. <https://doi.org/10.1016/j.gexpl.2008.08.002>
- Nordstrom DK (2011) Mine waters: acidic to circumneutral. *Elements* 7(6):393–398. <https://doi.org/10.2113/gselements.7.6.393>
- Nordstrom DK (2015) Baseline and premining geochemical characterization of mined sites. *Appl Geochem* 57:17–34. <https://doi.org/10.1016/j.apgeochem.2014.12.010>
- Nordstrom DK, Alpers CN (1995) Remedial investigation, decisions and geochemical consequences at Iron Mountain Mine, California. In: Proc, Sudbury '95—mining and the environment, vol II, pp 633–642
- Nordstrom DK, Alpers CN (1999) Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. *Proc Natl Acad Sci USA* 96(7):3455–3462. <https://doi.org/10.1073/pnas.96.7.3455>
- Nordstrom DK, Campbell KM (2014) Modeling low-temperature geochemical processes. In: Turekian HD, Holland KK (eds) *Treatise on Geochemistry*, vol 7. Elsevier, Amsterdam, pp 27–68. <https://doi.org/10.1016/B978-0-08-095975-7.00502-7>
- Nordstrom DK, Wright WG, Mast MA, Bove DJ, Rye RO (2007) Aqueous-sulfate stable isotopes—a study of mining-affected

- and undisturbed acidic drainage. US Geol Surv Prof Pap 1651:391–496
- Nordstrom DK, Nicholson A, Weing W, Mayer U, Maest A (2017) Geochemical modeling for mine site characterization and remediation. Management technologies for metal mining influenced water, vol 4, SME, Englewood
- Nuttall CA, Younger PL (2004) Hydrochemical stratification in flooded underground mines: an overlooked pitfall. *J Contam Hydrol* 69(1–2):101–114. [https://doi.org/10.1016/S0169-7722\(03\)00152-9](https://doi.org/10.1016/S0169-7722(03)00152-9)
- Oliveira CdR, Rubio J (2007) Adsorption of ions onto treated natural zeolite. *Mater Res* 10(4):407–412. <https://doi.org/10.1590/S1516-14392007000400014>
- Otero N, Soler AIG (2002) Sulphur isotopes as tracers of the influence of potash mining in groundwater salinisation in the Llobregat Basin (NE Spain). *Water Res* 36(16):3989–4000. [https://doi.org/10.1016/S0043-1354\(02\)00125-2](https://doi.org/10.1016/S0043-1354(02)00125-2)
- Otero N, Soler AIG (2003) Stable isotopes of dissolved sulphate as tracers of the origin of groundwater salinization in the Llobregat River (NE Spain). In: Presented at the international symp on isotope hydrology and integrated water resources management, Vienna, IAEA-CN-104:190–191
- Oyarzún R, Jofre E, Morales P, Maturana H, Oyarzún J, Kretschmer N, Aguirre E, Gallardo P, Toro LE, Muñoz JF, Aravena R (2015) A hydrogeochemistry and isotopic approach for the assessment of surface water-groundwater dynamics in an arid basin: the Limari watershed, north-central Chile. *Environ Earth Sci* 73(1):39–55. <https://doi.org/10.1007/s12665-014-3393-4>
- Oyarzún J, Núñez J, Maturana H, Oyarzún R (2018) The El Indio Mine closure plan effects over the water quality of the Upper Elqui Basin. *Environ Eng Geosci* 24(3):349–355. <https://doi.org/10.2113/EEG-2022>
- Parra A, Oyarzún J, Maturana H, Kretschmer N, Meza F, Oyarzún R (2011) Natural factors and mining activity bearings on the water quality of the Choapa basin, north central Chile: insights on the role of mafic volcanic rocks in the buffering of the acid drainage process. *Environ Monit Assess* 181(1–4):69–82. <https://doi.org/10.1007/s10661-010-1814-8>
- Pearse MJ (2005) An overview of the use of chemical reagents in mineral processing. *Miner Eng* 18(2):139–149. <https://doi.org/10.1016/j.mineng.2004.09.015>
- Pedretti D, Mayer KU, Beckie RD (2017) Stochastic multicomponent reactive transport analysis of low quality drainage release from waste rock piles: Controls of the spatial distribution of acid generating and neutralizing minerals. *J Contam Hydrol* 201:30–38. <https://doi.org/10.1016/j.jconhyd.2017.04.004>
- Playle RC, Wood CM (1989) Water chemistry changes in the gill micro-environment of rainbow trout: experimental observations and theory. *J Comp Physiol B* 159(5):527–537. <https://doi.org/10.1007/bf00694377>
- Plumlee GS, Nash JT (1995) Geoenvironmental models of mineral deposits—fundamentals and applications. Open-File Report—US Geological Survey OF95-0831:1–9
- Plumlee GS, Smith KS, Montour MR, Ficklin WH, Mosier EL (1999) Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. The Environmental Geochemistry of Mineral Deposits, vol 6A. Society of Economic Geologists, Littleton
- Pohl W (2011) Economic Geology – Principles and Practice – Metals, Minerals, Coal and Hydrocarbons – Introduction to Formation and Sustainable Exploitation of Mineral Deposits, 1st edn. Wiley-Blackwell, Chichester
- Polemio M, Bufo S, Paoletti S (1980) Evaluation of ionic-strength and salinity of groundwater—effect of the ionic composition. *Geochim Cosmochim Acta* 44(6):809–814. [https://doi.org/10.1016/0016-7037\(80\)90262-8](https://doi.org/10.1016/0016-7037(80)90262-8)
- Qian J, Wang L, Ma L, Lu Y, Zhao W, Zhang Y (2016) Multivariate statistical analysis of water chemistry in evaluating groundwater geochemical evolution and aquifer connectivity near a large coal mine, Anhui, China. *Environ Earth Sci* 75(9):747. <https://doi.org/10.1007/s12665-016-5541-5>
- Quatrini R, Johnson DB (2016) Acidophiles: Life in extremely acidic environments. Caister Academic Press, Poole
- Rao SR, Finch JA (1989) A review of water re-use in flotation. *Miner Eng* 2(1):65–85. [https://doi.org/10.1016/0892-6875\(89\)90066-6](https://doi.org/10.1016/0892-6875(89)90066-6)
- Ratié G, Quantin C, Jouvin D, Calmels D, Ettler V, Sivry Y, Vieira LC, Ponzevera E, Garnier J (2016) Nickel isotope fractionation during laterite Ni ore smelting and refining: implications for tracing the sources of Ni in smelter-affected soils. *Appl Geochem* 64:136–145. <https://doi.org/10.1016/j.apgeochem.2015.09.005>
- Razowska L (2001) Changes of groundwater chemistry caused by the flooding of iron mines (Częstochowa Region, Southern Poland). *J Hydrol* 244:17–32. [https://doi.org/10.1016/S0022-1694\(00\)00420-0](https://doi.org/10.1016/S0022-1694(00)00420-0)
- Reimann C, Garrett RG (2005) Geochemical background—concept and reality. *Sci Total Environ* 350(1–3):12–27. <https://doi.org/10.1016/j.scitotenv.2005.01.047>
- Rodrigues L, Valente TM, Correia A, Alves A, Foing B, Davies GR (2012) Contribution of eukaryotic microbial communities to the formation of Fe-rich accretions in an extreme acidic environment. *Geoph Res Abstracts* 14 (EGU General Assembly):EGU2012-14112
- Rózkowski A (2000) Coal mine water chemistry (Upper Silesian Coal Basin, Poland). In: Proc, 7th international mine water assoc congress, pp 634–644
- Rózkowski A, Rudzińska-Zapaśnik T (1983) Pochodzenie wód podziemnych w Górnoślaskim i Lubelskim Zagłębiu Węglowym [On the origin of groundwaters in the Upper Silesian and Lublin Coal Basin]. *Przeegl Geologiczny* 31(6):370–377
- Rubio J, Carissimi E, Rosa JJ (2007) Flotation in water and wastewater treatment and reuse: recent trends in Brazil. *Int J Environ Pollut* 30(2):197–212. <https://doi.org/10.1504/Ijep.2007.014700>
- Runnells DD, Shepherd TA, Angino EE (1992) Metals in water—determining natural background concentrations in mineralized areas. *Environ Sci Technol* 26(12):2316–2323. <https://doi.org/10.1021/es00036a001>
- Rüterkamp P, Meßer J (2000) Untersuchungen zur hydraulischen und hydrochemischen Situation in den drei Teilrevieren der gefluteten Flussspatgrube Straßberg, unpubl. Report No 1710–99-285. Deutsche Montan Technologie GmbH, Essen
- Schneider P, Nilius U, Gottschalk N, Süß A, Schaffrath M, Löser R, Lange T (2017) Determination of the geogenic metal background in surface water: benchmarking methodology for the rivers of Saxony-Anhalt, Germany. *Water* 9(2):75. <https://doi.org/10.3390/w9020075>
- Shen Y, Nagaraj DR, Farinato R, Somasundaran P (2016) Study of xanthate decomposition in aqueous solutions. *Miner Eng* 93:10–15. <https://doi.org/10.1016/j.mineng.2016.04.004>
- Singer PC, Stumm W (1970) Acidic mine drainage—rate-determining step. *Science* 167(3921):1121–1123. <https://doi.org/10.1126/science.167.3921.1121>
- Singh RN (1986) Mine inundations. *Int J Mine Water* 5(2):1–27. <https://doi.org/10.1007/BF02498098>
- Skierszkan EK, Mayer KU, Weis D, Beckie RD (2016) Molybdenum and zinc stable isotope variation in mining waste rock drainage and waste rock at the Antamina mine, Peru. *Sci Total Environ* 550:103–113. <https://doi.org/10.1016/j.scitotenv.2016.01.053>
- Skowronek E, Żmija M (1977) Określenie pochodzenia wody wpływającej z za obmurza szybu znakowaniem rodaminą B [Determination of the origin of water flowing out from behind a shaft lining traced with rhodamine B]. *Przeegl Gorn* 33(1):13–19

- Sloss L (2013) Quantifying emissions from spontaneous combustion. IEA Reports, vol CCC/224. Clean Coal Centre, London
- Smith JL, Beckie RD (2003) Hydrologic and geochemical transport processes in mine waste rock. In: Jambor JL, Blowes DW, Ritchie AIM (eds) Environmental aspects of mine wastes, vol 31, Mineralogical Assoc of Canada, Waterloo, Ontario, pp 51–72
- Søndergaard J, Asmund G, Johansen P, Elberling B (2010) Pb isotopes as tracers of mining-related Pb in lichens, seaweed and mussels near a former Pb-Zn mine in West Greenland. *Environ Pollut* 158(5):1319–1326. <https://doi.org/10.1016/j.envpol.2010.01.006>
- Spangenberg JE, Dold B, Vogt ML, Pfeifer HR (2007) Stable hydrogen and oxygen isotope composition of waters from mine tailings in different climatic environments. *Environ Sci Technol* 41(6):1870–1876. <https://doi.org/10.1021/es061654w>
- Sprenger M, Leistert H, Gimbel K, Weiler M (2016) Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes. *Rev Geophys* 54(3):674–704. <https://doi.org/10.1002/2015RG000515>
- Stephens FJ, Ingram M (2006) Two cases of fish mortality in low pH, aluminium rich water. *J Fish Dis* 29(12):765–770. <https://doi.org/10.1111/j.1365-2761.2006.00772.x>
- Stumm W, Morgan JJ (1996) Aquatic chemistry—chemical equilibria and rates in natural waters, 3rd edn. Wiley, New York
- Tóth J (1963) A theoretical analysis of groundwater flow in small drainage basins. *J Geophys Res* 68(16):4795–4812. <https://doi.org/10.1029/JZ068i016p04795>
- Tsujimura M, Abe Y, Tanaka T, Shimada J, Higuchi S, Yamanaka T, Davaa G, Oyunbaatar D (2007) Stable isotopic and geochemical characteristics of groundwater in Kherlen River basin, a semi-arid region in eastern Mongolia. *J Hydrol* 333(1):47–57. <https://doi.org/10.1016/j.jhydrol.2006.07.026>
- Valente TM, Leal Gomes C (2007) The role of two acidophilic algae as ecological indicators of acid mine drainage sites. *J Iberian Geol* 33(2):283–294
- Valente TM, Leal Gomes C (2009) Occurrence, properties and pollution potential of environmental minerals in acid mine drainage. *Sci Total Environ* 407(3):1135–1152. <https://doi.org/10.1016/j.scitotenv.2008.09.050>
- Van der Sloot HA, Van Zomeren A (2012) Characterisation leaching tests and associated geochemical speciation modelling to assess long term release behaviour from extractive wastes. *Mine Water Environ* 31(2):92–103. <https://doi.org/10.1007/s10230-012-0182-8>
- Viers J, Grande JA, Zouiten C, Freydier R, Masbou J, Valente TM, de la Torre M-L, Destrigneville C, Pokrovsky OS (2018) Are Cu isotopes a useful tool to trace metal sources and processes in acid mine drainage (AMD) context? *Chemosphere* 193:1071–1079. <https://doi.org/10.1016/j.chemosphere.2017.11.133>
- von Rohden C, Ilmberger J (2001) Tracer experiment with sulfur hexafluoride to quantify the vertical transport in a meromictic pit lake. *Aquat Sci* 63(4):417–431
- Vutukuri VS, Singh RN (1995) Mine inundation – case histories. *Mine Water Environ* 14(1–4):107–130. <https://doi.org/10.1007/BF02914857>
- Walkey AR (2017) Court upholds decision to block Taseko mine near Williams Lake. *The Globe and Mail* (2017-12-06)
- Walton-Day K, Poeter E (2009) Investigating hydraulic connections and the origin of water in a mine tunnel using stable isotopes and hydrographs. *Appl Geochem* 24(12):2266–2282. <https://doi.org/10.1016/j.apgeochem.2009.09.015>
- Ward AD, Trimble SW (2003) Environmental hydrology, 2nd edn. Taylor & Francis, Boca Raton
- Wedewardt M (1995) Hydrochemie und Genese der Tiefenwässer im Ruhr-Revier. DMT-Berichte aus Forschung und Entwicklung 39:1–250
- Wiederhold JG (2015) Metal stable isotope signatures as tracers in environmental geochemistry. *Environ Sci Technol* 49(5):2606–2624. <https://doi.org/10.1021/es504683e>
- Wolkersdorfer C (1994) Changes in mine water hydrology during the flooding of an abandoned uranium mine in the Erzgebirge/Saxonia/Germany. In: Proc, 5th international mine water congress, vol 1, Nottingham, UK, pp 43–55
- Wolkersdorfer C (1996) Hydrogeochemische Verhältnisse im Flutungswasser eines Uranbergwerks—die Lagerstätte Niederschlema/Alberoda. *Clausthaler Geowiss Diss* 50:1–216
- Wolkersdorfer C (2005) Mine water tracer tests as a basis for remediation strategies. *Chem Erde* 65(Supp 1):65–74. <https://doi.org/10.1016/j.chemer.2005.06.003>
- Wolkersdorfer C (2006) Acid mine drainage tracer tests. In: Proc, 7th international conf on acid rock drainage (ICARD), St. Louis, pp 2490–2501 [CD-ROM]
- Wolkersdorfer C (2008) Water management at abandoned flooded underground mines—fundamentals, tracer tests, modelling, water treatment. Springer, Heidelberg
- Wolkersdorfer C, LeBlanc J (2012) Regulations, legislation, and guidelines for artificial surface water and groundwater tracer tests in Canada. *Water Qual Res J Canada* 47(1):42–55. <https://doi.org/10.2166/wqrjc.2012.042>
- Wolkersdorfer C, Lopes DV, Nariyan E (2015) Intelligent mine water treatment—recent international developments. In: Paul M (ed) Sanierte Bergbaustandorte im Spannungsfeld zwischen Nachsorge und Nachnutzung—WISSYM 2015. Wismut GmbH, Chemnitz, pp 63–68. <https://doi.org/10.13140/RG.2.1.2441.5849>
- Wolkersdorfer C, Göbel J, Hasche-Berger A (2016a) Assessing subsurface flow hydraulics of a coal mine water bioremediation system using a multi-tracer approach. *Int J Coal Geol* 164:58–68. <https://doi.org/10.1016/j.coal.2016.03.010>
- Wolkersdorfer C, Shongwe L, Schmidt C (2016b) Can natural stratification prevent pollution by acid mine drainage? In: Proc, IMWA 2016—mining meets water—conflicts and solutions, Leipzig, Germany, pp 115–121
- Wright LT (1906) Controlling and extinguishing fires in pyritous mines. *Eng Min J* 81:171–172
- Wu J, Wu Y, Wang J, Zhou C (2012) Radon measuring to detect coal spontaneous combustion fire source at Bulianta mine, Shandong. In: Proc, 12th coal operators' conf, Wollongong, pp 300–304
- Wu Q, Mu W, Xing Y, Qian C, Shen J, Wang Y, Zhao D (2017) Source discrimination of mine water inrush using multiple methods: a case study from the Beiyangzhuang Mine, northern China. *Bull Eng Geol Environ* 2017:1–14. <https://doi.org/10.1007/s10064-017-1194-1>
- Yang Y, Li Z, Hou S, Li J, Si L, Zhou Y (2017) Identification of primary CO in coal seams based on oxygen isotope method. *Combust Sci Technol* 189(11):1924–1942. <https://doi.org/10.1080/0010202.2017.1340277>
- Yelapatyevsky PV (1995) Factors controlling metal content of mining waters. In: Kharaka YK, Chudaev OV (eds) Water-rock interaction, vol 8. Balkema, Rotterdam, pp 901–904
- Yin R, Feng X, Hurley JP, Krabbenhoft DP, Lepak RF, Hu R, Zhang Q, Li Z, Bi X (2016) Mercury isotopes as proxies to identify sources and environmental impacts of mercury in sphalerites. *Sci Rep* 6:18686. <https://doi.org/10.1038/srep18686>
- Younger PL (1997) The longevity of minewater pollution—a basis for decision-making. *Sci Total Environ* 194–195:457–466. [https://doi.org/10.1016/S0048-9697\(96\)05383-1](https://doi.org/10.1016/S0048-9697(96)05383-1)
- Younger PL, Banwart SA, Hedin RS (2002) Mine water—hydrology, pollution, remediation. Kluwer, Dordrecht
- Zamzow K, Chambers D (2017) Independent investigation of reclamation at exploration drill holes at the remote Pebble copper prospect, Alaska. In: Wolkersdorfer C, Sartz L, Sillanpää M, Häkkinen A (eds) IMWA 2017—mine water & circular economy, vol I. Lappeenranta Univ of Technology, Lappeenranta, pp 204–211
- Zhu C, Anderson GM (2002) environmental applications of geochemical modeling. Cambridge University Press, Cambridge



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