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Acid rock drainage prediction: A critical review

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A R T I C L E I N F O

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A B S T R A C T

Acid rock drainage (ARD) prediction is a very important issue in order to predict and prevent environmental pollution associated with mining activities. Nowadays, simple tests are widely applied and established in the mining and consulting business for ARD prediction. These tests have many known errors and problems, as that they do not account for the complexity of the mineral assemblage of an ore deposit, and therefore are not able to predict the geochemical behavior accurately. This critical review has the aim of first, highlighting the geochemical processes associated to the problems of ARD prediction. Secondly, the errors and limitations of the standard static and kinetic tests are highlighted. The currently applied calculation factor of 31.25 for sulfide acid potential calculation overestimates the carbonate neutralization potential by 100% in its geochemical assumptions. Thus, the calculation factor 62.5, based on the effective carbonate speciation at neutral pH, is recommended. Additionally, standard ABA procedure ignore the acid potential of Fe(III) hydroxides and/or sulfates and do not distinguish between different carbonate minerals. This can be critical, as for example siderite can be a net acid producing carbonate. Therefore, it is crucial to count on accurate quantitative mineral data in order to be able to accurately predict ARD formation and potential liberation of hazardous trace elements to the environment.

In many modern mining operations, quantitative mineral data is nowadays produced in order to enhance the recovery of the extraction process by the incorporation of geometallurgical information (e.g. quantitative mineralogy, mineral liberation, textural information, grain size distribution). Thus, the use of this very same existing data for ARD prediction can increase importantly the precision of ARD prediction, often without additional costs and testing. The only requirement is the interdisciplinary collaboration between the different divisions and data exchange in a modern mining operation.

Contents

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1. Introduction

Human history is an accumulation of conflicts about geo-resources (e.g. land, soil, water, metal, oil-gas). Therefore, mining has always had an essential role in the development of human history since the Neolithic Period. This has not changed today and most of the conflicts we observe nowadays have essentially the very same origin. Mining provides the metal supply of modern high-tech society. Although in daily life it is not very evident for most of the world's population, mining industry is the basis of economic wealth and technological development (Matsumoto et al., 2016), as can be observed in the industrial revolution in Europe (late 17th century) and the current information and energetic revolution world-wide. Although doubtless an essential industry, today's mining is facing severe problems for development, as the negative aspects of the mining activity are perceived to affect more and more people in a globalized world. Thus, the mining industry is struggling to obtain the social license in many parts of the world in order to develop new projects (Owen and Kemp, 2013). This is mainly due to the fact that most stakeholders, without direct benefit from the mining activity, perceive mining as a threat for their health and the environment, as for example by the formation of acid mine drainage (AMD) or more general acid rock drainage (ARD) and subsequent water pollution (Fig. 1). As metal extraction technologies have evolved, the amounts of mine wastes produced have increased tremendously, a trend, which will increase even more in the future. Hence, more precise ARD prediction methods are required to tackle this problem. ARD is the result of the oxidation sulfide-rich rocks, exposed by natural or anthropogenic processes to the atmosphere, process, which leads to high element concentrations in and acidification of the water. This process can result in a pollution of surface and groundwater resources. In this review the more general term ARD is used, as this applies also for any sulfide containing material extracted and deposited to oxidizing conditions, like for example in road, tunnel, or construction activities, or in natural oxidation processes.

In ancient times the metal supply was ensured by oxide ore deposits exposed on the surface of the earth crust (e.g. the gossan in the Iberian Pyritic belt from Roman time, or the silver gossans at Cerro de Pasco, Peru and Potosi, Bolivia pre-Inca and during the Spanish conquistador era (Abbott and Wolfe, 2003). Since the development of the flotation technique in the early 20th century (Bergh and Yianatos, 2011), it became possible to extract and separate metal sulfides from the primary zone of the ore deposit. This technological change, increased the dimension of mining, as now low-grade ores could be economically exploited. As a consequence, the amount of the waste material produced increased dramatically. Additionally, the phenomena of sulfide oxidation associated with the mining process could be first observed with the formation of acid mine drainage in coal mining (Colmer and Hinkle, 1947), which now is the main environmental challenge of the metal mining industry today (Dold, 2014).

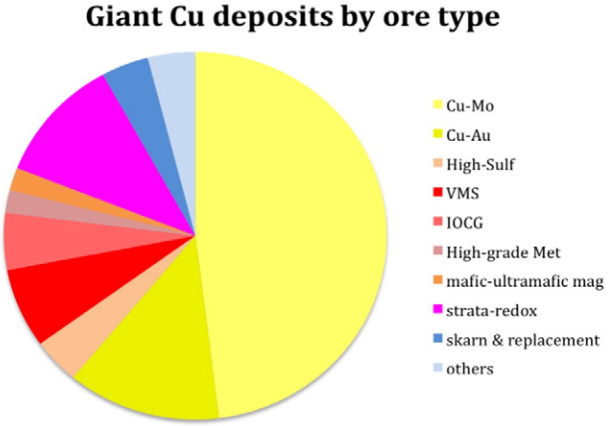

Fig. 1. Percentage of the different giant copper deposits by ore types to global copper production (n = 221). Giant Cu-Mo and Cu-Au porphyry deposits represent about 60% of the world copper production. The in yellowish to reddish colored ore types tend to produce ARD, while the bluish colored skarn and carbonate hosted deposits might have enough carbonates to neutralize the acid potential of the ore (modified after Laznicka, 2014).

As in the last decades environmental pollution has reached levels, which are directly critical for human health in some parts of the world (Rockstrom et al., 2009), the environmental and sustainable aspects have gained an important role in the last decades.

In order to get the dimension of the problem, the world production of some base metals through the importance of each exploited ore deposit type is analyzed (Laznicka, 1999, 2014; Singer, 1995). Plumlee (1999) highlighted the relationship between ore deposit type and final ARD composition, which allows the behavioral prediction for most deposit types with respect to ARD formation, assuming that a good knowledge of their mineralogical composition is available.

Giant (and super-giant) metallic ore deposits supply between 60 and 95% of global metallic resources on land, with several individual deposits monopolizing the supply (Laznicka, 2014), from which Cu has the highest number of super-accumulations followed by Au, Pb, Mo, Sb, and Sn (Laznicka, 1999). This is mainly due to the geochemical behavior of the different metals during enrichment processes in the earth crust. Cu, Au and Mo are mainly extracted from porphyry systems (60% of the world copper production is from porphyry Cu-Mo and Cu-Au deposits), and therefore the extraction of these elements is mainly done in huge mining operations (Gerst, 2008; Mudd et al., 2013). Thus, when considering these elements and the other ore deposit types, which host them (Fig. 1), it can be stated that most of the giant or super-giant deposits (except some carbonate hosted, skarn or placer deposits) will be very prone to produce ARD (Fig. 1).

ARD prediction is therefore an important issue due to the fact that ARD is one the principal environmental issue facing the mining industry nowadays (Fig. 2). Due to the increasing social pressure, governments and state agencies increasingly implement new regulations and laws to regulate mine waste management around the world, like for example the new mine closure law in Chile (in place since November 2012). Consequently, an accurate characterization of mine waste is required in order to evaluate the geochemical stability and predict if ARD might be an issue in the future that needs to be addressed and mitigated in time.

There are mainly two types of tests applied to predict the behavior of a rock sample concerning ARD production: The static tests, which evaluates if or not a sample will produce an acidic environment; and the kinetic tests, which evaluates, when the acidification will take place and which elements are liberated from the sample. In order to obtain this information, there are several tests widely used in the consulting and mining business and some are seen as standard methods.

The standard methods applied in ARD prediction are listed, explained and reviewed in several reports, books, and papers (Bouzahzah et al., 2014; Chotpantarat, 2011; Jacobs et al., 2014; Lottermoser, 2010; Parbhakar-Fox and Lottermoser, 2015; White and Jeffers, 1994; White et al., 1999) and will therefore not be all listed and addressed again in this review. It is also widely accepted that these tests have several limitations and sources of errors (Parbhakar-Fox and Lottermoser, 2015; White et al., 1999).

Parbhakar-Fox and Lottermoser (2015) have recently highlighted many of these problems associated with ARD prediction in an excellent review of ARD prediction. Here I will focus on some additional, fundamental errors (calculation factors) and limitations (only sulfides as proton source) of the current standard approaches. Most of these fundamental problems and errors are known and some were highlighted 25 years ago (Norecol Environmental Consultants Ltd., 1991). However, many of these errors and problems have been tolerated or ignored through time and it has reached a point where these test methods are established as standards in the mining and consultant

Fig. 2. Some examples of acid mine drainage. Above left: AMD pond with schwertmannite/goethite precipitating as sediment, Quiulacocha tailings impoundment, Cerro de Pasco, Peru. Above right: Collection channel for the AMD solutions from Excelsior Waste Rock Dump, Cerro de Pasco, Peru. Below left: Solid AMD in form of efflorescent salts precipitating at Pan de Azúcar tailings impoundments, Argentina. Below right: Schwertmannite terraces forming in the AMD effluent from Rio Tinto mine, Spain.

industries. They appear in guidelines and regulations, making it difficult to argue against them and promote new, more powerful approaches. Therefore, it is important to summarize these drawbacks once more in a comprehensive review and promote a modern use of mineralogical and geochemical data for ARD prediction.

In modern mining operations the importance of quantitative mineralogical characterization to increase the extraction efficiency by daily incorporation of mineralogical data for decision making in the mining process has been recently shown (Cruz et al., 2012), and together with the development of automated quantitative mineralogy gives nowadays new tools to improve the mining process (Gottlieb et al., 2000). Although this data exists in many modern, advanced mining operations, only sporadically it is also used for ARD prediction.

This review has the aim of summarizing and explaining the main problem of standard ARD prediction and convince the reader that the use of the often existing quantitative mineralogy used originally for geometallurgical purpose in a mining operation, could improve importantly also the ARD prediction, often without additional costs and testing.

2. Acid rock drainage and the importance of mineralogy

The goal of acid rock drainage prediction is very simple. It deals with the mineralogical composition of a geological sample (Fig. 3). This sample can contain different ratios of different minerals or mineral groups (e.g. silicates, carbonates, sulfides, sulfates, oxides). There are minerals which can produce acidity (e.g. sulfides through oxidation or Fe(III)hydroxides and/or sulfates through equilibrium reactions), which means they liberate protons (H^+) into solution and elements, which can hydrolyze to complexes (e.g. Fe, Al, Mn) in solution and by doing so deprotonize water, resulting also in a liberation of protons into solution; i.e. resulting in an acidification. If a solution is acidic it increases the mobility of heavy metals (e.g. divalent cations Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} among others), which can pollute water resources, rivers, lakes, sea, or groundwater.

On the other hand, there are minerals in a rock, which can neutralize these protons (e.g. carbonates, hydroxides, and silicates) and control

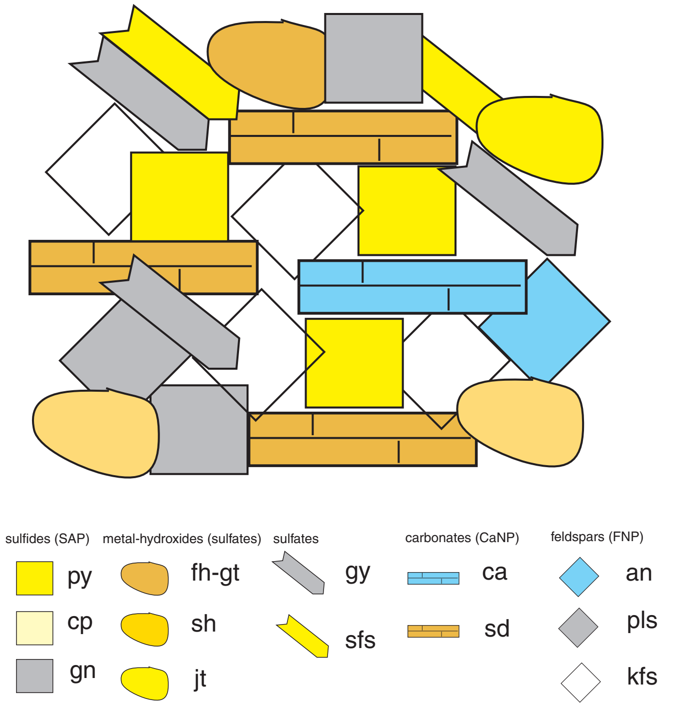

Fig. 3. Schematic mineral composition of a rock samples and the different minerals and mineral group producing acidity or neutralizing protons. Yellow colors indicate acid potential (AP), blue neutralization potential (NP), grey and white, none of both. Abbreviations: py = pyrite; cp = chalcopyrite; gn = galena; fh = ferrihydrite; gt = goethite; sh = schwertmannite; jt = jarosite; gy = gypsum; sfs = sulfo-salts; ca = calcite; sd = siderite; an = anorthite; pls = plagioclase; kfs = K-feldspar. SAP = sulfide acid potential; CaNP = carbonate neutralization potential; FNP = feldspar neutralization potential.

the pH as buffers at certain values (Langmuir, 1997; Stumm and Morgan, 1996). If a solution is alkaline, the mobility of elements, which are stable as oxyanions for example SO_4^{2-}, AsO_4^{3-}, MoO_4^{2-}, CrO_4^{2-} among others, is increased (Langmuir, 1997; Stumm and Morgan, 1996).

In order to predict if a rock (sample) will produce an acid, neutral or alkaline environment and/or liberate and possibly mobilize certain elements, it is necessary to know as exact as possible how much of each mineral is present in the sample (and its composition; i.e. the trace element composition). Thus, any prediction technique has the goal to quantify the reactive minerals in the sample. From an analytical point of view, this is a very difficult task. There exist only two traditional analytical techniques to characterize a mineral properly (i.e. define it's crystalline parameters): Optical microscopy and X-ray diffraction (XRD). Both techniques have strong limitation for quantification. In case of optical microscopy, a semi-quantification can be done by point counting, which is a very slow and labor intensive technique by highly qualified mineralogist, thus very expensive. X-ray diffraction has a high detection limit (2–5%), so that it is not suitable for detection of trace minerals. There are techniques available to lower this detection limit like differential XRD (Dold, 2003a), but are difficult to apply. Trace minerals can be most relevant for the environmental impact prediction, as clearly shown in the case of marine pollution associated to the tailings deposition in fjords at the Black Angel mine, Greenland (Elberling et al., 2002; Perner et al., 2010; Poling and Ellis, 1995).

The development of mineral quantification by the Rietveld method with XRD (Epp, 2016), give today the possibility of a semi-quantification of the mayor mineral phases in an mineral assemblage.

Do to these drawbacks for mineralogical quantifications; alternative faster and cheaper methods were needed for mineral quantification, specifically for ARD prediction. Subsequently, geochemical methods based on quantification of element concentrations in the sample and assumption for their mineral association in order to quantify indirectly the mineral content, were developed (e.g. Acid-Base Accounting (ABA); (Sobek et al., 1978), with modifications (Lawrence et al., 1989; Skousen et al., 1997), or correlations for quantification by the reactivity of the mineral assemblage (e.g. paste-pH, Fizz test, NAG) were drawn (White et al., 1999).

Parallel to this development of ARD prediction methods, due to the mentioned analytical limitations of the mineralogical techniques, a technique was needed for geosciences in general to quantify the mineral content of a sample in an automated and fast way, with higher accuracy and lower detection limit. This breakthrough was reached with the development of the SEM-EDX based automated quantitative mineralogy technique, also known as QEMSCAN® or Mineral Liberation Analysis (MLA) (Gottlieb et al., 2000).

In order to predict ARD for a rock sample, it is necessary to quantify the acid liberating minerals and calculate the moles of protons potentially liberated, which is called the Acid Potential (AP). On the other hand, the amount of minerals, which can neutralize the produced protons, are quantified, the so called Neutralization Potential (NP). The difference between both indicates if the sample has enough buffer capacity to neutralize all protons potentially produced (i.e. stays circum-neutral), or it will produce more protons than it can neutralize, which means that it will ultimately produce acidic conditions. This is called the Acid-Base Accounting (ABA). If there is a lack of acid buffer to maintain the system neutral, this buffer can be added, usually in form of carbonates (e.g. calcite or dolomite or sometime as lime). Therefore, the calculations are done as $tCaCO_3/1000$ t, in order to know how much carbonates are needed to maintain the material neutral.

As a result traditional, widely used standard prediction methods are applied, with many drawback and problems, and on the other hand, high-tech analytical techniques are available at a competitive price for the end-user. Thus, it can be predicted that it will be just a matter of time, when this change in the approach of ARD prediction will be accepted as new standard.

3. Acid rock drainage (ARD) formation

In this section, the geochemical and mineralogical basics necessary to understand the ARD prediction methodology are revised. For a more comprehensive review of the geochemical processes leading to ARD formation in mine waste, the reader is referred to the two open access publications (Dold, 2010, 2014) or other reference therein (Jambor and Blowes, 1994; Plumlee and Logsdon, 1999).

3.1. Acid liberation

Sulfide minerals form and are stable under reducing conditions. During mining these minerals can be exposed to oxidizing conditions, and subsequent, these minerals will undergo oxidation. This is usually highlighted in the literature with the example of pyrite oxidation, as this mineral is the most common sulfide and the one, which produces 4 mol of protons through its oxidation process (Colmer and Hinkle, 1947; Dold, 2014; Nordstrom, 2000; Singer and Stumm, 1970). This assumption is used in most ARD prediction method. Following Eq. (1), pyrite will oxidize in the presence of atmospheric oxygen and water, producing Fe(III)hydroxides, sulfate and 4 mol of protons per mole of pyrite oxidized by oxygen. Other sulfide minerals will produce different amounts of protons during oxidation under different geochemical conditions (Table 1). It can also be observed that mainly sulfide minerals containing iron produce net acidity via its oxidation, with exception of some lesser common sulfides like molybdenite, enargite, and stibnite. The liberated Fe^{2+} can oxidize automatically at $pH > 4$ or when catalyzed by bacterial activity at $pH < 4$ (e.g. *Acidithiobacillus* spp. or *Leptospirillum* spp.), a proton neutralizing process (Eq. (2)). The

Table 1

Overview of the oxidation reactions of the most relevant sulfide minerals via atmospheric oxygen, considering the hydrolysis of ferric iron and the final amount of protons liberated. Below, the oxidation via ferric iron is shown with the liberated amounts of protons. The equations have to be seen as idealized and partial reactions with different end products and amounts of protons liberated may occur in nature.

Sulfide mineral	Formula	Moles H^+
Oxidation via oxygen + hydrolisis of Fe^{3+}		
Pyrite (FeS_2)	$FeS_2 + 3.75O_2 + 3.5H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+$	4
Arsenopyrite ($FeAsS$)	$FeAsS + 2O_2 + 3H_2O = Fe(OH)_3 + SO_4^{2-} + HAsO_4^{2-} + 3H^+$	3
Chalcopyrite ($CuFeS_2$)	$CuFeS_2 + 4O_2 + 3H_2O = Cu^{2+} + Fe(OH)_3 + 2SO_4^{2-} + 2H^+$	2
Pyrrhotite ($Fe_{(1-x)}S$)	$x = 0.1$: $Fe_{(0.9)}S + 2.175O_2 + 2.35H_2O = 0.9Fe(OH)_3 + SO_4^{2-} + 2H^+$	2
Enargite (Cu_3AsS_4)	$Cu_3AsS_4 + 8.75O_2 + 2.5H_2O = 3Cu^{2+} + HAsO_4^{2-} + 4SO_4^{2-} + 4H^+$	4
Sphalerite (ZnS)	$ZnS + 2O_2 + = Zn^{2+} + SO_4^{2-}$	0
Galena (PbS)	$PbS + 2O_2 + = Zn^{2+} + SO_4^{2-}$	0
Covellite (CuS)	$CuS + 2O_2 + = Zn^{2+} + SO_4^{2-}$	0
Oxidation via ferric iron		
Pyrite (FeS_2)	$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	16/2[a]
Arsenopyrite ($FeAsS$)	$FeAsS + 13Fe^{3+} + 8H_2O = 14Fe^{2+} + SO_4^{2-} + HAsO_4^{2-} + 15H^+$	15/2[a]
Chalcopyrite ($CuFeS_2$)	$CuFeS_2 + 16Fe^{3+} + 8H_2O = Cu^{2+} + 17Fe^{2+} + 2SO_4^{2-} + 16H^+$	16/0[a]
Pyrrhotite ($Fe_{(1\text{-}x)}S$)	$x = 0.1$: $Fe_{(0.9)}S + 7.8\ Fe^{3+} + 4H_2O = 8.7Fe^{2+} + SO_4^{2-} + 8H^+$	8/0.2[a]
Enargite (Cu_3AsS_4)	$Cu_3AsS_4 + 35Fe^{3+} + 20H_2O = 3Cu^{2+} + HAsO_4^{2-} + 35Fe^{2+} + 4SO_4^2 + 39H^+$	39/4[a]
Sphalerite (ZnS)	$ZnS + 8Fe^{3+} + 4H_2O = 8Fe^{2+} + SO_4^{2-} + 8H^+$	8/0[a]
Galena (PbS)	$PbS + 8Fe^{3+} + 4H_2O = 8Fe^{2+} + SO_4^{2-} + 8H^+$	8/0[a]
Covellite (CuS)	$CuS + 8Fe^{3+} + 4H_2O = 8Fe^{2+} + SO_4^{2-} + 8H^+$	8/0[a]

[a] Amount of protons produced, considering if the amount of ferric iron has to be produced first through oxidation in the system, which neutralizes one mole of protons per mole of ferric iron (Eq. (2)).

produced ferric iron can then hydrolyze and produce Fe(III) hydroxides, process which liberates 3 mol of protons per mole of iron (Eq. (3)). Therefore, hydrolysis is the main acid producing process, so that any liberated element during weathering able to de-protonate the water molecule and hydrolyze (Ionic Potential (IP) between 4.6 and 5.6) can produce an excess of protons in solutions (e.g. Al, Fe, Mn), i.e. lower the pH. This is the reason that granites will produce acidic soils, although they do not contain sulfides.

$$FeS_2 + 15/4O_2 + 7/2H_2O \Rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{1}$$

$$Fe^{2+} + 1/4O_2 + H^+ \Longleftrightarrow Fe^{3+} + 1/2H_2O \tag{2}$$

$$Fe^{3+} + 3H_2O \Longleftrightarrow Fe(OH)_3(s) + 3H^+ \tag{3}$$

If pyrite is oxidized by ferric iron (Eq. (4)), 16 mol of protons are liberated per mole of pyrite oxidized. In this case it is crucial to have in mind that if the 14 mol of Fe^{3+} in Eq. (2) have to be produced in the system (i.e. in the fresh mine tailings impoundment or waste rock dump), 14 mol of protons will be neutralized (Eq. (2)), so that this reaction effectively produces 2 mol of protons, as in the case with oxidation via atmospheric oxygen. However, if a ferric iron-rich solution enters into a sulfide-rich system, then effectively 16 mol of protons are produced, as for example in the case of the Quiulacocha tailings impoundment and the Excelsior Waste-rock dump, Cerro de Pasco, Peru (Dold et al., 2009).

$$FeS_2 + 14Fe^{3+} + 8H_2O \Rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

Based on these assumptions it is generally established that one mole of pyrite produces 4 mol of protons through its oxidation and the associated precipitation of $Fe(OH)_3$ (Eq. (1)). This is used to calculate the AP of a rock unit based on its sulfur content and expressed as pyrite equivalent.

Another proton source, which is not considered by the standard ARD prediction tests, is the group of Fe(III) hydroxides and Fe(III) hydroxide sulfates (e.g. jarosite-alunite group, schwertmannite) together with metal chlorides and sulfates (e.g. eriochalcite, chalcanthite, rhomboclase), which might be the source of important amounts of acidity in ARD systems. The protons might be liberated due to dissolution-equilibrium reaction or due to mineral transformation due to meta-stability of the secondary mineralogy.

Dissolution-equilibrium.

$$\begin{aligned} &\text{Rhomboclase(dehydrated)}: HFe(SO_4)_2 + 3H_2O \\ &\quad = Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \end{aligned} \tag{5}$$

$$\begin{aligned} \text{Transformation}: \text{jarosite} \Rightarrow \text{goethite}: KFe_3(SO_4)_2(OH)_6 &\Rightarrow 3FeO(OH) \\ &+ K^+ + 2SO_4^{2-} + 3H^+ \end{aligned} \tag{6}$$

$$\begin{aligned} \text{Schwertmannite} \Rightarrow \text{goethite}: &\ Fe_{16}O_{16}(OH)_{10}(SO_4)_3 \\ &+ 6H_2O \Rightarrow 16FeO(OH) + 3SO_4^{2-} + 6H^+ \end{aligned} \tag{7}$$

3.2. Acid neutralization

The produced protons will interact with the gangue minerals of the rock and may undergo neutralization processes. Here, three mineral groups are the most relevant as potential neutralization agents: carbonates, hydroxides, and silicates.

3.2.1. Silicates

Among the silicates, quartz is considered as close to inert, and the dominant silicates for neutralization are the feldspars (Feldspar Neutralization Potential = FNP). Here are some important differences in the reaction kinetics to consider. While anorthite has acceptable relative reactivity in weathering processes, i.e. a relatively good FNP, plagioclase ($albite_{100–30}$) or orthoclase (K-feldspar) have very low relative reactivity (Table 2) and are therefore in general not considered in the evaluation of the overall neutralization potential (NP) of a rock unit (See Table 2), as equilibrium cannot reach in the contact time of the water with the mineral. In some cases high amount of intermediately fast weathering silicates like biotite and chlorite (~20%) for example from potassic and propylytic alterations, might add significant NP.

3.2.2. Hydroxides and hydroxide sulfates

Different metal hydroxides can have contrasting roles in a geochemical system. For example they can act as buffer by receiving protons, or de-protonate the water molecule due to hydrolysis (Eq. (3)) or they can liberate hydroxide ions into solution ($Ca(OH)_2$; portlandite), leading to alkaline pH conditions. The principal hydroxide buffers in the ARD environment or acid soils are dominated by the most abundant metal cations with the valence 3^+; i.e. Fe^{3+} and Al^{3+}. This is due to the ability of three valence cations to hydrolyze, given to their high ionic potential (IP) between 4.65 (Fe^{3+}) and 5.61 (Al^{3+}), forming solid hydroxide minerals like ferrihydrite, goethite, schwertmannite, jarosite-alunite, and gibbsite. These minerals represent buffers, which control the pH at ~4.3 ($Al(OH)_3$; gibbsite), ~3.5 ($Fe(OH)_3$; ferrihydrite, goethite), ~2.5–3.5 (schwertmannite), ~2 (jarosite). Thus, metal hydroxides represent important buffers in the acid pH ranges (Fig. 4).

3.2.3. Carbonates

As in ARD prediction, the most important question is to predict if the system maintain neutral pH or goes acid, therefore, the most important target minerals for the NP are the Ca-Mg carbonates, as they have a fast reactivity and tend to buffer the system a circum-neutral pH values (Table 2; Fig. 4). Therefore, it is crucial to apply the geochemistry of the carbonate system (Fig. 5) properly, in order to calculate and predict the NP accurately and the final ABA.

Calcite, and magnesite ($-\log K$ 8.48, $-\log K$ 8.24) are fast dissolving carbonates, (Table 2), while dolomite has lower solubility ($-\log K$ 17.09). Therefore, calcite is generally considered in calculations for NP and results are expressed as its equivalent. Calcite is the key buffer to maintain the pH at circumneutral conditions and is therefore the most important neutralizing agent in the mining environment. As long as calcite is available as a buffer in the system, its acid dissolution will liberate bicarbonate (HCO_3^-) to the solution (Fig. 5) (Sherlock et al., 1995) and is able to neutralize one mole of protons per mole of calcite dissolved (Eq. (8)). This is also true in an open system in the presence of $CO_{2(atm)}$,

Table 2
Relative reactivity in acid-neutralization capacity of minerals (after (Sverdrup, 1990).[a]

Group	Typical minerals	Relative reactivity (pH 5)
1. Dissolving	Calcite, dolomite, magnesite, aragonite, brucite,	1.0
2. Fast weathering	Anorthite, olivine, garnet, diopside, wollastonite, jadeite, nepheline, leucite, spodumene	0.6
3.Intermediate weathering	Enstatite, augite, hornblende, tremolite, actinolite, biotite, chlorite, serpentine, talc, epidote, zoisite, hedenbergite, glaucophane, anthophyllite	0.4
4. Slow weathering	Plagioclase (Ab100–Ab30), kaolinite, vermiculite, montmorillonite, gibbsite	0.02
5. Very slow weathering	K-feldspar, muscovite	0.01
6. "Inert"[a]	Quartz, rutile, zircon	0.004

[a] "Inert" is a relative expression, as in geological element cycling no mineral is inert.

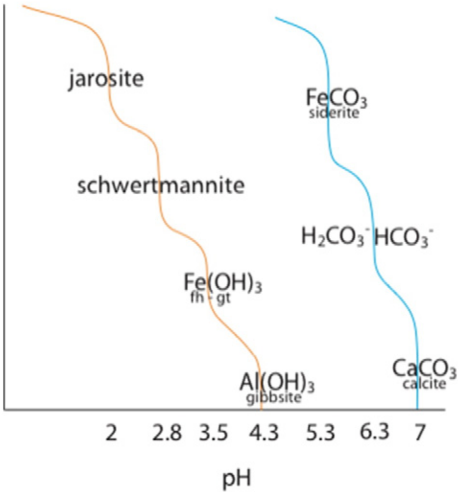

Fig. 4. Typical buffers and their pH in an ARD system (carbonates buffers and metal hydroxides-sulfates buffers).

which enhance the dissolution of carbonates (Eq. (9)). For a detailed review of the carbonate system refer to (Appelo and Postma, 2010; Stumm and Morgan, 1996).

$$CaCO_3 + H^+ \Longleftrightarrow Ca^{2+} + HCO_3^- \tag{8}$$

$$CO_{2(atm)} + H_2O + CaCO_3 \Rightarrow Ca^{2+} + 2HCO_3^- \tag{9}$$

If the pH is below pK1 (6.3), then carbonic acid is the dominant specie in solution (Eq. (10)).

$$CaCO_3 + 2H^+ \Longleftrightarrow Ca^{2+} + H_2CO_3^0 \tag{10}$$

Therefore, the carbonate system is able to neutralize 2 mol of protons at low pH (<6.3), but it is important to consider, that at pH < 6.3 the calcite buffer is destroyed and the aqueous carbonate species in solution become the only neutralization agent left in the system. Therefore, if calcite is still available as a buffer in the system, the dominant carbonate specie will be bicarbonate, as calcite buffers the pH around 7. This is the crucial consideration in acid base accounting calculations, and will be highlighted below in the discussion of the calculation factor.

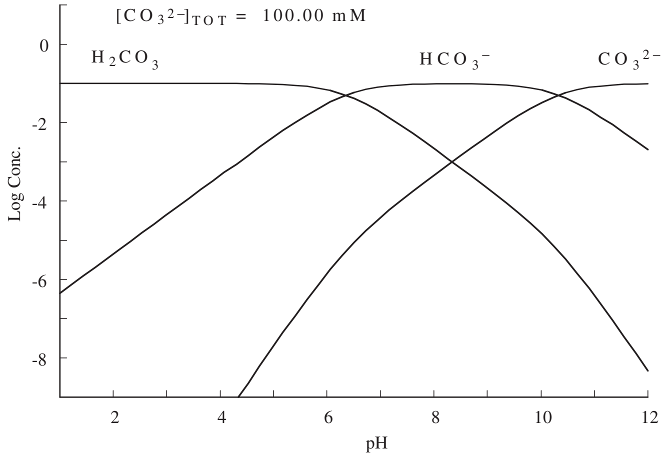

Fig. 5. Distribution of solute species in the aqueous carbonate system. Log concentration vs. pH for 100 mM CO_3^{2-}. The pK_1 is at 6.3 and pK_2 at 10.3.

It is additionally important to consider the differences in carbonate mineralogy, as they might have different reaction kinetics, solubility and for example siderite might even produce net acidity under certain conditions. Siderite is frequently found in porphyry copper systems (Dold and Fontboté, 2001). Thus a mineralogical approach is also essential for the estimation of the NP.

Siderite may act as a neutralizer under certain conditions, and under other conditions as an acid producer. The following dissolution reaction may take place and buffer the system at pH around 5:

$$FeCO_3 + 2H^+ \Longleftrightarrow Fe^{2+} + H_2CO_3^- \tag{11}$$

Combined with ferrous iron oxidation and ferrihydrate formation, the overall siderite dissolution-oxidation reaction is:

$$4FeCO_3 + O_2 + 10H_2O \Longleftrightarrow 4HCO_3^- + 4Fe(OH)_3 + 4H^+ \tag{12}$$

This indicates that under elevated pH, where bicarbonate is stable, the total reaction from dissolution of siderite to the formation of ferrihydrate gives a net acid production of one mole hydrogen ion per mol siderite dissolved. However, under more acidic conditions, where carbonic acid is stable, there will be no net acid production. But, it has to be considered that when ferrous iron is liberated, at low pH, it can be mobilized even under neutral pH condition and, and under oxidizing conditions downstream, it will oxidize and hydrolyze while liberating of protons and producing ARD far from the source.

If ferrous iron is present in a solution containing bicarbonate, the formation of siderite may occur by the following reaction:

$$Fe^{2+} + HCO_3^- \Longleftrightarrow FeCO_3 + H^+ \tag{13}$$

This reaction buffers the pH at around 5–5.5 and its reaction path may be an alternative to ferrous to ferric iron oxidation and the consecutive precipitation of Fe(III)oxyhydroxides. Geochemical studies by several authors have shown that in tailings impoundments and AMD affected aquifers the waters are frequently close to saturation or even oversaturated with respect to siderite (Blowes et al., 1991, 1994; Morin and Cherry, 1986), and siderite precipitation could be observed (Dold et al., 2009).

Before entering into details of the prediction techniques, it is helpful to highlight the ARD prediction problem with three simplified examples.

A.) Pyrite is the most abundant sulfide mineral in the Earth's upper crust and produces 4 mol of protons per mole of pyrite oxidized (Eq. (1)). Calcite is the most soluble carbonate and buffers at neutral pH, so that at these geochemical conditions one mole of protons can be neutralized per mole of calcite (Eq. (5)). If the molar weight of pyrite (120 g/mol) and calcite (100 g/mol) is set as 1:1 for simplification (accepting an error of 16.7%), it can be assumed that a rock with >20 wt.% of pyrite will always produce ARD, even if the rest of the sample is pure calcite ($20\% \times 4 = 80\%$ calcite needed to neutralize the protons from pyrite oxidation). Thus there are ore deposit types, which will always produce ARD due to their mineral composition (e.g. massive sulfide ore bodies).

B.) Porphyry copper deposits have usually only 2 wt.% pyrite in average, but due to the fact that the exploited ore has no or very little carbonate content (around 8 wt,% of calcite would be needed) and the silicate assemblage has very low reactivity due to hydrothermal alterations (mainly K-Feldspar), the mine waste of this deposit type is very prone to producing ARD (Dold and Fontboté, 2001).

C.) A granite contains no sulfides and no carbonates, it is a rock only composed of silicates and trace amounts of other mineral types; i.e. quartz, feldspars, micas, and some accessory minerals as for example hornblende, apatite, sphene, among others (Takaya, 2014). However, a weathered granite will most likely form an acidic environment (pH around 4.3–5.5) in the saprolite or soils (Liu et al., 2016); i.e. it produces ARD. This is due to the liberation of Al, and Fe through weathering process and the subsequent hydrolysis of these elements, in combination with the lack of carbonates and a feldspar assemblage of low relative reactivity.

4. Standard ARD prediction and its limitations

4.1. A historical background and mineralogical considerations

The so-called static testing of a rock sample for its potential to produce ARD tries, in a simplified geochemical way, to predict if a sample has an excess of AP or enough of NP to maintain the sample neutral. As a consequence, this has direct effects on the liberation and mobility of associated elements as stated above. This is normally done by a simplified geochemical quantification of sulfur in the bulk sample, which is assumed to be associated to the sulfide mineralogy (expressed as pyrite equivalent) and the carbonate mineralogy quantified by titration (expressed as calcite equivalent).

Most of the standard methods applied in this field were developed for other needs and were used for ARD prediction in sulfide metal mining without considering the complexity of a sulfidic mineral assemblage. This is, for example, the case for the most known ABA test, the so called Sobek test (Sobek et al., 1978), which was developed originally for coal mining. Therefore, the assumption that all sulfur is associated to pyrite was more or less correct in this geological environment. This test was then widely applied in the last decades also for ABA calculations in metal sulfide mining, where sulfur can be associated to many different minerals, which produce different amounts of acidity or produce no acidity at all (e.g. anhydrite-gypsum or sulfide, like sphalerite or galena, see Table 1). This problem was noted by (Lawrence et al., 1989), and several intents for improvement for the AP determination (Lawrence et al., 1989), as well for the NP estimation were published (Lawrence and Scheske, 1997; Paktunc, 1999). For example, a separation of the sulfate mineralogy from the sulfide mineralogy was attempted through the dissolution of sulfates with HCl (Lawrence et al., 1989), which is now better known as the "Modified Sobek test". Both tests assuming that only the sulfides are responsible for proton liberation. This assumption has to be expanded, as Fe(III)oxyhydroxides and Fe(III)oxyhydroxide sulfates like schwertmannite and jarosite, ferrihydrite and goethite, minerals which are often present in the ore geology, tend to acidify the solution due to equilibrium reactions (Alarcon et al., 2014; Dold, 2010), so that this mineralogy must also be included in an ABA (Dold and Weibel, 2013). Additionally, the HCl leach may attack some acid soluble sulfide or Fe(III) hydroxide sulfate minerals and has therefore a low selectivity.

A more selective separation of sulfur associated with the oxide fraction from the sulfide sulfur fraction can be done by a hot NH_4-oxalate leach (Dold and Fontboté, 2001), or by sequential extraction protocols established for a specific ore mineralogy e.g. (Dold, 2003a, 2003b), data which then gives the possibility of performing a high-resolution ABA, including the quantification of Fe(III)hydroxides and Fe(III)hydroxide sulfates and their respective AP. The Modified Sobek test (Lawrence and Scheske, 1997) can be seen as a two-step extraction method, were only the sulfur content is analyzed.

As mentioned above, there can be a substantial difference if calcite or siderite is present as carbonate. For this reason an additional correction for siderite might be necessary (Skousen et al., 1997).

4.2. ABA calculation

In addition to all of the problems related to the mineralogical considerations mentioned above, the key problem associated with standard ABA procedures remains the assumptions leading to the calculation factors applied to the geochemical data. While it is generally accepted that one mole of oxidized pyrite produces 4 mol of protons, there is disagreement between the amounts of protons neutralized by calcite. The following two Eqs. (14) and (15) are usually presented as the base for the calculation factor of 31.25 (e.g. GARD Guide (Verburg et al., 2009) etc.) for the AP of a sample applied to the total sulfur or sulfide sulfur concentrations of a sample.

$$CaCO_3 + 2H^+ \Longleftrightarrow Ca^{2+} + CO_2 + H_2O \tag{14}$$

$$CaCO_3 + 2H^+ \Longleftrightarrow Ca^{2+} + H_2CO_3 \tag{15}$$

This factor results from the assumptions that one mole of calcite can neutralize two moles of protons. As pyrite oxidation produces 4 mol of protons per mole of oxidized pyrite, and pyrite contains two moles of sulfur, the final assumption is that the protons produced by the oxidation of one mole of sulfur is neutralized by one mole of calcite. This leads to the following calculation:

$$100_{(\text{mole weight calcite})}/32_{(\text{mole weight sulfur})} \times 10_{(\text{tCaCO3/1000t})} = 31.25.$$

The factor 10 at the end is to present an applicable unit how much carbonate has to be added to the ARD forming material in tons of $tCaCO_3/1000$ t (or g/kg or ‰) to buffer the system (sometimes the factor is presented without this adjustment as 3.125 (White et al., 1999).

If it is accepted that calcite buffers the system at circum-neutral pH, and the general goal of mine waste management is to maintain the pH of the material neutral, then the carbonate specie present would be bicarbonate (at pH 7 > 85% HCO_3^- (Appelo and Postma, 2010); see Fig. 5 and Eq. (8)). Thus, Eq. (8) has to be considered for ABA calculations instead of Eq. (10) (or 14 and 15), latter overestimating the NP of calcite by about 100%. Therefore, a calculation factor of 62.5 should be applied, as two moles of calcite are needed to neutralize the acidity from one mole of sulfur:

$$2 \times 100_{(\text{mole weight calcite})}/32_{(\text{mole weight sulfur})} \times 10_{(\text{tCaCO3/1000t})} = 62.5.$$

Therefore, the product of the sulfur concentrations multiplied with the factor 62.5 instead of 31.25 gives the AP for ARD prediction, by including the amount of protons possibly produced (assuming pyrite oxidation as the only protons source) and the amount of protons able to be neutralized by the carbonates (assuming the presence of calcite) at neutral pH. As discussed above, it has to be considered a neutral pH for the carbonate NP, as only when the carbonate buffer is depleted the pH will decrease. This is different, if the amount of calcite has to be calculated to neutralize ARD. In this case, when the solution is acidic (pH < 6.3), calcite can neutralize two moles of protons per mole of calcite and therefore the factor 31.25 is correct (i.e. for treatment). This is contrary to ARD prediction, were it is evaluated if the system goes from neutral to acidic conditions in the future (Prediction). In a strict sense, before ABA can be properly calculated, the paste-pH should be performed to evaluate the correct calculation factor based on the dominant carbonate speciation.

The next step is the quantification of the NP in order to be able to calculate the final ABA. For standard ABA only the carbonate neutralization potential (CaNP) is considered. There are several approaches to quantify carbonates in a sample:

The easiest and cheapest method is the macroscopic quantification by a geologist in a hand specimen. However, this is a qualitative analisis as the detection of calcite by eye is not easy and usually HCl 10% is used to detect calcite in the field. This qualitative quantification follows the same principles as applied in the Fizz-test (Bouzahzah et al., 2015b) and can be very arbitrary, and is therefore not recommended for quantification of NP. Sobek et al. (1978) boiled the sample in HCl and later titrate with NaOH in order to quantify the carbonate species in the sample. (Lawrence et al., 1989) expose the sample at room temperature to HCl for 24 h and then titrate with NaOH. A modified method for NP determination (NP(pH 6) method) was developed taking in account to determine the "effective" NP or the calcium carbonate equivalent available in the sample to maintain the pH above 6, as discussed above (White et al., 1999). This method implies titration with 1 N sulfuric acid until pH 6 is reached, so that it might be the most realistic for carbonate NP determination.

Another possibility is to quantify the organic and mineral carbon by coulometric titration (E.g. Ströhlein® CS 702 or a LECO® CN-Analyzer). The mineral carbon concentrations are assumed to be associated to the carbonate minerals like calcite or dolomite and are expressed as $CaCO_3$.

If siderite is of concern, addition of H_2O_2 is applied to promote Fe oxidation before back-titration to account for the above mentioned "siderite problem" in ARD prediction (Skousen et al., 1997). The carbonate quantification has then to be expressed in $tCaCO_3/1000$ t, or g/kg, or ‰ in order to be able to calculate the final ABA with the AP. In general term, a good knowledge of the carbonate mineralogy is needed for ARD prediction.

Although there are many different ways to present the ABA results, the most common is the sulfide net acid potential (SNAP) or net neutralization potential (NNP)

$$NNP = NP - AP.$$

In the latter case, if the result is negative, this means that the material will form ARD, as there is an excess of AP (sulfides = pyrite) in relation to the carbonate content. If the result is positive, there is enough NP (carbonates = calcite) to maintain the material neutral. In some guidelines the range between −20 and +20 is called the "uncertain zone". However, with good knowledge of the mineralogy, this is not an area of uncertainty. For example, if a material has 1 wt.% pyrite (0.53 wt.% S) and no NP, the ABA will be −16,7 (calculated with the factor 31.25), but −33.4 with the factor 62.5, and this material will clearly produce ARD. A granite without any sulfides and in absence of carbonates will produce ARD although the NNP will be 0. Material from the oxidation zone of an ore deposit or tailings impoundment has an NNP of zero as there are no sulfides and carbonates left due to sulfide oxidation. However, this zone has a pH ranges between 2 and 4 due to the presence of Fe(III)hydroxides sulfates (Dold and Fontboté, 2001).

In some cases the regulations apply a criterion for the ABA calculations ranging from 1:1.2 to 1:3 (Nevada, California and Montana, respectively)(White et al., 1999), in order to ensure enough buffer capacity. However, if the standard calculation factor of 31.25 was applied, a criterion of 1:2 would represent simply the correct factor of 62.5 and no additional safety would be available. Only if a factor of 1:3 was applied, there would be some excess of buffer capacity for additional safety.

4.3. Kinetic testing

Above, the static tests were discussed in order to predict if a sample has the potential to acidify the geochemical system or if it will maintain neutral or even go alkaline. Kinetic testing is used to investigate in which time frame this will occur.

The standard tests (e.g. humidity cells; ASTM D5744-96) use columns or cells, were the samples are exposed to oxidation, and is flushed with deonized water after a certain time frame and the solution is analyzed for the solutes, representing the reaction products of the oxidation process. In the mostly applied ASTM D5744-96 humidity cell test, a one kilo sample with a grain size of <6.3 mm is exposed to 3 days humid air, 3 days dry air and the seventh day the system is flushed with water which is then analyzed for physical-chemical parameters and element concentrations. These cycles are recommended to be repeated 20–25 times to report the evolution of pH, Eh and dissolved elements like sulfate and Fe, Cu, Zn, Cd, Pb, As, Cr, among others.

Although widely applied in the mining and consulting business for ARD prediction, these kinetic tests often do not give conclusive results as shown in a study at the Andina porphyry copper mine, Chile (Weibel et al., 2011). In this example, although all samples were classified by ABA and mineralogical studies as ARD producing (Fig. 8), in the applied standard humidity cell tests (ASTM D5744–96), no acidification due to sulfide oxidation could be observed. From 78 samples only 11.5% reached final pH between 3.5 and 4.5, because of equilibrium reactions caused by the presence of Fe(III)hydroxides (these samples were located from the upper part of the ore deposit, suffering partial natural oxidation) and not due to sulfide oxidation during the experiment. The observed sulfate liberation was associated to anhydrite-gypsum dissolution present in the primary ore mineral assemblage. 64% of the samples maintained their circum-neutral pH (>6.3) and 14% reached final pH between 5.5 and 6.3 buffered by siderite. The evolution of the acidity concentrations, confirmed low ARD generation, were 73% of the samples remained stable, 10.2 had scarce acidity liberation, and 16.6% had a fast contribution associated to the samples containing Fe(III) hydroxides (Weibel et al., 2011).

Some unpublished test reports from high sulfide deposit types show a fast response of ARD formation in the recommended time frame. However, the scarce literature published on humidity cell tests of coal (Banerjee, 2014), carbonate containing sulfide rich tailings from Joutel tailings (Benzaazoua et al., 2004b) and of porphyry copper ores shows clearly that during the recommended time frame, mostly no acidification and increased element liberation could be observed, even if the ABA clearly suggests that the material should become acidic (Benzaazoua et al., 2004a; Filipek et al., 1999; Weibel et al., 2011). In a field study at the Talabre porphyry copper tailings at Chuquicamata, Chile, it was shown that the system need 3 to 5 years to acidify from the alkaline flotation conditions (pH 9.1) to a pH of 3.5–4 (Dold et al., 2004; Smuda et al., 2014). This is in the order of data shown in the GARD Guide of a cell test from an unknown ore type, where after 130 weeks the acidification and element release was observed. Thus, it can be stated that the recommended time frame is not suitable for many types of mineral assemblage, and a flexible set-up in time of these tests has to be proposed in order to ensure to document the geochemical behavior properly.

Several parameters control the kinetics of sulfide oxidation, like microtextures (Parbhakar-Fox et al., 2013), textural relation-ships between the minerals (Kwong, 1993), grain size, humidity, temperature, bacterial activity, availability of oxidants (e.g. oxygen or ferric iron) among others. Specifically it has shown by modifications of such cell tests, that a decrease in grain size, an increase of temperature and humidity results in an increase of the oxidation rates (Dold and Weibel, 2013; Dold et al., 2011). Too high water saturation might lower the oxidation rates (Bouzahzah et al., 2015a).

Thus, there are different possibilities to enhance the kinetics in the laboratory. Although the wet-dry cycle was introduced to simulate enhanced weathering cycles, the bacterial community oxidized most efficiently in a modified cell test, under constant experimental conditions. Best response was reached at constant 40 °C and 95% humidity during the whole cycle and only flushing on the 14th day. The results have shown a more rapid response in element liberation and pH drop than with the ASTM D5744-96 approach (Dold and Weibel, 2013; Dold et al., 2011), which was run in parallel.

Finally, in light of all the problems of the prediction the kinetics of ARD formation, it can be argued whether or not it is necessary to use kinetic testing. If the mineralogy and geochemistry suggest clearly that ARD will be an issue in the future of an ore deposit, immediate action must be taken to prevent ARD formation and to be able to control all effluent in future. Once ARD is formed it is extremely difficult to control it, thus prevention from the beginning of any mining activity must be the goal.

For example, it is easy to predict, only on the base of mineralogical composition that a porphyry copper tailings impoundment will first produce a sulfate plume (due to equilibrium reactions with gypsum-anhydrite), and later ARD (due to sulfide oxidation), both infiltrating and polluting the groundwater (Dold, 2014). With this knowledge prevention measures must be in place, before operation starts. In this regard, it is incomprehensible that there are still many mining countries, with new legislation for environmental protection in place, which still do not demand a basal impermeabilization for mine waste deposits in order to prevent infiltration of contaminated plumes into the groundwater.

5. Sample selection criteria for ARD prediction

It is most critical for ARD prediction, to select the correct samples for this purpose. In a mine waste environment, surficial samples from old oxidized mine tailings or waste rock dumps do not represent the full AP and NP, as they might have been affected by weathering processes. Therefore, samples must be extracted from depth, e.g. by drilling, in order to obtain samples for ARD prediction.

Also the geological and petrological classification as selection criteria is most relevant for correct ARD prediction. As discussed above, the vast majority of base metal production has its origin in igneous ore deposit types. >90% of the giant metal accumulations on earth relied on water as formation agents (Laznicka, 1999), such that hydrothermal processes are essential for most ore forming processes. Hereby, metal rich hydrothermal solutions interact with the host rock units and physio-geochemical changes (e.g. T, P, pH, redox) induce mineral precipitation and alteration. These processes can completely change the original mineral composition of the host rock, i.e. adding elements or minerals and/or altering minerals or transporting elements away (Fig. 6), so that sometimes only textural signs can be used for classification of the original rock unit (e.g. porphyric texture). For example when hydrothermal fluids interact with andesites or diorites along an active subduction margin, the alteration completely changes the original mineralogy and a Cu-Mo-Au porphyry deposit may form. From the ARD perspective, this mineralogical change is dramatic and crucial. Unaltered andesites or diorites do not have sulfides, thus their original AP is zero. They usually also do not have any carbonates, so that their CaNP is also zero. Andesite or diorites contain plagioclases like albite - anorthite, latter a feldpar with good FNP, meaning that this original rock suite would be able to neutralize some protons. However, the metals, sulfur, and acidity that were provided to the system during hydrothermal alteration, resulted in the precipitation of sulfide minerals like for example pyrite, chalcopyrite, enargite, and arsenopyrite, all of which are potential acid producers. These processes are also accompanied by a strong change of the gangue mineralogy. For example, the plagioclases are altered to muscovite (quartz-sericitic alteration) or to potassic feldspar (potassic alteration) or kaolinite (argillic alteration), minerals with very low reactivity kinetics and buffer capacity (Table 2) and therefore not helpful for ARD neutralization. Keeping this in mind, for ARD prediction of an ore body it is key that for sample selection procedure the hydrothermal alteration mineralogy classification is used, and not the original petrological or lithological classification (e.g. diorite or andesite), as sometimes observed.

- Thus, using the original petrological classification as sample selection criteria might also mislead geochemical modeling interpretations. For example, it is sometimes observed, that samples for ABA analysis are selected from petrological units like andesites or diorites, but no further mineralogical characterization is done and only the standard ABA data is used for prediction and setup for a geochemical model to predict future ARD quality. This gives way to the possibility of selecting samples outside the mineralized area (often no location of the samples in the ore deposit is given), and to assume that the feldspar specie is anorthite, which has acceptable neutralization properties. If equilibrium modeling uses the FNP without considering the reaction kinetics of the different feldspar species, unrealistic predictive geochemical modeling is the result and as a conclusion, it maybe stated that the unit will not produce ARD.

These examples highlight that it is crucial to understand which mineralogy will be exposed to a specific geochemical condition in order to predict ARD formation, or more generally, to predict mineral stability and subsequent element liberation processes and changes in the geochemical system.

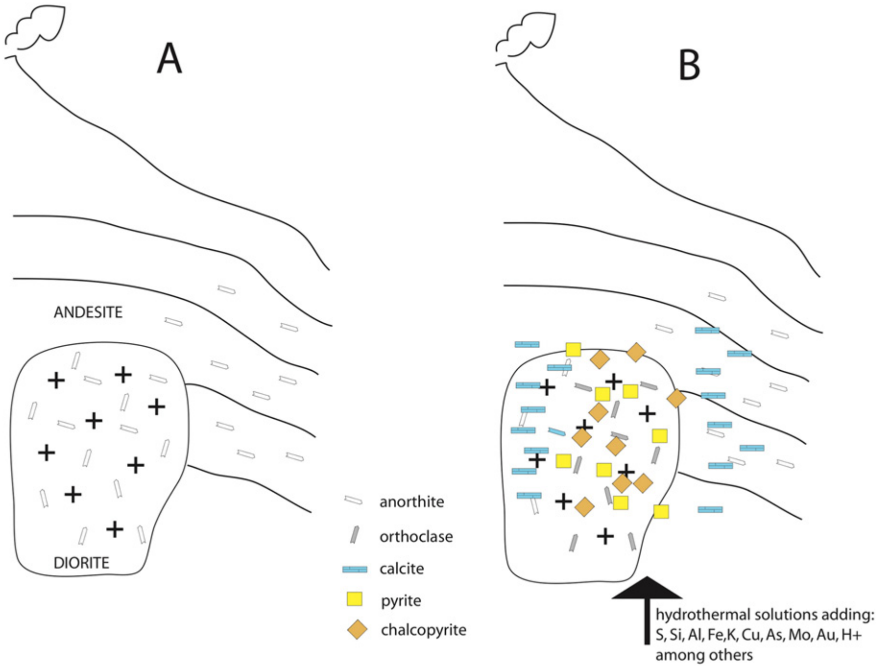

Fig. 6. A) Typical suite of andesitic flows intruded by a dioritic porphyry along the South American west coast. The ABA of these rock units would be zero. B) Change in mineral composition due to hydrothermal alteration with complete change of the ABA to negative values (excess of sulfides). Only in the external part of the ore deposit, the precipitation of calcite in the propylitic alteration zone adds CaNP to the original rock units.

6. Suggested characterization methodology for ARD prediction

The key information to predict ARD or any element liberation of a geological material, is the mineralogical composition of the sample. The mineralogy is the pool of potentially liberated and neutralization of protons through the above presented geochemical processes, and the subsequent liberation of elements to the environment in form of ARD or also as neutral to alkaline solutions. Variables like climate, microbial interactions, grain size, textures, relationships between minerals (e.g. electrochemical bridges), play also a important role in these processes, but mainly control the kinetics of the processes leading to ARD, not the overall acid-base balance. Therefore, the efforts should be concentrated in identifying the minerals present in a deposit, their quantification, their relations and whether these minerals have potentially hazardous trace elements associated.

In most cases, a simple overview of the ore deposit type and trace element composition gives a good first estimate if it will produce ARD and which trace elements might be critical for the environment, and actions can be taken for ARD control or prevention (e.g. impermeabilization of the waste deposition sites and solution control), or further investigations conducted.

The first step should always be a thorough revision of the literature of the ore deposit. Publications in scientific journals (e.g., Mineralium Deposita, Economic Geology, Ore Geology Reviews, Journal of Geochemical Exploration, among others) usually have excellent data on the mineralogical characterization of the ore deposits. However, only seldom they do present quantitative mineralogical analysis data. But as shown above, with the information of the ore deposit type and the specific minerals present in an ore, a good first estimate of the ARD behavior can be given; see also Plumlee (1999).

The second step, should be a characterization to obtain quantitative mineralogical data (can nowadays be done by automated quantitative mineralogical analysis; e.g. QEMSCAN® or MLA).

Many modern mining operations already use automated quantitative mineralogy and mineral liberation analysis for geometallurgical purposes to increase the recovery of their extraction process (Cruz et al., 2012). The very same data can and should be used for ARD prediction (Dold and Weibel, 2013), and no additional standard ABA tests are needed at no additional costs. As mentioned above, the standard ABA tests have to be seen only as a very simple, rough approach to attempt to quantify the ARD susceptible mineralogy through the use of geochemical data. In order to highlight which minerals are considered in the different methodologies and what data is given by the different techniques, these and the subsequent differences in the NNP are shown in Fig. 7 and Table 3.

Although a good calibration and quality control for each ore and special care for sample preparation is necessary for accurate quantification of the mineralogy, these relatively new techniques are able to produce the necessary data in reasonable time frames and competitive prices (Nowadays an analysis by Automated Quantitative Mineralogy costs in the same range as a mineralogical interpretation of a thin section by a qualified mineralogist). Additionally they can quantify trace mineral amounts, not detectable with any other analytical technique (Menzies et al., 2015). This can be specially relevant if some trace elements are associated to soluble minerals like metal sulfates or chlorides. However, in order to be able to predict trace element behavior, a more detailed geochemical characterization should be additionally performed on the minerals. This can be done for example by sequential extractions, where the trace element concentrations of reactive mineral groups can be quantified (Dold, 2003b). Additionally, sequential extractions have advantage in terms of turnaround time and prices in relation to some of the other techniques and give data for high- resolution acid-base accounting. Although, no prices for the different analysis in commercial labs can be given here, as they change with country and demand, the standard ABA tests are very expensive in relation of the information they deliver. For example the modified Sobek test (Lawrence), which is essentially a two step sequential extraction in which only sulfur is analyzed with an additional titration for the CaNP costs usually half or even more of the price, which costs a seven step sequential extraction with analysis of 31 elements in each leach. Thus, the geochemical information obtained by sequential extractions is much cheaper and gives much more information on the sample in relation to simple standard ABA procedures. Additional advanced analytical tools for geochemical characterization might be necessary like SEM-EDS, microprobe or Laser-ICP-MS, where trace metal concentration of specific minerals can be detected and quantified and therefore their liberation under specific geochemical conditions can be predicted.

In Fig. 7 only quantitative mineralogy is able to account on the different sulfide minerals, which produce different amounts of protons through their oxidation. Also the AP from Fe(III)hydroxides and sulfates can be quantified, as well the differences in NP between calcite and siderite and the different feldspars can be considered. Sobek would account any sulfur as sulfide sulfur in form of pyrite and siderite as full CaNP. It also does not account the AP from iron hydroxides and sulfates.

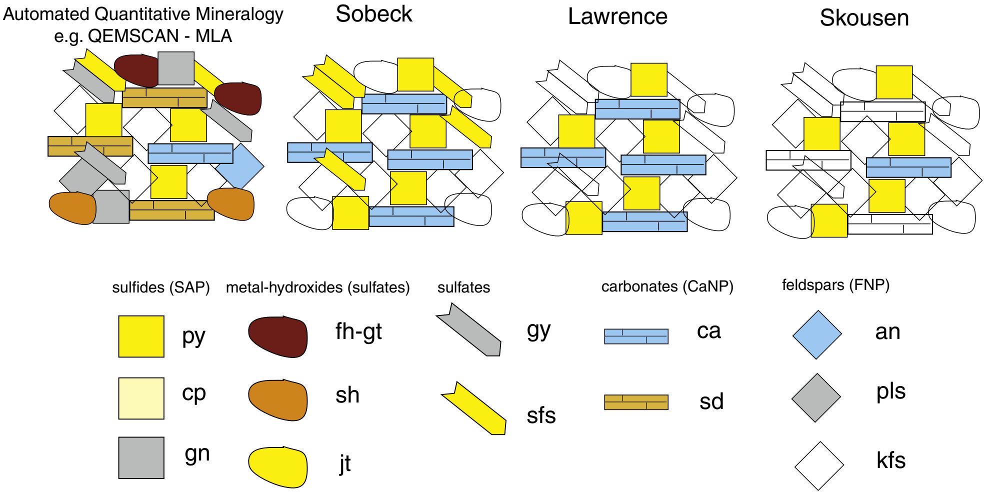

Fig. 7. Schematic illustration which minerals are detected and/or considered in the different techniques and calculated as acid potential or neutralization potential. Yellow colors indicate acid potential, blue neutralization potential and grey and white none of both. Abbreviations: py = pyrite; cp = chalcopyrite; gn = galena; fh = ferrihydrite; gt = goethite; sh = schwertmannite; jt = jarosite; gy = gypsum; sfs = sulfosalts; ca = calcite; sd = siderite; an = anorthite; pls = plagioclase; kfs = K-feldspar. SAP = sulfide acid potential; CaNP = carbonate neutralization potential; FNP = feldspar neutralization potential.

Table 3
Overview of a typical sample from a porphyry copper deposit and the results of the different standard ABA approaches in relation to the quantitative mineralogy by QEMSCAN®.

	Quantitative mineralogy e.g. QEMSCAN					Sobek		Lawrence		Skousen (siderite corrected)	
				31.25	62.5	31.25	62.5	31.25	62.5	31.25	62.5
Mineralogy	wt.% S	wt.%	wt.% S	SAP (‰$CaCO_3$)	SAP	SAP	SAP	SAP	SAP	SAP	SAP
Pyrite	53.3	1	0.53	16.66	33.31	16.66	33.31	16.66	33.31	16.66	33.31
Chalcopyrite	34.87	1	0.35	5.45**	10.9**	10.90	21.79	10.90	21.79	10.90	21.79
Sphalerite	32.86	0.5	0.16	0	0.00	5.13	10.27	5.13	10.27	5.13	10.27
Galena	13.38	0.5	0.07	0	0.00	2.09	4.18	2.09	4.18	2.09	4.18
Gypsum–Anhydrite	23.52	3	0.71	0	0.00	22.05	44.10	0	0	0	0
Total SAP				16.66	33.31	56.83	113.66	34.78	69.56	34.78	69.56
	wt.% C	wt.%	wt.% C	CaNP (‰)* (‰$CaCO_3$)	‰						
Calcite	12	0.5	0.06	5.30	5.30	5.30	5.30	5.00	5.30	5.30	5.30
Siderite	10.3	6	0.62	0	0.00	54.57	54.57	54.57	54.57	0.00	0.00
Total CaNP				5.30	5.30	59.87	59.87	59.57	59.87	5.30	5.30
ABA (NNP)				*−11.36*	*−28.01*	*3.04*	*−53.79*	*24.79*	*−9.69*	*−29.48*	*−64.26*

* Calculation factor for CaNP is 88.3.

** For chalcopyrite only 2 mol of H+ is considered ⇒ factor is 31.25/2 or 62.5/2.

Green: ABA calculated based on quantitative mineralogy. Orange: ABA calculated after mostly applied prediction protocols.

Lawrence improve in the sense that it does not account gypsum or anhydrite as sulfide sulfur, but the AP from sulfosalts and Fe(III)hydroxide sulfates is also not considered. Lawrence does consider siderite as full NP. Skousen accounts for the siderite problem and corrects the NP.

In Table 3 the different ABA (NNP) interpretations resulting through the characterization of a sample by the different test methods are highlighted: quantitative mineralogy with QEMSCAN, Sobek (Sobek et al., 1978), Lawrence (Lawrence et al., 1989), and siderite corrected (Skousen et al., 1997).

This hypothetical sample, typical for a porphyry copper deposit, shows which of the minerals or mineral groups are addressed in the different methodologies. On the left side is the mineralogy detected by microscopy and quantified by QEMSCAN. From the detected sulfide minerals pyrite is producing 4 mol of protons by its oxidation, chalcopyrite 2 mol, sphalerite and galena zero, and the sulfates gypsum-anhydrite also produce zero. These differences can be considered, if quantitative mineralogy is available, while the Sobek method assumes all sulfur containing minerals as acid producers and thereby overestimates the AP strongly. With respect to carbonate neutralization potential, Sobek strongly overestimates this value, as siderite is also included. The Lawrence method takes into account sulfates like gypsum, which do not produce acidity, but also overestimates the sulfur AP, as it considers sphalerite and galena as acid producers. Lawrence also overestimates the CaNP as siderite is considered as a neutralizer. Even if Lawrence is corrected for siderite (Skousen), it overestimates the AP, and applies the wrong calculation factor as shown by the difference with the standard calculation coefficient of 31.25 and the suggested 62.5 (see Section 4.2).

As a result, with quantitative mineralogy it is predicted that the sample has an NNP of −28.1 $tCaCO_3$/1000 t (‰). Calculated with the wrong, but widely used factor (31.25) the conclusion is that it lies in the uncertainty area with tendency to ARD foramtion (−11.36‰). In contrast, Sobek and Lawrence would predict that the sample is not ARD producing. Only if corrected for siderite, the NNP is also negative (−29.48). If, for all 3 standard tests the factor 62.5 instead of 31.25 were applied, in all cases the NNP would be negative. The same trend can also be observed in a data set of 200 samples from the Andina porphyry copper mine in Fig. 8. This clearly shows the importance of a correct mineral quantification and correct geochemical calculations in order to properly predict the ARD potential.

However, it is interesting to observe that sometimes, although a strong data set of quantitative mineralogy and geochemical data exists in a project, responsible managers spend additional money for the standard ABA tests, which illustrates how well established these tests are in the mining industry and state agencies, despite all the above-mentioned drawbacks and errors.

7. Conclusions

Standard static acid rock drainage prediction methodologies are based on simple geochemical tests with the goal to quantify potential acid production and NP of a geological sample. Due to the simplicity of the approach and it's basic assumptions, these tests have many problems and drawback, not able to account for the complexity of the mineral assemblage of an ore deposit, and therefore not able to accurately predict ARD formation. Also, standard kinetic testing is not able to produce concordant data for ARD prediction in the proposed time frames.

On the other hand, mineral characterization and automated mineral quantification has experienced in the last decades important development (e.g. QEMSCAN® and MLA). These data are increasingly produced in modern mining operation, nowadays mainly for geometallurgical purposes to increase the recovery from the ore. It can be predicted that this data will be available in the near future in most competitive mining operations. Thus, it is suggested to use the very same data of quantitative mineralogy for ARD prediction with no additional costs and testing, instead the very limited and problematic standard ARD prediction tests.

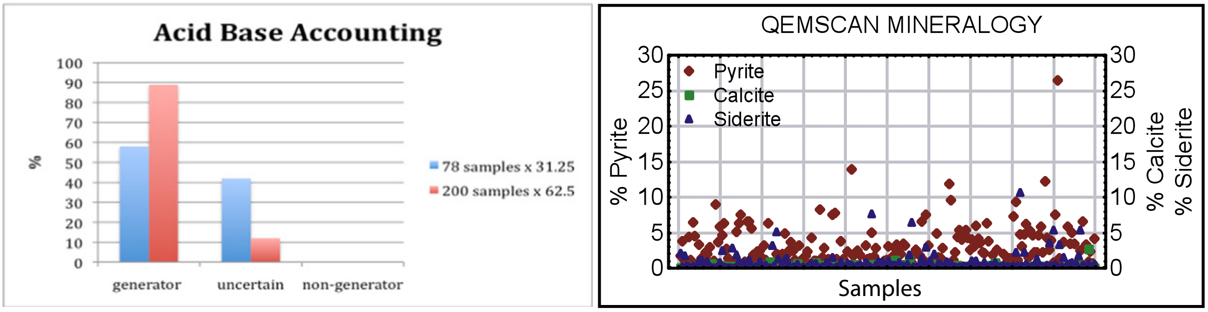

Fig. 8. Left: Blue bars: Percentage of the 78 samples plotting into the generator, uncertain (−20–20) and non-generator ABA from the Andina porphyry copper deposit (Weibel et al., 2011), obtained by the modified ABA (Lawrence et al., 1989) and calculated with 31.25. Red bars: high-resolution ABA obtained from sequential extraction data (Dold, 2003a, 2003b) from 200 samples from Andina and calculated with 62.5 (Dold et al., 2011). Right: Quantitative mineralogy of the same 200 samples obtained by QEMSCAN®, showing clearly that calcite are very minor traces and only siderite is available as carbonate NP, thus, all samples are clearly ARD producers.

However, if standard testing is applied for ARD prediction, following improvements should be applied:

1. Based on the paste-pH of the sample, the calculation factor of the sulfide AP should be chosen: If the paste pH is >6.3 the factor 62.5 must be applied (i.e. for ARD prediction). If the paste pH is <6.3, 31.25 is the correct factor for calculation, i.e. for ARD treatment.
2. The separation of the sulfate sulfur from the sulfide sulfur is the correct way, as applied by Lawrence et al. (1989). However, the use of HCl is not very selective, as many sulfides may suffer partial dissolution. A leach with 0.2 M NH$_4$-oxalate, pH 3, at 80° for 2 h has shown to completely dissolve all ferric iron oxides and hydroxides sulfate minerals present in sulfide ore deposits (Dold, 2003b), and is therefore recommended as more selective leach for this approach. The use of sequential extractions can improve importantly the resolution and precision of the ARD prediction (Dold, 2003b; Dold and Weibel, 2013).
3. For the determination of the NP, the Modified NP(pH 6) Method (White et al., 1999) is the most realistic. It considers the real pH conditions were the neutralization processes take place for ARD prediction, and considers the carbonate speciation in the system, and is therefore recommended.

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