CrossMark

A contribution to improve the calculation of the acid generating potential of mining wastes

Aurélie Chopard [a, *], Mostafa Benzaazoua [a], Hassan Bouzahzah [a], Benoît Plante [a], Philippe Marion [b]

[a] Research Institute on Mines and Environment (IRME), Université du Québec en Abitibi-Témiscamingue (UQAT), Rouyn-Noranda, QC, Canada
[b] GeoRessources, Université de Lorraine (UL), École Nationale Supérieure de Géologie (ENSG), Vandoeuvre-lès-Nancy, France

HIGHLIGHTS

- Oxidation rates of sulfidic tailings can be estimated from their sulfides content.
- A kinetic factor is suggested in the calculation of the acid-generating potential.
- Arsenopyrite, pyrrhotite, and gersdorffite have a strong influence on the kinetics.

ARTICLE INFO

ABSTRACT

Mine wastes from sulfide-bearing ore extraction and processing are often stored at the surface of mine sites and could generate mine drainage. Prediction tests are completed to predict the water quality associated with the deposition of mining wastes. Static tests can quickly assess the acid-generating potential (AP) and the neutralization potential (NP). Whereas some studies recommend to take into account a mineral reactivity factor for the NP determination, the reactivity rates of acidifying minerals are not considered in the AP calculation. The aim of this study is to bring contribution to the improvement of the static test determination by adding kinetic factors in the AP determination. Eight sulfides (pyrite, Ni-pyrite, pyrrhotite, Ni-pyrrhotite, chalcopyrite, galena, sphalerite, arsenopyrite) and a sulfosalt (gersdorffite) were separately submitted to kinetic tests in modified weathering cells. This test was selected for its rapidity of results and for the low amount of material used, as it is somewhat difficult to obtain pure minerals samples. Five synthetic tailings were composed by mixing pure sulfides in various proportions and submitted to the same kinetic tests. The oxidation rates of synthetic tailings were compared with the weighted combined oxidation rates of individual pure sulfides. The oxidation rates of the synthetic tailings calculated from those of pure sulfides are within the same order of magnitude than those obtained through the kinetic experiments. The AP of synthetic tailings were calculated according to standard equations of the literature and compared with the new method.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Mining industry worldwide is of economic importance for many countries. However, this industry impacts the environment, particularly through the various wastes generated. The solid mine wastes, mainly waste rocks (resulting from ore extraction) and tailings (generated by ore processing) are mostly stored at the surface of mine sites in waste rock piles and tailings impoundments. These wastes often contain sulfide minerals, and are exposed to climatic conditions and leaching, which can lead to poor water quality. Sulfides, upon exposure to water and oxygen, generate acidic effluents in the absence of neutralizing minerals. The phenomenon, well-known as acid mine drainage (AMD) or acid rock drainage (ARD), is a complex process of chemical, physical and biological reactions. AMD is probably the main environmental problem associated with polymetallic sulfide deposits mining (Adam et al., 1997; Aubertin et al., 2002; Blowes et al., 2014).

AMD is mainly produced by the oxidation of iron-bearing sulfides, mainly pyrite and pyrrhotite, commonly found in

polymetallic and precious metals deposits. Iron plays a role in the reactivity mechanisms of these sulfides. Their oxidation produces SO_4^{2-}, Fe^{2+} and H^+. Then, the oxidation of Fe^{2+} to Fe^{3+} and the precipitation of iron oxides and hydroxides will produce additional acidity. Fe^{3+} is a more effective oxidant than oxygen and catalyzes the reaction (Nordstrom et al., 2015). Other iron-bearing sulfides, such as chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS) or iron sphalerite (((Zn,Fe)S), also oxidize, either directly by water and oxygen action, or indirectly by the Fe^{3+} action. The oxidation of sulfide minerals is catalyzed by microbial activity (Nordstrom and Southam, 1997; Blowes et al., 2014) particularly at acidic pH.

Mine wastes presenting a strong potential for the generation of acid drainage and metal releases have to be managed more carefully to respect the surrounding environments. Therefore, the prediction of the drainage quality is an essential step towards the development of best practices for mine wastes management and for controlling generation of acidic solutions and/or release of contaminants into the environment. Various prediction tests were developed in the last decades, like the static and kinetic tests, developed in the past 30 years (Sobek et al., 1978; Lawrence and Scheske, 1997; Paktunc, 1999b; Plante et al., 2012). A general summary of ARD prediction methods can be found in MEND (1991), Lappako (2002), MEND (2004), INAP (2009) and Plante et al. (2012).

Despite the complexity of the phenomena involved, current practices still use the simple static tests to roughly assess the quality of mine drainage. The principle of the static tests is the balance between the acid-generating potential (AP) and the neutralization potential (NP) of a material, at a given time, without taking into account the kinetics of the reactions, which vary considerably from one mineral to another (Chopard et al., 2015). Each sulfide, depending on its crystal-chemistry and on many other external parameters, presents specific oxidation rate and typical geochemical behavior. For instance, pyrrhotite has long been known to be more reactive than pyrite (Kwong and Ferguson (1990)).

A static test is a one-time determination and is largely used, because it is rapid, simple and relatively low cost. Static tests can be accomplished on many samples and are can be used as a first screening to assess which samples (or orebody unit) will be problematic and which will need additional testing (kinetic tests and/or modelling). In contrast, kinetic tests involve repeated cycles or continuous leaching for extended periods (months to years) and are sampled on a periodic basis. Thus, kinetic tests can provide information on weathering rates and elemental concentrations in the leachates, including all possible geochemical interactions, which are not provided by static tests (Blowes et al., 2003; Hageman et al., 2015). Moreover, the static tests are based only on basic balance calculations from chemical assay or on the amounts of the different mineralogical phases present in the material (Bouzahzah et al., 2013).

AP and NP are separately evaluated and can be determined by chemical and/or mineralogical approaches. The Sobek test (Sobek et al., 1978) was the first chemical static test proposed, and remains the most popular in North America. The NP is determined by acid-base titration. The AP is calculated based on the total sulfur content in the sample, considering all sulfides occurrences as pyrite and based on the stoichiometry of the pyrite/calcite oxidation/neutralization (Equation (1); Sobek et al. (1978)). This AP value can be misestimated if significant quantities of non-sulfide species are present and as it considers all sulfur is present as pyrite. Moreover, the rates of acid generation of other sulfides, on a molar basis, are not considered.

AP and NP can also be calculated by mineralogical methods, by summing the individual contributions of each acidifying and neutralizing mineral, based on their proportions in the sample.

These methods consider the contribution of the various minerals. Many authors suggested NP calculations based on the mineralogical composition of the samples (Kwong, 1993; Morin and Hutt, 1994; Lawrence and Scheske, 1997; Lawrence and Wang, 1997; Li, 1997; Paktunc, 1999a, 1999b; Miller et al., 2010). For the AP calculation, Paktunc (1999b) proposed an equation based on the theoretical number of moles of sulfuric acid formed by the oxidation by oxygen of one mole of each sulfide present (Equation (2); Paktunc (1999b)).

$$AP = 31.25 \times \%Ssulfide \quad \left(kg\ CaCO_3 \cdot t^{-1} \right) \tag{1}$$

$$AP = \sum_{s=1}^{m} \left(\frac{n_s \times 98 \times X_s \times 10}{w_s} \right) \quad \left(kg\ H_2SO_4 \cdot t^{-1} \right) \tag{2}$$

AP: acidification potential;
n_s: number of moles of H_2SO_4 formed by the oxidation of one mole of sulfide mineral s;
98: molecular weight of H_2SO_4 (g.mol^{-1});
10: conversion factor for recasting in kg.t^{-1};
X_s: amount of sulfide mineral s in wt.%;
w_s: molecular weight of sulfide mineral s (g.mol^{-1});
m: number of sulfide minerals in the sample.

This equation improves the AP calculation as it considers other sulfides than pyrite. Based on Paktunc's equation, Bouzahzah et al. (2013) suggested a modified equation to attempt to include the reaction's kinetics of each sulfide. The relative experimental acidity production of each sulfide was used to calculate a relative "reactivity factor" (Equation (3); Bouzahzah et al. (2013)). As it is calculated by the average of the acidity produced during a kinetic test in modified weathering cells, it should be called a relative "acidity production factor". The statement of Bouzahzah et al. (2013) was that, for example, the calculated AP for 10 wt.% sphalerite (100.7 kg $CaCO_3.t^{-1}$) is greater than the calculated AP for 10 wt.% arsenopyrite (60.2 kg $CaCO_3.t^{-1}$) with Paktunc's equation. However, kinetic test results show that arsenopyrite generates 10 times more acidity (≈ 850 mg $CaCO_3.L^{-1}$) than sphalerite (≈ 90 mg $CaCO_3.L^{-1}$) when submitted to similar oxidation conditions. The relative acidity production factor was determined experimentally by calculating the average of the total acidity produced by each sulfide in the leachates of the kinetic tests during 200 days. Six common sulfides have been tested by the authors: arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), galena (PbS), pyrite (FeS_2), pyrrhotite ($Fe_{(1-x)}S$, $0 < x < 0,17$) and sphalerite ((Zn,Fe)S).

$$AP = \sum_{s=1}^{m} \left(\frac{n_s \times 98 \times X_s \times 10}{w_s} \right) * \mathbf{r_s} \tag{3}$$

With r = 1 for pyrite and pyrrhotite, 0.06 for galena, 0.23 for chalcopyrite, 0.26 for sphalerite and 2.54 for arsenopyrite, meaning that arsenopyrite produces about 2.5 times acidity than pyrite.

However, this factor does not really consider the oxidation rates of each sulfide - and thus the kinetics of the reaction - as this factor is based on the acidity production in average and does not refer to a reaction rate. The acidity production was measured in the laboratory and the interpretations and reliability of this measure can be affected by several parameters like the chemical instability of samples (Kirby and Cravotta, 2005b, 2005a).

Moreover, this factor does not consider the influence of minerals between them. These influences, occurring between semiconducting minerals, called galvanic interactions, modify (inhibit or activate) the geochemical behavior of sulfide minerals. As sulfides are mostly semi-conducting minerals, galvanic interactions