



Research article

Evaluation of pyritic mine tailings as a plant growth substrate

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ABSTRACT

At the Kidston gold mine, Australia, the direct establishment of vegetation on tailings was considered as an alternative to the use of a waste rock cover. The tailings acid/base account was used to predict plant growth limitation by acidity, and thus methods capable of identifying tailings that would acidify to pH 4.5 or lower were sought. Total S was found to be poorly correlated with acid-generating sulfide, and total C was poorly correlated with acid-neutralizing carbonate, precluding the use of readily determined total S and C as predictors of net acid generation. Therefore, the selected approach used assessment of sulfide content as a predictor of acid generation, and carbonate content as a measure of the acid-neutralizing capacity available at pH 5 and above. Using this approach, the majority of tailings (67%) were found to be non-acid generating. However, areas of potentially acid-generating tailings were randomly distributed across the dam, and could only be located by intensive sampling. The limitations imposed by the large sample numbers, and costly analysis of sulfide and carbonate, make it impractical to identify and ameliorate acid-generating areas prior to vegetation establishment. However, as only a small proportion of the tailings will acidify, a strategy of re-treating acid areas following oxidation is suggested. The findings of the present study will assist in the selection of appropriate methods for the prediction of net acid generation, particularly where more conservative measurements are required to allow vegetation to be established directly in tailings.

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1. Introduction

The Kidston mine was a large, low-grade gold mining operation located 260 km south-west of Cairns in far north Queensland, Australia. During the first phase of mining, approximately 6.0 million tonne of ore per annum was processed using a cyanide leach and carbon-in-pulp process. Gold-bearing ore was prepared for this process by grinding to $\leq 160 \mu\text{m}$. Following extraction of the gold, the tailings were placed by subaerial deposition in a storage facility covering approximately 300 ha. A preliminary geochemical evaluation of the tailings indicated that the dam, as a whole, would not be acid generating. However, density segregation of pyrite during deposition of the tailings resulted in areas where the

oxidation of sulfide minerals would produce low pH conditions. Two rehabilitation strategies were considered for the tailings storage facility (TSF); (a) cover the area with several metres of non-acid generating waste rock, or (b) direct establishment of vegetation into the tailings. A critical factor determining which rehabilitation strategy would be adopted for this TSF was the extent to which the establishment and sustained growth of native plant species in tailings would be restricted by acidity.

A range of approaches can be utilized for the prediction of net acid generation from mine wastes, such as short-term field tests, static methods, kinetic methods, and mineralogical classification (for example, see the review by Parbhakar-Fox and Lottermoser (2015)). Each of these general approaches has a range of advantages and disadvantages, including differences in cost, accuracy, and experimental duration (Parbhakar-Fox and Lottermoser, 2015). Of the static methods, acid-base accounting (ABA) and net acid generation (NAG) are the two most common approaches. The ABA requires the measurement of the maximum potential acidity (MPA) and the acid-neutralization capacity (ANC), with the difference between the two being the net acid producing potential (NAPP, also referred to as the net neutralizing potential, NNP). For NAG,

Abbreviations: ABA, acid base accounting; ANC, acid neutralization capacity; MPA, maximum potential acidity; NAG, net acid generation; NAPP, net acid producing potential; NNP, net neutralizing potential; TSF, tailings storage facility.

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hydrogen peroxide is added to the sample with solution pH measured after the reaction is complete (Finkelman and Giffin, 1986; Urrutia et al., 1992).

Of particular interest in the present study is ABA, which is comparatively inexpensive and commonly used. In this approach, MPA is typically determined by measurement of the total S concentration. However, it is well-known that total S often overestimates the MPA (to varying extents) due to the inclusion of non-acid forming S forms in measurements of total S, such as from gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Parbhakar-Fox and Lottermoser, 2015). Direct measurement of sulfides (c.f. total S) is more accurate but also more expensive. The ANC is most commonly measured by titration with a strong acid (Sobek et al., 1978), although several expansions and modifications of this method exist (Jambor et al., 2007; White et al., 1999). For example, Capanema and Ciminelli (2003) added 1 N HCl twice during their test which was found to be more accurate than the standard Sobek method. Other authors have measured concentrations of carbonates rather than titrating with acid (Borden, 2003; Hutt and Morin, 2000; Lengke et al., 2010). Whilst this approach has advantages (as discussed in detail later), it can underestimate the ANC, particularly in highly acidic systems. For example, examining a database of ca. 45,000 samples, Hutt and Morin (2000) reported that non-carbonate minerals provided the primary contribution to neutralization in up to 20% of samples.

The aim of the present study was to examine the suitability of ABA as a predictor of acid generation for tailings at the Kidston gold mine (Australia) by examining the physical, mineralogical, and geochemical properties of the tailings. Most studies utilizing ABA focus on acid mine drainage (AMD) and hence attempt to identify mine wastes that will generate highly acidic drainage water. However, in the present study we considered the growth of plants directly within the tailings – this requiring the final pH of the tailings to remain at pH values sufficiently high that acidity will not limit growth (for example, $\text{pH} > 4.5$). As a result, we examined the suitability of different approaches for measuring MPA and ANC for tailings to be used directly for the growth of plants. Based upon our findings, the TSF was then sampled to identify areas of potentially acid-generating tailings – this enabling an assessment as to whether it is practical to accurately predict acid-generating areas prior to vegetation establishment. Reliable methods for the prediction of acid-generation by mine wastes are of importance not only to mining companies but also to government regulators and to the general public.

2. Materials and methods

To obtain a representative collection of the tailings, the TSF was divided into eight regions on the basis of surface appearance and time since deposition. Nine cores (10 cm diameter, 60 cm deep) were extracted from each of these areas (total of 72 cores) and divided into four 15 cm depth increments (288 samples). The samples were air-dried and ground to ≤ 100 mesh ($150 \mu\text{m}$) prior to laboratory analysis.

The capacity of the tailings to generate acidity was investigated in two phases. A preliminary assessment of the geochemical characteristics of the tailings was conducted to quantify the proportions of potentially acid forming and non-acid forming tailings present at the surface. The methods used in this assessment were primarily developed to identify mine wastes which will generate highly acidic drainage water. However, a more conservative assessment was required in this situation, as the tailings were to be used as a plant growth media. Additional investigations were conducted using selected samples to provide a more accurate assessment of the acid-generating potential of the tailings.

2.1. Preliminary evaluation

The mineralogy of selected tailings samples was determined using X-ray diffraction techniques to identify the presence of the sulfide, carbonate and silicate minerals associated with the process of acid mine drainage. Eleven samples were selected to represent the range of geochemical conditions present. Samples were finely ground ($< 1 \mu\text{m}$) and diffraction patterns of randomly oriented powder samples were analysed using a Phillips PW-1840 spectrometer. The phases present were identified using Fein-Marquart's μPDSM search match program (Marquart, 1986).

For all 288 samples, the pH and EC of the tailings were determined in 1:5 soil:water suspensions. Total S was determined by high temperature oxidation using a LECO HF-10 C and S analyser, with the concentrations of S subsequently used to calculate the maximum potential acidity (MPA) of the tailings. Inherent buffering capacity was determined using the acid-neutralization capacity (ANC) method of Sobek et al. (1978), where tailings samples are reacted with a known excess HCl then back titrated with NaOH to quantify the acid neutralizing capacity of the sample. The net acid producing potential (NAPP) was calculated using the following equation (Sobek et al., 2000):

$$\text{NAPP} \left(\text{kg H}_2\text{SO}_4 \text{ t}^{-1} \right) = \text{MPA} (\% \times 31.25) - \text{ANC} \left(\text{kg H}_2\text{SO}_4 \text{ t}^{-1} \right). \quad (1)$$

The net acid generation (NAG) test was undertaken on selected samples. This approach uses hydrogen peroxide (15%) to oxidise reactive sulfide minerals in the tailings. The acid generated by this oxidation reacting with any neutralizing components of the sample (Miller and Jeffery, 1995), with the end result representing a direct measure of the capacity of the sample to generate acid.

2.2. Detailed assessment

A subset of 30 samples, representative of the range of NAPP identified in the tailings, were selected for more detailed analysis. Total C and S were determined by high temperature oxidation using a LECO CNS 2000 analyser. In preliminary investigations, acceptable recovery of S ($102\% \pm 2$) and C ($109\% \pm 2$) was obtained using vanadium pentoxide (V_2O_5) as an accelerant ($\approx 0.1 \text{ g sample} + 1.0 \text{ g of } \text{V}_2\text{O}_5$), and this approach was adopted for all experimental samples. Sulfide-S was determined using a sequential nitric acid oxidation method (Dacey and Colbourn, 1979). Briefly, samples were refluxed in 2 M HCl for 2 h at 105°C to remove sulfate-S, then refluxed in 2 M HNO_3 for the same period of time and at the same temperature to remove sulfide-S. Sulfide-S was subsequently measured using inductively coupled plasma atomic emission spectroscopy (ICPAES).

The neutralization potential was determined using the ANC method of Sobek et al. (1978). This ANC is the capacity of the sample to neutralize strong acid and hence will include components of the tailings that only react at low pH (< 3). However, as the tailings are to be used as a plant growth medium, the final pH of the tailings after oxidation must be sufficiently high that acidity will not limit growth ($\text{pH} > 4.5$). Thus, much of the ANC measured will not be available. An effort to assess the “available” ANC was made using two approaches. Firstly, slow acid titration of the tailings samples was examined as outlined by Miller and Jeffery (1995), with this slow titration measurement of ANC hereafter referred to as ‘available ANC_T’. Titrant additions (0.02 mL of 0.1 M HCl per 40 s) were made to a slowly-stirred, 1:125 soil:water suspension using a Radiometer Copenhagen™ TIM900 titration manager with an ABU901 autoburette. The titration duration was dependent on the

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