Characterisation of Secondary Minerals to Minimise Post Rehabilitation Downstream Water Quality Issues at Legacy Mine Sites

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Abstract

The remediation of legacy mine sites can be more challenging than operating mines because the waste rock at legacy sites is often substantially oxidised. Oxidised material can contain immediately leachable acidity and metals as well as poorly soluble acidic secondary minerals such as potassium jarosite. The validation of a method to quantify the amount of jarosite, and its implications for the remediation of waste rock at Rum Jungle in Australia is addressed here. Quantifying poorly soluble acidic secondary minerals should be a key component of geochemical characterisation programs and remediation programs for oxidised sulfidic material producing acid mine drainage.

Keywords: acid mine drainage, secondary minerals, jarosite, waste neutralisation, rehabilitation

Introduction

The downstream effects of legacy or abandoned mine sites due to acid and metalliferous drainage (AMD) represent, in the mind of the community, one of the most negative aspects of the mining industry. However, the rehabilitation of these sites to meet contemporary standards can be challenging since, in contrast to operating mine sites that are mining and managing fresh material, sulfidic waste at legacy sites is often broadly distributed across the landscape and already substantially oxidised. This oxidised material can contain immediately leachable acidity and metals as well as poorly soluble acidic secondary minerals such as potassium jarosite - $KFe_3(SO_4)_2(OH)_6$. Thus, achieving protection of the receiving environment from this partly oxidised material can be more complex than for fresh waste rock where protection from oxidation alone can be an effective management strategy.

The former Rum Jungle mine legacy site (Rum Jungle) in Australia's Northern Territory has a long history of adverse effects on downstream water quality and aquatic ecosystem health in the East Branch of the Finniss River (EBFR) and the main Finniss River (Mudd and Patterson 2008). Major rehabilitation works undertaken in the mid-1980s succeeded in reducing (by up to 70%) the loads of acid and metals released from the site, resulting in substantive recovery of the aquatic ecosystems in the EBFR (Jeffree et al. 2001). Despite this extent of improvement, metal concentrations in the EBFR do not meet contemporary water quality standards for ecosystem protection. Additionally, the site is on traditional aboriginal land, with it currently not being in a condition suitable for return to the groups involved.

Since 2009 the Northern Territory and Australian Governments have been working together and engaging with traditional Aboriginal owners, the Kungarakan and Warai peoples, under the framework of a National Partnership Agreement (NPA) to develop a final rehabilitation strategy for the site (fig. 1).

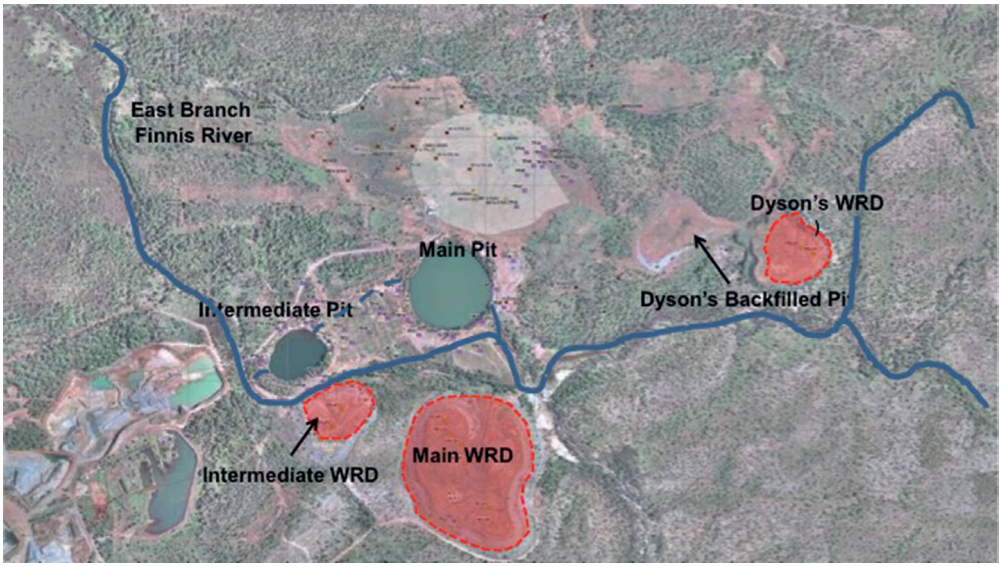

Figure 1 Current configuration of Rum Jungle showing the three covered waste rock dumps (WRD) and the two flooded open pits in close proximity to the east branch of the Finnis River.

Descriptions of the current layout and status of the site, and full details of the proposed rehabilitation strategy, are provided in the recently released Environmental Impact Statement and supporting technical documentation (DPIR 2020). Summaries of the geochemical characterisation program and environmental performance assessment for the proposed works are provided in Jones et. al. (2017) and Ferguson et al. (2017) respectively.

The key objectives of the geochemical characterisation program completed in support of the rehabilitation plan are to:

1. Determine the physical and geochemical properties of Potentially Acid Forming (PAF) and Non-Acid Forming (NAF) waste rock in the existing Waste Rock Dumps (WRDs) and other locations on site; and to
2. Identify PAF waste rock types in the three existing WRDs and surface disseminated material and prioritise for re-location as pit backfill or to a new waste storage facility to minimise future release of existing sulfide oxidation products and ongoing AMD generation from the re-located materials.

Critical to objective 2 is estimating the amount of neutralant required to neutralise existing acidity in re-located PAF materials, so as to reduce as much as practicable the future potential for this existing load to be released to the environment. Existing acidity comprises directly titratable acidity and acidity from poorly soluble secondary minerals. The first of these components can be easily measured by titration. However, quantifying the amounts of secondary minerals present is more challenging. The implementation and validation of a chemical method to quantify the amounts of poorly soluble secondary minerals, and the implications of secondary mineral content for the remediation of waste rock material at Rum Jungle is the focus here.

Methods

Details of the site and the methods of sample collection and preparation and analysis by the standard suite of static tests used for conventional Acid Base Accounting (ABA) to estimate AMD potential (AMIRA 2002, Price 2009, Preventing Acid and Metalliferous Drainage 2016) have been described previously (Jones et al. 2017). The ABA work on material from Rum Jungle was

done by a commercial laboratory (Australian Laboratory Services – ALS, Brisbane).

The mineralogy of a selection of samples was determined by quantitative powder X-Ray diffraction at the Queensland University of Technology, Brisbane. It was identified by this method that the higher PAF category of material contained substantial (up to 5 wt.%) quantities of jarosite, and no detectable alunite or barite. Since the jarosite component comprised a substantial proportion of the existing acidity in these selected samples it was concluded that all of the samples that had been characterised by the conventional ABA approach should also be screened for their jarosite content. A less costly and time-consuming method than X-ray mineralogy was needed to be applied to the large numbers of samples collected for this work. There are three chemical methods that have been evaluated for accuracy in the determination of jarosite:

1. Overnight extraction at room temperature with 4M hydrochloric acid
2. Pyrolysis at 550 °C for 1 h, followed by extraction with 4M HCl for 30 min. (Li et al. 2007).
3. Extraction with boiling sodium carbonate solution (MEND 2009)

In summary, these methods involve the determination of total sulfate in a sample, from which the water-soluble sulfate is subtracted to yield secondary mineral sulfate by difference. Sulfate comprises 38.3% by weight of potassium jarosite.

However, as noted by Price (Price 2009, Chapter 12) the efficacy of chemical methods to quantitate the amount of jarosite often depends on the provenance of this phase. Consequently, it was necessary to validate the recoveries of each of the potential methods against the XRD-determined jarosite contents for material from Rum Jungle, prior to screening the large numbers of samples required (Jones 2015).

Method 1 has been reported to underestimate the amount of sulfate associated with jarosite, although it has been suggested that 16h extraction should be long enough to recover at least 80% (Li et al. 2007). The muffle furnace pre-treatment functions by converting all sulfide sulfur in the sample to volatile sulfur dioxide, which is lost from the furnace. The jarosite is thermally altered to a much more soluble form such that only a sort time (ca. 30min) extraction with the 4M HCl should be sufficient (Li et al. 2007).

Each of the three methods was evaluated for jarosite recovery using a number of samples with different jarosite content, with the XRD-determined values for jarosite used for comparison (Jones 2015). It was found that Method 1 substantially underestimated (by >50%) the jarosite content. Method 2 was found to provide good recovery of jarosite, albeit with somewhat variable results. However, it would be a more difficult and time-consuming method to carry out for a large number of samples given the requirement for the muffle furnace pre-treatment.

Overall, Method 3 was found to provide the most consistent agreement with the jarosite content as determined by XRD (see Results and Discussion). It was also a very easy method to apply for the large number of samples required for the Rum Jungle project. The samples were sent to the ALS laboratory in Vancouver British Columbia Canada, which had a routine implementation of the method (ALS method GRA06).

Results and discussion

The identification of a reliable and robust method for the determination of jarosite in the variably oxidised Rum Jungle waste rock was key to efficiently quantifying the total existing acidity and hence neutralant demand of the material. The process of testing of three candidate methods was summarised above. Final confirmation of the efficacy of the sodium carbonate extraction method (Method 3) was provided by comparing XRD values with Method 3 for 10 samples spanning a wide range of jarosite contents (fig. 2). The correlation is high as demonstrated here in Figure 2.

The two existing acidity components (titratable and jarosite) are summarised below (tab. 1) for the three PAF classes defined for the waste from Rum Jungle (Jones et al. 2017). It can be seen in this summary that jarosite is by far the dominant component of total existing acidity.

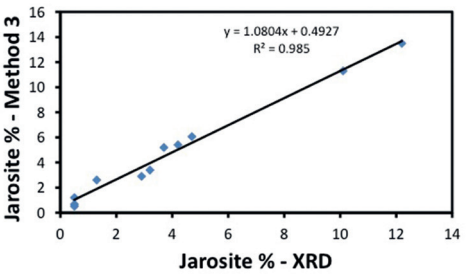

Figure 2 Correlation between jarosite content determined using Method 3 (sodium carbonate extraction and quantitative XRD.

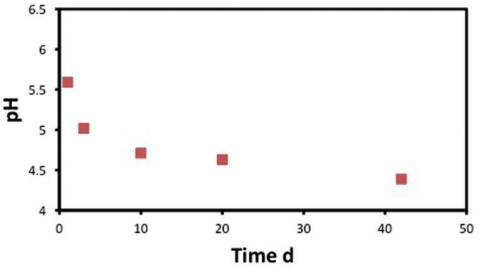

Figure 3 Decline in pH through time if only titratable acidity in waste rock is neutralised.

The data in Table 1 show that for the Rum Jungle site, measuring only readily titratable acidity would have resulted in a gross underestimate of neutralant demand for the waste and hence failure to add sufficient neutralant to stabilise this component of acid (and hence leachable metal) load. In particular, a neutralisation QC program that used short term pH alone as an indicator of success would not have detected that anything was wrong with the remediation work. The consequence of incomplete neutralisation would be that over time the acidity contained in the slowly reacting jarosite would buffer the pH downwards to around pH 3 to 4, resulting in the redissolution of initially precipitated and immobilised metals. This effect is shown (fig. 3) for a sample of waste rock containing 15 kg H_2SO_4/t jarosite acidity and 4 kg H2SO4/t titratable acidity, to which sufficient finely ground $CaCO_3$ was added to account for the titratable acidity only. The starting pH prior to neutralant addition was 3.4.

Finely ground agricultural lime – $CaCO_3$ – was selected as the neutralant of choice for the waste remediation project based on the findings from mixing tests that indicated the bulk of target metals were removed from solution by the pH (ca. 7) that could be achieved with this neutralant (Jones et al. 2017). Excess neutralant will be added according to the conservative dosing regime that has been determined for each of the PAF categories (Jones and Ferguson 2019).

Conclusions

The room temperature hydrochloric (HCl) acid extraction method currently routinely used to determine jarosite content in AMD assessments was found to substantially underestimate the amount of jarosite present in the Rum Jungle waste rock. Of the two methods tested that did yield good recovery, the one using extraction with boiling sodium carbonate is recommended for routine application.

The existing acidity (neutralant demand) of the acidic samples that were tested from Rum Jungle was found to be dominated by jarosite. This is a critical finding since failure to quantify the acidity contributed by jarosite would have resulted in a gross underestimate of the amount of neutralant needed to account for this source of acidity. The findings from this work emphasise the need for a validated method for the measurement of acidic low solubility secondary minerals to be applied for those remediation projects involving oxidised waste rock.

Table 1 80th Percentile Values for PAF Rock Types.

Type	%S	AMD Potential	Jarosite Acidity kg H_2SO_4/t	Titratable Acidity kg H_2SO_4/t	Total Existing Acidity kg H_2SO_4/t
PAF-I	5.1	High	14.8	2.8	17.6
PAF-II	1.5	Medium	13.1	1.5	14.6
PAF-III	0.8	Low	3.2	1.2	4.4

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