In situ calcite formation in limestone-saturated water leaching of acid rock waste

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ABSTRACT

The result of leaching of a 75% acid rock/25% limestone column with limestone-saturated solution has shown that the pH of the effluent recovered from 2.5, after apparent loss of acid neutralizing capacity after 4 years with water leaching, to pH 7 in less than 3 years. Bulk assay results, XRD and SEM/EDS analyses of samples from the column at 384 weeks (pH 3.6) and 522 weeks (pH 6.9) during this recovery have suggested that this is due to formation in situ of fine calcite. Calcite, initially blended to the column material at 25 wt.% was not found in the XRD of the 384 week sample but is clearly found in the 522 week XRD. This increased calcite content appears to be derived from the limestone-saturated water as finely divided solid precipitated in the drying cycles in the column. This result is confirmed by assessment of the 522 week sample as non-acid forming. Loss of some reactive aluminosilicate minerals, formation of secondary, precipitated, surface-attached gypsum and loss of fine secondary jarosite occurs across this pH range but fine, surface-attached jarosite is still found in the 522 week sample implying relatively slow dissolution kinetics. In comparison with the 384 week sample, armouring of highly reacted pyrite particles by surface layers of iron oxyhydroxides and aluminosilicates has become more extensive at 522 weeks after return of the pH to neutral values. This is consistent with results from Freeport field samples from limestone blended test pads where pyrite armouring was also substantially increased at higher pH. The results suggest that it may be possible to effectively maintain neutral pH and passivate pyrite, reducing oxidation rates by more than an order of magnitude, using limestone-saturated solution dump feed rather than bulk limestone blending or covers.

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1. Introduction

The management of acid and metal drainage from sulfide-containing mining waste, mainly stored as rock dumps (i.e. acid rock drainage, ARD), is of fundamental importance to the continuing social acceptance of mining industries and to the environmental management costs of current, exhausted and abandoned mine sites. In Australia alone, it is estimated that current ARD waste management costs of operating mines exceed $120M p.a. at >100 sites plus >$650M in inherited liability at abandoned sites (Harries, 1997; Chatwin, 2008). In the USA, there are more than 200,000 acid rock drainage (ARD) sites (Gallinger and Fleury, 2006). In the last decade, this has elevated assessment and management of acid rock drainage to one of the highest priorities in mining and minerals processing management in programs like the International Network for Acid Prevention

(INAP), a consortium sponsored by the world's leading mining companies (Gallinger and Fleury, 2006).

Assessment and classification of the acid producing potential of rock wastes is based on standard methods of acid–base accounting such as the net acid producing potential (NAPP) and the peroxide-accelerated net acid generation (NAG) tests. These test procedures are described in the AMIRA/EGi ARD Test Handbook (2002) and in the recent international Guide to Acid Rock Drainage (GARD) Handbook (www.inap.com). For wastes assessed to be acid producing in rock and overburden dumps, strategies to isolate the waste and reduce the rate of oxidation are the main control options while limestone addition is the main treatment option adopted by most operating sites. Limestone amendments, blended and layered in preparation or added as covers, have been extensively studied in both lab and field sites over more than 10 years and have demonstrated effective short-term control of ARD (e.g. Miller et al., 2003a,b, 2006). Probably the most extensive long-term study of this kind is the Grasberg operation in the Papua Province of Indonesia, a large copper (chalcopyrite with some bornite, chalcocite and covellite) and gold open pit mine operated by PT Freeport Indonesia (PTFI) (Rusdinar, 2006; Miller

et al., 2003a,b, 2006, 2009) The Grasberg ore body itself is low in carbonate but a substantial amount of limestone (more than 85% calcite with a NAPP value of −850 kg H_2SO_4/t) together with low-grade, high pyrite ore, has been mined to gain access to the copper-bearing ore. The overburden stockpiles have been constructed adjacent to the mine with a final elevation range from about 3500 m at the toe of the lowest stockpile to 4500 m at the final top surface. The annual precipitation varies from about 3000 mm to 5000 mm over short distances around the Grasberg mine, but the average daily precipitation is about 10 mm per day and leaching of the overburden is continuous throughout the year. A major focus of ARD investigations at Freeport has been aimed at developing strategies to maximise the beneficial use of the significant quantities of limestone mined from 2003 to the end of the open pit.

Laboratory columns and field test pad investigations have examined limestone blends, layers and covers. Full-scale trial dumps comprising truck blends, conveyor/stacker blends and truck placed limestone covers have been constructed and monitored. Site investigations, design and operational performance of a 450 million tonne limestone blended dump are reported in Miller et al., 2006. Trials have demonstrated that run-of mine truck-constructed blended dumps are not fully effective because the finer sulfide size fractions do not necessarily receive adequate adjacent limestone. Stacker-built blended dumps can be effective provided the blend ratio is based on achieving adequate acid neutralising capacity (ANC) within the finer fractions. Because the sulfur content increases and the acid neutralis-ing capacity decreases with decreasing particle size in limestone blends at Grasberg, the amount of limestone required to achieve this ANC greatly exceeds (at least 1.5 times) the stoichiometric reaction requirement (Miller et al., 2006). Stacker-built blended dumps can be effective provided the blend ratio is based on achieving adequate acid neutralising capacity (ANC) within the finer fractions. Because the sulfur content increases and the acid neutralising capacity decreases with decreasing particle size in limestone blends at Grasberg, the amount of limestone required to achieve acid–base balanced condi-tions across all size fraction within the blend greatly exceeds (at least 1.5 times) the theoretical amount required to produce an acid–base balanced bulk sample (Miller et al., 2006). With these blending specifications, however, the pH of the dump effluent has been maintained above 6 for more than 6 years.

Evaluation of limestone covers for treatment of ARD wastes at Grasberg has also been reported in Miller et al. 2003b. Pad 2 in this trial provides a useful example of the behaviour of limestone covers over longer periods of time. Pad 2 was constructed from 500 tonnes of −300 mm PTFI Blue waste blended with 10 wt.% PTFI limestone. The PTFI Blue waste has 2 wt.% S with pyrite as the dominant sulfide and minor chalcopyrite and trace bornite and covellite (total 4500 ppm Cu). It is classified as potentially acid forming based on standard tests of NAPP of 46 kg H_2SO_4/t and NAG pH 2.8 and sequential NAG to pH 7 of 27 kg H_2SO_4/t. The pH trends clearly showed that the 10% limestone blend provided only a short period of pH control with the pad leachate falling to pH 4 within 6 months and to pH 3 after 12 months. A 2 m limestone cover was placed over Pad 2 at day 400. About 16 months after placement of the cover, the pH slowly increased to 4 and after 2.5 years the pH rapidly increased from about 4 to 6. The pH has remained at about 6 to 6.5 for 5 years. The cover has effectively reduced the dissolved copper concentration by more than four orders of magnitude.

In the blended and cover limestone amendment trials, leach columns, test pads (Miller et al., 2003b, 2009) and dumps (Miller et al. 2006), there has been a reduction of acid sulfate generation rate (ASGR), relative to that expected from full oxidation of the sulfides in the ARD wastes, by more than 90% (up to 99%) when the pH is maintained above 6. Recent studies of model systems (Schumann et al., 2008, 2009) compared with field samples from test pads and dumps (Miller et al., 2009) have shown that this pyrite passivation

results from silicate-stabilised oxyhydroxide surface layers, limiting the availability of oxygen at the pyrite surface, maintained in circum-neutral pH but not found (or unstable) at lower pH. These layers inhibiting pyrite oxidation, similar to those reported by other researchers (without noting the role of silicate) (Nicholson et al., 1990; Calderia et al., 2003), have the following properties:

- at the pyrite surface, a thin, continuous and conformal layer of amorphous iron oxyhydroxide containing minor concentrations of silicate, sulfate and carbonate;
- a further overlayer of amorphous iron oxyhydroxide stabilised by higher concentrations of silicate;
- then a (semi-)crystalline layer of goethite-like material, and in cases where clay minerals are in the ARD waste (e.g. PTFI), another thick coating (armouring) by strongly adhering micaceous particles;

The inclusion of silicate in the stable layers under neutral conditions is well established (Schumann et al., 2008, 2009; Miller et al., 2009) but the mechanism is not yet fully understood. It is possible that this involves formation of amorphous iron hydroxy silicate that then crystallizes as the very stable botryoidal silicate-modified form of goethite but this needs to be proved (part of our current work). The evidence reported (Schumann et al., 2008, 2009; Miller et al., 2009) shows that the layers are much less stable without the silicate in neutral conditions and unstable at low pH. The paper by Kargbo and Chaterjee (2005) confirming the suppression of pyrite oxidation due to the formation of stable coatings of Fe^{3+}-silica and/or Fe^{3+}-hydroxy-silica complexes over pyrite surfaces in near-neutral and neutral solution pHs is also relevant. They show that there is no convincing experimental evidence that these coatings exist under low pH environments.

The growth of the iron oxyhydroxide coatings on pyrite has recently also been studied by Huminicki and Rimstidt (2009). They suggest that this occurs in two stages. In the first stage, Fe oxyhydroxide colloids form and then attach to the pyrite surface to produce a slight reduction in oxidant transport. In the second stage interstitial precipitation of Fe oxyhydroxide material between the colloidal particles reduces the oxidant's diffusion coefficient by more than five orders of magnitude causing the pyrite oxidation rate to decline as the square root of time. Extrapolation of the results to longer times predicts that pyrite-bearing materials need to be treated with alkalinity for several decades to produce coatings that are thick enough to be sustained by alkalinity levels typical of groundwater. They suggest that, once the coatings develop no additional treatment is needed and further pyrite oxidation simply causes the coating to grow thicker and denser until the entire pyrite grain is pseudomor-phically replaced by goethite.

In other studies, Barnes and Gold (2008) tested the efficiency of three slurries for treating acidity caused by pyrite weathering at pilot scale. Slurries of Bauxsol™, powdered limestone, and brucite [Mg (OH)$_2$] were sprayed onto 10-ton masses of pyritic aggregate, and the acidity and sulfate concentrations of outflows were monitored for 21.5 months. In their study, limestone control of pH was limited by armouring of the calcite by gypsum and by restricting of water flow to channels so that most of this slurry remained unreacted. These additional factors in field application are acknowledged and have been addressed in other studies on the Grasberg field trials (Miller et al., 2003a,b).

The results of the lab and site trials on the PT Freeport limestone amendments suggested that leaching from the limestone in this high rainfall environment, rather than direct reaction between carbonates and oxidising sulfides in situ, may be contributing to the slow but very effective recovery of ARD control at Grasberg. This might suggest an alternative treatment strategy based on limestone leach water control and flow rather than direct addition of large quantities of limestone as blends, layers or covers. This strategy would be important at sites where access to limestone is limited.