ARD Control by Limestone Induced Armouring and Passivation of Pyrite Mineral Surfaces

Stuart Miller¹, Russell Schumann², Roger Smart ³ and Yuni Rusdinar⁴

¹ Environmental Geochemistry International Pty Ltd, 81A College Street, Balmain, NSW 2041, Australia. egi@geochemistry.com.au
² Levay & Co. Environmental Services, Ian Wark Research Institute, University ofouth Australia, Mawson Lakes, SA 509, Australia.
³ ACeSSS, University of South Australia, Mawson Lake, SA 5095, Australia.
⁴ PT Freeport Indonesia, Tembagapura, Papua, Indonesia

ABSTRACT
At the PT Freeport Grasberg Mine in Papua, Indonesia, investigations have been ongoing since 1996 to evaluate the long-term performance of limestone blends and covers for ARD control. In addition to the site program involving leach columns, test pads, trial dumps and sampling of full-scale dumps, detailed surface chemistry and mineralogy studies have been conducted through a 6 year research project facilitated by AMIRA International.

Extensive armouring of pyrite was observed in limestone blends and has persisted for more than 10 years. The armouring layers were observed on samples collected during the first sampling event after 2 years of operation of the test pads, and water quality data suggest that effective armouring may have developed within 9 to 12 months following construction of the test pads. Armouring involves the formation of a thick jarositic/iron oxide layer on the pyrite surfaces onto which layer alumino silicates are strongly attached.

The results of the surface chemistry investigations suggest that pyrite continues to react when armoured but also confirms that maintaining the pH near neutral in a limestone blended mix retains the inhibiting surface layer and clay armouring and significantly reduces the rate of oxidation. The ongoing slow rate of oxidation at the pyrite mineral surface is considered an important mechanism for maintaining the armouring layers and enhancing the performance of the limestone blends for ARD control.

This paper presents the results from dump scale trials and 12 years operation of field scale test pads and detailed mineralogical investigations examining the nature, formation and role of limestone induced armouring for long term ARD control.

Additional Key Words: jarosite, surface chemistry, acid rock drainage, laboratory columns, field trials, calcite.

INTRODUCTION
The PT Freeport Grasberg Open Pit Mine in Papua, Indonesia commenced in 1988. Approximately 1,500 Mt of waste rock have been mind to the end of

¹ Paper presented at Securing the Future and 8th ICARD, June 23-26, 2009, Skelleftea, Sweden
2008 and placed in engineered overburden stockpiles located around the open pit. Mining of the open pit is planned to continue to at least 2015 at which time approximately 2,750 Mt of overburden will have been produced. Mining from current and future underground operations, located in the vicinity of the Grasberg deposit is planned to continue to at least 2045.

Almost all waste mined and placed around the pit in overburden stockpiles up to 2003 was potentially acid forming, fast reacting and with minimal lag before onset of acid conditions. Material with an acid generating capacity up to 35 kg\(\text{H}_2\text{SO}_4\)/t is labelled as Blue Waste and material with a higher capacity is either Red Waste or heavy sulphide zone material (HSZ). HSZ is defined as material containing more than 20% pyrite (i.e. more than 10% pyritic sulphur). The production of limestone (labelled Green Waste) from mine start up to 2003 was minimal and accounted for less than 5% of the annual waste rock production.

Limestone production increased to about 20% from 2004 to end 2006 and is estimated to account for at least 55% of all overburden from 2007 to end of the Grasberg pit operation. This large component of limestone was recognised by PTFI as providing an opportunity to mitigate existing acid rock drainage (ARD) and implement strategies that would reduce long term ARD issues. Other factors that influence the use of limestone for ARD control at Grasberg are fast reacting acid generating blue and red waste; continuous rainfall leaching; high infiltration rates and high dump permeability.

In addition, since underground mine operations and processing facilities are planned to continue for at least 30 years beyond the completion of the Grasberg Pit, active management of ARD will continue through the post-closure period. This will enable the performance of the limestone based ARD control strategies to be monitored and the long term overburden stockpile (OBS) geochemistry to be confirmed. The impact on final closure of the mine can then be assessed and any need for additional work identified and implemented prior to final site closure.

The ARD management strategy at Grasberg is based on collection and treatment of ARD from Blue, Red and HSZ dumps and the use of limestone for construction of the blended Lower Wanagon dump and as a final cover over all dumps. The Wanagon Basin and Carstensz dumps will also receive substantial amounts of limestone from 2007 to closure of the pit with limestone accounting for 51% of the waste rock reporting to Carstensz and 54% for the Wanagon Basin dumps. The remaining balance of these dumps will in effect be a partial blend of limestone and acid generating rock. The heavy sulphide zone (HSZ) material is being placed in designated areas towards the back of the Upper Wanagon OBS and within the ARD capture zone. Some of the HSZ material contains inherent buffering due to the influence of limestone at the contact. Although this buffering can provide some lag before onset of acid conditions, the ARD potential of the HSZ material is substantial and presents significant implications for long-term OBS geochemistry management.
This paper describes ARD control through limestone induced armouring and passivation of pyrite surfaces observed in limestone blended waste rock at the Grasberg mine. The purpose of the limestone blended dumps is to prevent ARD from the outset. Limestone covers are also being used at Grasberg to provide a source of alkalinity and calcium to progressively mitigate ARD in dumps that are deficient in limestone or have ineffective blends. Further information on the design and performance of limestone covers is presented in Miller et al 2003a and 2006.

INVESTIGATION PROGRAM
The investigation program includes static and kinetic testing of representative samples of individual waste rock types and limestone blends and laboratory columns, field test pads, a trial dump and operational scale monitoring.

A description and findings of the columns and test pads set up and operation are presented in Miller (2003a) and Miller (2003b), respectively. The trial dump design is presented in Andrina (2003) and Miller (2003a).

The bulk mineralogy of fresh Blue and Red waste based on a combination of XRD, SEM, QEM-SEM and optical microscopy include quartz, alkali feldspar, mica (including phlogopite and muscovite), plagioclase (albite and anorthite), chlorite (including clinochlore), olivine, pyrite, chalcopyrite, covellite, bornite, olivine and magnetite.

The technique used for examination of surface layers and armouring was XRD, multi-elemental analysis, analytical scanning electron microscopy (SEM) providing both topographical imaging and compositional analyses (using energy dispersive x-ray spectroscopy EDXS).

SEM imaging has been carried out in two modes: secondary images which essentially show surface structure and topography; and back scattered images which emphasise differences in composition (based on average atomic number) between different regions.

The micrographs chosen for presentation of evidence relating to conclusions necessarily represent a small subset of images recorded. Many pyrite grains were examined visually in each sample before choosing grains that best represent surface layers and changes between samples and after processing.

Ultrasonic agitation was used to remove loosely held fine particles from pyrite surfaces. This technique is used to detach adsorbed and precipitated particles whilst not disturbing composite (locked) fine structure.

Each of the samples was examined as-received to image and analyse the reacted surfaces of the pyrite and any surface coatings or armouring. All samples were then subjected to ultrasonication and the pyrite surfaces re-examined. Samples from limestone blended trails were equilibrated in pH4 (H₂SO₄) for 24h before further examination. This treatment was undertaken to test whether reducing pH caused the removal of armoured clay particles and/or
surface coatings. These samples were also subjected to ultrasonication and re-examination of the pyrite surfaces after pH 4 treatment.

Detailed sampling and analysis of solid and leachate samples was carried out on all trials. All solids were assayed for total sulphur, acid neutralising capacity (ANC), net acid generation (NAG) and total copper. Selected samples were assayed for multi-elements, mineralogy, sequential NAG and kinetic NAG based on methods described in AMIRA, 2005.

ARD EVOLUTION KINETICS IN BLUE AND RED WASTE
ARD generation and release from Blue and Red waste rock at Grasberg occurs rapidly. There is little or no lag phase with acid pH conditions developing within days to weeks following exposure.

Figure 1 shows the sulphate release rate (SRR) for a red waste column (Col 47) and the red waste test pad at Menado (Pad 8). Figure 2 shows the pH and acid release rate (ARR) trends for these samples. These trends clearly demonstrate the ARD evolution kinetics for Grasberg red waste. Blue waste follows a similar trend but with lower acid loads and slightly higher pH.

![Figure 1. Sulphate release rate (gSO\(_4\)/t/d) from red waste column and test pad](image)

Figures 1 and 2 show that the sulphate and acid release rate peaks after 1 to 2 years and then decreases, rapidly for 2 years and then at a slower decay rate. Within 5 years, the acid generation rate decreases by more than an order of magnitude from the peak rate and by 10 years the residual acid generation rate is about 2 orders of magnitude less than the peak rate.

The sulphur leached from the material after 10 years is about 50% of the total sulphur contained in the original sample and the leaching trends show that most of this is removed within the first 5 years.
Although some sulphate is stored in secondary minerals such as jarosite, site investigation indicate a low content of stored oxidation product within the dump compared to other sites in lower rainfall regions where the net infiltration is lower. This information is contained in unpublished internal report to PTFI and based on water and EDTA extractions techniques described in Tran et al 2003.

Figure 3 is a scanning electron micrograph (SEM) backscatter image of a pyrite particle from Blue waste after 6 years weathering.

This sample has pyrite particles that expose 25-50% of their surfaces and do not appear to be protected by any surface layer formation. The exposed areas appear to have a very thin iron oxyhydroxide layer that is easily removed (possibly formed following sample collection due to evaporative concentration of the iron). Adherent clay particles are easily detached by ultrasonic agitation.
and reaction is relatively uniform across the pyrite fracture surfaces. These pyrite particles appear to be in fully oxidative reaction although there may be partial inhibition by surface layer formation, particularly during periods of lower leaching rates.

In summary, the findings of geochemical testing and field observations show that Blue and Red waste have little or no lag period and generate acid within days to weeks of exposure. The peak acid generation rates occur within 1 to 2 years and decrease by almost 2 orders of magnitude after 10 years. Rates after 8 to 10 years reduce to approximately 1 to 2 g/t/day from peak rates of 100 to 150 g/t/day. This fast ARD evolution kinetics is most likely assisted by the high and continuous rainfall infiltration and leaching of oxidation products from mineral surfaces.

Andrina et al (2009) provide detailed information on field oxidation rates and scale up relating to ARD evolution kinetics at Grasberg.

**LIMESTONE BLENDS**

The aim of blending limestone with Red and Blue waste is to prevent ARD and metal leaching (in particular copper). Sufficient limestone must be used to provide effective neutralisation, reduce the sulphide oxidation rate and promote passivation and/or armouring of sulphide minerals. Natural analogues of this type of mineralogy blend are high carbonate pyrite skarns. However, for a mine operational blend of potentially acid generating waste and limestone, the proportion of limestone needs to be greater than for a skarn where the carbonate and sulphide are inherently in direct contact. Further discussion on blend requirements, operational specifications and field performance at Grasberg are presented in Miller et al 2006 and Andrina et al 2009.

Figure 4 shows the pH and sulphate release rate trends for limestone blended test pads. Pad 3 is a 25% limestone blend with blue waste and Pad 7 is a 50% limestone blend with red waste. The results show that the pH has remained circum neutral for the 10 years of operation of the pads that have been exposed to natural rainfall and climatic conditions prevailing at Grasberg. The sulphate release rate (SRR) is about 1 to 2 g/t/d from the Blue waste blend (Pad 3) and 2 to 3 g/t/d from the Red waste blend (Pad 7). These rates are 2 orders of magnitude less than peak rates for unblended Red and Blue waste as shown previously on Figure 1.

Figure 4 also shows that the sulphate release rate is relatively constant after about 9 to 12 months. This suggests that armouring may have become effective within this timeframe.
Figure 4: pH and sulphate release rate (gSO$_4$/t/d) from limestone blended red waste (Pad 7) and blue waste (Pad 3). 50% limestone with red waste and 25% limestone blend with blue waste.

Figure 5 shows the pH and calculated sulphate release rate for the three year monitoring period at Lysimeter 1, Panel 7 (L1P7) of the Batu Bersih trial dump (Andrina et al 2003). This panel was constructed using a stacker and is a 25% limestone blend constructed by alternately placing 3 units of Blue/Red waste and 1 unit of limestone. The unit was 14m$^3$ and sized to simulate a full-scale operational dump (Andrina et al, 2003). Figure 6 is a photograph of an excavation into the blended section of this panel.

Figure 5 shows that the pH remained circumneutral with a calculated sulphate release rate of 0.2 to 0.5 g/t/d. This rate is lower than observed in the columns and test pads and most likely due to preferentially flow paths and precipitation of gypsum. Mineralogical analysis of a sample collected at site L1P7 on Figure 6 after 3 years weathering indicated that about 5 to 10% of the sample mass was gypsum, CaSO$_4$(H$_2$O)$_2$.

Figure 5: pH and sulphate release rate trends in the limestone blended panel at Batu Bersih (Panel 7, Lysimeter 1)
Figure 6: Limestone Blended Trial. Panel 7, Batu Bersih Dump. November 2004

Figure 7 is a secondary electron image (SEI) of an as-received sample from L1P7. About 5 kgs of material was taken and placed in sealed bags. The samples were sieved through a 5mm aperture sieve and the minus 5mm size material was placed in a sealed plastic bag. The samples were then riffle split with a 1 kg sub-sample placed in a sealed bag and dispatched to the laboratory for analysis. Many grains from each sample were examined visually before choosing the sample shown in Figure 7 as representative of those occurring in the panel. The image shows complete coverage of the pyrite grain with silicate minerals. Figure 8 is a back-scatter electron image (BEI) of a pyrite sample after ultra-sonic cleaning. This shows oxidising pyrite surfaces with some residual and firmly fixed jarositic/alumino silicate layers.

Figure 7: Secondary Electron Image (SEI) of as-received samples from L1P7
Previous mineralogical and surface chemistry investigations of pyrite particles collected from the Test Pad trials identified similar surface layering and armouring. In the limestone blended samples, it is apparent that pyrite particles have thick iron hydroxy sulphate layers (of a jarosite type) totally adherent across the surface. This layer is covered by a strongly fixed layer of aluminosilicate minerals that have been identified as phlogopite, clinochlore and illite.

EDS probing of the jarosite type layer indicates that it is a complex mineral containing variable amounts of Ca as well as the jarosite mineral components of S, Fe, O. Alumino silicates also seem to be embedded in the layer.

Jarosite is a typical product of pyrite oxidation and has the following general chemical formula:

$$XFe_3(SO_4)_2(OH)_6$$

where X is typically K in sulphide mine waste but can be substituted by Na, NH$_4$ and H$_3$O$^+$. Jarosite is thermodynamically unstable at pH values more than about 4 and hence the ubiquitous occurrence of this mineral as a key component of the surface armouring of pyrite in these blended materials at circumneutral pH is likely to be a key factor in the mechanism of formation and their role in ARD control.

Although work is continuing on investigating the nature of the armouring layers the current premise is that the jarositic layer is composed of two distinct forms. A gel-like or amorphous layer in contact with the pyrite surface composed of Fe, S and O as hydroxides and sulphates (this has been determined by EDS and XPS analysis). The gel-like layer grades to a more crystalline jarosite with an overall thickness of 1 to 2 microns. Mica and clay type minerals are strongly fixed to the jarositic layer.
The persistence of the jarositic layer is critical to maintaining the armouring layer since without it, the negatively charged clay and mica minerals are highly unlikely to bond with pyrite mineral surfaces. The persistence of the jarositic layer is likely due to low pH (below 4) at the mineral surface while the pore water and effluent is pH neutral. It is apparent that the armouring is a consequence of neutralisation slowing the oxidation rate by removing ferric ion as ferric hydroxide and jarosite. As the jarosite forms and adheres to the pyrite surfaces, the clay and mica minerals can attach.

There is also evidence that oxidation of pyrite continues below the armouring layer but at a slow rate due to continual removal of ferric ion and slow oxygen diffusion to the pyrite surface. It is expected that the jarosite layer would continue to grow as it replaces pyrite. In the long term, when all pyrite is depleted, the jarosite may then dissociate and release acidity, again at a slow rate. This acidity would then be neutralised by excess limestone within a blend and/or by alkalinity from covers.

Continued slow oxidation at the pyrite mineral surface is therefore likely to be an important mechanism for maintenance of the jarositic ‘glue’ that binds the aluminosilicate minerals that further slow the oxidation rate.

The results of the surface chemistry investigations suggest that pyrite continues to react when armoured but also confirms that maintaining the pH near neutral in a limestone blended mix retains the inhibiting surface layer and clay armouring and significantly reduces the rate of oxidation.

CONCLUSIONS
Investigations have been ongoing for 12 years and have involved laboratory and field programs including column leach tests, test pads and a large scale trial dump. In addition, detailed surface chemistry and mineralogy studies have been conducted to investigate the nature of pyrite grains and surface coatings on these grains under the various limestone treatments (blends, covers and combined blends and covers). Mechanisms of formation and growth of armouring layers and passivation of pyrite oxidation have been developed.

Grasberg sulphidic waste rock generates low pH ARD almost immediate upon exposure to atmospheric conditions whereas blends of this rock with limestone produce circumneutral pH and sulphate release rates that are 2 orders of magnitude lower than unblended rock. In all the limestone blended trials extensive armouring of pyrite was observed involving the formation of a jarosite/iron oxide layer on the pyrite surfaces onto which layer aluminosilicates are strongly attached. The mechanism of formation and persistence of the armouring layer is not fully understood but the current understanding is described in the report.

With respect to the implications for mine operations, the findings of these investigations confirm that the limestone particles must be in close association with pyrite for blending to be fully effective for the prevention of ARD. This is because a key function of the limestone is to reduce or prevent ferric ion oxidation of pyrite and promote precipitation of iron to initiate the armouring mechanism.
REFERENCES


