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# Geochemical characteristics of a sulphidic waste rock and implications for environmental rehabilitation

E. Mylona [1,*], A. Xenidis[1], G. Gaidajis[2], K. Adam[3]

*[1]Laboratory of Metallurgy, School of Mining and Metallurgical Engineering,
National Technical University of Athens, 15780 Zografos, Athens, Greece
[2]Department of Production Engineering & Management, Democritus University of Thrace,
University Library Building, 67100 Xanthi, Greece
[3]Environmental, Chemical & Metallurgical services (ECHMES) Ltd.
40-42 Mikras Asias st., Athens 11527, Greece*

## ABSTRACT

The geochemical behaviour of the sulphidic waste rock produced from the Stratoni mines, Greece, was investigated in the present study. An extensive laboratory testwork, including the execution of chemical-mineralogical analysis, static and kinetic tests on a bulk waste rock sample (-50mm) and its different particle size fractions was conducted. Based on the acid base accounting test results, the whole sample assaying 2.9% S had neutralisation potential ratio (NPR) of 5.5 and was classified as non-acid generating. The majority of the contained sulphur, i.e. 85%, was distributed in the -4mm waste rock size fraction, whereas all the different size fractions had significant neutralisation potential, i.e. 380-590kg $CaCO_3$/t, derived from the contained calcite and dolomite. Acid leaching of the bulk waste rock sample indicated that only 2.8% of the contained alkalinity was sufficiently reactive to neutralise the acidity introduced. The respective amount of the -4mm size fraction was higher, i.e. 6.4%, and may be attributed to the higher percentage of reactive fine particles and the more uniform distribution of water flow. Homogeneous mixing of the -4mm size fraction with ground limestone further increased the reactive alkalinity resulting in the effective neutralisation of acidity throughout the test period of 30 weeks. © 2005 SDU. All rights reserved.

Keywords: Waste rock; Sulphides; Acid drainage; Limestone; Rehabilitation

## 1. INTRODUCTION

One of the most challenging aspects in the environmental management of mine wastes is the prediction and control of acid drainage generation from sulphidic waste rock. Waste rock produced from ore exploitation, as opposed to tailings produced from ore processing operations, is a heterogeneous material usually characterised by a wide grain size distribution (boulders to silt and clay particles), variable chemical composition depending on its origin and complex hydrology.

Traditionally, acid-base accounting (ABA) has been used as a tool for assessing the acid generation potential of sulphide wastes. ABA is based on reaction (1) that describes pyrite oxidation and subsequent neutralisation by calcite.

$$FeS_2(s) + 2CaCO_3(s) + 3.75O_2(g) + 1.5H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2(g) \qquad (1)$$
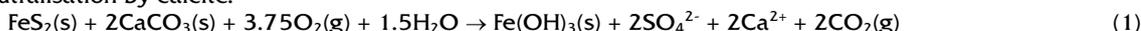
In ABA, acid generation potential (AP) is determined based on the sulphur content of material and the neutralisation potential (NP) is determined by back titration (Sobek *et al.*, 1978). The test results are expressed in terms of equivalent parts of $CaCO_3$ per 1000 parts of mine waste. Based on the ABA screening criteria recommended by the British Columbia Ministry of Employment and Investment of Canada, sulphide wastes with neutralisation potential ratio (NPR=NP:AP) <1 are classified as likely acid generating, whereas samples with NPR>4 are non acid generating.

The acid drainage potential of materials with 1<NPR<4 is considered uncertain and kinetic testwork should be conducted (Price *et al.*, 1997). Based on ABA test results, the amount of alkaline addition required to control acid generation from sulphide wastes can be also determined (Komnitsas *et al.*, 2000).

* Corresponding author. E-mail: mmmpem@central.ntua.gr

The balance between acid generating and acid consuming material is not, however, the sole parameter controlling the drainage quality of sulphide wastes and dictating the effectiveness of any alkaline addition. Other factors such as the homogeneous distribution of sulphides and carbonates, their particle size and reactivity and the formation of secondary minerals around the pyrite and limestone grains are parameters known to affect the kinetics of both the acid generating and alkalinity producing reactions (Mehling *et al.*, 1997; Scharer *et al.*, 2000). For waste rock piles, preferential flow has also a dominant influence on the drainage quality (Eriksson *et al.*, 1997; Morin and Hutt, 2000).

Data provided by Price and Kwong (1997) illustrated that ABA test performed on the whole waste rock sample may overestimate the physically available neutralisation potential. This was attributed to the reduced reactivity of coarse particles and the importance of separate analysis for the fine particle size fraction was demonstrated. Based on the study of Stromberg and Banwart (1999), it was deduced that there is a large difference in weathering rates between the fine waste rock and larger particles (>0.25mm). The -0.25mm waste rock size fraction, representing 27% of total mass contributed to approximately 80% of the sulphide and silicate dissolution. Furthermore, calcite within particles larger than 5-10mm reacted too slowly to neutralise the acid produced from sulphides. Scharer *et al.* (2000), who evaluated the neutralisation potential of various limestone particle size fractions, reported that 20% or less of the NP of the 6.4mm size fraction was exhausted at the onset of acidic conditions. Kinetic data on the depletion rate of the neutralising minerals and geochemical modelling suggested that waste rock with NPR as high as 5.0 may turn acidic in the long term. Miller *et al.* (2003) studied the effectiveness of limestone covers and blends in controlling acid rock drainage from potentially acid forming overburden at the Grasberg mine, Indonesia. Based on the results, it was deduced that it is necessary to ensure that all size fractions within the blend receive adequate alkalinity to buffer the potential acidity. Due to the fact that the sulphur content increased whereas the acid neutralising capacity decreased with decreasing particle size, the required amount of limestone greatly exceeded the stoichiometric requirement. Similar results were obtained from the geochemical investigation of waste rock dumps at the Ok Tedi mine, Papua New Guinea (Rumble *et al.*, 2003). The acid generation potential of the finer material (-2mm) was significantly higher than that of the coarser material. To minimise the risk of acid generation within the dumps, a sufficient amount of limestone should be added to ensure that neutralisation potential of all size fractions is in excess of acid potential.

Channelling is also an important parameter for the water flow in the waste rock piles. It has been reported that infiltration through waste rock contacts as little as 5-20% of the rock surfaces (Morin and Hutt, 2000). Due to preferential flow, waste rock drainage quality depends on the flow path length within acid neutralising rock separating zones of acid generating rock. The authors' analysis indicated that waste rock with a bulk NPR value of 300 could still release acidic drainage.

In the present study, the geochemical behaviour of sulphidic waste rock produced from Stratoni mines, Greece was investigated in laboratory scale. Based on previous studies (Gaidajis *et al.*, 2004), grab samples collected from the waste rock piles were classified from potentially acid generating to non acid generating. Furthermore, it was found that the major portion of sulphur contained in the waste rock is encountered in the finer grains. Sulphide oxidation and subsequent generation of acidic waters, i.e. pH: 3.0 contaminated with Fe, Zn, Pb, As, Cd and Mn was observed at the waste rock sites.

Based on the above, the objective of the present study was to investigate the geochemical characteristics of the different waste rock size fractions as compared with the whole material and assess the feasibility of separating the sulphide rich size fraction and its homogeneous mixing with limestone in order to inhibit acid generation.


## 2. MATERIALS AND METHODS

The waste rock sample used in the study was collected from the Karakoli stockpile at Stratoni mines, Greece. For practical reasons, particles larger than 50mm were removed and the rest of the sample, representing 80% of the total sample mass, was used in the laboratory testing.

For the characterization of the different waste rock size fractions, a representative split of the sample collected was sieved using 25, 9.5, 7.0, 4.0, 1.0, 0.5, 0.25, 0.125 and 0.063mm screens. The weight of each size fraction was recorded in order to determine the particle size distribution of the sample. Each sub size fraction was then analysed for As, Ca, Cd, Cu, Fe,mg, Mn, Pb and Zn, $S_{total}$ and $S(SO_4)$. Chemical analysis was performed by Atomic Absorption Spectrometry (AAS, Perkin Elmer 2100) following acid digestion with aqua regia ($HNO_3/HCl$). Sulphur measurements were carried out using a LECO analyzer; Sulphates concentration was determined gravimetrically. The neutralisation potential of each size fraction was determined by the standard Sobek method (Sobek *et al.*, 1978; Adam *et al.*, 1997). Mineralogical analysis by X-ray diffraction (XRD) and optical microscopy on thin and polished sections was also conducted on the bulk and selected size fraction samples.

Based on the results of chemical-mineralogical analysis and acid base accounting tests, kinetic humidity cell tests (MEND, 1991) were then conducted on the bulk -50mm waste rock sample (WR) and the fine -4mm size fraction (FWR). Furthermore, two humidity cells, involving the homogeneous mixing of the -4mm size material with limestone in amounts 16% and 28% wt. were set up (FWR16L and FWR28L respectively). Quarry quality limestone, consisting of calcite and dolomite (11%) was used in the tests. The limestone material had particle size finer than 1mm with 25% wt. being finer than 0.074mm.

The humidity cells used in the kinetic tests were constructed of plexi-glass. Cells of 2L capacity being 10.4cm in diameter and 30.3cm in height were used for the testing of the -4mm size fractions. The cells were loaded with approximately 2kg of sample. A larger cell design was necessary in order to accommodate the larger particle sizes of the bulk waste rock sample. A 30L capacity cell loaded with 35.7kg of material, with 30cm in diameter and 49cm in height internal dimensions, was constructed (Figure 1).

The operation of the humidity cells involved weekly cycles, comprised of three days of dry air (less than 10% humidity) and three days of water-saturated air (relative humidity > 90%) pumped up through the sample, followed by a leach with deionised water (weeks 0-5) or standard 0.1N $H_2SO_4$ solution on the seventh day. Leaching of the samples with sulphuric acid solution rather than deionised water aimed at accelerating the oxidation-neutralisation reactions and assess the geochemical behaviour of waste rock under acidic conditions. A 400ml volume of leachant was introduced in the cells FWR, FWR16L and FWR28L, involving the fine -4mm size fractions. The corresponding volume for the bulk waste rock sample (cell WR) amounted to 7L.

Immediately after collection of the leachate, parameters including leachate volume/weight, pH, oxidation-reduction potential, conductivity and acidity/alkalinity were measured. Then, solutions were analysed for both major and trace elements contained in the waste rock, i.e. As, Ca, Cd, Fe,mg, Mn, Pb, Zn and $SO_4$.
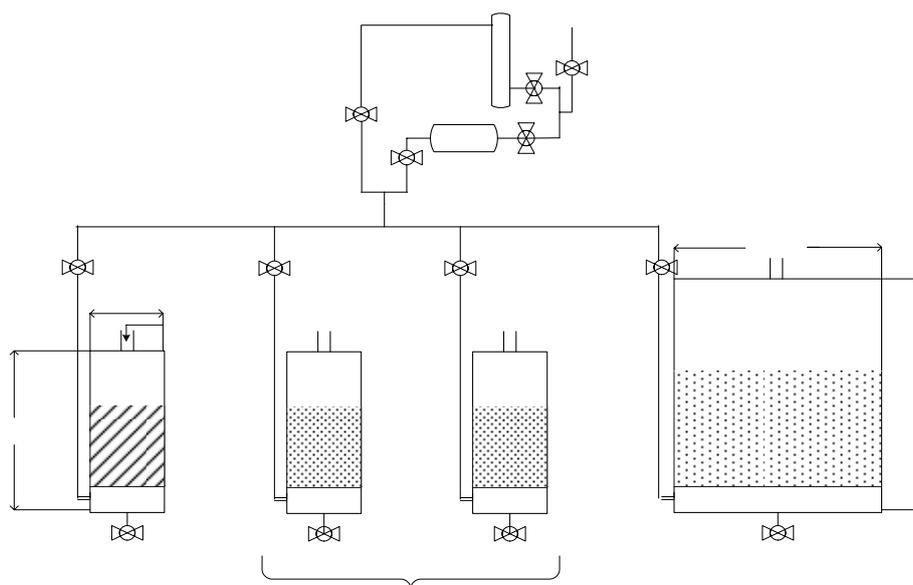


Figure 1. Experimental set up

The humidity cell tests were run for a total period of 35 weeks. After the completion of the tests, the solid residues were subjected to chemical analysis and acid base accounting tests.

## 3. RESULTS AND DISCUSSION

### 3.1. Geochemical characteristics of waste rock size fractions

The particle size distribution of the waste rock sample tested is shown in Figure 2.

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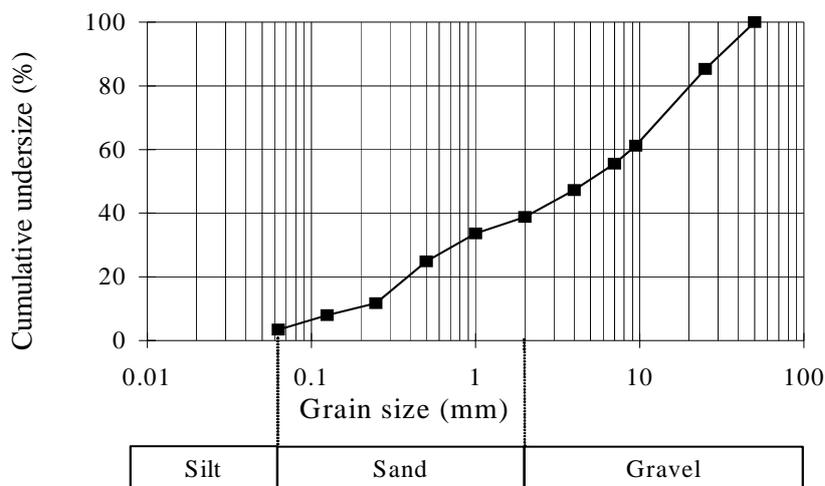
Figure 2. Particle size distribution of Stratoni waste rock sample

It was found that the major percentage of the material, i.e. 61% had a particle size in the range of gravel (2-50mm), whereas the fines (-0.074mm) content of the material was 4%.

The chemical analysis of the different waste rock size fractions is given in Table 1.

Table 1
Chemical assays of the different waste rock size fractions (analyses %)

| Size fraction (mm) | As | Ca | Cd | Cu | Fe | Mg | Mn | Pb | $S_{total}$ | $S(SO_4)$ | Zn | Insoluble |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| -50+25 | <0.02 | 18.24 | 0.004 | 0.05 | 1.72 | 2.17 | 0.12 | 0.24 | <0.1 | 0.00 | 0.73 | 38.84 |
| -25+10 | <0.02 | 18.06 | 0.002 | <0.01 | 1.00 | 3.04 | 0.16 | 0.05 | 0.56 | 0.00 | 0.08 | 36.72 |
| -10+6.0 | 0.06 | 15.84 | 0.009 | 0.01 | 2.52 | 2.30 | 0.34 | 0.99 | 1.75 | 0.06 | 1.40 | 32.36 |
| -6.0+4.0 | 0.19 | 12.63 | 0.008 | 0.02 | 4.22 | 2.27 | 0.47 | 0.21 | 2.80 | 0.10 | 1.31 | 40.00 |
| -4.0+2.0 | 0.21 | 13.95 | 0.006 | 0.02 | 3.70 | 2.41 | 0.42 | 1.42 | 4.00 | 0.17 | 1.00 | 38.70 |
| -2.0+1.0 | 0.20 | 13.96 | 0.010 | 0.03 | 5.58 | 2.27 | 0.37 | 1.52 | 5.34 | 0.31 | 1.76 | 38.38 |
| -1.0+0.5 | 0.19 | 12.14 | 0.010 | 0.03 | 6.15 | 1.53 | 0.34 | 2.54 | 6.93 | 0.31 | 1.91 | 36.04 |
| -0.5+0.25 | 0.18 | 14.61 | 0.009 | 0.04 | 5.06 | 1.43 | 0.36 | 1.79 | 5.47 | 0.47 | 1.54 | 31.02 |
| -0.25+0.125 | 0.26 | 17.06 | 0.009 | 0.05 | 5.76 | 1.34 | 0.40 | 1.86 | 5.60 | 0.17 | 1.85 | 26.88 |
| -0.125+0.063 | 0.33 | 15.92 | 0.008 | 0.04 | 5.75 | 1.47 | 0.40 | 1.64 | 6.01 | 0.69 | 1.49 | 28.60 |
| -0.063 | 0.30 | 14.25 | 0.008 | 0.05 | 5.05 | 1.55 | 0.38 | 1.73 | 5.30 | 1.41 | 1.47 | 29.06 |
| Total | 0.13 | 15.72 | 0.006 | 0.02 | 3.44 | 2.18 | 0.29 | 0.98 | 3.07 | 0.22 | 1.05 | 35.49 |

The results indicated that all the waste rock size fractions contained a significant amount of Ca, ranging from 12 to 18%, whereas the concentrations of sulphur and metals such as Fe, Pb and Zn were increasing with decreasing particle size. A similar trend in the $S(SO_4)$ content was observed; 27% of total sulphur content of the finer <0.063mm size material was in the sulphate form indicating the presence of past oxidation products.

Based on the mineralogical analysis of the bulk waste rock sample and the fine -4mm size fraction, pyrite ($FeS_2$), galena (PbS), sphalerite (ZnS) and chalcopyrite ($CuFeS_2$) were the major sulphide minerals identified. The samples contained a significant amount of carbonates, including calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Feldspars (orthoclase ($K(Al,Fe)Si_2O_8$), albite ($(Na,Ca)Al(Si, Al)_3O_8)$), muscovite ($H_2KAl_3Si_3O_{12}$), clinochlore ($(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$), actinolite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$ and quartz ($SiO_2$) were also detected. Furthermore, mineralogical analysis revealed the presence of gypsum ($CaSO_4.2H_2O$), limonite ($FeO(OH).nH_2O$) and anglesite ($PbSO_4$), common secondary products of sulphides oxidation and subsequent carbonates dissolution-neutralisation reactions.

Based on the acid base accounting test results, the acid potential (AP), neutralisation potential (NP) and neutralisation potential ratio (NPR) of the different waste rock size fractions is shown in Figure 3.
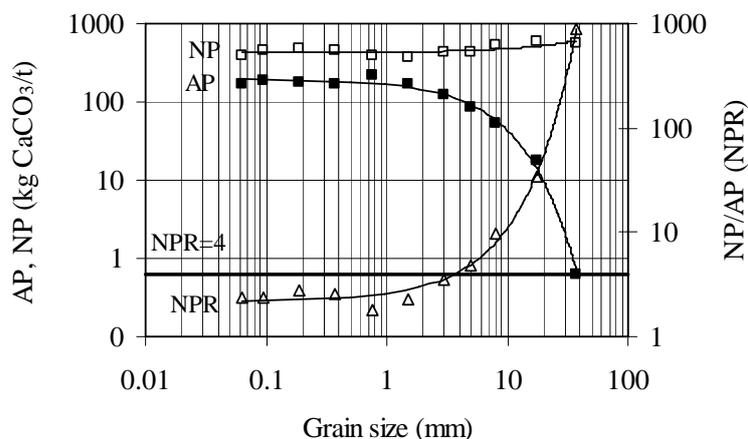
Figure 3. AP, NP and NPR vs. particle size of the waste rock material

Acid potential of the coarser waste rock size fraction, i.e. +4mm, was significantly decreased as compared to the finer material. On the contrary, all the size fractions exhibited a significant neutralisation potential ranging from 380 to 600kg $CaCO_3$/t. Based on the chemical-mineralogical analysis of the waste rock samples, their neutralising capacity was mainly attributed to the contained calcite and dolomite. Given that, NP values were also calculated from Ca and Mg content of the samples (Hutt and Morin, 2000), using Eq. (2). The results are compared with NP values measured by the ABA test in Figure 4.

$$NP_{(Ca+Mg)} \ (kg \ CaCO_3 /t) = \left( \frac{X_{Ca}}{40.08} + \frac{X_{Mg}}{24.31} \right) \times 100.09 \times 10 \qquad (2)$$

where $X_{Ca}$ and $X_{Mg}$ is Ca and Mg content of the sample respectively in wt. %, 40.08 and 24.31 is the atomic weight of Ca and Mg, respectively and 100.09 is the molecular weight of $CaCO_3$.
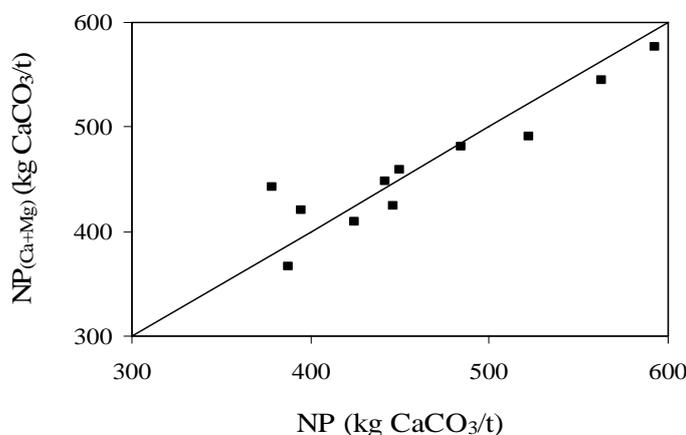


Figure 4. Calculated $NP_{(Ca+Mg)}$ vs. measured NP of the different waste rock size fractions

It was seen that the calculated values of NP were within ±10% of the NP measurements, indicating that the neutralising capacity of the samples was predominantly derived from the contained carbonate minerals and the Ca and Mg content of the samples was mainly originated from calcite and dolomite. Other minerals including actinolite and chlorite contained in the waste rock samples have been reported to be moderately reactive, also contributing to NP (Price and Kwong, 1997).

The NPR values ranged from 1.9 (-0.5+0.25mm) to 900 for the coarser -50+25mm waste rock size fraction. The coarser than 4mm material exhibited NPR > 4 and was classified as non acid generating based on the conservative screening criteria developed in British Columbia (Price *et al.*, 1997). The finer size fractions, having NPR: 1.9-3.7 had low potential for acid drainage. Considering that the contained alkalinity is derived from fast dissolving carbonates, the material would not be expected to produce any acidity.

### 3.2. Kinetic tests

To obtain further information on the geochemical behaviour of waste rock, particularly regarding the effectiveness of the contained alkaline minerals in neutralising acidity and drainage chemistry, kinetic humidity cell tests were conducted on the whole sample and the fine -4mm size fraction. Based on the chemical analysis, it was deduced that separation of the sulphide rich -4mm size fraction would result in the segregation of the 85% of S, 88% of Pb, 70% of Zn and 85% of As contained in the sample. Kinetic tests were also conducted on homogeneous mixtures of the fine -4mm size fraction with limestone. The alkaline material was added to the waste rock at amounts of 16% wt. and 28% wt. increasing thus the NPR value to 3.5 and 4.6 respectively (Table 2).

Table 2
Acid base accounting parameters of the humidity cells

| Code | Cell | $S_{sulphide}$ (%) | AP | NP | NNP | NPR |
|------|------|--------------------|-----|-----|-----|-----|
| | | | (kg CaCO₃/ t) | | | |
| WR | Waste rock (-50mm) | 2.85 | 89.02 | 492.11 | 403.11 | 5.53 |
| FWR | Waste rock (-4mm) | 5.79 | 180.94 | 451.44 | 270.50 | 2.50 |
| FWR16L | Waste rock (-4mm) mixed with 16% wt. limestone | 4.81 | 150.31 | 518.01 | 367.69 | 3.45 |
| FWR28L | Waste rock (-4mm) mixed with 28% wt. limestone | 4.13 | 129.06 | 593.72 | 464.65 | 4.60 |

### 3.2.1. Waste rock samples

pH and conductivity of the leachates produced from the whole -50mm size waste rock (WR) and the fine -4mm size fraction (FWR) vs. time is shown in Figure 5 (a) and (b) respectively.



(a)                                        (b)
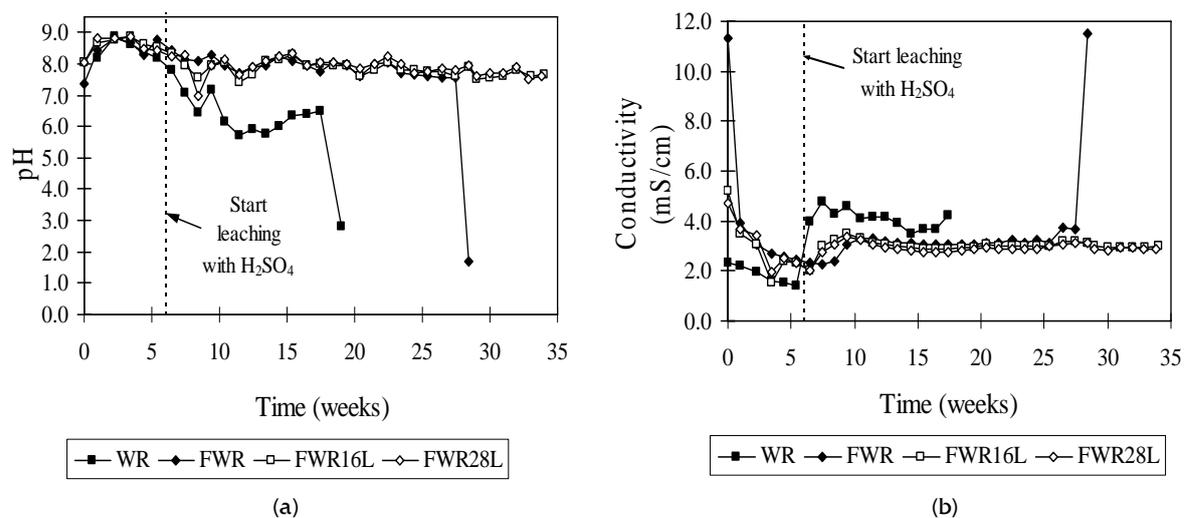
Figure 5. Variation of (a) pH and (b) conductivity vs. time in the leachates of waste rock and limestone amended humidity cells

The temporal variation of dissolved Zn, Mn, Ca and Mg concentrations in the leachates produced from the waste rock samples is shown in Figure 6 (a)-(d).
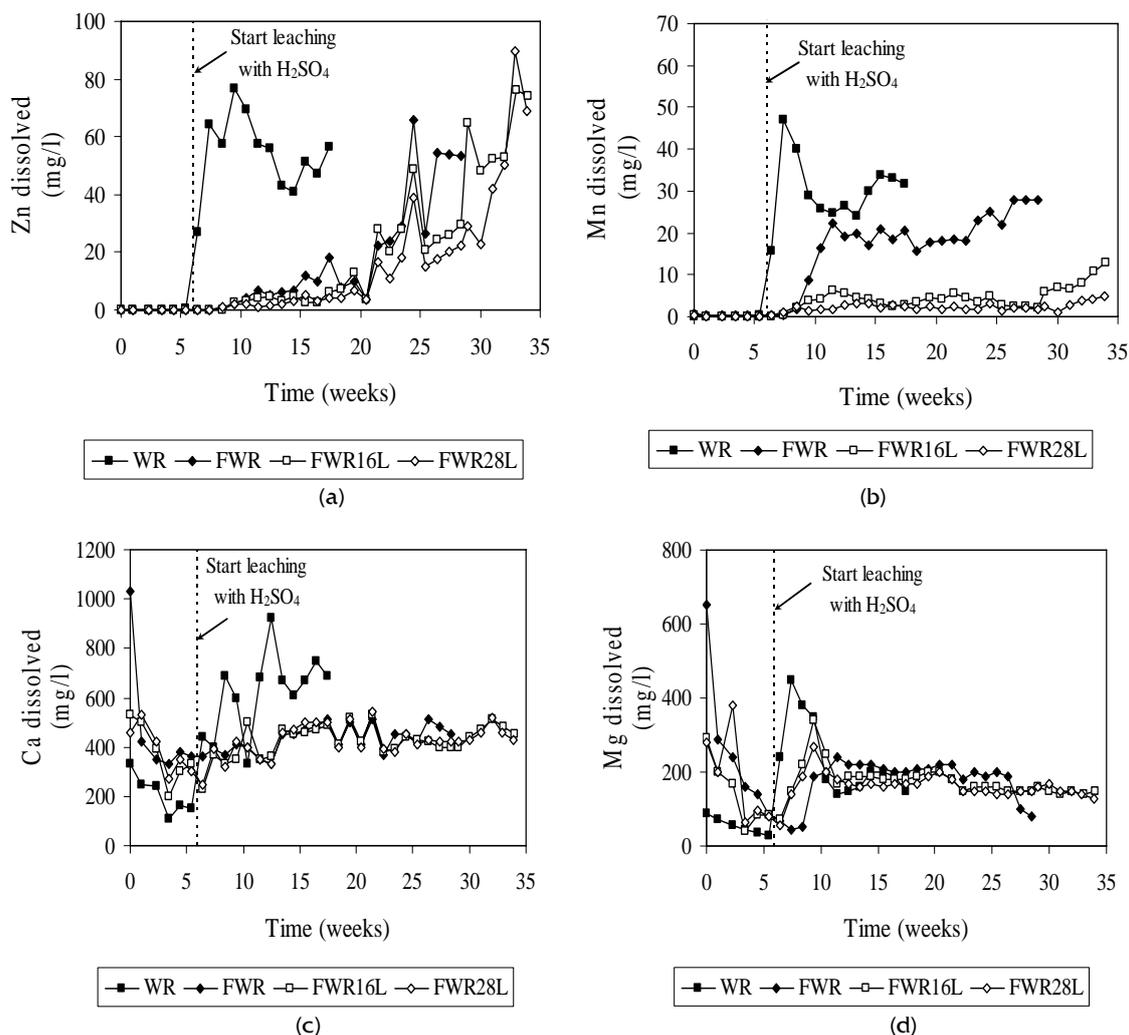
Figure 6. Variation of (a) Zn, (b) Mn, (c) Ca and (d)mg dissolved concentrations in the leachates of waste rock humidity cells

During the initial cycles (weeks 0-5), involving addition of de-ionised water in the samples tested, pH in the leachates of the cells WR and FWR was alkaline averaging, pH:$8.4\pm0.5$ and $8.5\pm0.3$ respectively. The concentration of dissolved Fe, Pb and As was below detection limit, i.e. <0.1, 0.5 and 1.0mg/l respectively and dissolved Zn and Mn levels were found below the limits for industrial effluents discharge, i.e. <2mg/l. Sulphate, Ca and Mg were the major ions in the solutions associated with the dissolution of pre-existing salts.

Leaching of the cells with sulphuric acid solution adversely affected the drainage quality of the waste rock samples tested. The effect was more intense for the whole -50mm waste rock sample, although it had a high neutralisation potential, NP: 492kg $CaCO_3$/t. The pH of WR cell leachates decreased from 8.4 to slightly acidic values, i.e. pH: 5.7-6.3 and after 13 cycles of acid leaching it dropped to pH: 2.8, Figure 5 (a). During acid leaching, the conductivity was also increased from 1.5mS/cm to $4.1\pm0.4$mS/cm and was associated with the increased dissolution of Zn, Mn, Ca,mg and $SO_4$.

Zinc and Mn exhibited similar dissolution patterns. An intense increase in the dissolved levels to Zn: 77mg/l and Mn: 47mg/l was observed after the initial cycles of acid leaching; thereafter dissolved concentrations gradually decreased to values Zn: 40-50mg/l and Mn: 25-30mg/l (Figure 6). Iron and Pb dissolved concentrations ranged from <0.2 to 19mg/l and <0.5 to 4mg/l respectively, whereas As level in solution remained below detection limit. Calcium and Mg concentrations in the leachates ranged from 330 to 920mg/l and 140 to 450mg/l respectively, while dissolved sulphate level ranged from 770 to

3,500mg/l. Geochemical modelling of the drainage, using MINTEQA2 (Allison *et al.,* 1990) predicted that saturation index (SI) values for gypsum were close to zero indicating that under the test conditions the solutions were near saturation with respect to this phase.

Under acid leaching conditions, the -4mm waste rock size fraction (cell FWR) produced alkaline leachates over a test period of 22 weeks. During this period, pH and conductivity of the cell leachates averaged 7.9±0.3 and 3.1±0.4mS/cm respectively (Figure 5). Iron, Pb and As concentrations in the solutions were undetected whereas Zn and Mn dissolution was increased to levels up to 66 and 30mg/l respectively. Dissolved Ca and $SO_4$ concentrations were in the range of 330-510mg/l and 1,680-2,800mg/l respectively and were mainly controlled by gypsum solubility. Magnesium concentration ranged from 47 to 240mg/l (Figure 6). After 22 cycles of acid leaching the drainage produced from FWR cell had acidic pH: 1.7, indicating that the alkalinity contained in the waste rock sample was no longer effective in neutralising the acidity introduced.

Based on above results, it was seen that although the whole -50mm waste rock sample and the fine -4mm size fraction had similar NP values, i.e. 492kg $CaCO_3$/t and 451kg $CaCO_3$/t respectively, they exhibited different values of available neutralisation capacity under the acid leaching conditions of the kinetic tests. More specifically, the total amount of acidity introduced in the bulk waste rock sample prior to the production of acidic pH, amounted to only 15.8kg $CaCO_3$/t, whereas the respective amount of the -4mm size fraction was estimated to 28.8kg $CaCO_3$/t. Furthermore, under acid leaching conditions, the fine waste rock size fraction produced leachates with higher pH and lower dissolved metals levels as compared with the bulk waste rock sample. Dissolved Fe levels generally remained below detection limit, suggesting that under the conditions encountered in WR and FWR cells, i.e. average drainage pH: 6.3 and pH: 7.9 respectively, the oxidation rate of pyrite was slow and precipitation of ferric iron in the form of hydroxide occurred. Lead dissolution was also minimal, that may be attributed to the low solubility of anglesite ($PbSO_4$), i.e. $logK_{sp}$=-7.79 (Allison *et al.,* 1990). On the other hand, increased leaching of Zn and Mn was observed. The cumulative amount of Zn and Mn dissolved in the drainage of WR and FWR cells, expressed in Mg of metal per kg of material, vs. time is shown in Figure 7 (a) and (b), respectively.
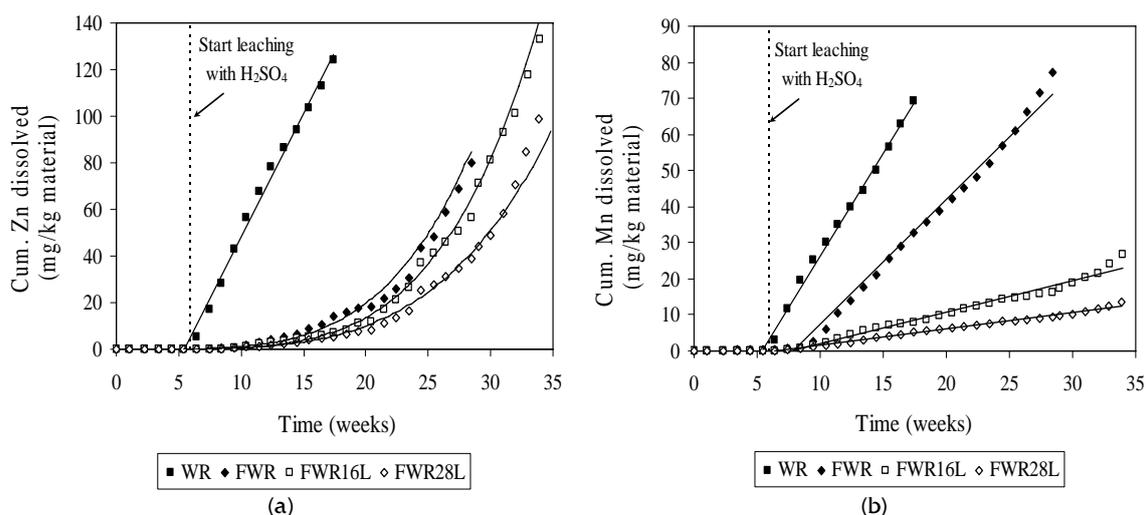


Figure 7. Cumulative amount of (a) Zn and (b) Mn dissolved in the leachates of the waste rock humidity cells

It can be inferred that the whole -50mm waste rock sample presented a different dissolution pattern of Zn as compared with the -4mm size fraction. The dissolution rate of Zn of the whole sample increased immediately after the start of acid leaching and remained roughly constant throughout the monitoring period, as indicated by the constant slope in Figure 7 (a). Under acid leaching conditions, Zn dissolution rate of the -50mm size sample was estimated to 10.8mg/kg per week. In contrast, Zn dissolution rate of the -4mm size fraction increased slightly until the 18th cycle of acid leaching; thereafter the rate increased from 2.2mg/kg per week to 9.8mg/kg per week, being close to the value estimated for the -50mm size sample. The dissolution rate of Mn of the -50mm waste rock sample was estimated to 6.0mg/kg per week. The respective value of the -4mm size fraction amounted to 4.0mg/kg per week, Figure 7 (b). Regarding sulphates dissolution, the cumulative amount of $SO_4$ dissolved in the drainage vs. the amount of $SO_4$ introduced in the waste rock cells is shown in Figure 8.
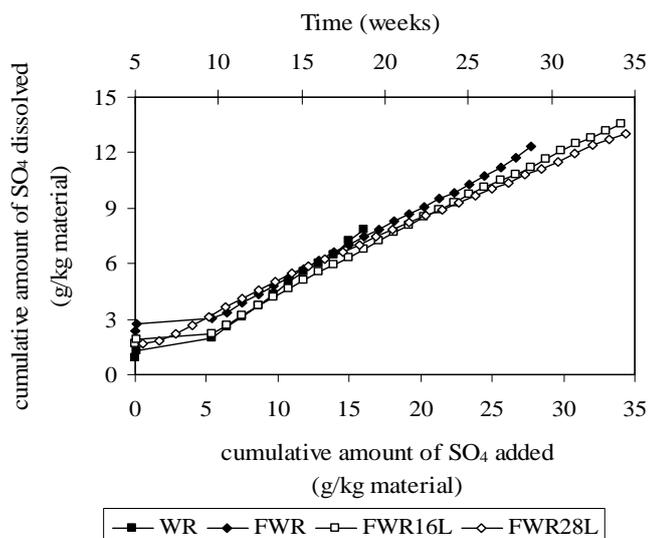
Figure 8. Cumulative amount of $SO_4$ dissolved vs. the cumulative amount of $SO_4$ introduced in the waste rock humidity cells

The dissolution rate of $SO_4$ of the -50mm and -4mm waste rock size fractions was estimated to 0.7g/kg per week and 0.4g/kg per week respectively as compared with the amount of 1g $SO_4$/kg per week introduced in the cells.

Regarding the consumption of calcite and dolomite contained in the waste rock samples, mass balance calculations indicated that under acid leaching conditions, a percentage of 2.8% of total alkalinity contained in the -50mm waste rock fraction was consumed to effectively neutralise the acidity introduced. The remaining alkaline potential of material could not balance the amount of acid added in the cell. The respective amount of the -4mm waste rock fraction was estimated to 6.4%.

The reduced effectiveness of waste rock samples in neutralising the acidity may be attributed to the reduced reactivity of limestone and dolomite grains due to their coarse size and/ or coating with gypsum and ferric hydroxides. Based on the particle size distribution of waste rock and the acid base accounting parameters of the different waste rock size fractions, it was drawn that the amount of neutralisation potential consumed during testing corresponded well with the NP contribution of the fine -0.063mm size fraction, as shown in Figure 9.
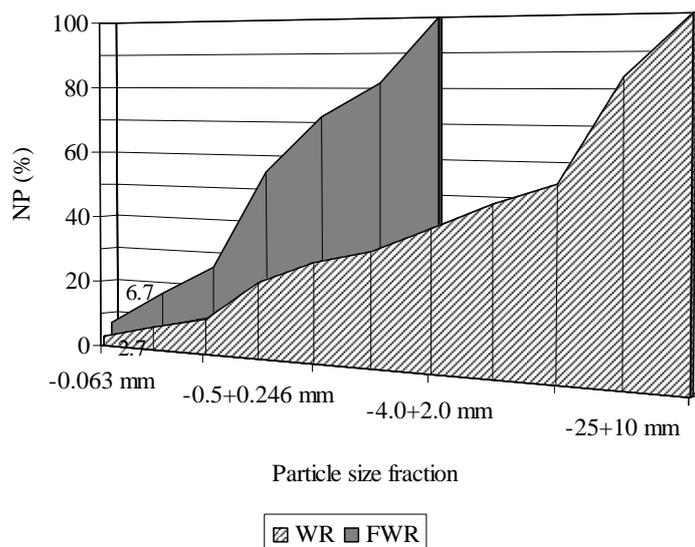


Figure 9. Contribution of the different size fractions to the NP value of the whole waste rock sample (WR) and the -4mm size fraction (FWR)

Physical parameters, such as the reduced hydraulic conductivity and the more spatially uniform distribution of water flow may have also contributed to the increased effectiveness of the fine -4mm waste rock size fraction as compared with the bulk waste rock sample in neutralizing the acidity introduced into the system and reducing metals dissolution.

### 3.2.2. Limestone amended cells

Under acid leaching conditions, the limestone amended cells produced leachates with alkaline pH, i.e. pH:7.8±0.2 (cell FWR16L) and pH: 7.9±0.3 (FWR28L), throughout the test period of 30 weeks, Figure 5 (a). The leachates produced had similar conductivity values, averaging 3.0±0.2mS/cm, as shown in Figure 5 (b).

The concentrations of dissolved Fe, Pb and As in the drainage of the amended cells were below detection limit, i.e. <0.1, 0.5 and 1.0mg/l respectively, throughout the test period. Dissolved $SO_4$ and Ca levels in the limestone amended cells during acid leaching averaged 2,100±200mg/l and 432±54mg/l respectively for FWR16L and 2,020±180mg/l and 435±57mg/l respectively for FWR28L. Sulphate and Ca yields were mainly controlled by gypsum solubility. Magnesium dissolved concentration in the drainage of FWR16L and FWR28L cells averaged 176±40mg/l and 166±27mg/l respectively.

The cumulative amount of Zn and Mn dissolved in the drainage of limestone amended cells vs. time as compared to the unamended waste rock samples is shown in Figure 7 (a) and (b) respectively. It was seen that limestone addition to the -4mm waste rock size fraction resulted in the significant reduction of Mn dissolution, i.e. 75-83%, whereas it was less effective in reducing Zn dissolution, i.e. 16-32%. The increased dissolution of Zn from sphalerite under acid leaching conditions is in agreement with previous studies (Gleisner and Herbert, 2002) indicating that metal mono-sulphides such as sphalerite, galena and chalcopyrite are degradable by proton attack. Furthermore, other studies have shown that galvanic interactions can lead to preferential leaching of Zn even under non acidic conditions (Kwong, 1995). Galvanic interactions occur when contacting sulphides are exposed to an oxygenated aqueous medium. Sphalerite and also galena have a considerably lower electrode potential than pyrite and thus oxidative dissolution of the former occurs at the anode, reaction (3) while the later is protected from oxidation at the cathode.

$$ZnS + 0.5O_2 + 2H^+ \rightarrow Zn^{2+} + S^0 + H_2O \tag{3}$$
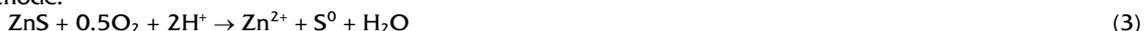
In the natural environment, the elemental sulphur produced in the galvanic reaction is subsequently converted to sulphate. Based on reaction (3), it is also seen that acidic conditions would facilitate the oxidative dissolution of the sulphide anode enhancing the release of Zn into solution.

Regarding Mn dissolution, MINTEQA2 simulation predicted that the saturation index values for rhodochrosite ($MnCO_3$) of the limestone cell leachates were above 0.1 suggesting that precipitation of this phase may be imposing an upper limit on dissolved Mn concentrations in the drainage.

The cumulative amount of $SO_4$ dissolved in the drainage of limestone amended cells represented 40% of the amount added as compared to 45% of the -4mm waste rock size fraction and to 52% of the bulk waste rock sample, indicating that the addition of limestone to waste rock enhanced the precipitation of sulphate, mainly in the form of gypsum.

The cumulative amount of the acidity introduced to the limestone amended samples during the kinetic testing corresponded to 35.5kg $CaCO_3$/t. Based on mass balance calculations, the alkalinity of FWR16L and FWR28L samples consumed was estimated to 37kg $CaCO_3$/t and 39kg $CaCO_3$/t respectively, representing 7.1% and 6.6% of total contained alkalinity. Assuming that the reactive alkalinity of limestone added to waste rock was encountered only in the fine -0.063mm size fraction, the available alkalinity of FWR16L and FWR28L samples was estimated to 61.8kg $CaCO_3$/t and 86.8kg $CaCO_3$/t respectively, being 115% and 200% higher as compared to the value obtained for the -4mm waste rock size fraction. The above results indicate that the amount of alkalinity contained in the fine material is an important parameter controlling the acid neutralisation reactions.

## 4. CONCLUSIONS

The bulk waste rock sample (-50mm size) examined had a sulphur content of 2.9% and a neutralisation potential ratio (NPR) of 5.5 and was classified as non-acid generating. Analysis of the different size fractions indicated that 85% of the contained sulphur was encountered in the -4mm size fraction, whereas all the different size fractions had significant neutralisation potential, i.e. 380-590kg $CaCO_3$/t.

Acid leaching of the -50mm size sample adversely affected the drainage quality. The kinetic test results indicated that only a portion of the contained alkalinity amounting to 2.8% was sufficiently reactive to neutralise the acidity introduced. Separation of the -4mm waste rock size fraction increased the available alkalinity to 6.4% resulting in the prolongation of acidity neutralisation and the reduction of metals dissolution, mainly Zn and Mn. This may be attributed to chemical parameters including the higher amount of reactive fine (-0.063mm) size material encountered in the -4mm waste rock size fraction as well as to

physical parameters such as the reduced hydraulic conductivity and the more uniform distribution of water flow in the -4mm size material.

Homogeneous mixing of the -4mm size fraction with ground limestone further increased the reactive alkalinity and resulted in the effective neutralisation of acidity throughout the acid leaching test period of 30 weeks. Furthermore, limestone addition to waste rock resulted in the significant reduction of Mn dissolution by 75-83%, whereas it was less effective in reducing Zn dissolution, i.e. 16-32%.

The alkalinity contained in the fine fractions is an important parameter controlling the acid neutralisation process in Stratoni waste rock. Although the bulk waste rock sample examined in the present study had a significant neutralisation potential of 492kg $CaCO_3$/t, its mixing with potentially acid generating waste rock would not be effective in inhibiting acid generation. Separation of the sulphide-rich fine fractions and subsequent mixing with ground limestone would increase the homogeneity of the mixture and would result in more uniform water flow, enhancing the effectiveness of the technique in controlling acid generation. To assess the performance of above mitigation technique under actual conditions, field trial tests were performed, and the results obtained after a monitoring period of three years were presented in Gaidajis *et al.* (2004).

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