EFFECTS OF NICKEL MINING ACTIVITIES ON WATER QUALITY[1]

C. Muzenda[2], and I. Pumure

Abstract. Acid Mine Drainage (AMD) originates from the sulphide mineral oxidation in the presence of water and oxygen, and to some extent bacteria, yielding sulphuric acid. The acid generated mobilizes some metals resulting in their increased bioavailabilities, creating a hazardous environment for aquatic animals and plants. The groundwater quality emanating from adjacent mine sites is a useful tool for measuring AMD. The purpose of this study was to determine extent of mine drainage from an active nickel mine and to develop mitigation. Major mining pollution sources were identified for constant monitoring. Recommendations for possible remediation and abatement of AMD were made. Several liquid samples were taken from selected sites along two streams, which flow out of the mining complex. Eight water samples were collected once a month from June to October. pH and conductivity were immediately measured followed by determination of Cu, Fe, Ni, sulphates, Total Suspended Solids (TSS) and Total Dissolved Solids (TDS).

Elevated concentrations of sulphate, high conductivity and TDS were observed indicating the presence of AMD. An increase in sulphate concentration, TDS and Conductivity levels for the Community Rivers was observed. This was caused by the water flowing from the nickel mine. The quality of the natural river water was grossly affected.

A passive treatment strategy would need to be developed. For the treatment process to succeed, a complete characterisation of the contaminated mine drainage is needed. Topsoiling and revegetation are other cheaper methods that can be used to reduce the extent of sulphide oxidation.

Additional Key Words: Acid Mine Drainage, oxidation of sulphides, pyrite, pyrhottite

Introduction

Acid mine drainage (AMD) is a major global environmental problem which affects the quality of both surface and ground waters. The influx of untreated acid mine drainage into streams can severely degrade both habitat and water quality often producing an environment devoid of most aquatic and unfit for desired uses (Kimmel, 1983). AMD is caused by oxidation and hydrolysis of metal sulphides in mine-dump ores resulting in the formation of several soluble hydrous iron sulphates, formation of acidity and the subsequent leaching of toxic heavy metals (Gray, 1998; Gray, 1996; Ridge and Seif 1998; Reddick and Todd, 1997).

High acidity, high salinity, turbidity, elevated concentrations of iron and sulphate and a variety of metals are an indicator of AMD (Gray, 1998; White and Jeffers, 1994). The lower the pH, the more severe the potential effects of mine drainage on aquatic life. High sulphate concentrations may have be harmful to the stomach and water an unpalatable taste.

Sulphate is produced during oxidation of iron sulphide minerals and an elevated concentration of sulphate is directly related to AMD production as indicated by the following reaction:

Iron sulphide + oxygen + water $\rightarrow$ Iron hydroxide + sulphuric acid + heat

AMD is characterized by high SO_4^{2-} concentration, high TDS, high conductivity and elevated Fe concentrations. The composition of mine drainage reflects not only its origin but also what it encounters along its flow path. Contaminated mine drainage waters usually find their way into communal rivers and when this results in severe water quality impacts affecting rivers and to some extent dams.

Prior to designing a passive treatment system, a complete characterisation of influent AMD is needed to determine which type of system is appropriate and how to design that system to meet treatment goals (Zipper and Jage, 2001).

Experimental

Sulphate analysis was done using the Turbidimetry method on a Spekol UV VIS at 420nm. A Shimadzu Atomic Absorption Spectrophotometer AA-6701/6601F was used to measure the concentration of Fe, Ni and Cu. The standard used was the SRM1646 estuarine sediment reference sample. Conductivity was measured using an Orion conductivity meter model 150 and pH was measured using an Orion pH meter model 420A immediately after collection of the samples.

Description of Mine Site

The nickel mine is an underground mine. At the mining complex there is a concentrator, a smelter and refinery plant. The nickel sulphide ore mainly a mixture of, pentlandite and millerite from underground is crushed and then separated from the waste by froth flotation at the concentrator plant. Waste rock from the underground mine is piled outside and the slimes tailings from the concentrator plant are conveyed in a pipe to the slimes tailings dam. The effluent from the froth flotation plant passes through a tank where ammonia is added to neutralize the acid. The waste rock from the underground is immediately wetted at the end of the conveyer belt to trap dust particles. A dam wall built in front of the waste rock mountain traps the runoff water from the fresh waste rock mountain. The nickel sulphide is transported to the smelter plant where it is roasted and smelted producing the nickel oxide and nickel matte respectively. The iron in the ore is oxidised during roasting and then it is converted to the silicate, which is removed as slag waste. The waste slag is piled up on a mountain 500m from the smelter plant. The final purification stage is by electrolysis at the refinery plant, which is, located 300m from the smelter plant.

Description of Samples and Sampling Sites

Eight water samples per month were collected from June to October from sampling sites indicated on the map shown in Figure 1.

The water sampling points are as follows:

W1:   is a surface water point at a bridge between the slimes tailings dam and the slag mountain along Stream A.

W2: is a surface water control point for Stream, A which is located 3km upstream of W1. Mining excavations have not affected this sampling site but it is within the mining complex.

W3: water sample taken from an active slimes tailings dam consisting of slimes of very fine particles from the concentrator, which are completely submerged under water.

W4: is a monitoring borehole behind the slimes tailings dam wall, which represents the quality of water which seeps off from the slimes tailings dam into the natural river system behind the dam wall.
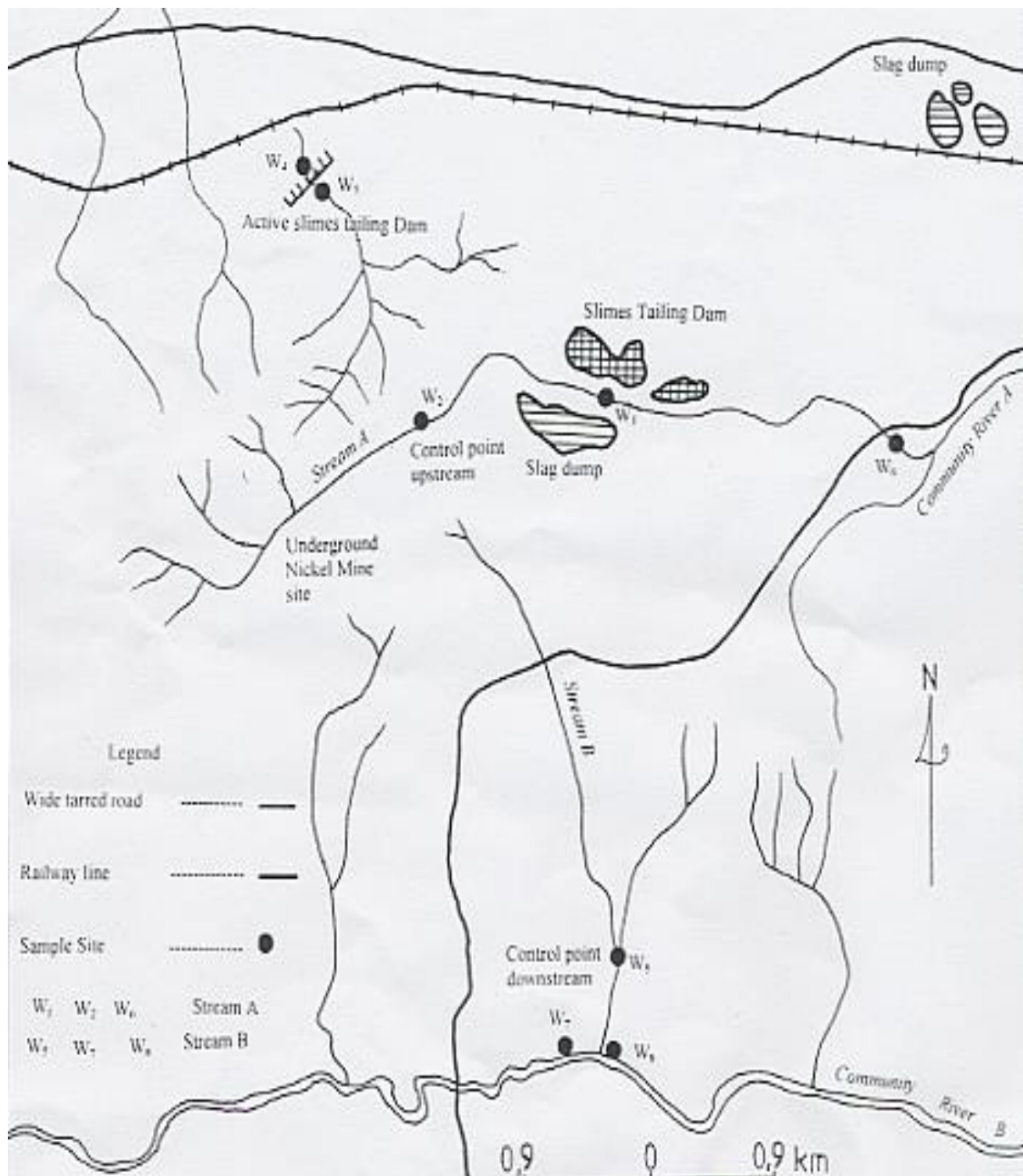
Figure 1: Facilities and monitoring points at the nickel mine.

W5: a point at a V Bridge, which traps particulate matter which occasionally spills from the waste rock and concentrator plant. The effluent flows into Community river B. The effluent from the concentrator and waste rock was later stopped from flowing through W5 in September and October by constructing a capturing dam. The V-bridge was kept flowing by the underground seepage from the constructed dam.

W6: a point 5km downstream of W1 along Stream A exiting the mine, which indicates the quality of water emanating from the nickel mining complex into the natural river system.

W7: is a surface water control point 300m upstream of Community River B representing the unaffected river water.

W8: is a surface water point 300m downstream after complete mixing of Stream B and Community river B in order to determine the impact of mining waters on the water quality.

Results and Discussion

All water samples were analysed for SO_4^{2-}, Conductivity, TDS and TSS, pH, Fe, Ni and Cu. The results are shown in the Tables and Figures below:

The sulphate concentrations measured in samples W1-W8 using the UV VIS are shown in Figure 2.

The SO_4^{2-} in W1 ranged from 991-1814mgL^{-1} while the background levels at W2 varied from 88.2-129mgL^{-1}.

Figure 3 shows TDS values for the samples ranging from 1390-2374mgL^{-1} in W1 while the background values range from 360-470mgL^{-1}.

Conductivity values in Figure. 4 are high in W1 and W6, which indicates some correlation with sulphate and TDS values in Figures 2 and 3.
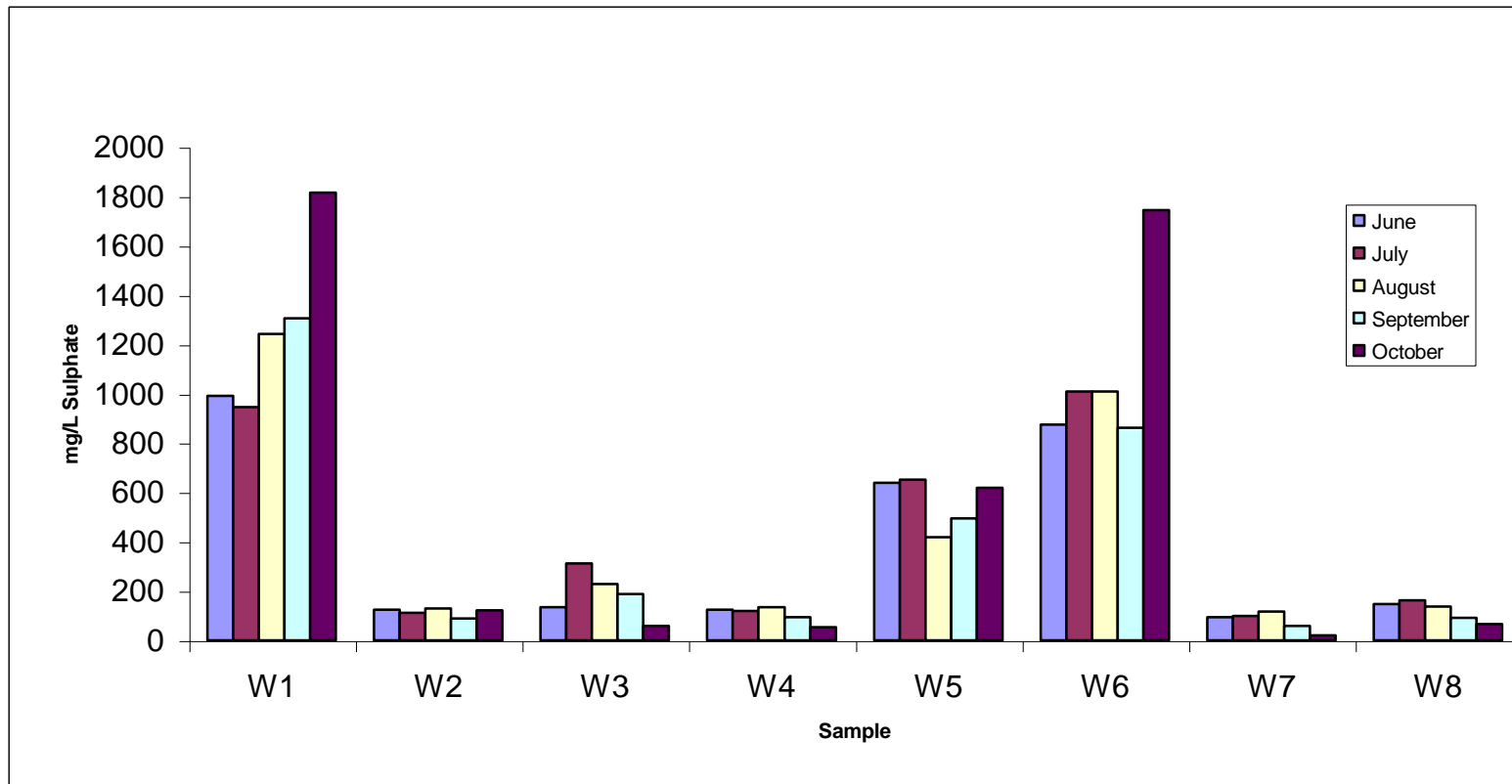
Figure 2. Variation of mg/L sulphate in water samples collected around the mining complex
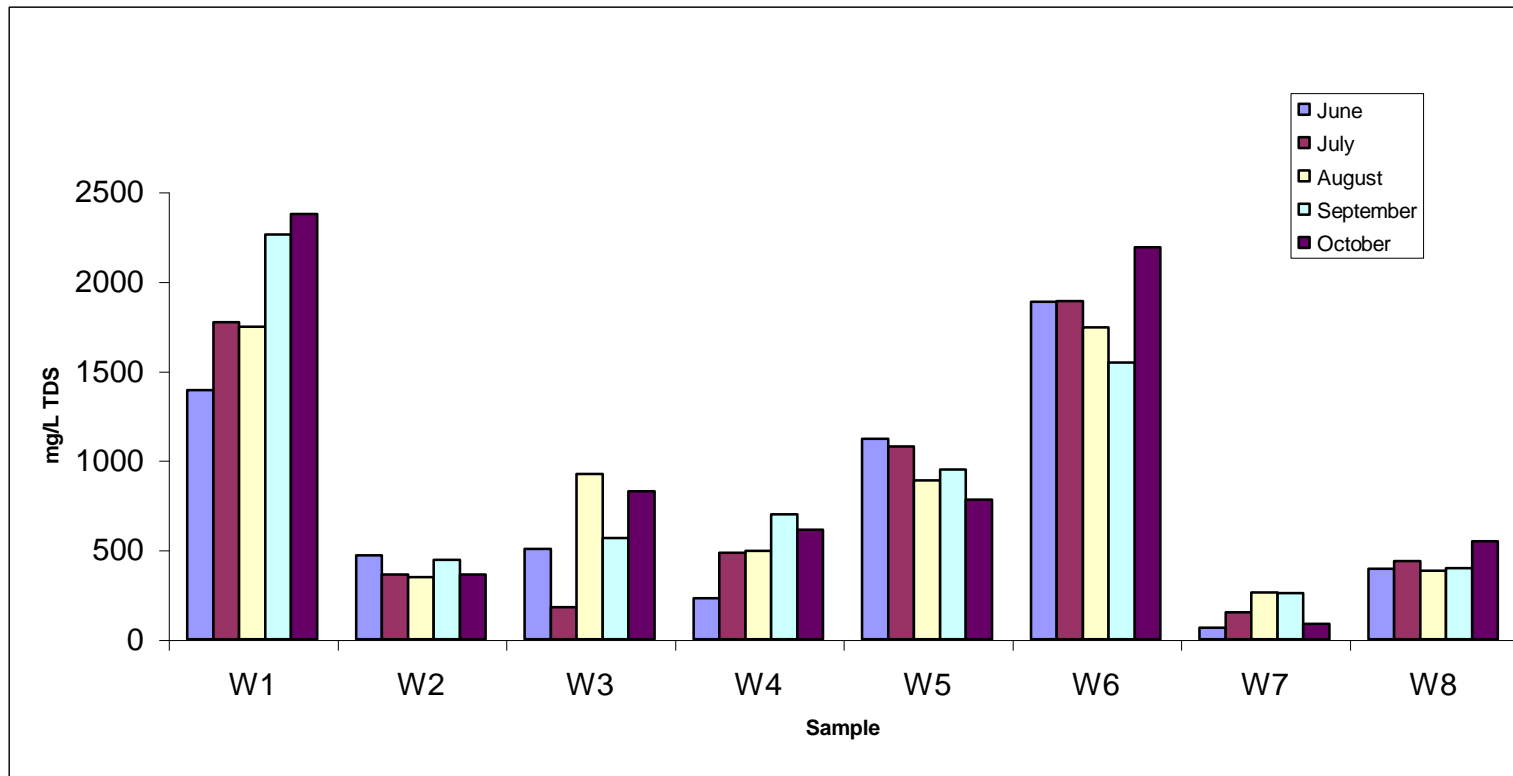
Figure 3. Variation of mg/L TDS in water samples collected around the nickel mining complex.
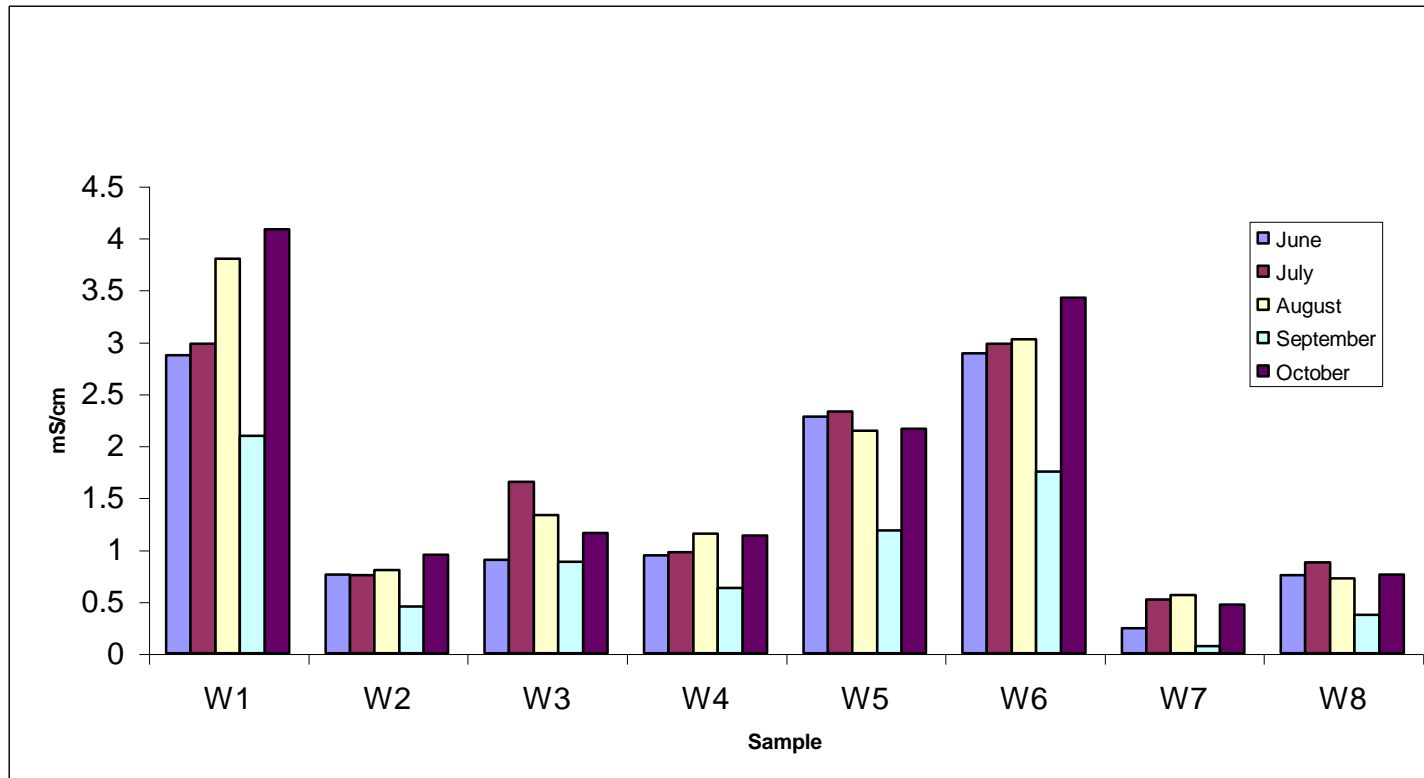
Figure 4: Variation of conductivity (mScm^{-1}) in water samples collected around the nickel mining complex

The pH values for the samples collected at points W1-W8 are shown in Table 1 below.

Table 1: Variation of pH in water samples collected around the nickel mine

	June	July	August	September	October
W1	7.1	6.2	7.4	7.5	7.2
W2	6.4	6.1	6.9	7.5	7.1
W3	7.9	6.0	6.8	6.9	6.8
W4	6.8	5.7	7.0	7.1	7.0
W5	7.0	8.0	7.4	5.9	6.5
W6	7.7	8.2	8.1	8.0	7.9
W7	7.4	7.0	7.9	7.3	7.6
W8	7.5	8.3	7.9	7.9	8.0

It appears that the mine waters are currently being neutralized not only by the naturally occurring carbonate rocks but also likely by the aqueous ammonia, which is added to the effluent from the concentrator plant before it is recycled or discharged.

The Fe concentration increased steadily from June to October due to concentration effects as the dry season progressed as shown in Figure 5 below. The background concentration W2 and W7 also showed the same trend. Iron concentrations observed were lower than expected due to the neutralization of AMD resulting in some of the iron precipitation as $Fe(OH)_3$.

Maximum Ni concentrations were recorded in June and July in W5 due to a sudden increase in effluent flow, which resulted from accidental pipe bursts, which occurred in June as shown in Figure 6. Nickel is also relatively high in background W2 which is an indication of the presence some nickel containing rocks in the riverbed. This sampling site is near the nickel mountain from which underground excavations take place.

Figure 7 shows almost constant Cu concentrations from June to October varying from 0.015-0.037mgL^{-1} while background levels ranged from 0.014-0.027mgL^{-1}.

High TSS values were recorded in June and July at W5 and W8 as shown in Figure 8. This is attributable to the pipe bursts mentioned earlier. The values ranged from 20-494mgL^{-1} in W5 and 14-256mgL^{-1} in W8.
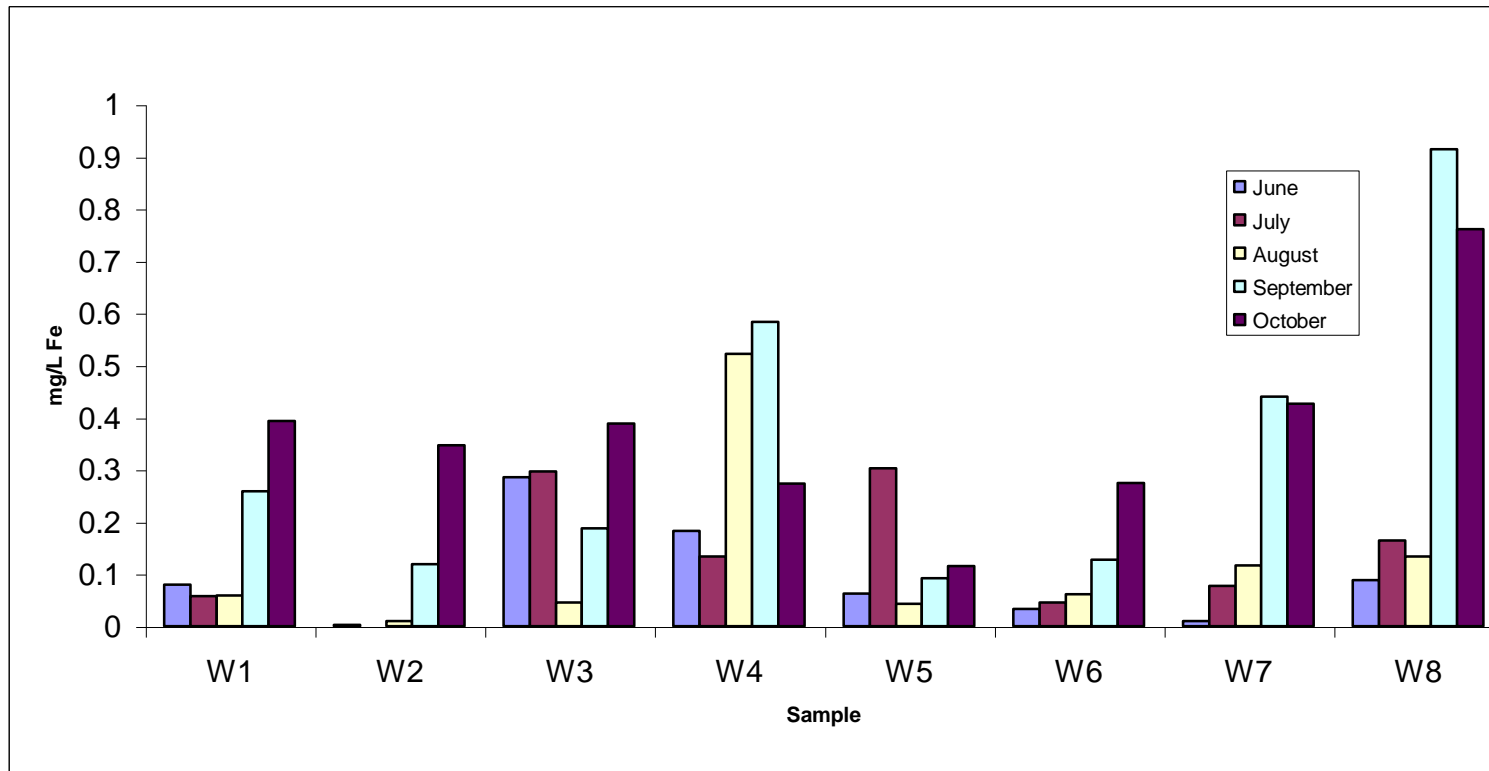
Figure 5: Variation of mg/L Fe in water samples collected around the nickel mining complex.
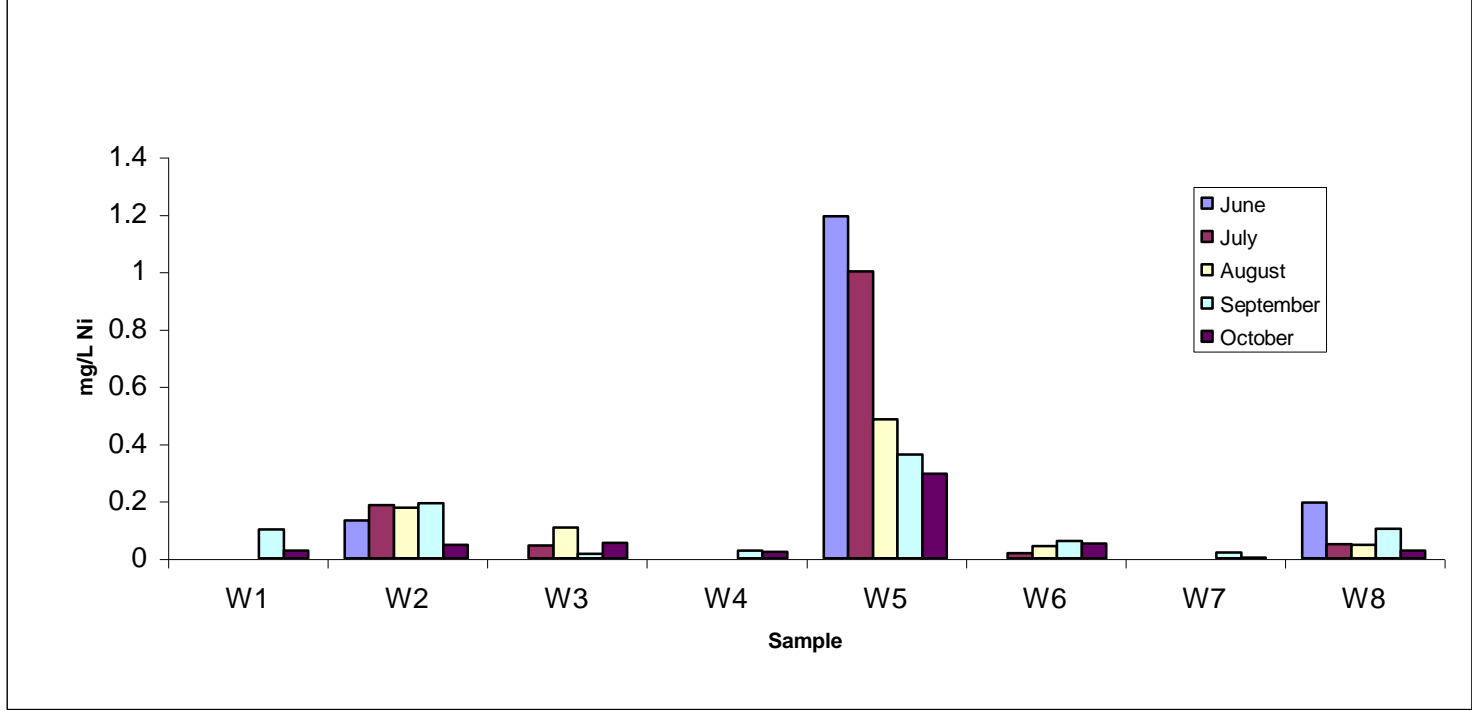
Figure 6: Variation of mg/L Ni in water samples collected around the nickel mining complex.
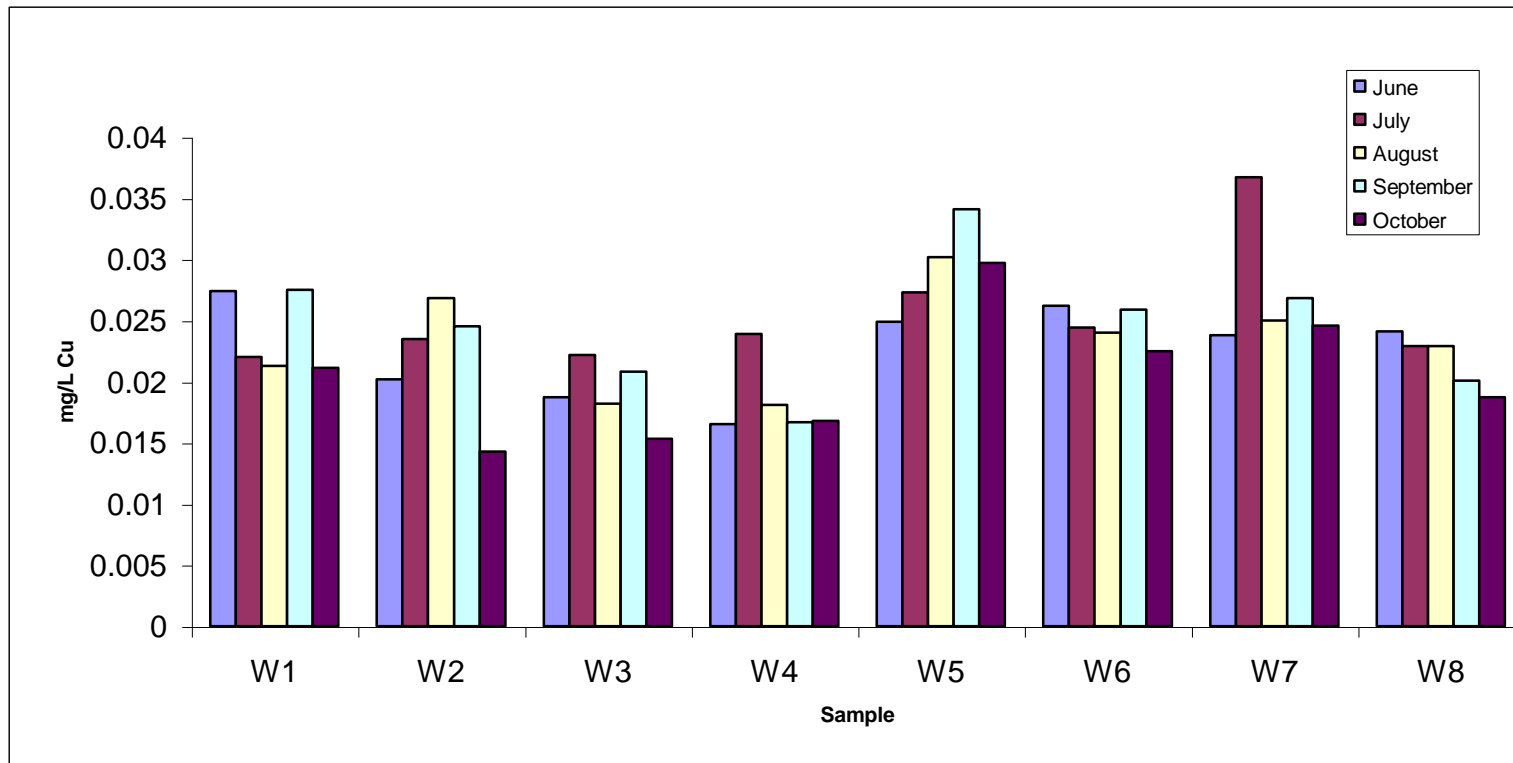
Figure 7: Variation of mg/L Cu in water samples collected around the nickel mining complex.
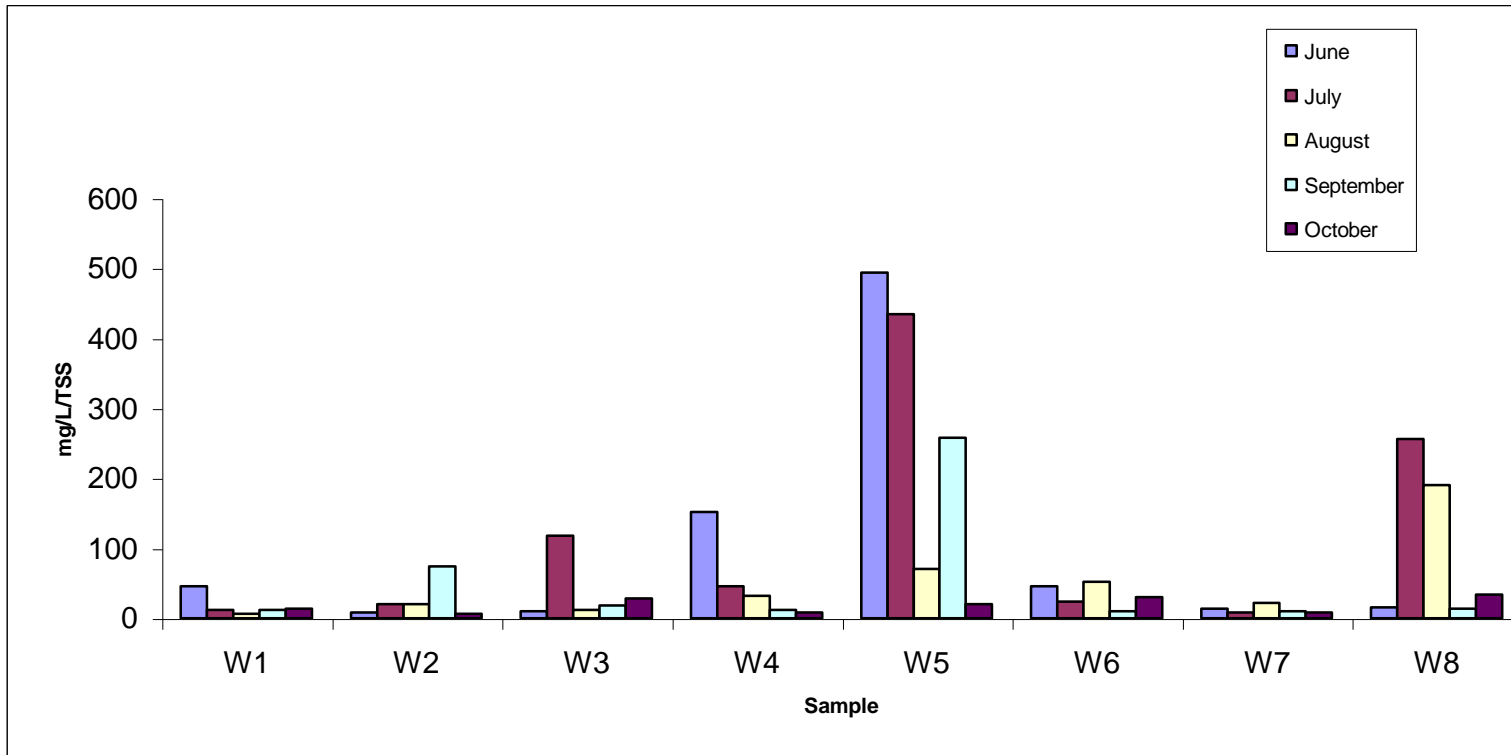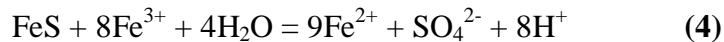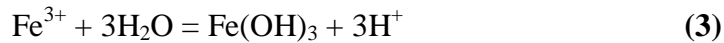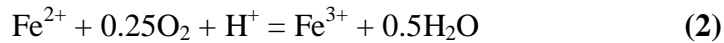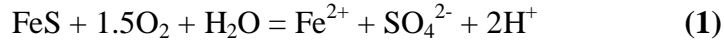
Figure 8: Variation of mg/L TSS in water samples collected around the nickel mining complex.

Mineralogical examinations on ore samples collected indicated the presence of pyrrhotite, pentlandite, chalcopyrite, pyrite and millerite in their decreasing order of abundance.

Pyrrhotite, one of the major sulphides found at the nickel mine, easily oxidizes and therefore is highly associated with AMD according to the following reaction mechanism:

$$FeS + 1.5O_2 + H_2O = Fe^{2+} + SO_4^{2-} + 2H^+ \qquad \textbf{(1)}$$

$$Fe^{2+} + 0.25O_2 + H^+ = Fe^{3+} + 0.5H_2O \qquad \textbf{(2)}$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \qquad \textbf{(3)}$$

$$FeS + 8Fe^{3+} + 4H_2O = 9Fe^{2+} + SO_4^{2-} + 8H^+ \qquad \textbf{(4)}$$

In reaction (4) above, Fe^{3+} generated from reaction (2) is used as the oxidizing agent for pyrrhotite and water resulting in acidity and elevation of sulphate concentration.

In Figures 1, 2 and 3, water samples collected from a point near the slag dump (W1), contained very high values of SO_4^{2-}, TDS and conductivity with reference to the background values. The SO_4^{2-} in W1 ranged from 991-1814mgL^{-1} while the background levels at W2 varied from 88.2-129mgL^{-1}. This is attributed to the acidic drainage discharge from tailings, which flow in the form of sulphuric acid. As the acidic drainage flows it is neutralized by the naturally occurring carbonate rocks yielding high SO_4^{-2} concentrations, which eventually flow into the nearby stream A.

Figures 9 and 10 show a very significant increase in the sulphate levels of the communal rivers. This is attributable to the contribution from the mine drainage contaminated Streams A and B when they flow into the natural river systems. This increase in the sulphate levels has an adverse effect on the quality of the community river waters.
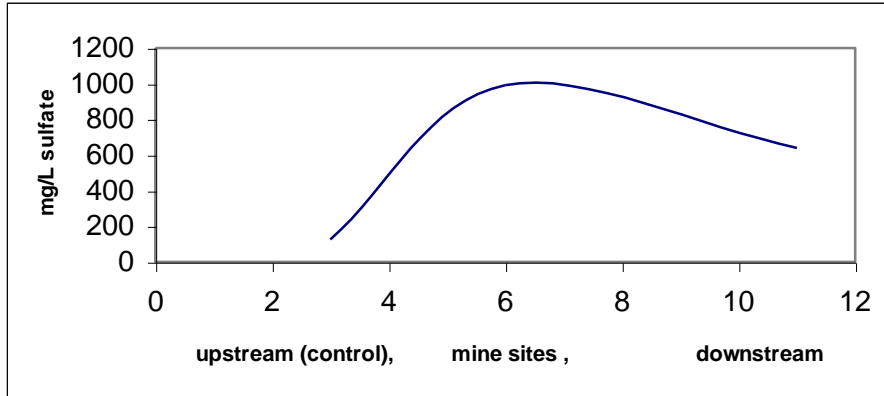
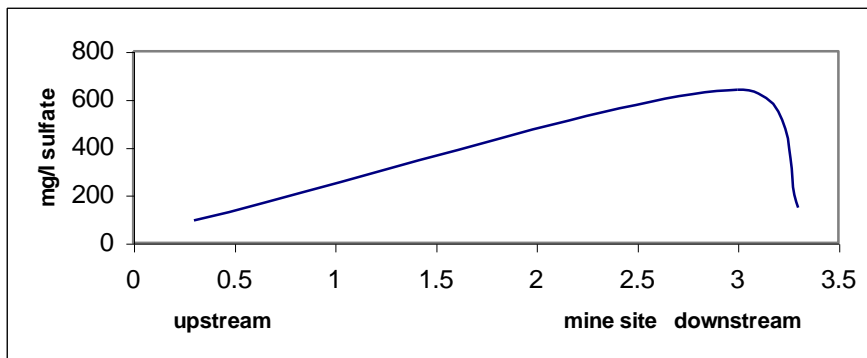Figure 9: Change in sulphate concentration with distance along Stream A

Figure 10: Change in sulphate concentration with distance along Stream B

AMD is further evidenced by high conductivity and TDS values which were obtained in sample (W1). A comparison of TDS and conductivity range of values for W1 and the upstream control point W2 for Stream A is shown below:

	TDS	Conductivity
W1	1390-2374mgL^{-1}	2.09-4.08mScm^{-1}
W2	348-470mgL^{-1}	0.45-0.95 mScm^{-1}

It can be observed that the TDS concentration for the water flowing from the control point W2 had increased by 299%-405% on passing through W1 which is a sampling point surrounded

by tailings dumps while conductivity had increased by 364% -329%. These high values of TDS and conductivity for W1 have a strong correlation with SO_4^{2-} concentrations.

Sulphate concentration, TDS and conductivity values obtained for W6 were also high. This is in agreement with the fact that the waters from W1 flow through W6 a downstream sampling point for Stream A which flows into Community river A.

Sample W5 represents the effects of mining activity on the quality of underground water. The sampling point W5 is kept overflowing perennially by a nearby spring which supplies water to stream B. The spring water is characteristic of the underground water composition and it represents the seepage from the mining complex. Samples collected at this point showed a relatively high concentration of sulphate, conductivity and TDS. The only surface water flow that passed through W5 was when there occurred an accidental pipe burst from the concentrator plant during the months of June and July. W5 was also affected by the runoff from the nickel mine rock storage during the months of June and July. For the upstream control point W7, SO_4^{2-} concentrations, TDS and Conductivity levels were found to vary as follows:

|	**Upstream control (W7)**	**W5**
SO_4^{2-}	21.2-116mgL^{-1}	418-652mgl^{-1}
TDS	66-260mgL^{-1}	780-1120mgL^{-1}
Conductivity	0.07-0.56 mScm^{-1}	1.18-2.33mScm^{-1}

The effluent from W5 flows into the Community river B via stream B and is subsequently diluted by W7 an upstream control point resulting in W8 which is a combination of water from the mine W5 and the unaffected community river water W7. W8 was found to have the following composition ranges in SO_4^{2-} concentration, TDS and conductivity:

	W8	**Upstream control (W7)**
SO_4^{2-}	65.9-162mgL^{-1}	21.2-116mgL^{-1}
TDS	382-546mgL^{-1}	66-260mgL^{-1}
Conductivity	0.37-0.76mScm^{-1}	0.07-0.56 mScm^{-1}

The results indicate an increase in the SO_4^{2-}, TDS and conductivity values in the mixture W8 when compared to W7 the upstream control point. The sulphate concentration from W7 to W8 increased by a range of 40%-211% which indicates a tremendous change in the Community river B water quality.

The slimes tailings dam aqueous phase W3 and the monitoring borehole water behind the slimes dam wall W4 showed a low discharge of sulphate 57.4-311mgL^{-1} and 54.3 –135mgL^{-1} respectively. This could be attributed to the fact that the fine particulate matter from the concentrator in the slimes tailings dam W3 is totally submerged in water and this prevents AMD from occurring. Conductivity values for W3 varied from 0.7 - 1.65 mScm^{-1} and is very similar to the background values.

The generation of sulphate in mine waters indicates AMD. High sulphate content and almost neutral pH obtained in the water samples suggest that the sulphuric acid produced is immediately neutralized forming sulphate and other species as follows:

$$H_2SO_4 \ + \ OH^- = H_2O \ + \ SO_4^{2-} \qquad\qquad (5)$$
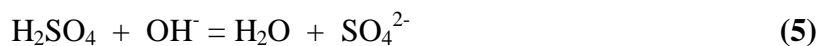
Passive methods of treating mine water use chemical and biological processes that decrease metal concentrations and neutralize acidity (Robert et. al., 1994). However, the failure of these passive treatment technologies (Hayman et.al. 1995), is attributable to improper characterisation of contaminated mine drainages and/or incomplete understanding of the water quality analysis and geochemistry of the drainages.

Reactive measures for the abatement of AMD

(i)   Addition of carbonate minerals such as $CaCO_3$ to   increase the NP values

(ii)   Use of bactericides or Detergents to destroy *Thiobacillus thiooxidans* and *Thiobacillus Ferrooxidans*, which facilitate AMD production.

(iii)   Lime addition in the form of CaO and Ca $(OH)_2$

(iv)   Use of ammonium hydroxide

(v)   Use of phosphate to reduce the amount of ferric and ferrous Fe in water

(vi)   Use of wetlands containing sulphate-reducing bacteria decreases sulphate concentrations. Others contain Hyperaccumulator plants, which selectively remove specific metals from the water bodies (Zipper and Jage, 2001).

Proactive measures

(i)   Top soiling and revegetation

(ii)   Use of wet and dry covers to prevent water and oxygen infiltration into mine spoils.

Conclusions

AMD is currently occurring at the nickel mine as evidenced by high SO_4^{2-} concentrations, TDS and conductivity. Neutralization of acidity resulted in water with high sulphate concentrations and low Fe due to some of the Fe content having precipitated as $Fe(OH)_3$. AMD can be treated and prevented by suitable proactive and reactive measures. Although there are multitudes of treatment methods used to contain AMD the only long-term, cheapest and relatively effective way is topsoiling and revegetation. Topsoiling and revegetation reduce the infiltration rate of water, decreases the influx of oxygen into underlying mine spoils and thus reduces the extent of sulphide oxidation. A full characterisation of the contaminated mine drainage water quality, and rock composition analysis is indispensable for the successful implementation of a recommended passive treatment technology.

Acknowledgements

Literature Cited

Gray, N.F. 1996. Field assessment of acid mine drainage contamination in Surface and ground water. Environmental Geology 27. p. 358-361. http://dx.doi.org/10.1007/BF00766705

Gray, N.F. 1998. Acid mine drainage composition and the implications for its impact on lotic systems. Wat. Res. Vol 32 No 7: p. 2122-2134. http://dx.doi.org/10.1016/S0043-1354(97)00449-1.

Greenood, N.N. and Earnshaw, A. 1994Chemistry of the Elements. First Edition. Department of Inorganic Chemistry and Structural Chemistry University of Leeds. Pergamon Press. p. 1330.

Hyman, D.M. and Watzlaf, G.R. 1995. Mine drainage characterisation for the successful design and evaluation of passive treatment systems. Paper presented at the 17th Annual National Association of Abandoned Mine Lands Conference. October 15-18. French Lick, IN. pp. 170-184.

Jaye, C. and Zipper, C. 2001. Passive Treatment of Acid Mine Drainage with vertical Surface Systems. Reclamation Guidelines for Surface Mined Land in South West Virginia. Virginia Cooperative Extension. Publication pp. 460-133.

Kimmel, W.G. 1983. The impact of acid mine drainage on the stream ecosystem. *In* S.K. Majumdar, and W.W. Miller eds. The Pa. Acad. Sci. Publ. Pennsylvania Coal: Resources, Technology and Utilization. pp. 424-437.

Reddick, K. and Todd, J. 1997. Acid Mine Drainage. Groundwater Pollution Primer. CE4594. Soil and groundwater Pollution Civil Engineering Department, Virginia Tech.

Ridge, T. and Seif, J.M. 1998. The Science of Acid Mine Drainage and Passive Treatment. Department of Environmental Protection. Bureau of Abandoned Mine Reclamation.

Robert, S. Hedin, R. Robert, W.N. and Kleinmann, R.L.P. 1994. Passive treatment of coal mine drainage. Bureau of Mines Information Circular/1994. IC 9389. United States Department of The Interior.

U.S. Environmental Protection Agency, December 1994. Acid Mine Drainage. Technical Document.

White W.W. and, Jeffers 1994 T.H. p. 608-630. Chemical predictive modelling of acid mine drainage from metallic sulphide bearing waste rock. Environmental Geochemistry of Sulphide Oxidation 550.