Implications of Non-Acid Metal Leaching on Mine Rock Management at a Nickel Mine in Permafrost Terrain:1 – Mine Rock Evaluation

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Abstract

Raglan is a nickel-copper-cobalt mine in the continuous permafrost region of Quebec. The management plan for waste rock at the mine was developed during the Environmental Assessment stage of the project and was based on acid based accounting (ABA) methods to identify acid generating and non-acid rock types with the intent to backfill the open pits and freeze the acid waste. The screening criteria were reexamined in 1999 to address nickel leaching and to develop more conservative and lower risk criteria than the ABA approach. A waste rock assessment study was initiated to focus on nickel leaching at neutral pH. The major rock types were characterized and humidity cell tests were established with regular distilled water and with pH adjusted (acetic acid to pH<7) water to determine nickel release rates from these materials.

The results showed that the waste rock solids exhibited high nickel to sulphur ratios that likely reflected traces of pentlandite sulphur in contrast to the more usual pyrrhotite sulphur in similar waste rock. Nickel leaching was evident for most rock types even when the sulphur contents in the rock were as low as 0.3%. In contrast to other studies that exhibited lag times of tens of weeks to observe nickel leaching, the absence of buffering above pH values of 8 in the Raglan materials resulted in nickel leaching within a few weeks of initiating the humidity cell tests. It was found that nickel leaching at neutral pH and not acid generation was the defining criteria for waste rock that required additional management. As a result, a significant decision was made to alter the mine plans and to revise the baseline assessment of the proposed mining areas as described in a companion paper (Nicholson et al., 2003).

INTRODUCTION

Base metal mining produces large quantities of waste rock that contain sulphide minerals which oxidize when exposed to atmospheric oxygen and moisture. The waste rock can be classified as either non-reactive or reactive. Non-reactive rock can be defined as rock appropriate for use as construction material, posing little to no risk of unacceptable drainage quality. Reactive rock can be defined as material that either generates acidic drainage or drainage containing unacceptable levels of metals for release to the environment.

Typically, management practices have utilized non-acid generating waste rock for construction materials and this rock is identified based on screening criteria associated with neutralization potential (NP) and acid potential (AP) for the waste rock. However, this in some cases, screening criterion fails to consider the issue of leachable metals, such as nickel, zinc or copper that can invalidate the conclusion regarding the reactivity of waste rock or selection of rock for uses other than controlled disposal in specific waste rock facilities. Experience has shown that metal leaching can dictate whether waste rock requires special management or may produce unacceptable leachate quality, regardless of whether acid generation occurs or not. The objective of this study was to develop criteria for the evaluation of waste rock from the Raglan nickel-copper mine in Northern Quebec to determine whether it should be classified as reactive or non-reactive.

METHODS

Eight grab samples were collected from the waste rock piles and were submitted for laboratory analysis for characterization and determination of metal content. Sulphide sulphur values were determined using Leco

Furnace at 550 °C. A temperature of 550 °C is typically used to evolve CO_2 from carbonates and sulphur from pyrite solids, but may not be sufficient to volatilize sulphur from pyrrhotite and pentlandite. Moreover, it is unlikely that the rock samples from Raglan contain appreciable 'non-sulphide' species of sulphur (e.g., gypsum). Discrepancy between total sulphur and sulphide sulphur results likely reflects the analytical method rather than the presence of other sulphur species, such as sulphate, that are likely rinsed from the solids during testing. Therefore, total sulphur values were interpreted as sulphide sulphur.

Humidity cell tests were conducted on selected samples representing various rock types from the Raglan site, including gabbro, argillite, peroxinite and aggregate rocks. The tests were conducted to determine the leaching characteristics of the various waste rocks. Based on the chemical characterization of the rocks, the primary constituent of concern for metal leaching was determined to be nickel.

Nickel solids (e.g., $Ni(OH)_2$) can form and represent an important control on nickel solubility at pH values above 8, but represents an ineffective control in an aquatic environment below a pH value of 7.5. An additional geochemical control on nickel concentrations is adsorption onto iron hydroxide coatings that can form on the rock surfaces when iron oxidation occurs. Iron hydroxides are precipitates that form when iron, released during oxidation of sulphide minerals, forms the low solubility solid $Fe(OH)_3$. The adsorption process is more complex than simple solubility, but can result in lower dissolved nickel concentrations than precipitation of solid $Ni(OH)_2$ (Smith et al., 1998; Theis and Richter, 1980). Adsorption is also pH-dependent, and is a more effective control on dissolved nickel concentrations at lower pH values than those that control $Ni(OH)_2$ solubility. Therefore, in addition to standard humidity cell tests (neutral pH), tests were conducted under conditions designed to minimize sorption and the formation of secondary nickel solids (i.e., pH less than 7). These tests provided insight into potential lag-times for nickel release that may occur if secondary solids were controlling nickel release rates.

The humidity cell tests included 1 kg of waste rock placed in each cell which was rinsed weekly for a total of 69 weeks with 1 L of de-ionized water or mild acetic acid. The rock was maintained moist but **n**ot saturated between weekly rinses. The leachate was collected and submitted for chemical analysis. Four standard tests were conducted with a de-ionized water leaching solution (neutral pH) and consisted of either gabbro, argillite, peroxinite or an aggregate waste rock sample. Three additional tests were conducted with an acetic acid leaching solution to maintain the pH between 6 and 7 and consisted of either gabbro, argillite, or peroxinite waste rock.

RESULTS

Solids Chemistry

Selected results of the rock sample chemistry is provided in Table 1. Waste rock at Raglan has a wide range of sulphur contents. The values observed in this study were as high as 9.2% (mean value of 2.1 %) with nickel content up to approximately 3.3% (mean value of 0.7%) for 9 grab samples collected form the site (Table 1). Sulphide sulphur values were less than total sulphur values and were as high as 4.3% (mean value of 0.84%). However, as previously discussed, due to restriction in the analytical method for sulphide sulphur, total sulphur values were interpreted as sulphide sulphur.

In general, the nickel to sulphur ratios (Ni/S) in the rock exhibit higher values relative to waste rock samples from other nickel deposits (e.g. Voisey's Bay in Labrador and Whistle deposit in Sudbury). It should also be noted that even the natural overburden typically contained elevated nickel values in the areas tested. The nickel and sulphur data for Raglan waste rock are plotted in Figure 1, together with data from Voisey's Bay. Because it is assumed that non-reactive material will have a sulphide content of less than 1%, data in Figure 1 was plotted to a maximum of 1%. Based on this data, the ratio of Ni/S in the

Raglan rock is about 0.55 (see slope on Figure 1).

Kinetic Tests

Standard Humidity Cell Tests

Standard humidity cell tests were conducted to assess the leaching characteristics of different types of waste rock under neutral pH conditions. In general, the results show that both nickel and sulphate exhibited relatively steady state concentrations in leachate after ten weeks of testing. Therefore, the mean, steady state nickel and sulphate concentrations were calculated as the average value from week 10 to week 69 and these values are provided in Table 2 together with maximum observed values.

TABLE 2: Selected results showing peak and mean, steady state nickel and sulphate concentrations in leachate from humidity cell tests.

Rock Type	Peak Concentration[1]		Mean, Steady State Concentration[2]	
	Nickel (mg/L)	Sulphate (mg/L)	Nickel (mg/L)	Sulphate (mg/L)
Standard Leach Test				
Gabbro	0.02	3	<0.010	0.6
Argillite	0.16	17	0.031	1.7
Peroxinite	0.11	28	0.019	5.0
Aggregate	1.60	120	0.41	13.3
Acid Leach Test				
Gabbro	0.26	10	<0.010	0.4
Argillite	1.20	20	0.035	1.6
Peroxinite	0.93	42	0.030	4.9

The mean, steady-state concentrations of sulphate in leachate ranged from 0.5 to 14.2 mg/L. Leachate from testing gabbro had the lowest value and leachate from testing the aggregate had the highest value. The mean, steady-state concentration for nickel ranged from <0.010 to 0.43 mg/L. Similar to sulphate, the lowest concentration was associated with gabbro and the highest value was associated with the aggregate. The peak sulphate concentrations ranged from 3 to 120 mg/L and were, in general, a factor of 5 to 9 times higher than the mean, steady state values. Peak nickel concentrations ranged from 0.02 to 1.6 mg/L and were generally a factor of 2 to 4 higher than the mean, steady state values.

Tests Conducted at pH Values Less Than 7

Three humidity cells were conducted using mild acetic acid rinse water (pH maintained between 6 and 7) to assess the leaching characteristics of different rock types under mildly acidic conditions. The results are provided in Table 2 in terms of peak concentrations and the mean, steady state concentrations of nickel and sulphate.

Similar to standard humidity cell tests, steady state sulphate and nickel concentrations were observed after approximately 10 weeks of leaching. Gabbro waste rock samples exhibited the lowest concentrations while leachate from testing the peroxinite waste rock had the highest concentrations. Peak sulphate concentrations were marginally higher than values observed in the standard tests. The peak nickel concentrations were a factor 10 times higher, on average, than values observed in the standard tests. However, the mean, steady-state sulphate and nickel concentrations were very similar to values observed in the standard tests.

These results suggest that, although pH values less than 7 can affect the amount of nickel leached initially, there is no observed affect of pH on leaching after 10 weeks of testing (steady state). In contrast to other nickel deposits (e.g. Voisey's Bay) that exhibited lag times to observe nickel leaching (Nicholson et al., 1999), there is no apparent delay in nickel release from the Raglan materials in the absence of buffering above pH values of 8.

DISCUSSION

Solids Assays Used for Screening Non-Reactive Waste Rock

The main waste sulphide that is generally associated with nickel sulphide deposits is pyrrhotite. Pyrrhotite (FeS) generally contains a maximum nickel content of about 1% by weight. The nickel content of the Raglan waste rock can therefore not be attributed to pyrrhotite only, as shown by the pyrrhotite line in Figure 1, which almost coincides with the horizontal axis. The line that shows the nickel-sulphide relationship for pentlandite ($\{Fe,Ni\}_8S_9$) is also plotted in Figure 1. The data from Raglan fall below, but is close to, the pentlandite line. This suggests that a significant fraction of the sulphide in the rock is composed of pentlandite, with the remaining sulphide likely composed of pyrrhotite.

For comparison, waste rock from the Voisey's Bay deposit (Labrador) and the Whistle deposit (Sudbury) exhibit Ni:S ratios of about 0.1 (Figure 1). The same Ni:S ratio in the Raglan waste rock is 5 times higher. The high Ni:S values at Raglan are likely attributed to the high proportion of pentlandite in the waste. This means that even with low quantities of sulphur in the waste rock (or natural overburden, for that matter) at Raglan, nickel concentrations tend to be relatively high. This also implies that if sulphur is present in waste rock considered "non-acid generating" based on sulphur content and NP/AP ratios, then substantial nickel may be available to leach and has the potential to produce drainage with unacceptable water quality.

Nickel Leaching

Results of the kinetic tests indicate that there is no apparent delay in Ni release from the Raglan waste rock in the absence of pH buffering above pH of 8. In contrast, Ni leaching studies on nickel waste rock from other mines have shown lag times of tens of weeks before nickel release (but eventually did have releases). Figure 2 presents the results of kinetic testing of waste rock with variable sulphur contents for the Voisey's Bay Mine site in Labrador (Nicholson et al., 1999). The results show that Ni concentrations remain below detection for a period of time, then increase to relatively high values after approximately 30 to 45 weeks. The time delay for nickel release from the solids is dependent on the sulphur and nickel contents of the rock. The waste rock with relatively low sulphur and nickel contents (S = 0.12 %) released nickel to the leachate several weeks later than the higher sulphur waste rock (S = 1.2 %).

The timing for nickel release is also pH dependent (Figure 3). The results show that certain threshold pH values, which are near neutral, control the release of nickel to the leachate. The threshold values are different for the different types of waste rock. This result likely reflects the greater abundance of Fe-solids present in the humidity cell (with higher S content) that tend to control nickel concentrations by sorption reactions.

The results of leachate monitoring for the Voisey's Bay site show that nickel can be released from low sulphur waste rock at neutral pH. This is similar to the results of this study, which show that although the peak Ni concentrations were highest in the tests conducted under acidic conditions, the average steady-state Ni loadings were, in general, similar for both neutral and acidic leaching. This implies acid generation has little effect on nickel release rates and that nickel leaching may produce unacceptable leachate quality at neutral pH. The results also highlighted the potential for nickel leaching as a result of natural weathering processes and subsequent elevated nickel concentrations in drainage from mineralized areas.

Predicting Loading Rates from Sulphur Assays

Sulphate loading rates for the Raglan waste rock were calculated and found to agree with a larger data set from Voisey's Bay and to be proportional to the sulphur content of the waste rock. The relationship is provided in Figure 4 for all rock types at Raglan and shows that:

$$\text{SO}_4 \text{ Loading Rate (mg-SO}_4\text{/kg/wk)} = 14\ (S_t) \quad [1]$$

where S_t represents the sulphur content of the waste rock. Because there is a strong correlation between nickel content and sulphur content in the waste rock (Figure 1), the Ni:S_t ratio (0.55) was used to modify Equation 1 to:

$$\text{Ni Loading Rate (mg-Ni/kg/wk)} = 7.7\ (S_t) \quad [2]$$

or

$$\text{Ni Loading Rate (Kg-Ni/t/a)} = 0.4\ (S_t) \quad [3]$$

Allowable Quantity of Waste Rock for Construction

Screening level calculations were made to determine the maximum amount of waste rock that can be stored (or used for construction) on site per unit area. This calculation was based on an assumed equivalent run-off of 100 mm/a (or flow rate of 1×10^5 $m^3/km^2/a$) and a surface water quality objective for nickel of 0.020 mg/L.

A maximum loading rate of 2.0 kg-Ni/km^2/a is required for the run-off (and resultant steady-state values in surface water bodies) to have a maximum nickel concentration of 0.020 mg/L. This loading rate was integrated into Equation 3 to develop a relationship between sulphur content in the waste rock and maximum quantity of waste rock that can be used for construction per unit area. The relationship is illustrated in Figure 5. This relationship is non-linear and the quantity of rock increases rapidly with a decrease in sulphur content. This relationship is also very conservative in that the rates are based on measurements from humidity cells reacted at room temperature. Moreover, the nickel leaching rates were assumed with no attenuation. The relationship, however, provides a first level of evaluating the acceptability of using rock with known metal leaching characteristics. The average run-off for this area was assumed to be 100 mm/a and if the actual value is higher than this, the allowance for sulphur bearing construction rock will increase above the current estimates.

CONCLUSION

Kinetic tests, including modified metal leaching tests, clearly showed that the Raglan rock can leach nickel at neutral pH, and that NP/AP ratios should not be the only tool to evaluate the risk associated with the material. The results of the waste rock assessment demonstrated that nickel leaching was a key issue for waste management at the Raglan mine (in addition to natural loadings). The implications of this study have resulted in modifications to the mine plan at Raglan to account for the nickel leaching issue, and a revised baseline assessment of the proposed mining areas, as described in a companion paper (Nicholson et al., 2003). The mine plan modifications have resulted in a reduction of more than 10 Mtonnes of mine rock with current reserves. These results have also been integrated into Raglan's ongoing management program to protect the environment.

REFERENCES

Nicholson, R.V., M.J. Rinker, G. Williams and W.A. Napier. 1999. Assessment of Water Quality Associated with Underwater Disposal of Tailings and Waste Rock from the Voisey's Bay Project, Labrador, Canada. *In* Sudbury '99 Mining and the Environment II Conference Proceedings. Sudbury, Ontario. 13-17 September.

Nicholson, R.V., G. Williams, M. J. Rinker, M.A. Venhuis and B. Swarbrick. 2003. Implications of non-acid metal leaching on mine rock management at a nickel mine in permafrost terrain: 2 – Environmental Baseline Investigation. *In* Proceedings Sudbury 2003 Mining and the Environment Conference. Sudbury, Ontario. 25-28 May.

Smith, K.S., J.F. Ranville, G.S. Plumlee and D.L. Macalady. 1998. Predictive Double-Layer Modeling of Metal Sorption in Mine-Drainage Systems. *In* E.A. Jenne. Adsorption of Metals by Geomedia: Variables, Mechanisms and Model Applications. Academic Press.

Theis, T.L., and Richter, R.O. 1980. Adsorption Reactions of Nickel Species at Oxide Surfaces. *In* Ed. Kavanaugh, M.C. and Leckie, J.O., Particulates in Water: Characterization, Fate, Effects and Removal. Advances in Chemistry Series 189, American Chemical Society, Washington D.C., U.S.A.

TABLE 1: Solids characteristics of Raglan waste rock.

Constituent	Waste Rock Sample ID								
	RWR-001	RWR-002	RWR-003	RWR-004	RWR-005	RWR-006	RWR-007	RWR-008	RWR-Z2
Co (mg/kg)	120	200	540	180	38	32	56	140	130
Cr (mg/kg)	1,300	2,000	1,300	880	170	100	2,100	36	1,700
Cu (%)	0.06	0.45	0.50	1.0	0.044	0.047	0.018	0.009	0.068
Ni (%)	0.33	1.20	3.30	0.92	0.02	0.02	0.12	0.0018	0.37
NP (kg $CaCO_3$/t)	69.8	17.8	28.7	26.8	20.4	15	64.2	40.7	37.8
AP (kg $CaCO_3$/t)	4.06	20.6	135	53.4	0.31	0.31	1.88	15.3	4.69
Total S (%)	0.56	2.05	9.22	3.96	0.05	0.03	0.47	1.72	0.69
Sulphide S (%)	0.13	0.66	4.32	1.71	<0.01	<0.01	0.06	0.49	0.15

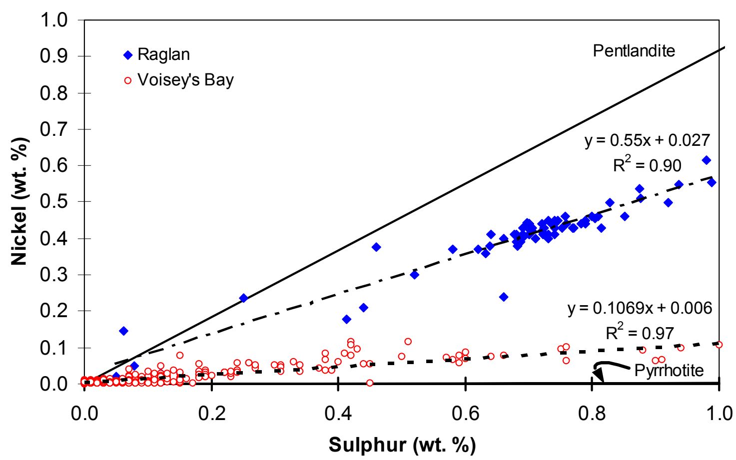

FIGURE 1: Plot of nickel versus sulphur content of waste rock from the Raglan site. Nickel versus sulphur content of waste rock from Voisey's Bay (Labrador) is provided for comparison.

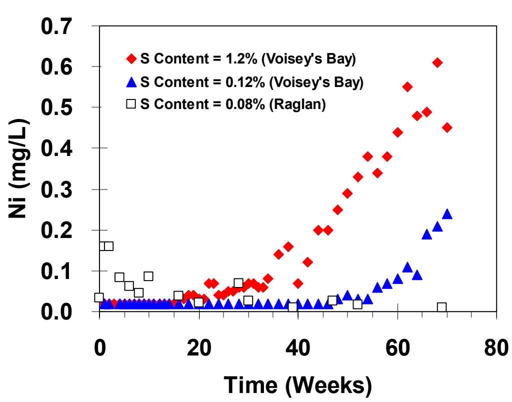

FIGURE 2: Results of nickel concentration versus time for leach testing of sulphide waste rock from Voisey's Bay (Labrador).

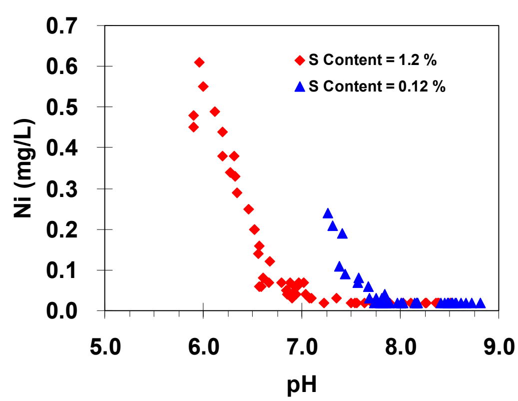

FIGURE 3: Results of nickel concentration versus pH for leach testing of sulphide waste rock from Voisey's Bay (Labrador).

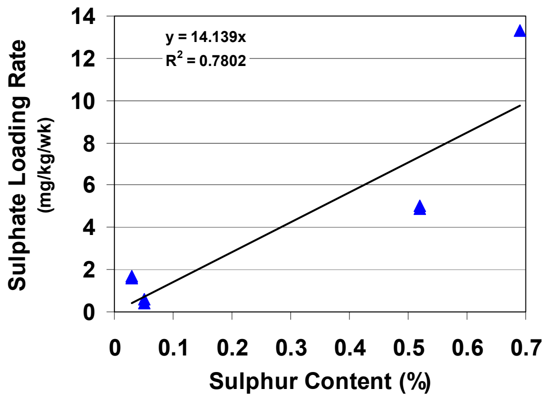

FIGURE 4: Sulphate loading rates as a function of sulphur contents in Raglan waste rock.

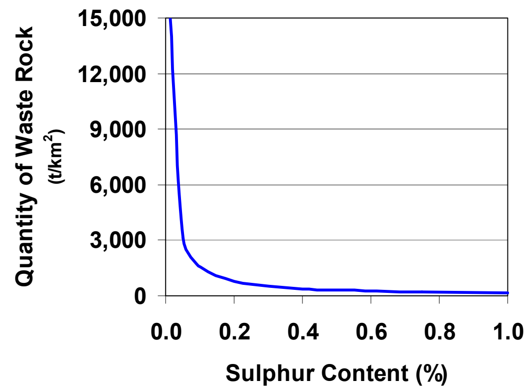

FIGURE 5: Relationship between the quantity of construction rock allowed for a specified sulphur content per square km of watershed capturing drainage from the rock.