

Field retention tests to evaluate nickel retention on mine waste rock

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ABSTRACT

A field retention test campaign was designed to verify the retention of nickel two field cells, one with “fresh” waste rock and one with “weathered” waste rock. They were watered with nickel-rich water over several hours and the nickel concentration in the effluent samples was monitored. It was found that the fresh waste rock was able to maintain very low Ni concentrations in its effluent, while the weathered waste rock released most if not all the Ni that was added with the input water, therefore had barely any retention capacity. The results from the field campaign confirm the hypothesis that sorption of nickel is a significant factor in contaminated neutral drainage (CND) generation at this mine site.

RÉSUMÉ

Une campagne de terrain a été entreprise pour vérifier la rétention du nickel sur deux cellules expérimentales, une contenant des stériles frais et l'autre contenant des stériles altérés. Les cellules ont été arrosées avec de l'eau riche en nickel et la concentration en Ni dans l'effluent a été analysée. L'effluent des stériles frais a conservé des concentrations en Ni faibles, tandis que les stériles altérés ont relâché presque la totalité du Ni ajouté par l'eau d'arrosage, donc n'avait que très peu de capacité de rétention. Les résultats de cette campagne de terrain confirment que la sorption du nickel est un facteur important dans la génération du drainage neutre contaminé (DNC) à ce site minier.

1 INTRODUCTION

Mining operations generate large amounts of waste rock that is generally stored in piles exposed to atmospheric conditions. Minerals present in the waste rock may react with surrounding water and air, which can affect the quality of water percolating through the waste rock. When the effluent has a pH near neutrality and contains concentrations of one or several metal species above the current norms, it is called contaminated neutral drainage (CND). A project was initiated to improve the knowledge on CND for a mine site dealing with Ni contaminated effluent from its waste rock pile.

Seven field test cells were installed at the mine site (using approximately 30 m³ of waste rock for each test cell). Effluent quality was monitored since installation in 2006. Laboratory tests were performed in parallel to the field tests to evaluate the geochemical behaviour of the tested materials. It was found that some minerals have significant nickel sorption capacity, and these results were correlated to the field data.

The work described in this paper presents a field test designed to validate laboratory results that suggested that retention (particularly sorption) capacity of fresh and weathered waste rock is different. The field cells are first described, followed by the procedure used and the results obtained in terms of effluent quality. Then, results interpretation is focused on the processes that may explain the behaviour observed during the test.

2 CELLS DESCRIPTION, MATERIAL PROPERTIES, AND SUMMARY OF GEOCHEMICAL BEHAVIOUR

Seven test cells were built in summer 2005 and instrumented to monitor the geochemical behaviour of different types of waste rock. Two of those cells are used in the present study. The cells contain approximately 30 m³ of waste rock placed in a square-based pyramid shape, as shown in Figure 1. The bottom of the cells was lined with impervious geomembrane (protected by two 20 cm layers of inert sand) to catch the rain water flowing through the waste rock, and a drainage system was installed to collect the water through a single outflow pipe. The outflow pipe is connected to a flow measurement system (pressure sensor HOBO U20).

The waste rock used in the cells has different ilmenite content and oxidation levels. Cell C1 is made of freshly blasted waste rock (within 1 month of cell construction) with a low hemo-ilmenite content of approximately 31%. Cell C4 also contains 31% hemo-ilmenite waste rock, but the waste rock has been exposed to ambient climatic conditions for approximately 25 years before being placed in the cell. A complete characterisation was performed at the beginning of the test in 2005 and results can be found in Pepin (2009). Selected relevant data for the current study are presented here. The mineralogical composition of the waste rock, determined by XRD, is presented in Table 1. Labradorite is the main gangue mineral, and ilmenite is the main titanium-bearing mineral. Geotechnical parameters are presented in Table 2. Specific gravity is slightly higher in C4 than C1, probably because of the different weight fractions of labradorite (G_s of 2.69) and enstatite (G_s of 3.2). The saturated hydraulic conductivity (k_{sat}) and air entry value (AEV) are similar for both cells, with k_{sat} of 0.2 cm/s and AEV < 10 cm. More details on geotechnical characterisation are available in Pepin (2009) and Peregoedova (to be published).

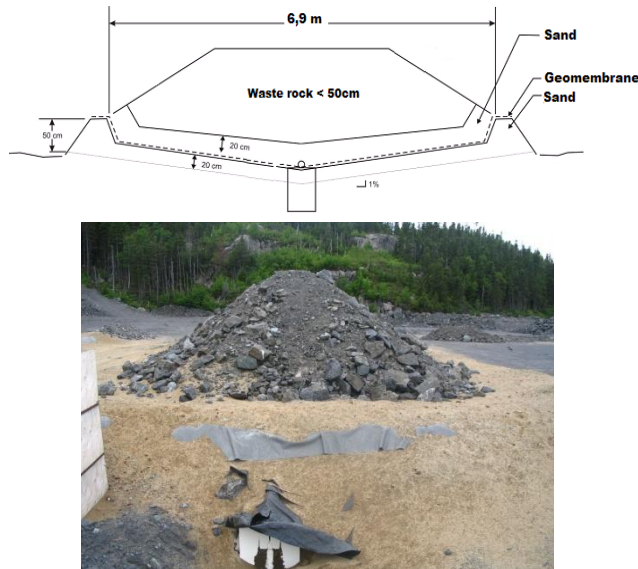


Figure 1: Configuration of the test cell (from Demers et al. 2010)

Table 1: Mineralogical composition (in %) of the waste rock

Mineral	C1	C4
Labradorite	45	32
Ilmenite	23	23
Hematite	8	8
Pyrite	1	1
Enstatite	6	25
Pigeonite	4	2
Biotite	2	< 1
Muscovite	< 1	1
Chlorite	3	3
Orthoclase	7	1

Table 2: Selected geotechnical and hydrogeological parameters of the waste rock

Parameter	Unit	C1	C4
G_s	-	3.087	3.271
k_{sat}	cm/s	0.2	0.2
AEV	cm of water	< 10	< 10

Figures 2 and 3 present the evolution of pH and Ni concentration in the effluent of cells C1 (fresh) and C4 (weathered). Their pH level is similar, from 6 to 9 for both cells. C4 has higher Ni concentrations that keep increasing with time, from 0.1 mg/L in 2006 to above 0.6 mg/L in 2010. C1 kept its Ni concentrations below 0.02 mg/L. The difference between the two type of test plots being the alteration level of the waste rock, it was postulated that retention of nickel by the fresh waste rock reduces the nickel concentration at the outlet. As the waste rock ages, its retention capacity is slowly decreased since its sorption sites are being saturated

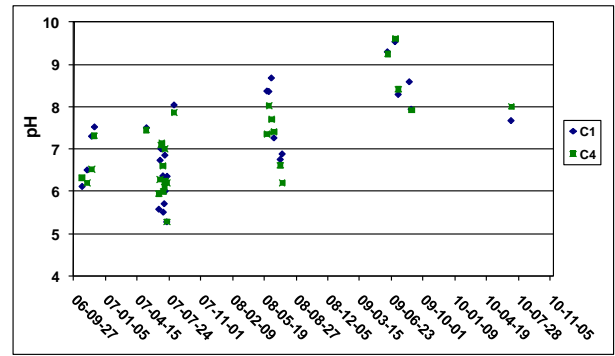


Figure 2: pH evolution in effluent of the two cells

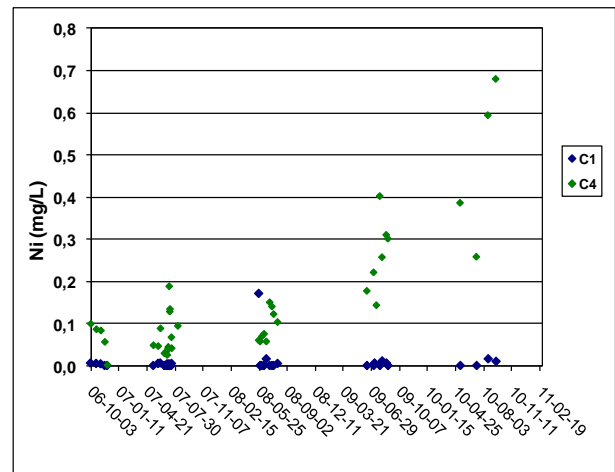


Figure 3: Ni evolution in the effluent of the two cells

3 FIELD RETENTION TESTS

A field retention test campaign was designed to verify the retention of nickel on the test plots and then validate the laboratory observations (Plante 2010; Plante et al., 2010a, b, c). Nickel rich water was collected on the mine site into 1000-L containers. Each container was analysed in situ for pH, ORP and Ni concentration using pH, conductivity and ORP probes, and colorimetry for Ni. Ni concentrations were later confirmed by ICP-AES. ICP-AES analyses also included the following elements: Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Pb, S_{tot} , Sb, Si, Ti, Zn. Some key results for each water container are presented in Table 3. Overall, the input water for C1 contained approximately 1.8 mg/L Ni at a pH value of 7, while the input water for C4 contained approximately 2 mg/L Ni at a pH value of 6.8.

Table 3: Main characteristics of the Ni-rich water before the retention tests

Container	pH	ORP	Ni (colorimetry)	Ni (ICP-AES)
C1-1	7.45	95.5	1.845	1.81
C1-2	7.05	103.2	1.65	1.8
C1-3	7.11	101.1	1.88	1.78
C4-1	6.83	NA	NA	1.9
C4-2	6.82	NA	NA	2.03
C4-3	6.72	NA	1.235	2.09

The nickel-rich water was watered by overhead irrigation on cells C1 and C4 over several hours using a garden sprinkler. A total of 3000 L was watered in two periods for C1 and C4 (see Figure 4). The effluent produced was sampled hourly using an automatic peristaltic sampler. Nickel concentration in the effluent samples was evaluated on site using colorimetry and in the laboratory using ICP-AES. The effluent's pH was measured sporadically using a pH probe and meter. The effluent flowrate was also evaluated sporadically using a graduated cylinder and a stopwatch.



Figure 4: Field set-up for retention tests: water sprinkler on top of cell (top) and colorimetry and pH/ORP equipment (bottom).

4 RESULTS

The results obtained are presented below. The Ni concentrations presented are those obtained through ICP-AES analyses (free mobilized analytes). Colorimetry was used on the field mostly as an indicator to estimate the Ni content of the feed water and a few times to check the effluent. The ICP results usually matched well those obtained by colorimetry.

4.1 Flowrate

Ni-rich water was sprinkled almost continuously for two periods for each cell, for a total of 530 minutes for C1 and 542 minutes for C4. The corresponding flowrate is 5.7 L/min for C1 and 5.4 L/min for C4. However, the measured flowrates, presented in Figures 5 and 6, are below these estimated values. The watering periods are indicated by the dark arrows. It suggests that part of the water added is retained in the cell, and that the duration of the watering was not enough to reach the steady state in terms of water flow. Also, it is possible that a portion of the water added was lost to evaporation and that a very low amount may have been projected outside the cell during sprinkling (minimal according to field observations).

4.2 Ni concentrations

Figures 5 and 6 show the trend of the Ni concentration in the effluent of both cells, with the watering period and the measured flowrates. For C1, the Ni concentrations remained low throughout the test, generally below 0.02 mg/L. During the second watering period, Ni concentrations reached 0.15 mg/L for a short period, then returned back to below 0.02 mg/L once watering was stopped. The Ni concentrations obtained in the effluent of cell C1 were well below the input concentration of 1.8 mg/L.

Cell C4 shows a different behaviour. The Ni concentration in its effluent rose rapidly with the water input for the watering from an initial concentration of 0.257 mg/L to 1.75 mg/L, and the concentration at the effluent stayed elevated even after the water input was turned off. During the second watering period, Ni concentrations rose above 2.5 mg/L, and slowly decreased to reach 1.26 mg/L by the end of the test.

4.3 Ca, Mg, S concentrations

Figure 7 to 10 present the evolution of the calcium, magnesium and sulphur concentration in the effluent of both cells. The three elements concentrations follow the same pattern for a given cell, with a spike in concentration shortly after the watering period. For C1, the first peak concentrations occurred within 8 hours of the beginning of the watering. Ca and S concentrations at the effluent rose to values near the input water concentration. When watering was stopped, Ca and S concentrations stabilized and then rose again with the second watering period. During that period, Ca and S concentrations at the effluent rose above the input concentration. Effluent concentrations decreased once watering was stopped. A similar behaviour was observed for Mg, however the input

water concentration was not reached in the effluent during both watering periods.

The peaks in Ca, S, and Mg concentrations in C4 effluent appears to be smoother than for C1. The slightly lower flowrate and slightly different physical properties of its waste rock may be responsible, at least in part, for the different shape of its concentration spikes. Ca, S, and Mg concentrations in the effluent rose during the first watering period, reaching approximately half of the input water concentration. When watering stopped, the Ca, S and Mg concentration steadily decreased, until the second watering period. The concentrations in the effluent were higher than during the first watering period, but lower than the input water concentration. The concentration in the effluent slowly decreased once watering stopped.

4.4 Co concentrations

Figure 11 presents the evolution of the cobalt concentrations in the effluent of cell C4. For C1, the Co concentrations were below the detection limit (<0.004 mg/L) throughout the test. The C1 input water had 0.5 mg/L Co while the input water for C4 contained 0.55 mg/L Co. Co concentration in C4 effluent followed the same evolution as Ca, S, and Mg. The Co concentration in the effluent rose to approximately 0.35 mg/L during the first watering period, then near 0.5 mg/L during the second watering period. The Co concentration in the effluent then decreased steadily to reach 0.2 by the end of the test.

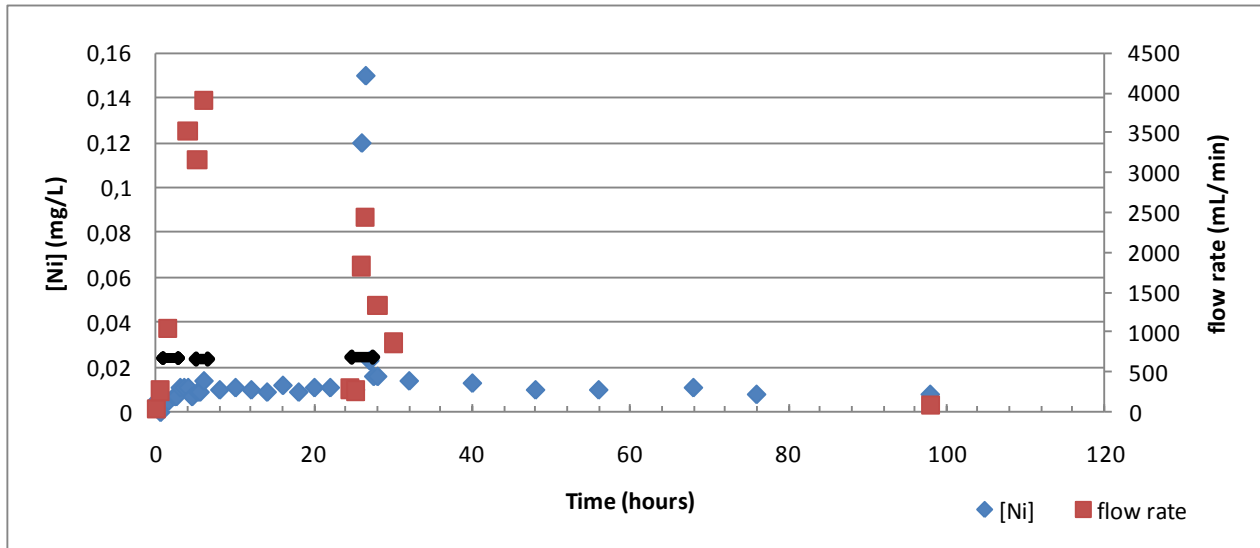


Figure 5: Ni concentration and flow rate measured at the effluent of cell C1. Dark arrows indicate watering periods.

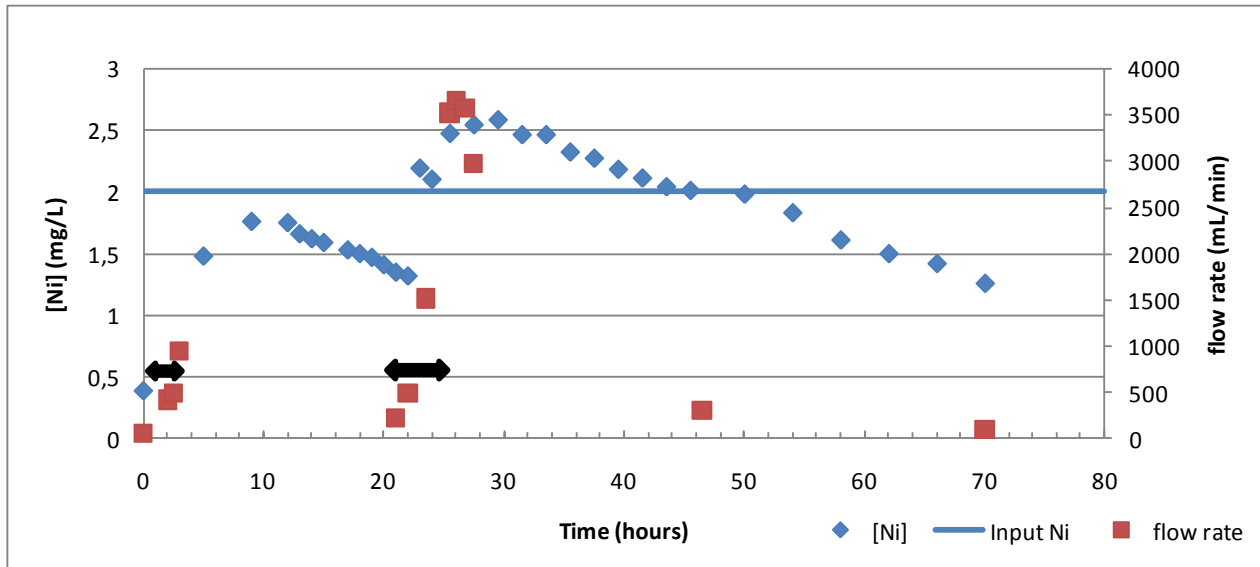


Figure 6: Ni concentration and flow rate measured at the effluent of cell C4 (points). Dark arrows indicate watering periods. Solid line indicates input water concentration.

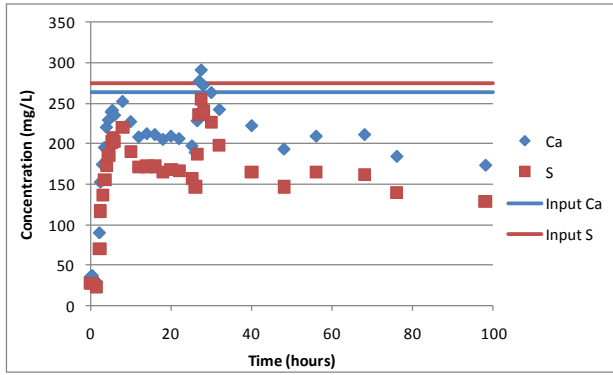


Figure 7: Ca and S concentration in C1 effluent (points). Solid line indicates input water concentration.

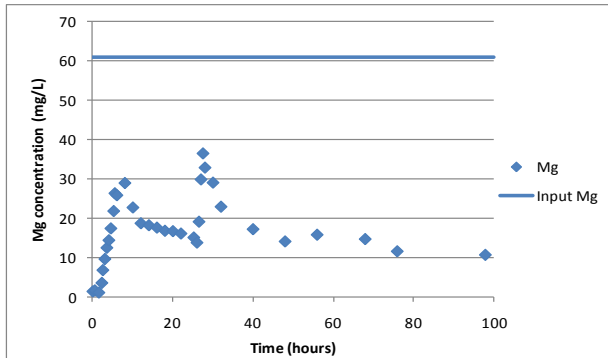


Figure 8: Mg concentration in C1 effluent (points). Solid line indicates input water concentration.

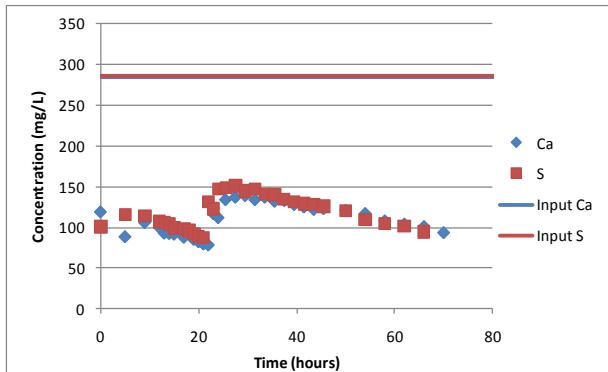


Figure 9: Ca and S concentration in C4 effluent (points). Solid line indicates input water concentration.

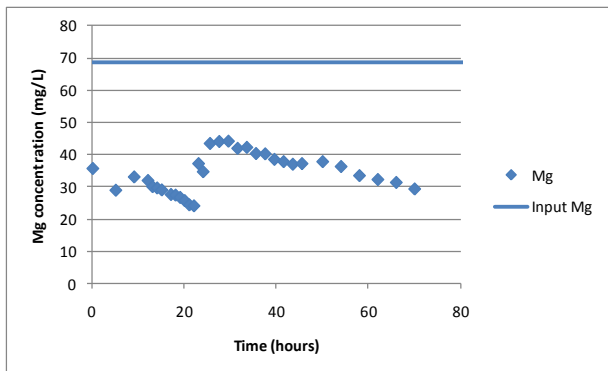


Figure 10: Mg concentration in C4 effluent (points). Solid line indicates input water concentration.

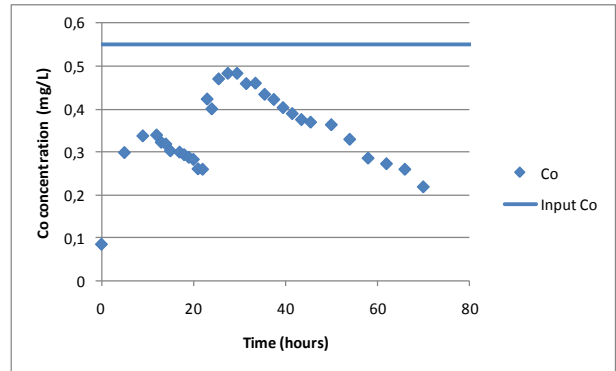


Figure 11: Co concentration in C4 effluent (points). Solid line indicates input water concentration.

5 INTERPRETATION

5.1 Dispersion behaviour

The retention test performed on both cells can be related to a tracer test in which the tracer is the input water. Therefore, the evolution of most metal concentrations in the effluents of C1 and C4 can be attributed to a typical plug-flow reactor with some degree of back-mixing (or dispersion; Levenspiel, 1972). To normalize the data, the fractional concentration F_t was calculated using:

$$F_t = C_t / C_0 \quad [1]$$

Where C_t is the concentration at time t and C_0 is the concentration in the input water. It is presented in Figures 12 and 13 for C1 and C4 respectively.

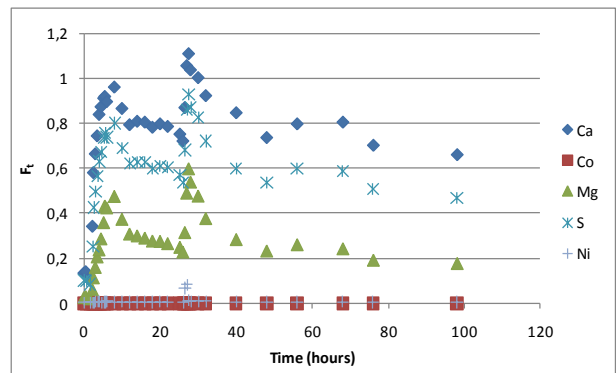


Figure 12: Fractional concentrations in C1 effluent

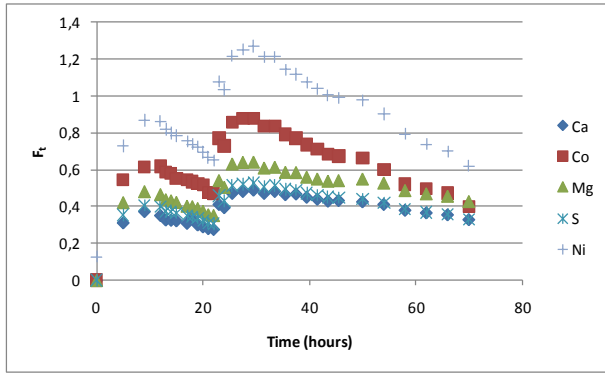


Figure 13: Fractional concentrations in C4 effluent

The fractional concentration evolution of a pulse tracer addition to a plug-flow reactor with dispersion can then be approximated by a solution to Fick's second law (Guthrie, 1993):

$$F_t = \frac{1}{2} \left(1 - \operatorname{erf} \left(\frac{1-\theta}{\sqrt{\frac{4D_E}{L\bar{U}}}} \right) \right) \quad [2]$$

Where Θ is the fractional holding time ratio (t/\bar{t}) (\bar{t} being the residence time), and $D_E/L\bar{U}$ is the dispersion number (or the inverse of the Peclet number). Figure 14 presents the comparison between the field data obtained for the first sprinkling period and a typical theoretical fractional concentration calculated using equation 2 with a dispersion number of 0.4. For C1, Mg fits relatively well equation 2, while Ca and S show higher fractional concentrations than the theoretical values, possibly because of dissolution of Ca and S-bearing minerals (sulphide oxidation neutralized by plagioclase dissolution). The elevated concentrations after the peak may be explained by some degree of dead volume (defined as material being retained in the cell for more than twice its residence time) (Guthrie, 1993). Ni concentrations remain very low throughout the test, so they cannot be approximated by equation 2, and the behaviour may not be attributed to a typical flow system in a plug-flow reactor with dispersion. In summary, Ca, S, and Mg behaviour in C1 may be explained by the dispersion mechanism of the flow, whereas Ni behaviour does not fit the model.

For C4, the behaviour of all elements (Ca, S, Mg, Ni, Co) presented in Figure 14 may be approximated by equation 2 with a dispersion number of 5. They all follow a similar pattern, with initial and final concentrations being different, however their behaviour may be attributed to a typical flow system in a plug-flow reactor with dispersion.

The plug-flow system with dispersion accounts for tracer migration within the cell, it does not incorporate any geochemical processes, such as precipitation, sorption, and dissolution.

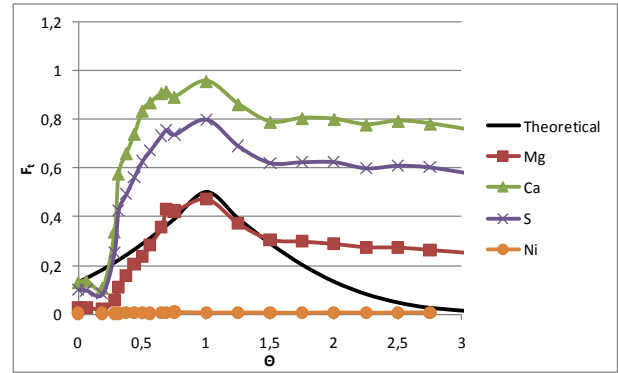


Figure 14: Comparison between measured F_t and typical theoretical F_t for C1 effluent for the first watering period.

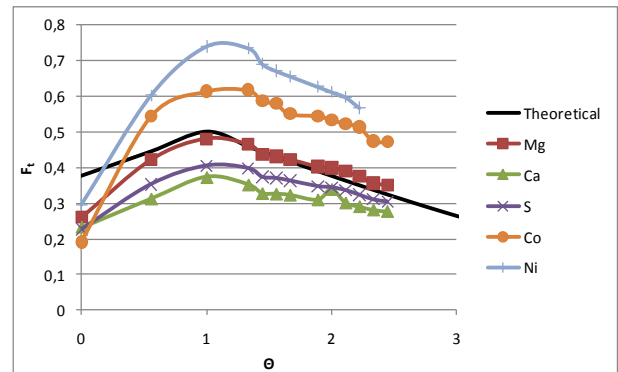


Figure 15: Comparison between measured F_t and typical theoretical F_t for C4 effluent for the first watering period.

5.2 Geochemical behaviour

Since nickel and cobalt behaviour in C1 cannot be approximated by the dispersion mechanism, other processes must influence their behaviour. Geochemical processes may explain the low concentrations obtained at the effluent, such as sorption and precipitation.

The geochemical behaviour of aqueous Ni is linked to the pH of the system. Figure 16 presents the speciation of Ni according to pH obtained with VMinteq (Felmy et al. 1984). For a pH value of approximately 7, Ni is mainly found as aqueous Ni^{2+} , whereas Ni hydroxide begins to occur mainly at pH above 9.

Geochemical modelling was used to further verify the possibility of Ni-bearing (and other) mineral precipitation for the conditions of the field test. The code VMinteq (Felmy et al. 1984) was used to calculate the saturation indices of a variety of minerals according to the effluent composition and conditions. No Ni- and Co-bearing minerals were identified as being in supersaturated state, therefore no secondary Ni or Co mineral should precipitate under the conditions of the test. Iron minerals, such as goethite, hematite, and lepidocrocite are supersaturated and may precipitate. Magnesioferrite, a Mg-bearing mineral is in supersaturated state, so may precipitate and retain some Mg within the cells. The precipitation may explain the lower concentrations observed at the effluent of both cells. No calcium or sulphate minerals were identified as supersaturated,

therefore Ca and S should remain in solution. However, an important assumption of geochemical modelling is that the system is at equilibrium, which may not be the case for the field test.

Considering that the possibility of Ni being retained as precipitate during the test is very low, sorption becomes the most likely mechanism that explains the low Ni (and Co) concentrations in the effluent of C1. Previous laboratory work performed on the same waste rock showed that the freshly blasted waste rock (i.e. C1) has significant Ni sorption capacity, while weathered waste rock (i.e. C4) has very limited sorption capacity (Plante et al. 2010a, 2010b). Previous laboratory results also identified the sorbed species as nickel hydroxide $\text{Ni}(\text{OH})_2$ (Plante et al. 2010c). The high sorption capacity of fresh waste rock corresponds well to the results obtained for C1, while C4 being made of weathered waste rock has exhausted its sorption capacity and can no longer retain Ni and Co by sorption.

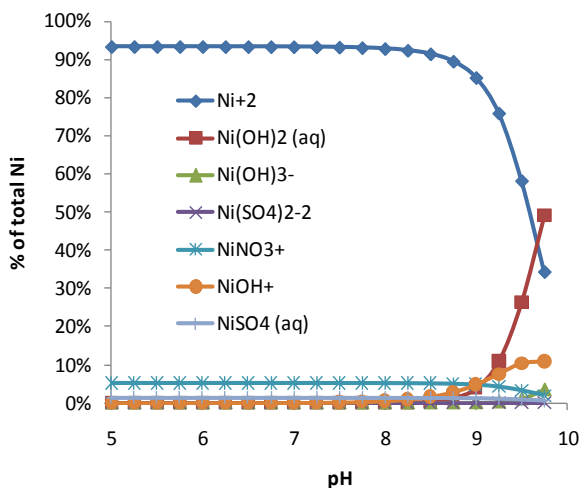


Figure 16: Aqueous Ni speciation for pH between 5 and 10

6 CONCLUSIONS

The objective if the field work was to validate laboratory results that suggested that sorption capacity of fresh and weathered waste rock is different. The watering of two waste rock field cells with Ni-enriched water showed that the fresh waste rock was able to maintain very low Ni concentrations in its effluent, while the weathered waste rock released most if not all the Ni that was added with the input water, therefore had barely any retention capacity. While the behaviour of calcium, magnesium, and sulphur can be attributed to dispersion, the behaviour of nickel and cobalt is explained by sorption in the case of C1. The behaviour of Ca, Mg, S, Ni, and Co in C4 can be explained, at least in part, by dispersion.

Geochemical modelling using VMinteq confirmed that no Ni- and Co-bearing minerals are likely to precipitate, assuming equilibrium conditions. Furthermore, under the test conditions, Ni is present mostly as aqueous Ni^{2+} ion.

The results from the field campaign confirm the hypothesis that sorption of nickel is a significant factor in

CND generation at this mine site. Further work, which involves numerical modelling of the water flow and geochemical evolution using numerical tools such as MIN3P and VADOSE, will be performed to better interpret the test results.

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