# **Geochemical Behaviour of Nickel Contained in Tio Mine Waste Rocks**

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## Abstract

In this study, humidity cells (ASTM D5744-96) were used for contaminated neutral drainage (CND) prediction from waste rock piles of an ilmenite deposit known to occasionally release above-level nickel loadings. The influence of mineralogy and in-situ alteration degree of waste rock on its geochemical behaviour are investigated, using samples of waste rocks having various mineral compositions and which underwent different alteration times in the waste rock piles (fresh to approximately 25 years old waste). The nickel adsorption potential of the studied waste rocks appears to play a significant role on the nickel geochemical behaviour.

## Introduction

Acid mine drainage (AMD) is often characterized by low pH, high acidity, and high metal loadings. The phenomenon received much attention in the past decades in terms of prediction, control, and remediation. However, many toxic metals such as nickel, zinc, cobalt, arsenic, and antimony are soluble at near-neutral pH, and can potentially lead to the contamination of mine effluents without the presence of acidic conditions; this phenomenon is called contaminated neutral drainage (CND) (Nicholson, 2004). Since many Canadian mines can potentially face nickel release from waste rock, and nickel geochemistry received much less attention than other CND-related elements (ex. As) in the past years, this work focuses on nickel geochemistry at near-neutral conditions.

The present study is performed on waste rock from the Lac Tio mine, an ilmenite deposit near Havre-Saint-Pierre, Québec, Canada, exploited through an open pit operation by QIT-Fer et Titane Inc. since the early 1950's. Waste rock piles from Lac Tio mine, estimated at over 70 Mt, cover approximately 92 ha and are between 20 and 80 meters high. Water draining from waste rock piles are near-neutral and sporadically show nickel concentrations slightly higher than those allowed by local regulations. Preliminary studies on this waste rock showed that nickel is generated mainly from the dissolution of nickel-bearing pyrite and pentlandite, sulphides that seem to be associated with ilmenite in the Lac Tio deposit, and that the waste rock beneficiate from an important metal retention potential most probably occurring via surface adsorption (Bussière et al., 2005).

## Materials and methods

In this work, 6 Lac Tio waste rock samples are investigated: 3 samples of freshly blasted waste rock and 3 "altered" samples from an old waste rock pile (approximately 25 years old) which underwent significant natural alteration. Table 1 lists the names and ilmenite content of the waste rock samples studied. Nickel content ranges from 0.028 to 0.043 wt% and sulphur content ranges from 0.142 to 0.384 wt% in the studied samples; altered samples have significantly lower sulphur values (<0.172 wt%) than fresh samples(>0.345 wt%), probably due to alteration. Such a sample configuration enables the evaluation of the alteration degree and ilmenite content effects on geochemical behaviour of the wastes, which was evaluated through the use of humidity cell tests (ASTM D5744-96). This procedure consists of weekly drying-wetting cycles ending with flushing of the studied material with deionized water, which is then analyzed for various geochemical parameters.

	C1	C2	C3	C4	C5	C6
Sample age	Freshly	Freshly	Freshly	25	25 years	25
	blasted	blasted	blasted	years		years
Ilmenite content	low	intermediate	high	low	intermediate	high
S (wt%)	0.384	0.345	0.472	0.142	0.164	0.172
Ni (wt%)	0.028	0.032	0.043	0.031	0.033	0.037

Table 1 General description of the Lac Tio waste rock samples studied

## **Results and discussion**

Some of the key geochemical results of the humidity cell tests are shown in Figure 1. Before approximately 150 to 200 days, "fresh" waste rock samples (C1, C2 and C3) generated drainage waters having pH values slightly higher than the 25 years old waste rock samples ("altered" samples C4, C5 and C6). The pH values from both fresh and altered waste rock samples gradually tend to show smaller differences. All pH values are between 6.5 and 9.0, with a slight decreasing tendency. Conductivity values are stabilized between approximately 15 and 70  $\mu$ S/cm from 150 days up to over 300 days. Fresh waste rock samples show higher conductivity values (between 25 and 70  $\mu$ S/cm) than the altered waste rock samples (between 15 and 25  $\mu$ S/cm).

Aluminum and calcium release are associated with gangue minerals, mainly plagioclase in the Lac Tio deposit. Aluminum levels of the fresh waste rock samples vary between 0.05 and 0.30 mg/L up until 250 days, where aluminum values gradually dropped below 0.10 mg/L from 275 days on. Aluminum values of the altered waste rock samples are generally close to or below the method detection limit (MDL) of 0.01mg/L illustrated with the dotted line. Calcium values show a tendency similar to aluminum values with the fresh waste rock samples (stabilized between 3 and 10 mg/L since 75 days) having higher values than altered waste rock samples (stabilized under 2 mg/l since 150 days). Calcium levels from the fresh waste rock samples show a decreasing tendency and are getting closer to the aluminum levels of altered waste rock samples.

Plagioclase dissolution is known to be incongruent, with aluminum and calcium being preferably dissolved at the surface. This dissolution generates an aluminum/calcium-poor thin layer at the mineral surface, which is consistent with the lower aluminum and calcium levels obtained in the leaching waters of the altered waste rocks. Sulphur levels associated to the oxidation of sulphide minerals are very similar for all waste rock samples and are stabilized under 2 mg/L since 125 days, suggesting similar sulphide oxidation kinetics for fresh and altered waste rock samples. Aluminum and calcium values seem to be related to sulphide values, suggesting that plagioclase depletion is a response to the acid-generating oxidation of the sulphide minerals. Nickel levels are close to the MDL (0.004 mg/L, dotted line) and no general tendency can be observed for nickel values.

The low nickel values obtained in humidity cell tests are inconsistent with field observations, where nickel concentrations are sporadically higher than those allowed by Canadian regulations (0.5 mg/L). Geochemical simulations of water quality demonstrated that nickel is soluble in the test conditions, eliminating secondary mineral precipitation as an explanation for the absence of nickel in leached waters. Consequently, these discrepancies between lab and field observations could be explained by the metal retention potential of the Lac Tio waste rock which is still active in the humidity cell tests. As a result, although nickel is actually generated in the humidity cell tests as demonstrated by sulphur release, it is retained by the waste rock until saturation of the retention sites.

The nickel adsorption potential of the freshly blasted waste rock samples (C1, C2 and C3) was verified using alteration cells (Cruz et al., 2001). Those small-scale humidity cell tests (alteration cells only require about 70 g of material) enable to work on smaller samples and are known to be slightly more aggressive than the humidity cell tests while rendering similar geochemical responses (Villeneuve et al., 2004). The waste rock samples in alteration cells were leached using nickel-contaminated water (2.0-2.5 mg/L nickel) taken from a pond at the mine site. Major ion analyses were performed at each lixiviation cycle both on the contaminated water and the water leached through the waste rock samples. Figure 2 shows that all waste rock samples show limited nickel adsorption capacities, as nickel concentrations coming out of the alteration cells become very close to the contaminated leaching water used after approximately 175 days, and may in the near future surpass the nickel level of the contaminated leaching water.



Figure 1 Partial geochemical results of the humidity cell tests on Lac Tio waste rocks

*Figure 2* Nickel retention of the freshly blasted waste rock samples from the lixiviation of contaminated waters in alteration cells



## Conclusions

Many geochemical processes influence nickel concentrations in the Lac Tio waste rock samples. This study highlights ilmenite content, alteration degree, and nickel surface adsorption as key parameters affecting nickel geochemistry of these waste rocks. Further research is underway, such as identification of the minerals responsible for retention, their retention capacities and stabilities, and determination of the nickel generation potential and mechanisms.

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