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Les effets potentiels du projet d'exploitation  
d'une mine et d'une usine de niobium à Oka  
sur les eaux de surface et les eaux  
souterraines ainsi que sur leurs utilisations  
Oka 6211-08-003



Le 15 ~~18~~ avril 2003

ENVIRONNEMENT  
REÇU LE

15 AVR. 2003

DIRECTION RÉGIONALE  
DES LAURENTIDES

**Madame Dorothee Benoit**  
MINISTÈRE DE L'ENVIRONNEMENT  
Direction régionale des Laurentides  
140, rue St-Eustache, 3<sup>e</sup> étage  
Saint-Eustache (Québec)  
J7R 2K9

**Objet : Rapport d'expertise concernant la problématique des fluorures dans  
les eaux souterraines – Projet minier Niocan**  
N/Réf. : 20611-000

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Madame,

Vous trouverez ci-joint deux exemplaires du rapport d'expertise portant sur la problématique des fluorures dans les eaux souterraines suite à l'entreposage de la pulpe de résidus miniers de l'exploitation du site Niocan dans les fosses du site St-Lawrence Columbium.

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Le rapport a été produit par le Dr. Frederick Michel, professeur associé au Département des Sciences de la terre de l'Université Carleton à Ottawa. Le Dr. Michel qui est hydrogéologue, a déjà été impliqué dans un projet d'étude de la présence de fluorures dans des eaux souterraines au Ghana. Le curriculum vitae du Dr. Michel est joint à la présente.

Comme vous pourrez le constater à la lecture du rapport d'expertise, le Dr. Michel est convaincu que la teneur en fluorures dans les eaux souterraines en aval des fosses demeurera inférieure au critère de 4 mg/L contenu dans la Politique de protection des sols et de réhabilitation des terrains contaminés.

Veuillez agréer, Madame, l'expression de nos sentiments les meilleurs.

Yves Thomassin, ing. f., M.Sc.A.  
Chargé de projet

c.c. M. Richard Faucher, dir. gén., Niocan inc.



**ENVIRONNEMENT  
RÉGULÉ**

**15 AVR. 2003**

**DIRECTION RÉGIONALE  
DES LAURENTIDES**

**EVALUATION OF THE IMPACT  
OF THE  
NIOCAN MINING PROJECT  
ON  
THE FLUORIDE CONTENT  
OF  
GROUNDWATER**

**For  
Roche Ltée, Groupe-conseil  
Sainte-Foy, Quebec**

**By  
Dr. F. A. Michel  
Department of Earth Sciences  
Carleton University  
Ottawa, Ontario**

**April 7<sup>th</sup>, 2003**

## **Executive Summary**

The highest fluoride concentrations in natural groundwaters of the area are found in gneisses marginal to the Oka carbonatite complex, where Ca-Na exchange reactions appear to be controlling the dissolved fluoride concentrations. Slurry waters that are to be discharged into the old open pits of the former St. Lawrence Columbian property by Niocan Inc. will react with abundant coarse-grained calcite in the pit walls and bedrock. Calcite dissolution will make fluorite solubility the controlling process for fluoride levels in the slurry waters. Elevated calcium concentrations, due to calcite dissolution, should lead to fluorite precipitation and dissolved fluoride concentrations of less than 1.5 mg/L, the CMAC guideline for drinking water, and well below the Ministry of Environment target for Niocan Inc. of 4.0 mg/L.

## **Introduction**

On February 28, 2003, I was asked by Mr. Yves Thomassin of Roche L  e to examine the impact on local groundwaters of elevated fluoride concentrations in process waters associated with the proposed mining activity of Niocan Inc. in the Oka carbonatite complex near Oka, Quebec.

It is my understanding that during mining operations Niocan Inc. plans to discharge a slurry containing about 30% solids into two old open pits at the nearby former St. Lawrence Columbian property. The slurry will contain approximately 15 to 35 mg/L fluoride due to the use of fluoric acid and fluorosilicic acid during treatment of the ore. The pit walls are considered to be fractured, which will permit the flow of fluids into the surrounding rock. The concerns of the Ministry of the Environment relate to the possible contamination of surrounding groundwater by raising the fluoride concentrations to in excess of 4.0 mg/L.

The purpose of this report is to examine the concerns of the Ministry of the Environment and the potential for high fluoride levels in the surrounding groundwaters.

## **Fluorine Geochemistry**

Fluorine occurs primarily as a free fluoride ion in natural waters, however, complexes can be formed with H, Al, Be, Fe, Si, and B under suitable conditions that generally include slightly to strongly acidic conditions. The concentration of fluoride in natural waters is usually less than 1.0 mg/L, but can increase to values exceeding 10 mg/L in certain geologic settings due to fluorite dissolution and various other chemical processes (Hem 1985, Apambire et al. 1997, Datta et al. 2000, Kundu et al. 2001). In addition to fluorite dissolution, fluorine can also be contained in the structure of minerals such as apatite, amphiboles, micas, certain clay minerals (illite, chlorite, smectites) and villiaumite. Elevated fluoride concentrations are often associated with granitic rocks, late stage pegmatitic rocks, and thermal waters associated with granitic plutons and recent

volcanism (Hem 1985, Hamilton et al. 1988). Hem (1985) has also noted that a number of sedimentary basins contain fluoride concentrations in excess of 1.0 mg/L.

Fluorite solubility is the main control on dissolved fluoride concentration in natural waters that contain calcium concentrations in excess of that required for fluorite equilibrium. A strong negative correlation usually exists between calcium and fluoride. In waters that experience cation exchange reactions (Ca-Na), the fluoride concentration increases with increasing sodium levels; the mineral villiaumite (NaF) is an extremely soluble salt. In many sodium-rich waters, the elevated fluoride concentrations actually occur because Ca - Na exchange reactions cause the waters to become deficient in calcium (thus undersaturated with respect to calcite and fluorite) and permit continued fluorite dissolution. As the calcium continues to be lost due to cation exchange, the fluoride concentration continues to increase. Due to the similar size of the fluoride and hydroxyl (OH) anions, competition for anion exchange sites on clays and aluminum complexes tends to favour increased fluoride concentrations in the water with increasing pH. The highest fluoride concentrations reported in the literature are for natural waters with a pH greater than 9.5 (Hem 1985, Gaciri and Davies 1993).

Artificially generated waters, such as mine process waters, are subject to the same geochemical controls as natural waters, however; these waters initially may not have the same broad distribution of ionic species as natural waters. Once these waters are discharged into holding ponds and encounter natural soil or rock materials, their chemistry will become modified and they will evolve toward natural waters and become subject to normal natural geochemical controls. Poulsen and Dudas (1998) experimentally demonstrated that acidic process water with elevated fluoride concentrations from a phosphogypsum plant underwent a rapid change in pH when it encountered calcareous soils, and the fluoride concentrations decreased to below the Canadian Maximum Acceptable Concentration (CMAC) guidelines for drinking water (1.5 mg/L). This same guideline is followed throughout Canada, including Quebec.

## **Health Considerations of Fluoride in Water**

Fluorine is required for the development of good bones and teeth in humans. Small quantities (1.0 to 3.0 mg/day) are beneficial, however; larger doses (>4.0 mg/day) can result in diseases such as dental and skeletal fluorosis. The World Health Organization (1994) has set an upper limit of 1.5 mg/L based on a daily water consumption rate of 2 L, an average adult body mass, and a standard diet containing 0.2 to 0.5 mg fluorine. Areas of the world where fluorosis is a problem have fluoride concentrations in the water exceeding 4 to 5 mg/L, or have hot climates that result in an increased daily water intake by the inhabitants (Apambire et al. 1997). Brouwer et al. (1988) found that in Senegal 68.5% of the children had mild dental fluorosis at the 1.0 mg/L level due to increased water consumption above the 2 L/day assumption.

## **Site Geology**

The Niocan mining project is located within the Oka complex, approximately 35 km west of Montreal and immediately north of Lake of Two Mountains. The area consists of rolling topography with a maximum relief of 92 metres and an oval-shaped depression overlying the complex. Bedrock topography has a relief of up to 215 metres and clearly defines a crater-like morphology (Gold 1972). Overburden thickness ranges from absent (outcrops) to as much as 120 metres in places.

The Oka complex is part of the Monteregian Hills Petrographic Province (Adams 1903), which contains a series of Cretaceous-age alkaline igneous intrusions. The Oka Complex is dominantly a carbonatite intrusion with a "distorted figure 8 shape" (Gold 1972). The five main rock types include carbonate-rich rocks underlying about half the surface area, pyroxenites, nephelinites (silica poor), glimmerites, and late intrusive breccias and lamprophyres (Gold 1972). The intrusion is within an inlier of Precambrian gneisses that are surrounded by Paleozoic sedimentary rocks.

The mineralization for the former St. Lawrence Columbian (Niobium) mine consists of pyrochlore-bearing sovite (Gold et al. 1986). Sovite is essentially a coarse-grained calcite (calcium carbonate) containing some pyroxene, biotite, apatite, and magnetite accessory minerals. Pyrochlore usually contains some fluorine in its mineral structure. The two open pits of the St. Lawrence mine will receive the slurry discharge from the Niocan mill.

The solid portion of the slurry discharge will reflect the mineralogical composition of the gangue minerals in which the ore minerals are contained. Since the dominant rock type (sovite) is essentially calcite, the slurry solids will be largely composed of crushed calcite. An analytical report by Golder Paste Technology Ltd. (1999) on the slurry solids, provided by Roche Ltee, shows that abundant calcite is present (CaO is 40% of total). An analysis on the liquid portion of the slurry was also provided by Roche Ltee. It indicates that the pH is slightly acidic (6.1) and that the liquid contains some calcium (45 mg/L) and a small amount of sodium (18 mg/L). Overall the total dissolved solids content of the liquid is low.

## **Groundwater and Water Geochemistry**

The headwaters of most streams in the area originate within the boundaries of the carbonatite intrusive and flow either northeast or southwest toward the margins. Thus shallow groundwater flow is expected to be primarily northwest and southeast toward these streams. The intrusive complex forms a large crater-like depression (bedrock surface) infilled by a varying thickness of sediment. Large hills occur southwest (Montagne du Radar) and northeast of the complex and may direct deeper groundwater flow toward the center of the complex. A figure provided by Roche Ltée, from a 1999

environmental impact study (project # 20611) undertaken for Niocan Inc., indicates that this is the case.

Groundwater geochemistry data for the area were obtained from the Ministère de l'Énergie et des Ressources, Québec (1985, 1986) and from Roche Ltée. The Ministry data indicate that fluoride concentrations in the center of the complex (along Chemin Sainte-Sophie) range from 0.1 to 0.8 mg/L, while calcium concentrations vary from approximately 25 to 120 mg/L. The highest fluoride concentrations in the area occur in groundwaters sampled from gneisses marginal to the complex, along Rang du Domaine (NE), Rang Sainte-Germaine (N), and Rang de l'Annonciation (W). Fluoride concentrations in these waters are up to 2.50 mg/L, while calcium concentrations are generally < 40 mg/L for the fluoride-rich waters. Fluoride concentrations decrease as calcium concentrations increase.

A number of surface water analyses were provided by Roche Ltée for the two open pits, decant tower outlet, and local streams. Fluoride concentrations in these waters ranged from 0.1 to 11.4 mg/L, while calcium concentrations ranged from 14 to 160 mg/L. Several well water analyses were also provided, but most of them did not contain fluoride values.

The geochemical data were analysed with the computer program SOLMINEQ, developed by the Alberta Research Council in 1988, to examine solubility controls for fluorine and saturation indices. Essentially all waters were found to be saturated with respect to calcite, which is not surprising given that the carbonatite complex contains calcite as one of the dominant minerals. The Quebec Ministry data did not include phosphate analyses, however; some of the data from Roche Ltée did. Whenever data for phosphate and fluoride were available, it was found that the waters were extremely oversaturated with respect to fluorapatite. This indicates that fluorapatite, which is present in the Oka rocks and may be one source of fluoride in the groundwater, does not precipitate easily and does not control the concentration of fluoride in the water.

Waters in the study area are generally low in sodium, however; in those instances where sodium concentrations exceed 100 mg/L, calcium concentrations tend to be low (< 40 mg/L) and fluoride concentrations increase. These samples are primarily in the gneisses surrounding the carbonatite complex and may indicate that Ca-Na exchange is occurring in those rocks. The pH of groundwaters and surface waters in the area is neutral to slightly alkaline (7.2 to 8.1) and appears to be controlled by carbonate dissolution. At these pH values, anion exchange reactions involving the hydroxyl ion are not expected to affect fluoride concentrations.

The presence of abundant calcite will make fluorite solubility the main control. A strong correlation between fluoride concentration in the area waters and the fluorite saturation index indicates that saturation with respect to fluorite is being achieved when fluoride concentrations reach approximately 2.0 mg/L and calcium concentrations are at 40 mg/L. Precipitation of fluorite should occur when fluorite saturation is achieved.

Determination of the degree of saturation for water with respect to fluorite is calculated from the solubility product for fluorite and the concentrations of calcium and fluoride dissolved in the water. The saturation index (S.I.) is given as:

$$\text{S.I.} = [\text{Ca}][\text{F}]^2 / K$$

where K is the solubility product of fluorite,  
and [ ] is the concentration of dissolved calcium and fluoride in the water.

The fluoride concentration is squared because there are two moles of fluorine for every mole of calcium in the fluorite mineral structure.

The slurry waters will encounter calcite in the pit walls and surrounding rocks, as well as the slurry solids. Prolonged contact between them will result in calcite dissolution, which will increase the amount of calcium and carbonate ions in the water. The carbonate ions will consume (complex with) any excess hydrogen ions and result in a slightly alkaline pH, similar to that seen in the local natural waters. The increased calcium concentrations will in turn lower the concentration of fluoride required for saturation conditions with respect to fluorite to be attained. Therefore, as long as calcite dissolution continues, the excess calcium will result in ongoing fluorite precipitation. Calcium concentrations greater than 40 mg/L should result in fluoride concentrations of less than 2.0 mg/L in the water. To achieve fluorite saturation with a fluoride concentration of 1.5 mg/L (CMAC drinking water guidelines) would require a calcium concentration of only 70 mg/L; less than that found in many of the local groundwaters. As noted earlier, the work by Poulsen and Dudas (1998) on fluoride-rich process water demonstrated that the presence of calcareous soils quickly raised the pH of the acidic process water and decreased the fluoride concentration to below CMAC guidelines. The same geochemical processes should be expected to control the chemistry of the Niocan slurry waters.

## Conclusions

Slurry waters discharged into the open pits of the former St. Lawrence Columbian property will react with coarse-grained calcite in the pit walls and adjacent bedrock, and with crushed calcite in the slurry solids. This will lead to a slightly alkaline pH of between 7.2 and 8.1 for the waters. Excess calcium will make fluorite solubility the controlling factor for fluoride concentrations in the water. Computer modelling of geochemical data for natural waters in the area indicates that saturation with respect to fluorite occurs at fluoride concentrations of approximately 2.0 mg/L and calcium concentrations of 40 mg/L. Higher calcium concentrations should lower the dissolved fluoride concentrations to below the CMAC and Quebec Ministry guidelines for drinking water (1.5 mg/L). Cation (Ca-Na) and anion (OH-F) exchange reactions are not expected to play a significant role in controlling fluoride concentrations in the slurry waters. Therefore, any slurry waters that flow into the bedrock and become part of the groundwater system should have fluoride concentrations well below the Ministry of Environment target for Niocan Inc. of 4.0 mg/L.

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