

MOBILIZATION OF MERCURY FROM A GOSSAN TAILINGS PILE, MURRAY BROOK PRECIOUS METAL VAT LEACHING OPERATION, NEW BRUNSWICK, CANADA¹.

D.R. Boyle² and C.N. Smith³

Abstract: A number of the massive sulfide deposits of the Bathurst mining camp in New Brunswick have well-developed gossans that have been mined and processed by cyanide vat and heap leaching to recover Au and Ag. The Murray Brook deposit is the largest of these gossans (1.9 million mt; 1.52 g/mt Au; 65.86 g/mt Ag). The Hg content of the gossan ranges from 10 to 220 ppm with an average of 36 ppm. Hg in the Murray Brook gossan is present in at least three mineral forms: (1) as an amalgam with native Au and Ag, (2) in cinnabar, and (3) in Sb-Bi-As hydroxy-sulfates. During vat cyanide leaching of the gossan ore, approximately 12% of the Hg is recovered by retorting; the remainder reports to the gossan tailings pile. Monitoring of the ground waters around the tailings pile shows that Hg is the only base metal being leached; during operation, levels of this element in ground waters reached 8,390 ppb (background <0.5 ppb). Time series analyses for monitoring wells show a strong correlation between residual cyanide and Hg levels in the ground waters. Since cessation of vat leaching operations, both the residual cyanide and Hg levels in ground waters have progressively decreased, with minor perturbations occurring during spring freshets. The mobilization of Hg from the gossan tailings pile is thought to be due to a slow kinetic reaction between residual cyanide and cinnabar.

Additional Keywords: mercury, cyanide, cinnabar, gossan, gold, ground water, vat leaching.

Introduction

During cyanide leaching operations at Au-Ag mining operations, special attention is given to the possible concentration and mobilization of such elements as Cu, Pb, Zn, Hg, Ni, Fe, and Co within the environments of these sites. This is because these elements form relatively stable complexes with cyanide and generally occur in the group of cyanide minerals (base-metal sulfides) that often plague the efficiency of cyanide leaching as well as effluent treatment. With the exception of Co^{3+} and Fe^{3+} , Hg forms stronger complexes with cyanide than the metals mentioned above, and given the presence of numerous mineral forms in which this element can occur and its potential bioaccumulative toxic effects in the environment it is important to understand fully the factors that control the concentration and mobilization of Hg in cyanide leaching operations, especially heap and vat leaching waste disposal piles where residual cyanide often remains for some time. Problems with Hg mobilization in these environments may also be compounded by the fact that Hg does not respond to traditional lime neutralization-precipitation processes.

The present study describes the geochemical behavior of Hg and cyanide in surface and ground waters at the first precious metal vat-cyanide-leaching operation to be established in Canada (Murray Brook Mine, New Brunswick).

Geology, Mineralogy, and Geochemistry

A number of the massive sulfide deposits of the Bathurst Mining Camp in New Brunswick have well developed overlying supergene zones which formed prior to the last glaciation (fig. 1). Tonnages for these gossan deposits range from 20,000 to just under 2 million mt (Murray Brook); three of these deposits have been mined for Au and Ag. The Murray Brook gossan deposit is the largest mined to date and contains 1.7 mt tonnes grading 1.52 g/mt Au and 65.86 g/mt Ag (Rennick and Burton 1992).

The gossan zone at Murray Brook is composed of goethite, quartz, secondary amorphous silica, a number of hydrated sulfate and oxide minerals containing combinations of K-Fe-Pb-As-Sb-Ag (beudantite, plumbojarosite, jarosite, bindheimite), scorodite [$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$], cassiterite (SnO_2), and trace amounts of cinnabar (HgS). Native Ag and Bi occur in the gossan, and Au, although not directly, is also assumed to

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²D.R. Boyle, Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, Canada, K1A 0E8.

³C.N. Smith, NovaGold Resources Ltd, 774 Main St., Beresford, New Brunswick, E0B 1H0.

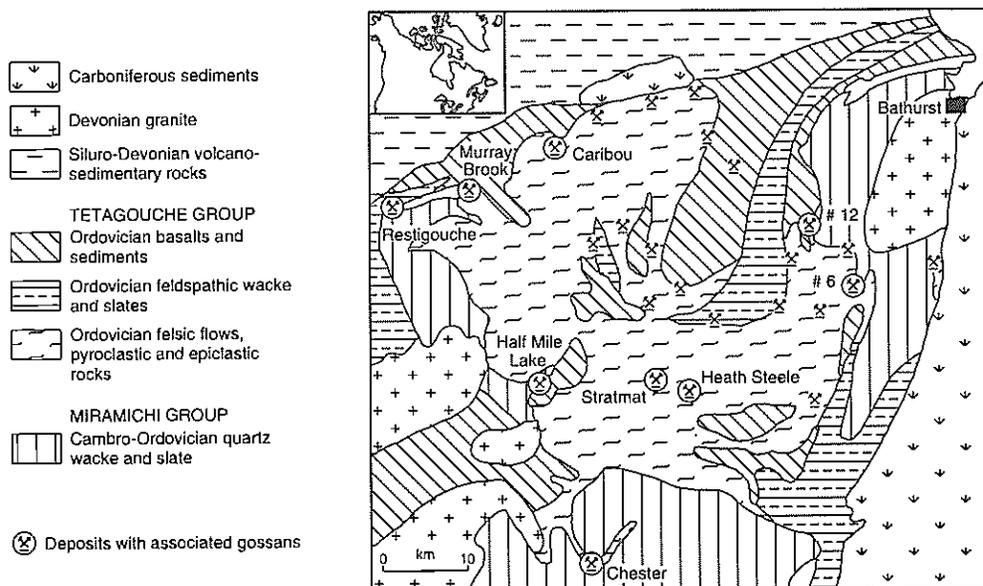


Figure 1. Geology of Bathurst Mining Camp showing locations of massive sulfide mineral deposits with associated supergene ore zones.

be in the native form (Boyle 1992). Pyrite in the gossan is only present in trace amounts at the gossan-supergene sulfide zone contact.

Mercury in the gossan has an average concentration of 36 ppm and a range of 10 to 220 ppm. Most of the Hg is present in the form of cinnabar (HgS), which occurs as submicron grains and veinlets in goethite, often associated with void structures. Some of the Hg is associated with native silver and presumably native gold. On average, the cyanide leaching process extracts 12% of total Hg, most of this is considered to be associated with native Au and Ag. Trace amounts of Hg are also associated with the hydrated sulfates, particularly beudantite.

Geochemistry and Mineralogy of Mercury

In the primary environment Hg may be present as a significant component in a wide variety of sulfide minerals (Jonasson and Boyle 1979). In the supergene oxidizing environment Hg is mainly present as cinnabar formed as the result of oxidation of Hg-bearing sulfide minerals. This mineral is perhaps the most stable of all sulfides in oxidizing environments, with solubilities of 5, 15, and 120 $\mu\text{g/L}$ at pH values of 3.0, 7.0, and 9.0, respectively (Schwartzbach and Widmer 1963). In weathered materials that make up the ore for many heap and vat cyanide leaching operations, cinnabar is the most common Hg-bearing mineral.

In the secondary environment, Hg is of great concern as a toxicant because during methylation processes, in both aerobic and anaerobic environments, it will readily form methyl-Hg complexes which are easily concentrated in the flesh of many forms of biota (Jonasson and Boyle 1979). In addition, Hg is a strong bioaccumulator in the aquatic food chain and may therefore accumulate in fish to such an extent that their consumption is hazardous to human health and the viability of fishing industries is jeopardized.

Physiography, Climate, and Hydrology

The Murray Brook deposit is located on the side of a hill with a 10° slope (fig. 2). The mill site, tailings pile, and treatment ponds are located at the base of the deposit with the entire operation forming the headland region of Gossan Creek valley. Overburden at the site varies in thickness from 1 to 2 m and consists mainly of sand and gravel glacial till. Bedrock underlying the overburden is strongly weathered and fractured.

The ground water table in the area varies from 2.5 to 5 m and generally follows surface relief; most of the overburden in the area is located in the vadose zone. Both surface and subsurface drainage in the area is channeled into Gossan Creek, which eventually flows into the Eighteen Mile Brook-Upsalquitch River system. Along its course, Gossan Creek receives surface drainage from two significant streams and many ground water springs (fig 2).

The mean annual precipitation in the area is approximately 980 mm, of which about 240 mm falls as snow and thus contributes to the spring freshet.

Mining and Milling Processes

The mining and milling process at Murray Brook began in September 1989 and continued without interruption until April 1992. Mining is carried out using opencast methods with ore being initially stored in a primary ore stockpile (fig 2). The gossan ore is crushed to minus 0.75 cm, and the fines are agglomerated with lime and cement before leaching. The leach material is placed in four indoor vats each with a capacity of 900 mt. Leaching by continuous sprinkling is carried out for 24 h using a free cyanide concentration of 0.7 to 1.0 g/L. The pregnant solution is processed for Au and Ag using the Merrill Crowe zinc dust precipitation method. Mercury, which reports to the precipitate during this process, is recovered by retorting. Because Cu, Zn, and sulfide concentrations are very low in this ore and Fe is not in the sulfide form, cyanide and process water recirculation at this site are optimum.

After vat leaching, the barren ore is washed with clean water for 4 to 6 h. The washed barren ore from the vats is then transported by front end loader to the tailings disposal area, where it is graded.

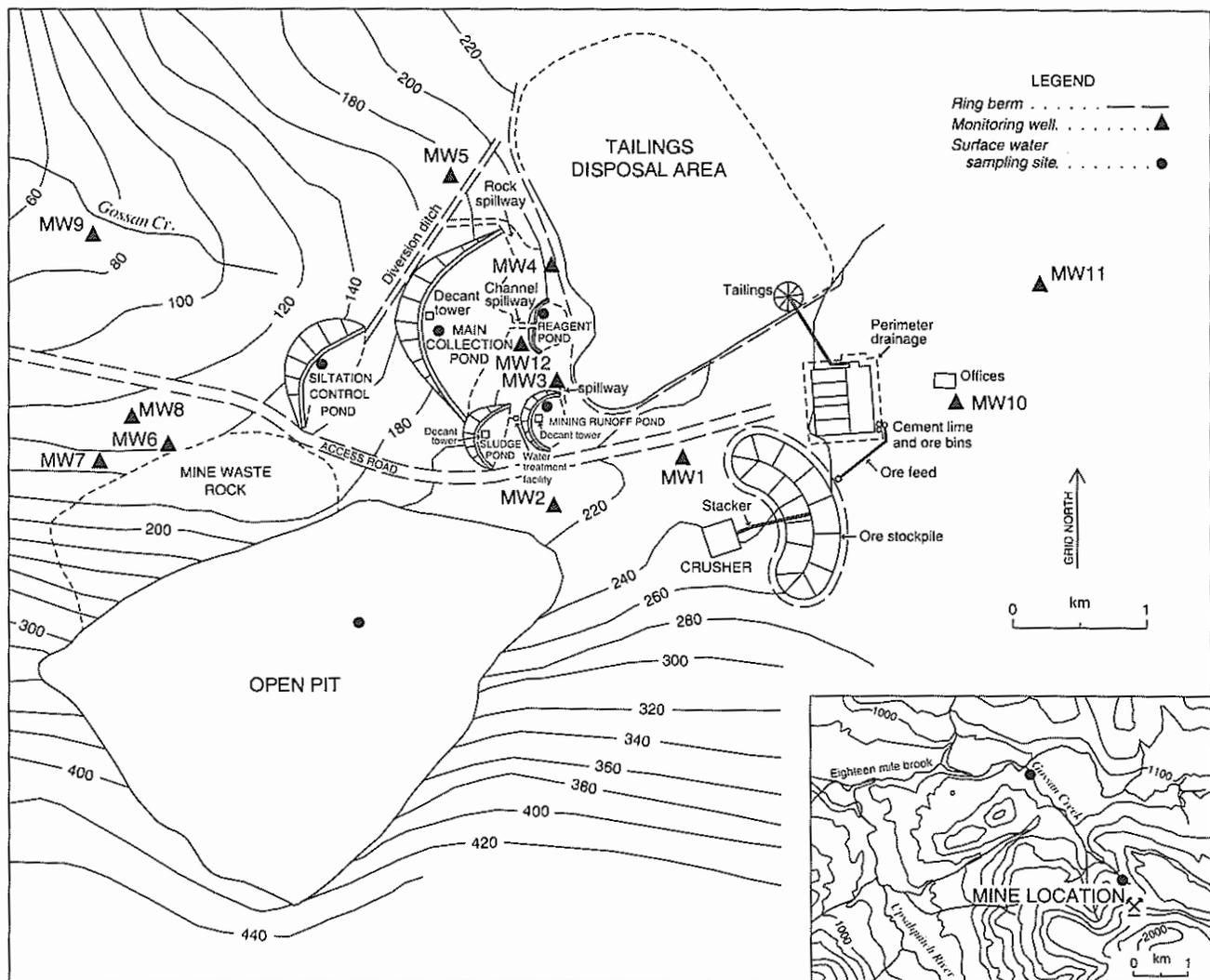


Figure 2. Murray Brook mining operation showing locations of surface and ground water monitoring sites for mine area and baseline study (inset).

Environmental Monitoring Program

Three years prior to mining, a baseline monitoring program was set up on the Gossan Creek-Eighteen Mile Brook-Upsalquitch River system (see insert, fig. 2). Shortly before mining commenced in September 1989, surficial and ground water monitoring networks were established on the site (fig 2). Surficial sampling was aimed at monitoring the composition of open pit water, runoff from various units of the mine site (tailings pile, ore stockpile, mill area), and various pond effluent waters. Twelve ground water wells were established to monitor composition of ground waters associated with the tailings disposal area (MW-4, MW-5, MW-9), the effluent pond environments (MW-3, MW-12), the waste rock pile (MW-6 to 8), the open pit area (MW-2), the ore stockpile (MW-1), the mill and office area (MW-10), and a background area just to the west of the operation (MW-11). All of the ground water monitoring wells are finished in bedrock with the overburden section sealed off from possible surface contamination. In all cases the water levels in these wells were within bedrock.

Surface drainage on the site is channeled through various drainage ditches to the collection ponds near the tailings disposal area, where it can be used as makeup water in the mill and eventually treated if necessary.

Monitoring sites were sampled biweekly from the start of site preparation in September 1989 and will continue to be sampled until the area is reclaimed and considered to be "chemically stable". It is expected that this will be a 'walk away operation' after reclamation.

Water samples from monitoring sites were analyzed consistently for pH, total cyanide, Cu, Pb, Zn, Fe, and Hg, and periodically for As. The pH was measured on site. Total cyanide was measured by a distillation-titrimetric method (method 4500-CN-C of Standard Methods for the Examination of Water and Wastewater, SMEWW), base metals by atomic absorption techniques, As by a hydride atomic absorption method, and Hg by cold-vapor atomic absorption spectrometry (method 3112-B of SMEWW). Ground water samples were not filtered and thus results for cyanide and Hg represent total concentrations.

Results and Discussion

Baseline Monitoring and Regulations

Results from the premining baseline monitoring program established low and high levels in the Gossan Creek-Eighteen Mile Creek watershed as follows: Cu, <0.01 and 0.033 $\mu\text{g/L}$; Pb, <0.01 and 7.9 $\mu\text{g/L}$; Zn, 0.025 and 0.169 $\mu\text{g/L}$; Fe, 0.027 and 0.963 mg/L , and pH, 7.17 and 8.01. At present the pH and concentrations of these metals at the regulatory environmental receiving site (mouth of Gossan Creek) are all within the premining baseline levels mentioned above. Although total cyanide and Hg were not included in the baseline studies, their levels at the receiving site have remained at <0.1 mg/L and <0.5 $\mu\text{g/L}$, respectively, since monitoring began at time of mining. The Federal and provincial regulatory levels imposed on this operation for total cyanide and total Hg at the receiving site are 1.0 mg/L and 10 $\mu\text{g/L}$ respectively.

Tailings Pile Characteristics

The tailings pile at Murray Brook covers an area of approximately 3 km^2 , has a maximum thickness of about 12 m, and constitutes about 1.1 million mt of gossan. Because of coarse crushing and the original porosity of the ore (average 21%), the pile is highly permeable to waterflow and O_2 diffusion.

The paste pH (using 0.01M CaCl_2 adjusted to pH 7.0) of 21 representative samples of the unleached gossan from the open pit averaged 5.20 with a narrow data range of 4.72 to 5.73, indicating that the gossan material will not be significantly acid generating once the lime-cement agglomerating material is dissolved out of the pile. The Hg concentrations of these pH paste solutions were all < 1.0 $\mu\text{g/L}$.

To determine the amounts, variation with depth, and interrelationship of labile cyanide and Hg in the pile, five profile samples of the gossan material were sampled at 1-m intervals to a depth of 6.5 m and leached in the laboratory. The static leaching method consisted of adding 2 kg of gossan to 1.5 L of de-ionized water that had been purged of dissolved oxygen by bubbling N_2 gas through it for 24 h. The gossan was leached without shaking for 48 h, and the leachates were then decanted, filtered (0.45 μm), and stabilized with NaOH solution to pH 12 for total cyanide determination and with concentrated nitric acid to pH 2 for mercury analysis. The results of this experiment (table 1) indicate that total cyanide has degraded considerably in the upper 2 m of the pile compared with lower depths. Roughly half of the cyanide in the 0 to 2 m depth interval has either oxidized in situ or been mobilized by meteoric precipitation, or a combination of both. Using an average total cyanide

concentration for the lower depths of the pile (>2 m) of 5.0 mg/kg and a date of April 1992 for last addition of material to the pile,

a degradation rate for cyanide of about 2.5 mg/kg/yr can be calculated. Given the fact that degradation is probably not linear with depth, this would have to be considered a maximum rate. Using this rate, it would take about 2 yrs for the cyanide in the pile to degrade to nondetectable levels. This compares well with the investigations of Engelhardt (1985), who found that 85% of the free cyanide in a heap leach operation in Arizona was destroyed within 15 months of shutdown.

The data in table 1 show an almost one to one correlation between labile total cyanide and labile mercury in the pile. For the highly stable $Hg(CN)_4^{2-}$ complex, the stoichiometric ratio of Hg to cyanide is 2:1. About half of the cyanide present in the pile can therefore be accounted for as a cyanide-mercury complex. The other half is probably present as other metal-cyanide complexes, particularly $Fe(CN)_6^{3-}$. The pH of ground waters leaving the pile ranges from 5.8 to 7.2, depending on climatic conditions; any free cyanide in solution will therefore be in the HCN form.

Table 1. Results of static leaches, Murray Brook gossan tailings.

Sample depth, m	Total cyanide, mg/kg	Mercury, mg/kg
0.5	2.4	2.7
2.0	2.1	3.6
3.0	7.0	6.4
4.5	4.0	4.2
6.5	5.6	3.0

Surface Water Chemistry

Throughout the monitoring program at Murray Brook, the concentration of total cyanide in stream waters at the head of Gossan Creek has remained consistently below 0.1 mg/L. The Hg concentration at this site remained at background levels until December 1991 and then began to rise steadily to peak at a level of 75 $\mu g/L$ in March 1993, after which it has been steadily decreasing (fig. 3). At the time of peak Hg concentration in stream waters at the head of Gossan Creek, the concentration at the environmental receiving site (mouth of Gossan Creek) remained at baseline levels of <0.5 $\mu g/L$, well below the regulatory level of 10 $\mu g/L$. Based on the Hg results and the response of other elements in this system, waters (surface and ground waters) entering the head of Gossan Valley are diluted before reaching the receiving site by a factor of at least 200.

During the mining operation, the concentration of Hg in the open pit water remained below 0.5 $\mu g/L$ even when the pit water went strongly acid (pH 2.5) when the gossan-sulfide contact was reached. The low concentration of Hg in pit water agrees well with the results for Hg in the pH paste solutions of fresh unleached gossan material.

Ground Water Chemistry and Flow

For ground waters representing subsurface flow from the ore stockpile (MW-1), the open pit (MW-2), the mine waste rock pile (MW-6 to 7), the southern portion of Gossan Creek valley (MW-9), and background lithology away from mining (MW-11), the Hg and total cyanide concentrations have been consistently at background levels from start of mining until the present (<0.5 $\mu g/L$ and <0.1 mg/l, respectively). Ground waters in monitoring wells associated with the effluent and runoff pond environments (MW-3, MW-12) show sporadic increases in Hg and total cyanide, consistent with the times at which these ponds were used to store effluent before recycling to the mill or before liming, cyanide destruction, and passage into the collection and siltation control ponds. In these wells, Hg and total cyanide concentrations reached levels of 850

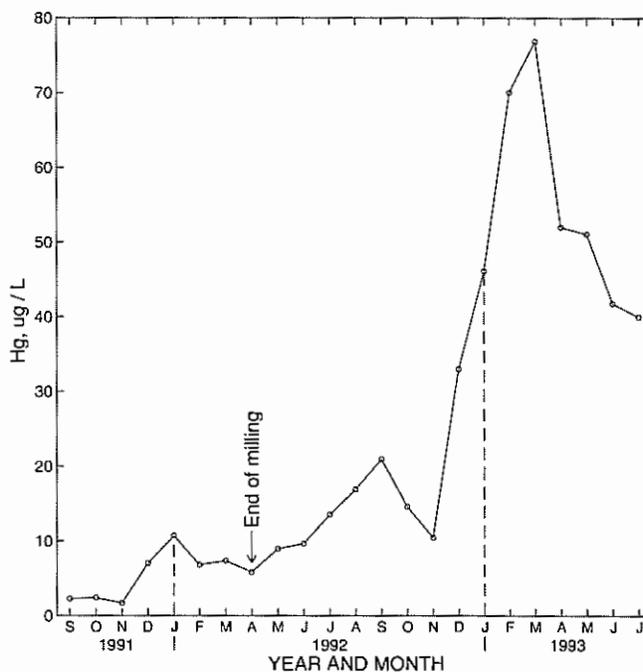


Figure 3. Monthly averages for Hg in stream water at the head of Gossan Creek. Total cyanide was consistently below 0.1 mg/L over this period.

$\mu\text{g/L}$ and 1.8 mg/l, respectively, but generally decreased within a few months to background levels after introduction of effluents into the ponds was stopped.

Of main concern to this study are the waters associated with baseflow from the tailings disposal area (MW-4, MW-5). Well MW-4 receives baseflow from tailings material deposited in the first two years of operation and MW-5 from material deposited mainly over the last year of mining. The monthly averages for total cyanide and Hg in MW-4 ground waters are plotted in figure 4. Apart from an obvious strong correlation between cyanide and Hg, there is a gradual decrease in the yearly averages for these two parameters from 1990 to 1993. After the end of milling (April 1992), there is a significant decrease in cyanide and Hg compared to the mining period, with a peak increase occurring only at the time of the spring freshet in 1993. Present levels for MW-4 are at background for total cyanide ($<0.1 \text{ mg/L}$) and are approaching background for Hg (now about $250 \mu\text{g/L}$).

For MW-5 ground waters (figure 5) there is also a strong correlation between total cyanide and Hg, but levels of both these parameters have remained high from late 1990 to the present. The differences between the concentration patterns for total cyanide and Hg in MW-4 and MW-5 ground waters are most likely due to a longer period of time for cyanide destruction for the portion of the pile monitored by MW-4. The comparative data between these two wells suggest that concentrations of Hg in pore waters within the pile and dispersion of this element out of the pile are controlled by the destruction and mobilization rates of residual cyanide. In figure 5 there is a slight offset in the times that cyanide and Hg initially reach MW-5. This is probably due to almost total destruction of free and complexed cyanide during the initial stages of baseflow from the northern portion of the tailings pile.

From the breakthrough time of Hg into monitoring well MW-5 (fig. 5), the time of travel for ground waters in bedrock downslope from the tailings pile is estimated to be about 40 m/yr. This would result in an initial influx of ground waters from the pile into the headwaters of Gossan Creek at the end of 1992, which correlates quite well with results for Hg monitoring of this creek (fig. 3). The decrease of Hg in Gossan Creek after early 1993 probably represents overall increased destruction of free cyanide and cyanide-Hg complexes, with greater partitioning of Hg into the solid phases of the overburden-bedrock environment. Figure 6 shows the correlation between total cyanide and Hg for all analyses of ground waters at the site. Also shown on this plot is the line for stoichiometric $[\text{Hg}(\text{CN})_4]^{2-}$. Many of the ground waters at Murray Brook contain more Hg than can be accounted for as a Hg-cyanide complex; this is especially so for the ground waters at MW-5. With greater destruction of the cyanide-Hg complex, by both inorganic and organic agents, more of the Hg is free to enter into solid adsorption

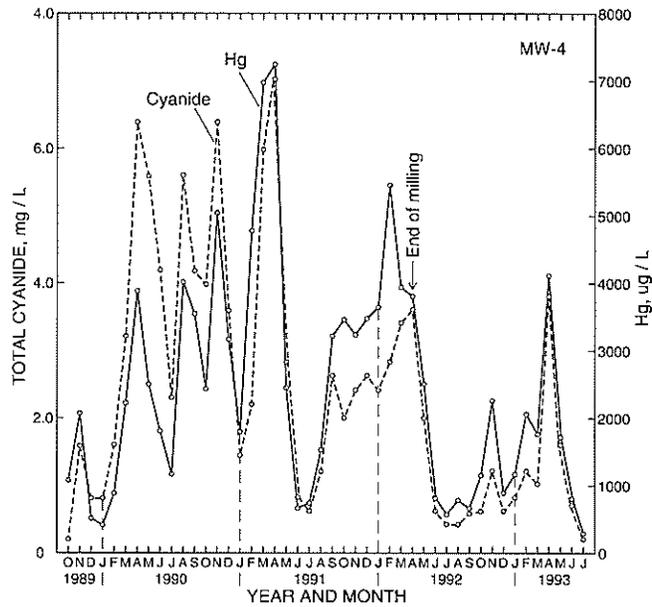


Figure 4. Monthly averages for total cyanide and Hg in ground waters of monitoring well MW-4.

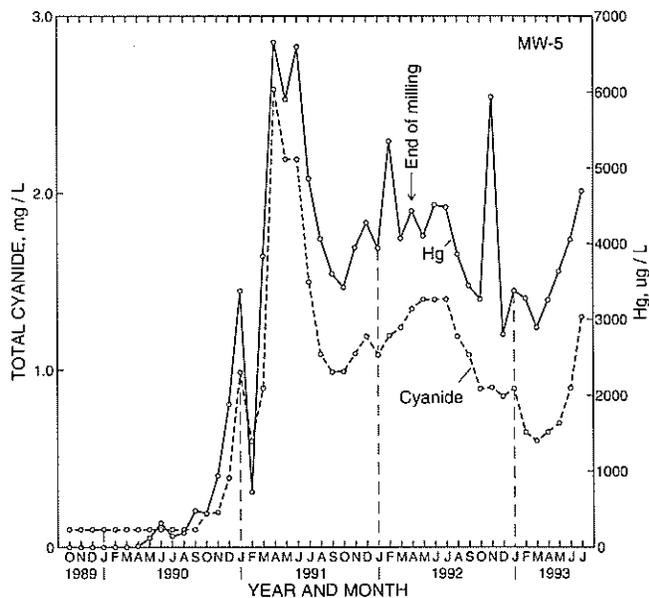


Figure 5. Monthly averages for total cyanide and Hg in ground waters of monitoring well MW-5.

processes. Provided the supply of Hg from the pile is attenuated by cyanide destruction within the pile, solid phases should not become saturated and the influx of Hg into the Gossan Creek streamflow system will not reach critical proportions. Given the fact that the environmental receiving site is at the mouth of Gossan Creek and there is an almost 200:1 dilution factor along this creek, the influxes of Hg should be environmentally manageable. However, if this operation had been much larger, with a greater mined tonnage or higher Hg content, the mobilization of Hg could conceivably have been a serious problem.

Behavior of Cinnabar in Cyanide Solutions

To determine if cinnabar, which is the principal Hg-bearing mineral in this deposit, was the major contributor of Hg to ground waters, a literature search was made for information on the behavior of cinnabar in cyanide solutions. Nothing was found and it was then decided to run some preliminary experiments. Results of three leaches of cinnabar using 1, 10 and 250 mg/L free cyanide solutions are presented, together with controls, (table 2). Considerable amounts of Hg can be leached from cinnabar in even weak cyanide solutions. Depending on the concentration of cyanide, the solubility of cinnabar in cyanide solutions (tables 1 and 2) is 270 to 800 times greater than in neutral noncyanide waters.

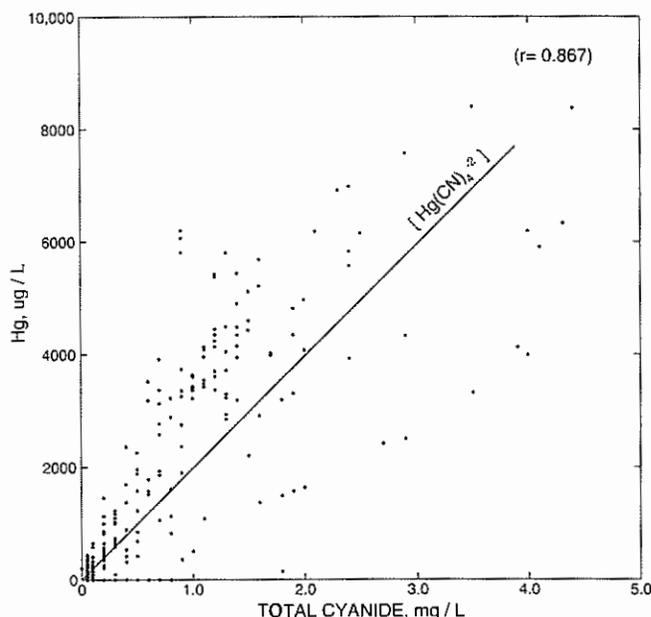


Figure 6. Plot of Hg versus total cyanide for all ground water analyses at Murray Brook. Line of stoichiometric composition of dominant $[\text{Hg}(\text{CN})_4]^{2-}$ complex also given.

Table 2. Cyanide leaching of cinnabar (HgS)¹.

Conditions	Leaching solution		
	Cyanide, ppm	Hg, ppb	Hg leached, mg/g
Control 1	0	81	0.020
Control 2	0	94	0.024
Leach 1	1	2,150	0.538
Leach 2	10	4,350	1.090
Leach 3	250	12,200	3.050

¹Leaches carried out on 1 g of cinnabar (Almaden Mine, Spain) with 250 mL of NaCN solution for 48 h with gentle agitation every 12 h. Control leaches carried out using de-ionized water. Both cyanide and control leach solutions were adjusted to pH 10 using NaOH.

Although the kinetic rates of this reaction still need to be determined, it would appear from the mill recovery of Hg (12% of total contained Hg), the strong correlation between cyanide and Hg in ground waters (fig. 6), and the constant uptake of Hg in pore waters of the tailings pile, that the dissolution rate of cinnabar in even weak cyanide solutions is high enough to be of environmental concern.

Conclusions

The following conclusions can be drawn from this research:

1. At Murray Brook Mine, the concentration of Hg in pore waters of mill tailings containing significant amounts of cinnabar (HgS) is related to the amount of residual cyanide remaining in the pile and, more importantly, to cyanide mobilization and cyanide destruction within the pile and along ground water flowpaths.

2. Clearly more research is required on the behavior of cinnabar in the cyanide leaching of various types of oxidized ores, especially since cinnabar is a common mineral in these ores and Hg is a very difficult element to remove from effluents.

3. Consideration should be given to methods of accelerating the rate of cyanide destruction in vat and heap leaching waste materials containing high concentrations of Hg (generally greater than 10 to 20 ppm) as cinnabar.

4. In Canada, indoor vat cyanide leaching methods will be the method of choice for certain types of Au-Ag ores owing to the severe climatic conditions of the country. For oxidized and volcanic epithermal Au-Ag ores, in which Hg is present in significant amounts as cinnabar, future vat leaching operations should utilize lined catchment reservoirs for mill tailings.

Acknowledgments

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