



**MERCURY REMOVAL
FROM INDURATION OFF GAS
BY WET SCRUBBERS**

COLERAINE MINERALS RESEARCH LABORATORY

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By 
Blair R. Benner
Program Director – Minerals

Approved by 
David W. Hendrickson, Director
Coleraine Minerals Research Laboratory

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University of Minnesota Duluth
Natural Resources Research Institute
5013 Miller Trunk Highway
Duluth, Minnesota 55811

Coleraine Minerals Research Laboratory
P O Box 188
One Gayley Avenue
Coleraine, Minnesota 55722

Mercury Removal from Induration Off Gas by Wet Scrubbers

SUMMARY

During the induration of taconite pellets, green balls are heated to greater than 2200°F. A previous study¹ indicated that greater than 90 percent of the mercury contained in the green balls is volatilized during induration. Some of the volatilized mercury is removed by the gas scrubbers. Studies²⁻⁴ on coal burning power plants indicate that the mercury in flue gas is present as either elemental mercury or as divalent mercury. In power plant scrubbers, the majority of the divalent mercury is removed, but very little elemental mercury is removed by the scrubbers. The particulate matter in the off gas appears to remove a significant portion of the mercury that is removed. It is thought that the off gas chemistry and the scrubber water chemistry could affect the removal of mercury. To determine if the scrubber water chemistry could affect the removal of mercury from taconite pelletizing off gases, the Minnesota Department of Natural Resources' (MNDNR) environmental cooperative funded a study to sample around the scrubbers from the plants equipped with wet scrubbers to determine if water chemistry affects mercury removal. Another objective of the study was to determine the role of solids entrained in the off gases and removed by the scrubbers. These solids are returned to the process. If they were discarded, then some amount of mercury could be eliminated from the system, but at a cost of iron units.

Samples were obtained from Minntac, EVTAC, Minorca, Hibtac and Northshore. With the exception of the mercury analyses, all chemical analyses were conducted at Coleraine. Mercury analyses were run by Frontier Geosciences of Seattle, Washington.

While the various plants have different scrubber configurations and scrubber water chemistries, these differences appeared to have no significant affect on mercury removal. Accurate mercury balances were not possible because mercury content in the fired pellets from all of the plants was below the detection limit of about 0.6 parts per billion (ppb). Solids entrained in the off gases removed significantly more mercury than the scrubber water. Of the mercury removed in the scrubber systems, the amount contained in the solids ranged from 75 percent at Northshore to greater than 99 percent at EVTAC. The minus 10 micron fraction of the solids in the off gases appears to remove the most mercury. Analysis of the solids that are continually recycled to the Minorca wet scrubbers indicates a high capacity for mercury removal (the solids assayed over 3000 ppb mercury). This result indicates that the mercury should remain with the solids and should not leach if the solids were sent to the tailings basin.

INTRODUCTION

During the pelletizing process, the majority of mercury contained in the green balls is vaporized and leaves with the off gases. Wet scrubbers remove some of this mercury. Mercury that is removed is either dissolved in the water or is associated with the solids entrained in the off gas stream. It is generally assumed that mercury removed by the scrubber water and solids is present as divalent mercury and mercury that is not removed by the scrubbers is present as elemental mercury. Based on research on coal fired power plant emissions, most of the removed mercury is associated with the solids that are generally recovered in the electrostatic precipitators and that the amount of carbon, chlorine, and sulfur in the off gas can affect the amount of mercury removed. It is possible that other elements in the indurating off gas may also affect the amount of mercury removed by the wet scrubbers.

In most cases, the solids contained in the scrubber water are recovered and are recycled to green ball feed. This practice tends to increase the amount of mercury in the green balls. One of the objectives of this program is to determine how much mercury is being recycled and how much iron would be lost if the material was wasted instead of recycled.

The MNDNR's environmental cooperative funded a study by the Coleraine Minerals Research Laboratory (CMRL) to sample the various plants and conduct chemical analyses of the various streams. Sampling was conducted at the five operating taconite plants (Hibtac, Minntac, EVTAC, Minorca, and Northshore) that are equipped with some type of wet scrubbers on the indurating off gases. The main objective of the sampling program was to determine if scrubber water chemistry could be related to mercury removal by the wet scrubbers. The test program was **not** designed to provide a mercury balance around the indurating plant. Data contained in this report cannot be used to accurately calculate the amount of mercury being released to the atmosphere by any of the sampled plants.

SAMPLING PROGRAM

Grab samples were taken of the materials entering the system: green balls, solid fuel (if any), and scrubber inlet water; and exiting the system: fired pellets, scrubber water out, and multiclone solids (if any). Sampling devices were cleaned with dilute acid and distilled water prior to the sampling. Each of the sampling devices were purged with the material being sampled. All samples were brought to the Coleraine Minerals Research Laboratory (CMRL) for filtering and chemical analysis. (Samples from Hibtac were from a previous sampling program conducted by Hibtac in October of 1998.) All liquid samples were filtered through 0.45 micron paper, with the solids content being measured. All solids samples were dried, with the moisture content being recorded. All solids processing equipment was thoroughly cleaned and was purged with the material being processed (when possible). Splits of the solids and water samples were sent to Frontier Geosciences in Seattle for mercury analysis. All remaining analyses were run at CMRL by ICP.

OFF GAS TREATMENT SCHEMES

Each of the plants has slightly different wet scrubbers. Minntac has the simplest flowsheet, Figure 1, where the exhaust from the grate-kiln system is sent to one scrubber per line, fresh water is added to the scrubber, and the water with entrained solids is removed and sent to a thickener. Both the water and solids are eventually recycled to the process, but nothing is recycled to the scrubber.

EVTAC also employs the grate-kiln system, but has a more complicated scrubber flowsheet, as shown schematically in Figure 2. EVTAC's system consists of a scrubber and a de-misting tank. Fresh water is added through slats in the top of the de-misting tank. That water plus the water and solids from the scrubber are sent to a thickener. The thickener overflow is recycled to the scrubber. Thickener underflow is sent back to the process. In steady state, the water added at the slats (slat water) is equal to the amount of water removed with the thickener underflow.

Minorca has a traveling grate machine with two separate gas streams going to the scrubber as shown in Figure 3. The first (hood exhaust) goes directly to the scrubber, while the second and larger stream (window exhaust) goes to a series of "multi clones" to remove most of the entrained dust. Gas from the multi clones goes to the scrubber. Water to the scrubbers is continuously recycled, with fresh water being added to maintain sump level.

Hibtac is similar to Minorca in that it has a traveling grate and a dry dust removal step prior to the wet scrubbers, as shown schematically in Figure 4. It is not known if all of the off gas passes through the dry dust removal section, but all of the off gas is treated by the wet scrubbers. Scrubber water is not recycled directly to the scrubber.

Northshore also employs a traveling grate machine and has two off gas streams, as shown in Figure 5. Unlike Minorca and Hibtac, there is no dust removal prior to the scrubbers and there are separate scrubbers for each exhaust stream. Fresh water is added to the scrubbers with no direct recycle.

WATER CHEMISTRY

Chemical analyses for the water samples taken in the test program are given in Table I. All of the analyses are in parts per million (ppm) except for the mercury analyses, which are in nanograms per liter (ng/l) or parts per trillion (ppt).

For Minntac there were only two water samples; scrubber water in and scrubber water out. Looking at the Minntac analysis in Table I, the mercury results appear to be wrong in that the scrubber in water has more mercury than the water out. Previous work¹ showed a mercury content of 2.05 ng/l in the water in and 491.55 ng/l in the scrubber out water. The scrubber in water analysis was a quality control sample for Frontier, which means that it was run in duplicate and was run with a known addition. The duplicate analyses were 74.5 and 83.3 ng/l for an average of 78.9 ng/l report in Table I. Frontier's reports for all samples with the quality control results are given in Appendix I. Since the duplicate analyses were reasonably close, it appears that the mercury analysis of the

scrubber in water is truly the mercury content on the sample sent to Frontier. It is possible that the scrubber out sample was accidentally poured into both the scrubber in and scrubber out bottles that were sent to Frontier. Based on the cation and anion analyses for the Minntac waters (Table I), samples were taken of the scrubber in and scrubber out waters.

For EVTAC there were five water samples as shown in Table I. EVTAC has two thickeners for the scrubbers; therefore, there is an overflow and underflow sample for each thickener as well as the makeup water (slat spray water). Again, there appears to be a problem with the mercury analyses. In this case, thickener overflow 2A appears to be too high in mercury. The other analyses look appropriate.

For Northshore there were also five water samples (Table I), since both lines 11 and 12 were sampled. With the exception of the Waste Gas Water from line 11, the analyses look consistent. The reason for the low cation and anion concentrations in line 11 waste gas water is unknown. Northshore has the most unique water chemistry due to the addition of soda ash to soften the water.

Only two water samples were obtained from Minorca - the recycled scrubber water and the make up water. As would be expected from recycling the water, the Minorca scrubber water had the highest mercury content of 112 ppt.

Hibtac supplied three water samples for analyses. It appears that only the make-up water and the scrubber water are germane to this study.

As mentioned above, some sampling of scrubber water was conducted as part of a previous study in 1997¹. Mercury analyses of those waters were significantly different from the current study, as shown in Table II. For Minntac and Hibtac, there was a large decrease in the mercury content of the water coming out of the scrubber, while the mercury concentration in the water from the Northshore scrubbers increased, especially line 11. For Hibtac and Northshore, the mercury content in the scrubber input water had increased. The 1997 mercury analyses were also conducted by Frontier Geosciences.

SOLIDS CHEMISTRY

Solids from the sampling program were analyzed for mercury by Frontier. The samples were analyzed at Coleraine for total iron, ferrous iron, silica, CaO, MgO, alumina, sulfur and carbon (coal sample only). Results are given in Table III. Frontier Geosciences' reports of mercury analysis for the solid samples are included in Appendix I. Values in Table III are in dry weight percent except for the mercury, which are in ng/g (ppb).

For Minntac there were four solid samples: the greenballs, fired pellets, solids contained in the scrubber discharge, and coal. Fired pellet mercury content was below the detection limit of 0.6 ppb. For Minorca there were also four solid samples: the greenballs, fired pellets, multiclon dust, and the solids in the recycling scrubber water. As with the Minntac sample, the fired pellet mercury content was below detection limits. For EVTAC there were 7 solid samples: greenballs, fired pellets, coal, two thickener underflows (A & B), and two thickener overflows. Again, the fired pellets were below the mercury detection limits (0.69 ppb in this case). Hibtac provided 7 solid samples: filtercake, concentrate, greenballs, limestone, bentonite, fired pellets and multi-tube dust.

Unfortunately, Hibtac did not supply a sample of the solids in the scrubber discharge. Again, the fired pellets were below the mercury detection limits of 0.69 ppb. For Northshore there were eight samples (four per line): greenballs, fired pellets, solids from the hood exhaust scrubber and solids from the waste gas scrubber. Line 12 fired pellets were reported to contain 1.85 ppb mercury, which is most likely a mistake. Line 11 fired pellets were below the detection limit as were all the other fired pellet samples from the other plants.

Comparing the greenball mercury analysis with the 1997 study indicated essentially the same mercury concentration for both studies, as shown in Table IV.

Part of the work on the solids included screening selected samples on a 10 micron screen and having mercury analyses run on the size fractions. Samples screened were the two thickener underflow samples from EVTAC and the multitube dust from Hibtac. Results are given in Table V. As was expected, there was very little minus 10 micron material in the multitube dust. About 30 percent of the thickener underflow solids was minus 10 micron. Due to the relatively small amount of minus 10 micron material, no analysis was performed on that fraction. Mercury concentration in the minus 10 micron fraction was calculated from the head mercury, the mercury in the plus 10 micron fraction and the weight split. Mercury was concentrated in the minus 10 mesh fractions. All of the minus 10 mesh material had a calculated mercury concentration of greater than 1 ppm.

ESTIMATED MERCURY BALANCES

Estimated mercury balances for the various plant scrubbers are given in Table VI. Since all of the fired pellet mercury analyses were below detection limits, a value of 0.5 ng/g (ppb) was assumed for all fired pellets. Also included in Table VI is the mercury balance if the pellets contain 0 ng/g and 0.69 ng/g (detection limit).

Minntac - For the period tested, the greenball feed rate was 450 tph at a moisture of 9.5 percent. Coal was added at the rate of 13,000 lb/hr and the flow rate to the scrubber was 2,960 gpm. As shown in Table VI, the greenballs added 3.355 grams per hour (g/hr) of mercury to the system; the coal added 0.149 g/hr and the scrubber water added 0.0067 g/hr. (a value of 10 ng/l was assumed for the scrubber in water). Coming out of the system the fired pellets (at the assumed mercury content) removed 0.194 g/hr mercury; the solids with the scrubber water removed 0.115 g/hr and the scrubber water removed 0.0447 g/hr. Based on the calculated tonnage of solids with the scrubber water and the iron analysis (Table III) of the scrubber, there are about 0.832 tph of iron in the scrubber solids. Assuming 100 percent operating time (8,760 hours per year), not recycling the scrubber solids would result in about 2.2 pounds of mercury being removed from the system with a loss of about 7,300 tons of iron units per year.

Northshore - Line 11 was being fed 196 tph of greenballs at 10.1 percent moisture with an estimated scrubber feed rate of 1,000 gpm. As shown in Table VI, this results in 0.258 g/hr mercury being added to the system with the greenballs and 0.0016 g/hr being added with the scrubber water. Coming out of the system, the fired pellets removed 0.0847 g/hr (using the assumed mercury content in the fired pellets); the combined scrubber solids removed 0.021 g/hr; and the combined scrubber water removed

0.007 g/hr. Line 12 was very similar, as shown in Table VI. As was the case for Minntac, more mercury was removed with the scrubber solids than with the scrubber water.

EVTAC - The system was being fed 600 ltp of greenballs at 9.5 percent moisture. Coal was being added at a rate of 7.52 ltp and slat water at 980 gpm. At these rates, the greenballs added 6.627 g/hr mercury; the coal added 0.0788 g/hr; and the slat water added 0.0012 g/hr as shown in Table VI. Exiting the system, the fired pellets removed 0.2619 g/hr mercury, the combined solids in the thickener underflows removed 0.7761 g/hr mercury; and the thickener underflow water removed 0.0040 g/hr mercury. Assuming 100 percent operating time, discarding the thickener underflow solids would remove 14.99 pounds of mercury a year from the system with a loss of about 5,423 tons of iron units.

Minorca - Since there was no estimate of the amount of dust from the multiclone, there was no way to estimate a mercury balance. It is of interest to note the high mercury concentration (3.179 ppm) in the solids recycled with the scrubber. This indicates that magnetite dust has a high capacity for removing mercury and would suggest that any scrubber solids sent to the tailing basin would not be leached by the water.

Hibtac - As with Minorca, there was no estimate of the rate of multitube dust production. That, combined with a lack of the solids contained with the scrubber water, precluded the calculation of a mercury balance.

CONCLUSIONS

Sampling around the scrubbers at five taconite plants has indicated that the majority of the mercury that is removed by the various scrubbers is removed by the solids, either wet or dry. Mercury in the solids appears to be concentrated in the minus 10 micron fractions. There was no indication that the scrubber water chemistry had any affect on the amount of mercury removed by the water. Discarding the solids from the scrubber system could remove significant amounts of mercury from the system without a catastrophic loss of iron units. Results from Minorca's scrubber solids recycling indicates that the scrubber solids have a relatively high capacity for the deposition of mercury, which implies that the scrubber solids would retain the mercury in the tailings basin. Since the fired pellet mercury analyses were all below detection limits, no accurate mercury balances could be calculated. Using an assumed value of 0.5 ng/g mercury in the fired pellets, the fired pellets removed a significant amount of mercury compared to the scrubber solids and water.

REFERENCES

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3. Gibb, Clarke, and Mehta, The Fate of Coal Mercury During Combustion, Fuel Processing Technology, Vol. 65-66, pp 365-377, 2000.
4. Galbreath and Zygarlicke, Mercury Speciation in Coal Combustion and Gasification Flue Gases, Environmental Science and Technology, Vol. 30, No. 8, page 2421, 1996.

Table I - Chemical Analysis of Water Samples

	Hg, ng/g	pH	IC	Na	K	ppm		SO4	Cl	F	TOC
						Ca	Mg				
Minntac											
Scrub in	78.90	8.11	41.00	73.23	26.26	117.14	176.81	717.60	141.80	2.91	3.70
Scrub out	66.50	6.62	5.60	74.57	27.47	135.63	180.27	878.10	163.80	8.00	2.80
Inland											
Process water	5.67	7.88	37.10	41.41	9.72	32.69	52.46	74.70	82.00	5.79	3.80
Scrub out	112.00	4.57	1.40	52.07	14.61	62.03	73.63	154.20	205.70	47.50	2.80
Northshore											
Feed Water	7.05	9.71	36.90	738.50	53.33	22.57	6.08	426.30	395.00	35.80	6.70
Hood Exhaust 11	32.80	7.65	30.30	780.60	56.01	24.32	7.12	531.60	436.30	130.90	6.80
Hood Exhaust 12	15.70	7.54	31.40	808.30	53.01	23.42	7.00	504.30	458.30	136.30	7.80
Waste Gas Wat 11	29.10	7.81	34.20	441.40	33.70	19.65	7.17	279.30	266.70	68.50	5.00
Waste Gas Wat 12	15.70	7.79	44.60	851.30	63.77	25.29	7.34	518.10	487.20	130.90	9.10
Evtac											
Thick unflo 2A	15.48	4.44	2.76	103.38	20.83	175.16	67.73	752.10	79.50	31.70	5.12
Thick oflo 2A	82.22	3.92	2.96	103.50	20.26	168.11	65.29	766.50	84.10	45.70	5.81
Thick unflo 2B	18.12	4.49	2.61	100.26	18.82	146.36	67.62	704.10	76.00	38.80	5.44
Thick oflo 2B	24.35	4.53	3.32	98.92	18.69	136.31	65.30	668.40	78.20	40.40	5.17
Slat Spray Water	5.25	7.25	29.24	74.30	10.89	44.57	55.74	246.60	55.00	12.00	6.41
Hibtac											
Conc water	8.61	7.99	90.89	58.75	10.80	74.79	128.89	265.20	64.20	8.30	7.92
Make-up water	5.37	8.00	40.79	58.31	16.26	40.32	74.58	204.90	57.20	9.80	3.62
Scrub water	11.95	7.63	22.79	58.95	16.94	41.23	74.77	267.60	62.30	18.00	2.84

**Table II - Comparison of Mercury Content in Water Samples
From 1997 and Current Study.**

		Hg, ng/l		
		1997	Current	Current
Minntac	Scrubber in	2.05	78.9	
	Scrubber out	491.55	66.5	
Hibtac	Scrubber in	2.81	5.37	
	Scrubber out	63.35	11.95	
Northshore			Line 11	Line 12
	Scrubbers in	2.21	7.05	7.05
	Hood Exhaust out	6.61	32.8	15.7
	Waste Gas out	10.87	29.1	15.7

Table III - Chemical Analyses of Solid Samples

	Percent									
	Hg, ng/g	Fe	SiO2	CaO	MgO	Al2O3	Sat Mag	Fe+2	S	C
Evtac Greenball	12.00	66.60	6.14	0.80	0.48	0.10	66.53	22.92	0.016	
Evtac Fired Pellet	<0.69	64.90	6.18	0.72	0.48	0.10	0.58	0.79	0.003	
Evtac Coal	10.30	0.09	2.01			0.95			2.980	74.63
Evtac Thickner Unflow 2A	527.00	55.00	17.56	0.98	1.25	0.74	39.56	14.50	0.064	
Evtac Thickner Oflow 2A	233.00	49.60	23.64	0.85	1.68	1.08	28.53	11.89	0.083	
Evtac Thickner Unflow 2B	367.00	57.20	15.53	0.87	1.06	0.53	43.86	14.93	0.099	
Evtac Thickner Oflow 2B	826.00	48.30	24.21	1.31	1.81	0.90	28.47	11.83	0.074	
Hibtac Filter Cake	13.90	67.90	4.17	0.31	0.30	0.07	68.90	22.88	0.015	
Hibtac Concentrate	18.20	68.40	3.97	0.16	0.28	0.05	68.12	23.24	0.005	
Hibtac Limestone	3.72	0.02	0.46	55.05	0.69	0.11			0.285	
Hibtac Multi-tube Dust	154.00	66.90	4.56	0.28	0.32	0.13	38.01	12.58	0.028	
Hibtac Greenball	16.70	67.60	4.69	0.31	0.30	0.18	68.67	21.39	0.022	
Hibtac Bentonite	26.40	3.03	61.47	0.09	1.91	17.60			0.295	
Hibtac Fired Pellet	<0.69	66.20	4.62	0.31	0.33	0.17	1.99	1.09	0.000	
Northshore Waste Gas 11	211.00	61.20	5.94	3.80	1.25	0.35	52.76	16.49	0.030	
Northshore Waste Gas 12	110.00	62.20	4.34	3.96	1.12	0.32	52.74	16.40	0.022	
Northshore Hood Exhaust 11	26.00	63.20	3.92	3.68	1.02	0.33	56.68	18.53	0.030	
Northshore Hood Exhaust 12	26.40	62.70	4.56	3.72	1.04	0.35	54.26	17.01	0.031	
Northshore Greenball 11	1.44	63.20	3.86	3.85	1.03	0.28	63.33	20.73	0.013	
Northshore Greenball 12	1.10	63.10	4.06	3.85	1.04	0.32	62.81	20.29	0.018	
Northshore Fired Pellet 11	<0.69	63.30	4.42	3.91	1.05	0.34	2.01	0.21	0.011	
Northshore Fired Pellet 12	1.85	63.20	4.25	3.94	1.04	0.33	1.76	0.18	0.014	
Minntac greenball	8.10	62.90	4.48	3.27	1.12	0.18	62.88	21.00	0.016	
Minntac fired pellet	<0.6	63.60	4.64	5.58	1.13	0.20	1.45	0.20	0.014	
Minntac scrubber out	87.00	64.00	4.57	2.19	1.10	0.25	52.50	15.20	0.015	
Minntac coal	25.30	0.20	0.86			0.74			0.327	66.39
Minorca scrubber solids	3179.00	55.40	14.13	2.88	1.78	0.22	13.85	4.38	0.050	
Minorca multiclone dust	193.00	49.40	5.18	9.63	4.94	0.15	13.47	4.26	0.058	
Minorca green balls	7.80	61.10	4.29	4.35	1.39	0.15	61.00	20.99	0.014	
Minorca fired pellet	<0.6	62.60	4.38	4.52	1.45	0.15	6.44	1.47	0.004	

Table IV - Comparison of Mercury Content in Greenballs and Fired Pellets From 1997 and Current Study.

		Hg, ng/g		
		1997	Current	Current
Minntac	Greenballs	7.5	8.1	
	Fired Pellets	0.65	<0.60	
Hibtac	Greenballs	16.2	16.7	
	Fired Pellets	0.94	<0.69	
Northshore			Line 11	Line 12
	Greenballs	0.83	1.44	1.1
	Fired Pellets	0.29	<0.69	<0.69

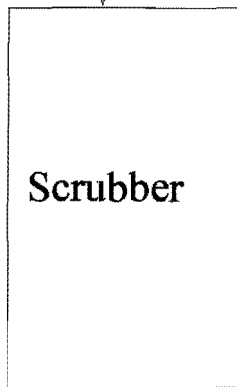
Table V - Distribution of Mercury Between Plus and Minus 10 Micron Fractions

	Sample	Wt, g	Wt %	Hg, ng/g	Hg Dist, %
EVTAC Un'flow 2A	+10 microns	2.75	66.91	38.8	4.93
	-10 microns	1.36	33.09	1514.2	95.07
	head			527.0	
Un'flow 2B	+10 microns	4.70	73.90	48.6	9.79
	-10 microns	1.66	26.10	1268.5	90.21
	head			367.0	
Hibtac Multitube Dust	+10 microns	5.40	93.43	86.8	52.66
	-10 microns	0.38	6.57	1108.9	47.34
	head			154.0	

Table VI - Estimated Mercury Balances for the Various Plants

		Hg Analysis	Flow Rate	Total Hg g/hr	% solids
Minntac	IN				
	Greenball	8.1 ng/g	450 ltph	3.3547	90.50
	Coal	25.3 ng/g	13000 lb/hr	0.1493	
	Scrubber water	10 ng/l	2960 gpm	0.0067	
	Total in			3.5107	
	OUT				
	Pellets	0.5 ng/g	382.5 ltph	0.1945	
	Scrubber solids	87 ng/g	1.33 tph	0.1150	
Scrubber water	66.5 ng/l	2960 gpm	0.0447	0.18	
Total out			0.3542		
Northshore Line 11	IN				
	Green Balls	1.44 ng/g	196 ltph	0.2583	89.90
	Scrubber water	7.05 ng/l	1000 gpm	0.0016	
	Total in			0.2599	
	OUT				
	Pellets	0.5 ng/g	166.6 ltph	0.0847	
	Waste Gas Solids	211 ng/g	0.08 tph	0.0171	0.08
	Waste Gas water	29.1 ng/l	400 gpm	0.0026	
Exhaust Solids	26 ng/g	0.15 tph	0.0039	0.10	
Exhaust water	32.8 ng/l	600 gpm	0.0045		
Total out			0.1129		
Line 12	IN				
	Green Balls	1.1 ng/g	184 ltph	0.1852	90.00
	Scrubber water	7.05 ng/l	1000 gpm	0.0016	
	Total in			0.1869	
	OUT				
	Pellets	0.5 ng/g	156.4 ltph	0.0795	
	Waste Gas Solids	110 ng/g	0.09 tph	0.0100	0.09
	Waste Gas water	15.7 ng/l	400 gpm	0.0014	
Exhaust Solids	26.4 ng/g	0.09 tph	0.0024	0.06	
Exhaust water	15.7 ng/l	600 gpm	0.0021		
Total out			0.0955		
EVTAC	IN				
	Green balls	12 ng/g	600 ltph	6.6265	90.50
	Slat water	5.25 ng/l	980 gpm	0.0012	
	Coal	10.3 ng/g	7.52 ltph	0.0788	
	Total in			6.7064	
	OUT				
	Fired pellets	0.5 ng/g	515 ltph	0.2619	
	Underflow water	18.12 ng/l	980 gpm	0.0040	
Underflow solids a	527 ng/g	0.49 tph	0.2621	0.40	
Underflow solids b	826 ng/g	0.61 tph	0.5140	0.50	
Total out			1.0420		

Water In



Scrubber



Water and Solids Out

FIGURE 1 - SCHEMATIC OF MINNTAC SCRUBBER

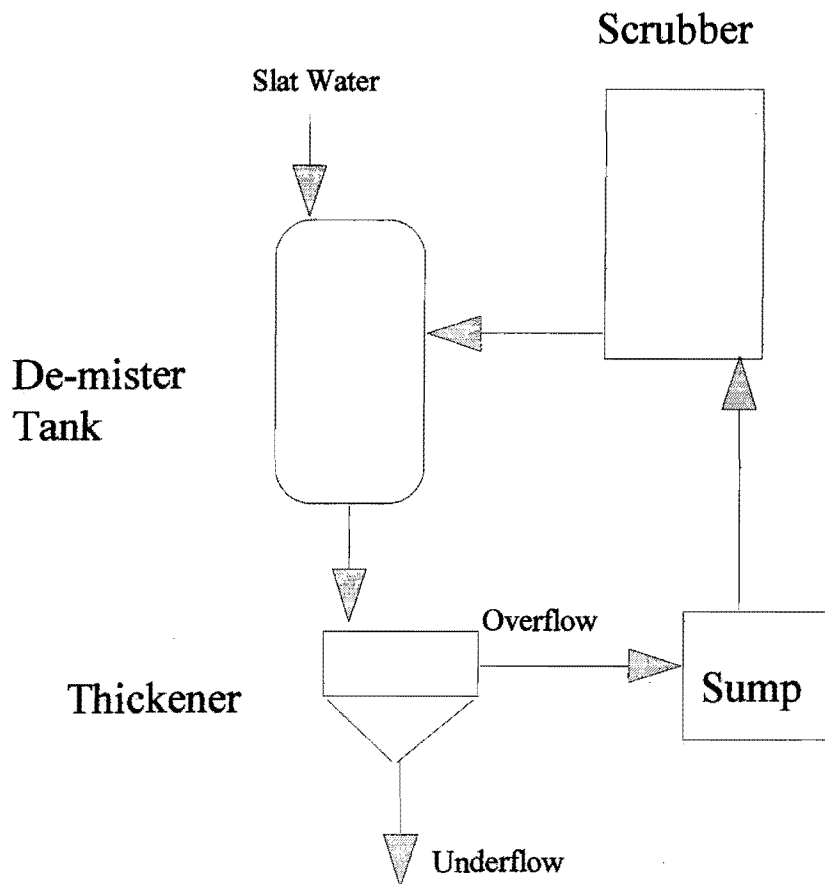


FIGURE 2 - SCHEMATIC OF EVTAC SCRUBBER

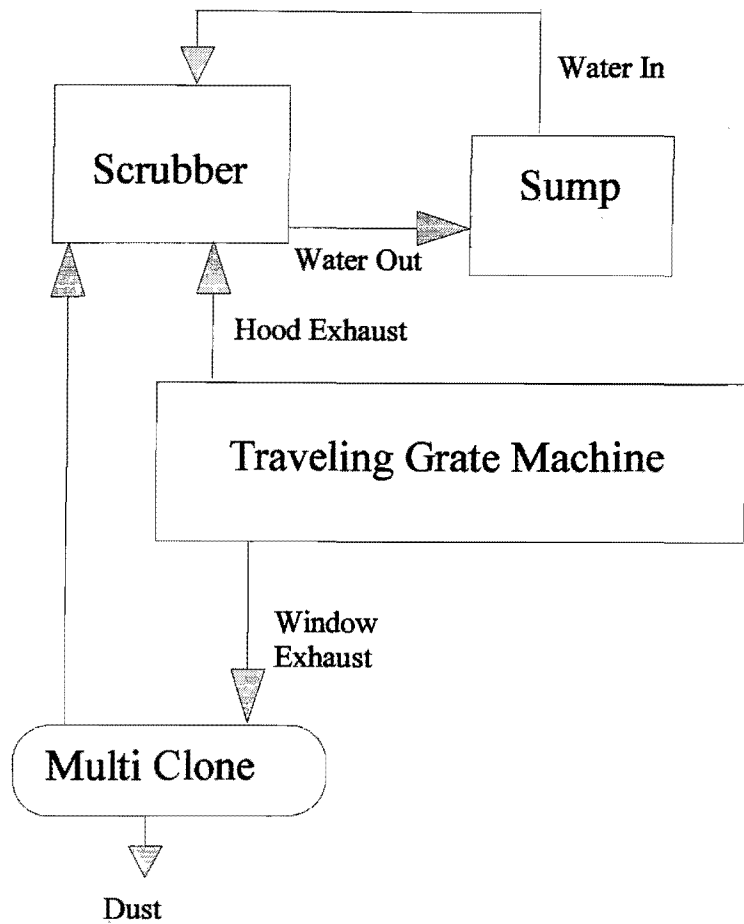


FIGURE 3 - SCHEMATIC OF MINORCA SCRUBBER

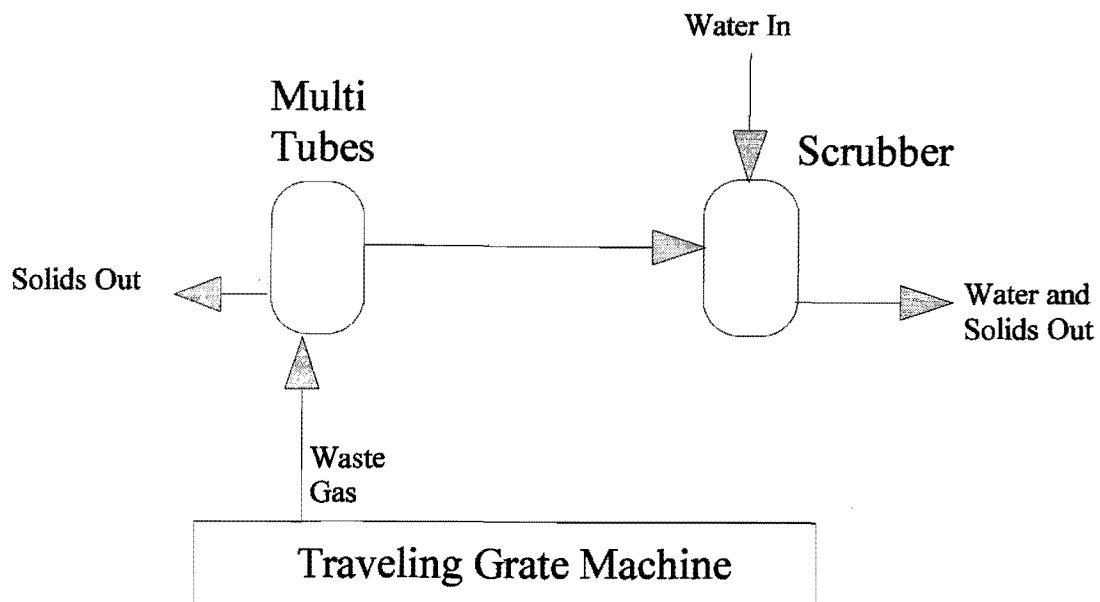


FIGURE 4 - SCHEMATIC OF HIBTAC SCRUBBER

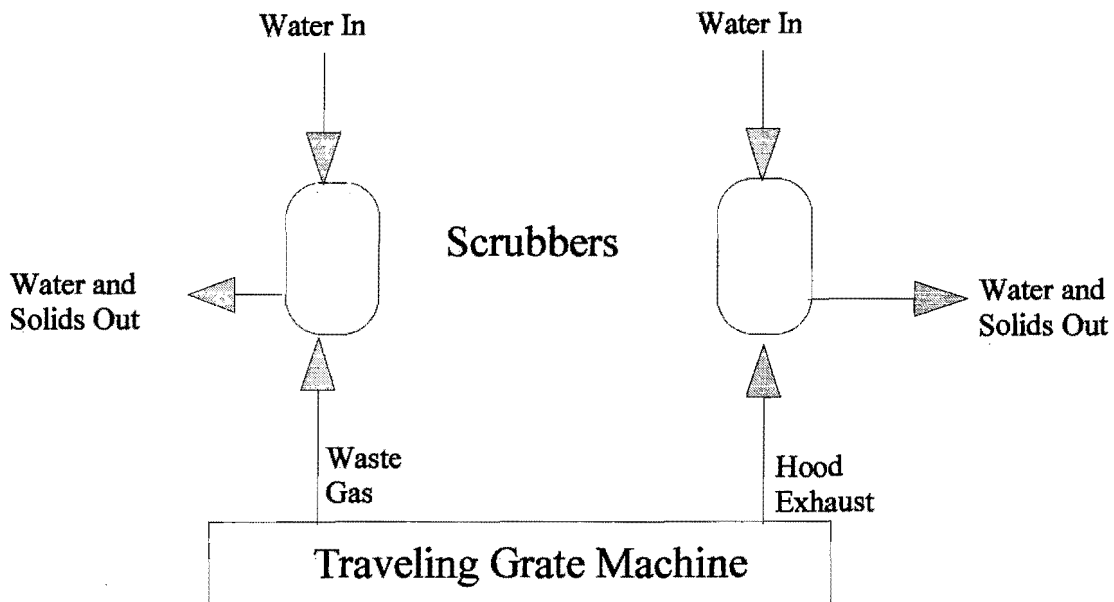


FIGURE 5 - SCHEMATIC OF NORTSHORE SCRUBBERS

**APPENDIX I - MERCURY ANALYSES REPORTS FROM FRONTIER
GEOSCIENCE**

Total Hg in Solids (University of Minnesota)

analyzed by:

Frontier Geosciences R&C 414 Pontius Avenue North, Suite B, Seattle WA 98109

phone: (206) 622-6960 fax: (206) 622-6870 email: nicolasb@frontier.wa.com

Sample Identification	Dry Fraction	Total Hg, ng/g*	
		wet wt basis	dry wt basis
Evtac Green Ball	1.000	12.0	12.0
Evtac Final Pellet	0.999	ND(<0.69)	ND(<0.69)
Evtac Coal	0.998	10.3	10.3
Evtac Thickener Un'flow 2A	0.999	526	527
Evtac Thickener O'flow 2A	0.998	233	233
Evtac Thickener Un'flow 2B	0.997	366	367
Evtac Thickener O'flow 2B	0.996	823	826
Hibtac Filter Cake	0.998	13.9	13.9
Hibtac Concentrate	0.999	18.2	18.2
Hibtac Limestone	0.999	3.72	3.72
Hibtac Mult-tube Dust	1.000	154	154
Hibtac Green Ball	1.000	16.7	16.7
Hibtac Bentonite	0.980	25.9	26.4
Hibtac Fired Pellet	1.000	ND(<0.69)	ND(<0.69)
North Shore Waste Gas Line 11	0.999	211	211
North Shore Waste Gas Line 12	0.999	110	110
North Shore Hood Exhaust Line 11	0.998	25.9	26.0
North Shore Hood Exhaust Line 12	1.000	26.4	26.4
North Shore Green Ball Line 11	0.999	1.44	1.44
North Shore Green Ball Line 12	1.000	1.10	1.10
North Shore Fired Pellet Line 11	0.999	ND(<0.69)	ND(<0.69)
North Shore Fired Pellet Line 12	1.000	1.85	1.85

*Blank corrected

ND-less than estimated MDL

Total Hg in Solids (University of Minnesota)

analyzed by:

Frontier Geosciences R&C 414 Pontius Avenue North, Suite B, Seattle WA 98109

phone: (206) 622-6960 fax: (206) 622-6870 email: nicolasb@frontier.wa.com

Sample Identification	Dry Fraction	Total Hg, ng/g	
		wet wt basis	dry wt basis

Method Blanks

Blank-1		0.89	
Blank-2		1.96 ^a	
Blank-3		0.49	
Blank-4		0.49	
Mean method blank		0.62	
Estimated MDL		0.69	

^aExcluded from calculation of mean method blank

Standard Reference Materials

NIST-2709		1,529	
recovery		109.2%	
reference value		1,400	

Total Hg in Solids (University of Minnesota)

analyzed by:

Frontier Geosciences R&C 414 Pontius Avenue North, Suite B, Seattle WA 98109

phone: (206) 622-6960 fax: (206) 622-6870 email: nicolasb@frontier.wa.com

Sample Identification	Dry Fraction	Total Hg, ng/g*	dry wt basis
--------------------------	-----------------	-----------------	--------------

Matrix Duplicates

North Shore Hood Exhaust Line 11		25.89	
North Shore Hood Exhaust Line 11 MD		25.85	
Mean		25.87	
RPD		0.2%	
North Shore Fired Pellet Line 11		-0.01	
North Shore Fired Pellet Line 11 MD		1.32	
Mean		0.66	
RPD		203.1%	
Evtac Green Ball		11.98	
Evtac Green Ball MD		11.95	
Mean		11.97	
RPD		0.3%	

Matrix Spikes

North Shore Fired Pellet Line 11 MS		9,980	
spiking level		9,488	
net		9,979	
recovery		105.2%	
North Shore Fired Pellet Line 11 MSD		9,868	
spiking level		9,901	
net		9,867	
recovery		99.7%	
RPD		5.4%	

*Blank corrected

Total Mercury in Process Water (University of Minnesota)

analyzed by

Frontier Geosciences R&C 414 Pontius North, Suite B Seattle WA 98109
 phone: 206-622-6960 fax: 206-622-6870 e-mail: nicolasb@frontier.wa.com

sample ID	description	[Hg], ng/L	comments
#8	evtac thickener u'flow water 2A	15.48	
#20	evtac concentrate water	8.61	
#12	evtac slat spray water	5.25	
#10	evtac thickener u'flow water 2B	18.12	
#22	hibtac scrubber water	11.95	
#21	hibtac makeup water	5.37	
#9	evtac thickener o'flow water 2A	82.22	
#11	evtac thickener o'flow water 2B	24.35	
B-1	blank-1	0.12	
B-2	blank-2	0.16	
B-3	blank-3	0.16	
	mean	0.15	
	estimated MDL	0.07	
#12	evtac slat spray water rep 1	4.97	
#12	evtac slat spray water rep 2	6.21	
	mean	5.25	10.5% RPD
	matrix spike level	40.40	
#8	evtac thickener u'flow water 2A + MS	53.71	94.6% recovery
#8	evtac thickener u'flow water 2A + MSD	54.77	97.3% recovery
	mean	52.24	2.1% RPD
NIST-1641d	NIST certified water CRM rep 1	7,751	diluted 200x
NIST-1641d	NIST certified water CRM rep 2	7,054	diluted 200x
	mean	7,403	9.4% RPD
	certified value	7,950	93.1% recovery
	analysis date	2-Jul-01	

Total Mercury in Process Water (University of Minnesota)

analyzed by

Frontier Geosciences R&C 414 Pontius Avenue North, Suite B Seattle WA 98109

phone: (206) 622-6960 fax: (206) 622-6870 email: ericv@frontier.wa.com

sample ID	description	[Hg], ng/L	comments
#9	N.S. Feed Water	7.05	
#10	N.S. Hood Exhaust Water Line 11	32.8	
#11	N.S. Hood Exhaust Water Line 12	15.7	
#12	N.S. Waste Gas Water Line 11	29.1	
#13	N.S. Waste Gas Water Line 12	15.7	
B-1	blank-1	0.05	
B-2	blank-2	0.10	
B-3	blank-3	0.05	
	mean	0.06	
	estimated MDL	0.09	
#11	N.S. Hood Exhaust Water Line 12	15.72	
#11	N.S. Hood Exhaust Water Line 12	17.67	
	mean	15.89	11.7% RPD
	matrix spike level	40.40	
#11	N.S. Hood Exhaust Water Line 12 + MS	57.94	97.2% recovery
#11	N.S. Hood Exhaust Water Line 12+ MSD	56.11	92.9% recovery
	mean	57.03	3.2% RPD
NIST-1641d	NIST certified CRM (diluted 200x)	8,042	101.2% recovery
	certified value	7,950	
	analysis date	July 9, 2001	

Total Mercury in Taconite Mill Substances (Coleraine Minerals Research Lab)

analyzed by

Frontier Geosciences Inc. 414 Pontius North, Seattle WA 98109

phone: 206-622-6960 fax: 206-622-6870 e-mail: nicolasb@frontier.wa.com

sample #	sample description	[Hg]	units	date analyzed	comment
#01	Mintac scrubber in water	78.9	ng/L	18-Jul-01	QC sample
#02	Mintac Scrubber out water	66.5	ng/L	18-Jul-01	
#03	Inland process water	5.67	ng/L	18-Jul-01	
#04	Inland scrubber water	112	ng/L	18-Jul-01	
#05	Mintac greenball	8.1	ng/g	31-Aug-01	QC sample
#06	Mintac fired pellet	< 0.6	ng/g	31-Aug-01	
#07	Mintac scrubber out solids	87.0	ng/g	31-Aug-01	
#08	Mintac coal	25.3	ng/g	31-Aug-01	
#09	Inland scrubber water solids	3,179	ng/g	31-Aug-01	
#10	Inland multi-clone dust	193	ng/g	31-Aug-01	
#11	Inland fired pellet	< 0.6	ng/g	31-Aug-01	
#12	Inland greenball	7.8	ng/g	31-Aug-01	
#13	Evtac thickener 2A + 10m	38.8	ng/g	31-Aug-01	
#14	Evtac thickener 2B + 10m	48.6	ng/g	31-Aug-01	
#15	Hibtac multi-tube dust + 10m	86.8	ng/g	31-Aug-01	
	solids blank #1	0.4	ng/g	31-Aug-01	
	solids blank #2	0.4	ng/g	31-Aug-01	
	solids blank #3	0.2	ng/g	31-Aug-01	
	solids blank #4	0.8	ng/g	31-Aug-01	
	solids blank #5	0.3	ng/g	31-Aug-01	
	solids blank #6	0.2	ng/g	31-Aug-01	
	mean	0.4	ng/g	31-Aug-01	estimated MDL = 0.6 ng/g
	water blank #1	0.05	ng/L	18-Jul-01	
	water blank #2	0.06	ng/L	18-Jul-01	
	water blank #3	0.09	ng/L	18-Jul-01	
	mean	0.07	ng/L	18-Jul-01	estimated MDL = 0.06 ng/L

Total Mercury in Taconite Mill Substances (Coleraine Minerals Research Lab)

analyzed by

Frontier Geosciences Inc. 414 Pontius North, Seattle WA 98109

phone: 206-622-6960 fax: 206-622-6870 e-mail: nicolasb@frontier.wa.com

sample #	sample description	[Hg]	units	date analyzed	comment
#05	Mintac greenball	8.3	ng/g	31-Aug-01	
#05	Mintac greenball dup	7.8	ng/g	31-Aug-01	
	mean	8.1	ng/g	31-Aug-01	6.2% RPD
#05	Mintac greenball + 93.5 ng/g MS	97.4	ng/g	31-Aug-01	
	% recovery	95.6			
#05	Mintac greenball + 99.7 ng/g MSD	107.2	ng/g	31-Aug-01	
	% recovery	99.4			3.9% RPD
	NIST-2709 (soil)	1,367	ng/g	31-Aug-01	certified = 1,400 ng/g
	% recovery	97.6			
#01	Mintac scrubber in water	74.5	ng/L	18-Jul-01	
#01	Mintac scrubber in water dup	83.3	ng/L	18-Jul-01	
	mean	78.9	ng/L	18-Jul-01	11.2% RPD
#01	Mintac scrubber in water + 202 ng/L MS	292.5	ng/L	18-Jul-01	
	% recovery	105.7			
#01	Mintac scrubber in water + 202 ng/L MSD	279.7	ng/L	18-Jul-01	
	% recovery	99.4			6.4% RPD
	NIST-1641d (water)	7,926	ng/L	18-Jul-01	certified 7,950 ng/L @ 200x dilution
	% recovery	99.7			

Frontier Geosciences Inc.

Environmental Research & Specialty Analytical Laboratory

414 Pontius Ave N · Seattle WA 98109

Mr. Blair Benner
University of Minnesota Duluth
Coleraine Minerals Research Lab
P.O. Box 188
Coleraine, MN 55722

July 16, 2001

Dear Mr. Blair,

Enclosed please find our results for the determination of total Hg in 22 solids samples which were received on June 25 and July 2, 2001 and 8 water samples received on July 2. Following receipt, the water samples were preserved with 1% (v/v) 0.2N BrCl and allowed to oxidize at least overnight prior to analysis.

One gram aliquots of the samples were accurately weighed into HF cleaned Teflon bombs, and 25 mL of a mixture of 2:1:1 (v/v) HNO₃ + HF + HCl were added. The samples were digested for 12 hours at 100°C. We find that even though common soils and rocks will easily go into solution in less than 4 hours under these conditions, the "conc." and "pellet" samples did not fully solubilize even after the full 12 hours. Although certain ores, including taconite and bauxite, do not fully solubilize during digestion, we have performed intercomparison exercises with thermal volatilization and aqua regia digestion which suggest that grinding to a powder, followed by HF/HNO₃/HCl digestion is never-the-less the most effective way to liberate the Hg for analysis.

After digestion, the samples were cooled and diluted to 100 mL with reagent water, and stored in their respective digestion bombs until analysis. Aliquots (2.0 mL) of the digests were analyzed using SnCl₂ reduction, purge and trapping on gold coated sand, and cold vapor atomic fluorescence spectrometry (CVAFS) detection. Overall, the analysis went very well, with excellent spike and CRM recoveries, and low blanks. One of the four blanks prepared and analyzed with the set was noted to be higher than the other three, and was excluded from calculation of the mean blank employed to blank correct the data.

206 622 6960
fax 206 622 6870
email: info@Frontier.WA.com
www.FrontierGeosciences.com

Frontier Geosciences Inc.

Environmental Research & Specialty Analytical Laboratory
414 Pontius Ave N • Seattle WA 98109

July 24, 2001

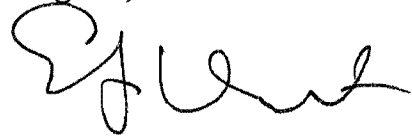
Mr. Blair Benner
University of Minnesota-Duluth
Coleraine Minerals Research Lab
P.O. Box 188
Coleraine, MN 55722

Dear Mr. Benner,

Enclosed please find our results for the determination of total mercury in process water samples received on July 2, 2001. The samples were received in good condition and immediately oxidized with 1% (v/v) 0.2N BrCl. All samples were allowed to oxidize at least overnight prior to analysis.

Aliquots of each sample were analyzed using SnCl₂ reduction, dual gold amalgamation, and cold vapor atomic fluorescence (CVAFS) detection. Analysis went very well, with no analytical problems encountered. Please feel free to contact me if you have any questions regarding these results.

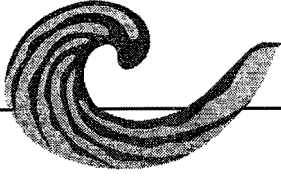
Regards,



Eric J. von der Geest
Analytical Chemist

206 622 6960
fax 206 622 6870
email: info@Frontier.WA.com
www.FrontierGeosciences.com





**FRONTIER
GEOSCIENCES INC.**

ENVIRONMENTAL RESEARCH & SPECIALTY ANALYTICAL LABORATORY

(206) 622-6960 • fax: (206) 622-6870

E-mail: info@frontier.wa.com

414 PONTIUS NORTH • SEATTLE, WA 98109

Mr. Blair Benner
University of Minnesota Duluth
Coleraine Minerals Research Lab
P.O. Box 188
Coleraine, MN 55722

September 9, 2001

Dear Mr. Blair,

Enclosed please find our results for the determination of total Hg in 11 taconite process solid samples and 4 waters, which were received on July 16, 2001. This is a hard copy report of the data table already forwarded to you by e-mail on September 8, 2001.

One gram aliquots of the solid samples were accurately weighed into HF cleaned Teflon bombs, and 25 mL of a mixture of 2:1:1 (v/v) HNO₃ + HF + HCl were added. The samples were digested for 12 hours at 100°C. We find that even though common soils and rocks will easily go into solution in less than 4 hours under these conditions, some ore samples do not fully solubilize even after the full 12 hours. Although certain ores, including taconite and bauxite, do not fully solubilize during digestion, we have performed intercomparison exercises with thermal volatilization and aqua regia digestion which suggest that grinding to a powder, followed by HF/HNO₃/HCl digestion is never-the-less the most effective way to liberate the Hg for analysis. After digestion, the samples were cooled and diluted to 100 mL with reagent water, and stored in their respective digestion bombs until analysis. Water samples were digested by the addition of 1% (v/v) of 0.2 N BrCl in 12N HCl to the original sample bottle, and allowing to sit over night at room temperature prior to analysis.

Aliquots (0.1-2.0 mL of the solids digests, or 5-50 mL of the waters) were analyzed using SnCl₂ reduction, purge and trapping on gold coated sand, and cold vapor atomic fluorescence spectrometry (CVAFS) detection. Overall, the analysis went very well, with excellent spike and CRM recoveries, and low

blanks. One sample (Inland scrubber water solids) went off scale, but was re-analyzed on a different analyzer on the same day.

Please feel free to call or e-mail me if you have any questions, or are in need of additional analytical or contract research services.

Best Wishes,

A handwritten signature in black ink, appearing to read 'Nicolas Bloom', with a stylized flourish at the end.

Nicolas Bloom
Sr. Research Scientist