

CAMECO CORPORATION

**THE DECOMMISSIONING OF THE
B-ZONE WITH ECOLOGICAL
ENGINEERING**

1994 FINAL REPORT

January 31, 1995

EXECUTIVE SUMMARY

Within the decommissioning scenarios for the B-Zone waste rock pile, a passive treatment approach for seepages which might emerge from the recontoured and revegetated pile is being considered. The muskeg areas to be used are within the waste management area, located between the waste rock pile and the pit or Ivison Bay. Design criteria for a scale-up of the process to relegate As and Ni to sediments in these areas are based on 3 years of laboratory and field work. In collaboration with CANMET biotechnology, the forms of As and Ni which would be retained in the wetland sediments were determined and found to be environmentally stable under prevailing condition. Both elements are primarily complexed as organic particulates which are formed in association with the decomposition of added organic materials. In this form, the As and Ni settle to the sediment where they are transformed into insoluble metal precipitates as favourable Eh and pH conditions are encountered in the deeper portions of the sediment.

Estimates of removal rates based on the experiments are 0.046 to $0.25 \text{ g.m}^{-2}.\text{day}^{-1}$ for As and 0.05 to $0.36 \text{ g.m}^{-2}.\text{day}^{-1}$ for Ni. Loading from the waste rock pile seepages are estimated as $153\text{-}398 \text{ kg.yr}^{-1}$ for As and $551\text{-}1,397 \text{ kg.yr}^{-1}$ for Ni for 1992 to 1994 based on 7 % of precipitation reporting as run-off.

An open water muskeg in the vicinity has an area of 2.4 ha and therefore theoretically sufficient to accommodate the annual loadings from the pile. Design criteria for scale-up are presented.

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- Appendix 4 Fyson, A., Kalin, M. and Smith, M.P. (1995) Nickel and Arsenic Removal from Mine Wastewater by Muskeg Sediments. Proc. 11th. Annual Biominet Meeting, Ottawa, January 16, 1995, pp.103-115
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1.0 INTRODUCTION

The decommissioning plans for the B-Zone waste rock pile are being developed. Recontouring and revegetation are options under consideration which would reduce, to a large extent, the seepages which emerge from the waste rock pile. At present, the seepages are collected in a ditch system and pumped to the mill site treatment plant. A decommissioning plan ideally would not require perpetual collection, pumping and treatment of the seepages and therefore, the elimination of the ditch system is being considered.

Boojum research has been contracted since 1992 to evaluate the potential of using passive polishing approaches. The company specialises in the utilization of natural cleansing processes which contain contaminants within the mine waste management area. These processes take place in wetland sediments. As the waste rock pile is surrounded by a raised water table with muskeg and open-water ponds, using these areas for such a passive approach is an attractive option for consideration as it potentially eliminates the need for seepage collection.

Stimulation of sediment microbiology has been proven to raise pH and remove metals in acid mine drainage (Kalin, 1993). In the B-Zone muskeg sediments, such processes could be enhanced through the addition of readily degradable organic materials such as potato waste or alfalfa pellets. This was tested both in laboratory reactor experiments and in field enclosures in the BT-2 area adjacent to the waste rock pile.

This report summarises all of the laboratory and field work and identifies the forms of As and Ni which are formed in the sediments. The waste rock pile seepage characteristics are described and related to waste rock type. Estimates of loadings are derived from the hydrology data and scale-up design criteria are presented.

2.0 ARSENIC AND NICKEL REMOVAL BY MUSKEG SEDIMENT

The seepages from the B-Zone waste rock pile exhibit large fluctuations in pH, As and Ni concentrations. They are collected in a ditch system surrounding the waste rock pile and pumped to a treatment facility at the mill. Within the options to be considered for decommissioning of the waste rock pile, the conventional treatment approach for the pit and the seepages is not attractive, as it produces sludges which require further maintenance and disposal. Passive treatment approaches involve utilization of the muskeg sediments, located between the waste rock pile and the flooded open pit. The muskeg areas (BT-1 and BT-2) surrounding the waste rock pile represent a perched water body, thus suitable for use as a treatment vessel for the seepages which might emerge from the recontoured waste rock pile.

The microbial activity of the muskeg sediments could be enhanced through addition of easily degradable organic material. Consequently As and Ni is removed from the water through organic complexation with decomposition products. The pH would be elevated due to microbial iron reduction. In the deeper portions of the sediments, where low Eh is prevailing, metals form either carbonates or sulphates, which would result in environmentally stable metals.

These As and Ni removal processes, expected to take place in the sediments, formed the working hypothesis which was tested both in the laboratory and in the field since 1992. The laboratory reactor work is summarized in Section 2.1 and the BT-2 field enclosure studies in Section 3.0. The chemistry and hydrology of the waste rock pile and vicinity is summarised in Section 4.0. In Section 5.0 the results are compiled to arrive at design criteria for the scale up using the muskeg sediments.

2.1 Summary of Laboratory Experiments

Five laboratory experiments have been carried out in 2.5 L reactors to characterize the removal rates and processes of Ni and As from B-Zone waste rock pile seepage water. The reactors represent static conditions (i.e. no continuous flow). The removal rates determined in the reactors, dictate the required retention time of water to be treated in the muskeg. The area of the sediments inside the reactor (78.6 cm²) represents the area which is considered to be active in the removal process with the volume of water overlaying the sediments. Design criteria for the scale up of the process can therefore be derived from the reactor experiments which are to be verified with removal rates observed in the field enclosures.

The main findings from the reactors as follows:

- Muskeg sediments remove As and Ni
- Organic amendments increase rates of As and Ni removal
- Diluted and full strength seepages are effectively treated by sediments (the combined seepage collected at 6.11; diluted 6.11 water simulating run-off events and seepages directly emerging at the foot of the pile were tested)
- As is removed principally as organic complexes
- Ni is removed as organic complexes and as carbonates and sulphates.
- Maximum removal rates from stn 6.11 water were 0.17 mg.m⁻².min⁻¹ for As and 0.25 mg m⁻².min⁻¹ for Ni.
- Sediment removal capacity is at least 59.3 g.m⁻² for Ni and 52.2 g.m⁻² for As.

In Table 1, a chronological summary of the experimental series is presented, listing for each experiment the objectives of each experiment, the type of seepage water and

Table 1: Summary of Laboratory Reactor Experiments

Expt. #	Date set-up	Objective	Reference
1	July 1992	To test ability of BT2 and to remove As and Ni from water. Designed to mimic conditions	1,3
2	November 1992	To test reproducibility of As and Ni removal	3,5
3	March 10 1993	To compare removal from station 6.11 and diluted station 6.	5
4	May 10 1993	To compare alfalfa and peat stimulation of As and Ni removal To determine role of sediment To determine form of As and Ni	2,3
5	January 20 1994	To determine sediment treatment efficiency g/L mg/L ()	2,3,4,6

1 CAMECO Collins Bay B-Zone Decommissioning

2 CANMET Arsenic and nickel removal from water, vol. 1, pp 109-118

3 Fyson, A., Kalin, M. and Adrian, L.W. 1994, Environmental Science and Technology, vol. 28, pp. 103-117

4 Fyson, A., Kalin, M. and Smith, M.P. 1995

5 Boojum Progress Report No 2, April 7, 1993

6 Appendix 6 this report

organic amendments used. The main results obtained at the end of the experiments are also summarized in the table and references are given for the Appendices, where methodology and detailed results are outlined. The first two experiments basically determined that BT muskeg sediments are able to remove As and Ni from WRP seepage (stn 6.11) water. Seepage was used at a 5 five fold dilution, as it was felt that addition of the seepage at full strength would provide a shock to the microbial system in the sediment. In addition, under field conditions, the seepage will always be diluted with some fraction of fresh water. Arsenic concentrations were increased through adding spikes of arsenic. As the removal of both As and Ni was very effective after 112 days. A second experiment was set up to test the reproducibility of the removal process. Ninety percent (90 %) of the As was removed and 95 % of the Ni in 45 days. Measurement intervals in the second experiment were much shorter, thus the rates of removal, based on the first experiment, where after 112 days effective removal was noted could be revised to 45 days. The results were reported previously in the Collins Bay Decommissioning report and formed part of a paper presented at the Pittsburgh Acid mine drainage conference. The information is included for ease of reference as Appendices 1 and 3 .

The 2nd experiment, which tested reproducibility (6 identically set-up reactors) was allowed to sit up to 115 days, at which point experiment 3 was started. New water was added to the same reactors, this time representing full strength 6.11, seepage collected at the toe of the Waste rock Pile (WRP-P) and diluted 6.11 water. The reactors were run without addition of more organic amendment. The measurement intervals were decreased in the third experiment, to determine the removal rate. After 21 days significant removal has taken place in all seepage types. Controls were run where amendment was tested in the absence of sediment to determine the role of the sediment. In the absence of sediment microbial community, limited removal was noted. This removal is through adsorption of the metals to organic surfaces. The detailed results are summarized in an internal progress report given in Appendix 5.

The sediments from Experiment 4 were used as for sequential extraction which determined the amounts of various forms of As and Ni held in sediments. This technique employs extraction in KNO_3 to remove ion exchanged metals, $\text{Na}_4\text{P}_2\text{O}_7/\text{EDTA}$ to remove complexed ions, ammonium acetate to remove acid soluble precipitates (some oxides) and HNO_3 to extract the remaining precipitates (mainly carbonates and

The results of the first experiment were encouraging. A second experiment was set up to determine the reproducibility of the results obtained. The data collected 115 days after setup are summarized in table 4. Eh values remained positive, but were sufficiently low that denitrification and dissimilatory nitrate reduction could proceed in the water column. These processes, which reduce nitrate to $\text{H}_2\text{O}/\text{N}_2$ and NH_4 , respectively, can generate alkalinity and help establish conditions for further precipitation reactions, through lowering Eh and raising pH. The low NO_3 concentrations (0.41 to 1.94 mg/L) after 115 days also suggest that one or both of these processes has taken place. Sulfate reduction is indicated by the pour of H_2S and decline in the SO_4 concentration. As and Ni concentrations showed a rapid decline in all reactors. More than 90 % of both elements was removed within 44 days. After 115 days, As concentrations were in the range 0.1 to 0.3 mg/L and Ni concentrations were in the range of 0.05 to 0.14 mg/L. These values are in the same range as the first experiment.

Table 2. Ecological and elemental characteristics of sediments.

Parameter	Sediment		
	BT1-200	BT2-250	BT2-350
Bacteria..... /mL	86,000,000	140,000,000	170,000,000
Sulfate reducers... /mL	1000	50,000	ND ¹
Molds..... /mL	410,000	410,000	1,800,000
Algae..... /mL	1,500,000	1,400,000	1,900,000
ATP..... ng/mL	54	51	33
Arsenic..... ug/g	21	57	411
Nickel..... ug/g	<97	195	786
Sulfur..... ug/g	678	2,335	982
Iron..... ug/g	3,585	5,058	22,683
Phosphorus..... ug/g	97	681	687
Aluminum..... ug/g	10,756	13,132	102,121
Calcium..... ug/g	1,647	4,961	5,990
Magnesium..... ug/g	1,550	2,043	11,881
Loss on ignition.... %	38	84	11

ND¹ Not determined

Table 3. Arsenic and nickel removal by sediments.

Sediment	As, mg/L			Ni, mg/L		
	87	116	229 days	87	110	237 days
BT2-250	3.00	1.10	0.40	0.12	0.11	0.05
BT2-350	1.90	0.20	0.40	0.06	0.10	0.03
BT1-200	0.60	0.75	0.70	0.06	0.06	<0.01

Table 4. Reactor water chemistry 115 days after setup.

Parameter		Reactor						Mean
		E6-1	E6-2	E6-3	E6-4	E6-5	E6-6	
pH at set up.....	units	6.30	6.36	6.23	6.30	6.25	6.27	6.29
pH.....	units	6.44	6.55	6.73	6.07	7.00	7.00	6.63
Eh.....	mV	+88	+100	+163	+102	+129	+189	+129
Conductivity.....	uS/cm	639	620	585	715	523	554	606
Iron.....	mg/L	5.86	5.15	1.38	7.30	1.20	1.56	3.74
Arsenic.....	mg/L	1.30	0.40	0.10	0.30	0.60	0.60	0.55
Nickel.....	mg/L	0.05	0.05	0.08	0.08	0.06	0.14	0.07
Sulfate.....	mg/L	18	33	71	40	69	76	51
Acidity.....	mg/L	3.9	1.7	10.0	5.9	8.1	2.9	5.4
Alkalinity.....	mg/L	190	223	231	205	192	208	208
Phosphate.....	mg/L	0.29	0.26	0.33	0.37	0.76	0.49	0.42
Ammonium.....	mg/L	1.5	0.7	2.2	6.5	1.4	1	2.2
Nitrate.....	mg/L	1.94	0.48	0.88	0.41	0.75	1.36	0.97

A third experiment examined the amount of metal removal when organic material was added as a surface layer over sediments, rather than mixing the organic material into the sediment.

Control Reactors

In the control reactors, where organic amendments were not added, only minor changes in the water chemistry were observed in 70 days. The pH slightly increased in the first 16 days and thereafter declined slowly to original levels of 4.2 (fig. 1a). Acidity (fig. 1b) and Eh (fig. 1c) remained fairly constant. The iron concentration initially decreased, then abruptly increased (up to 21 days) and decreased again (by 34 days) to near initial levels (fig. 1d). Nickel concentrations declined steadily during the course of the experiment (fig. 1e). Arsenic concentrations remained steady for 21 days and then declined (fig. 1f). The NH_4 concentrations remained steady (fig. 1h) whereas the NO_3 concentrations (fig. 1i) declined from 63 to 12 mg/L (34 days). The PO_4 concentrations decreased somewhat (fig. 1j).

Potato Waste Reactors

In the potato waste reactors, there was an increase in pH from 4.1 to 5.1 (mean of 2 reactors) from day 8 onwards to 34 days after set-up (fig. 1a). This trend continued and by day 64, the mean pH of the two reactors was 6. The Eh decreased during the first 16 days of the experiment (fig. 1c). The abrupt decline in Eh between 10 and 14 days after set-up occurred at the same time as the dramatic increase in acidity (fig. 1b) due to release of reduced iron, and possibly organic acids (from microbial decomposition of starch), from the sediment.

The dramatic increase in iron concentration observed between day 10 and day 21 (fig. 1d) was likely due to ferrous iron concentration increases diffusing from the sediment, following microbial iron reduction, and likely accounts for the reduction in Eh. A much smaller increase in iron (from 0.45 mg/L at day 1 to 3 mg/L at day 20) was observed in the control jars, indicating that some oxidized iron precipitates initially present in the solution were reduced, and/or that the potato waste contains minor amounts of iron.

The observed decreases in phosphate concentrations (fig. 1j) are likely related to the increasing pH over the course of the experiment. As pH increased, more HPO_4^{2-} dissociated into PO_4^{3-} and precipitated primarily with aluminum. Increases in NH_4 during the first 10 days (fig. 1h) can be attributed to the decomposition of protein in the potato waste. Decreases in NO_3 observed between 7 to 10 days (fig. 1i) were likely due to denitrification, facilitated by the decline in Eh and the provision of organic acids as electron donors and carbon sources. A reduction in nitrate concentration was also observed in the absence of a sediment (table 5).

Table 5. Chemistry of control jars without sediments.

Treatment	Days	pH	Eh, mV	Cond, uS/cm	Temp, C	Fe, mg/L	Ni, mg/L	As, mg/L ²	SO ₄ , mg/L	NH ₄ , mg/L	NO ₃ , mg/L	PO ₄ , mg/L	Acidity, mg/L ³	Alkalinity, mg/L ³
Potato waste	1	4.12	445	1,620	21.9	0.45	74	50	ND	16	60	59	136	0
	3	4.37	425	1,660	21.8	3.10	74	50	ND	21	51	45	111	0
	8	5.53	90	1,670	13.2	1.10	74	50	594	21	57	59	97	59
	20	4.28	306	1,590	21.6	3.10	64	80	540	12	.3	47	ND	0
	51	6.42	181	1,536	21.9	0.10	73	100	100	18	0	96	103	116
Alfalfa	1	4.44	444	1,510	21.9	0.31	74	50	ND	18	60	48	87	0
	3	5.94	-237	4,100	21.8	0.52	40	50	ND	36	51	57	487	ND
	8	5.72	71	6,120	13.2	3.30	61	50	342	36	7	62	649	2,161
	20	5.69	-119	5,990	21.8	0.40	53	95	160	69	<.2	42	ND	ND
	51	6.83	111	6,110	21.9	ND ¹	17	75	400	500	ND	47	291	2,155

ND¹ Not determined.

²Interference with sulfides suspected in ASTM 3500-As Mercuric Bromide Stain method.

³mg/L CaCO₃ equivalent.

