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 $g.m^{-2}.day^{-1}$ for As and 0.05 to 0.36 $g.m^{-2}.day^{-1}$ for Ni. Loading from the waste rock pile seepages are estimated as 153-398 $kg.yr^{-1}$ for As and 551-1,397 $kg.yr^{-1}$ 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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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 cm^2) 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 Exp

Expt. #	Date set-up	Objective		Reference
1	July 1992	To test ability of BT2 and remove As and Ni from wa Designed to mimic conditi		1,3
2	November 1992	To test reproducibility of A		3,5
3	March 10 1993	To compare removal from stn 6.11 and diluted stn 6.		5
4	May 10 1993	To compare alfalfa and p stimulation of As and Ni r To determine role of sedir To determine form of As		2,3
5	January 20 1994	To determine sediment tr	g/L mg/L l)	2,3,4,6

1 CAMECO Collins Bay B-Zone Decommissic
2 CANMET Arsenic and nickel removal from
3 Fyson, A., Kalin, M. and Adrian, L.W. 1994 , vol. 1, pp 109-118
4 Fyson, A., Kalin, M. and Smith, M.P. 1995 va, pp. 103-117
5 Boojum Progress Report No 2, April 7, 199
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.

With the reproducibility and the observed rates of removal the approach to seepage treatment looked very promising. The next step in process development was to test the role of the sediment in the removal process, to test alternative organic amendments to mulch and alfalfa as well as determine the chemical form in which both arsenic and nickel might be present in the sediment.

The reactor sediments from the previous experiments were sacrificed for the determination of the chemical forms of As and Ni. A new set of reactors was set-up with sediments collected from the field enclosure (E-6) prior to addition of organic amendments in the field. This assured, that the same microbial community is active in the reactors and the field enclosures. From the results of the fourth experiment it was determined, that the organically amended sediments indeed removed Ni and As more effectively than when no organic amendment was added. The details of the experiment were previously reported in a CANMET report and are summarized in the Pittsburgh proceedings which are included as Appendices 2 and 3.

In the last experiment, Experiment 5, the reactors were used to test the maximum removal capacity of the sediments. This was achieved through weekly additions of new 6.11 water until the removal capacity was exhausted. After standing from day 129 to day 274, additions of 6.11 water recommenced. By day 305 As removal ceased and the removal rate of Ni was much reduced. The early results of the final experiment are given in Appendices 2, 3 and 4 and the later results in Appendix 6.

2.2 Form of As, Ni and Fe in Sediments

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, $Na_4P_2O_7$/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 sulphides). The applicability of the technique to these highly organic sediments was tested with spikes of known quantity of both Ni, As and Fe. The sequential extractions yielded good mass balances for As and Fe but yielded highly variable results for Ni, and element which has a very high adsorption affinity for organic material. The details of the recovery are summarised in Appendix 2.

The sequential analyses carried out on the sediments from the reactors and from the field enclosures suggest that much As is held by the sediment in organic complexes. In the presence of organic amendments in the reactors, a substantial amount of precipitate was present. This indicates that reducing conditions, established through addition of potato waste or alfalfa pellets, can lead to removal of arsenic as precipitates. The Eh/pH phase diagram suggests that the conditions found soon after addition of the organic amendments were favourable for formation of arsenite (Appendix 4). This form of As has recently been detected in anaerobic soils contaminated by waste waters from a gold mine (Bowell et al 1994). In the reactors Eh/pH conditions were reached, which would also allow for the formation of sulphide forms of arsenic. It can be expected that such precipitates would be stable and that, in the field, such conditions are prevailing in the deeper parts of the sediments.

The Ni data from the sequential analysis is too variable for quantitative estimation of forms removed. Reducing conditions where achieved in the reactors through the microbial decomposition of organic matter, which based on the Eh/pH diagrams, can lead to precipitation of Ni salts. Using the data generated during the last experiment, and fitting them into Eh/pH phase diagram for Ni, it is evident that data points fall into the zone where equilibria favour dissolved Ni^{+2}. The data indicate that at the onset of decomposition activity when very low Eh values are coupled to low pHs (4-5), sulphide formation is possible (Appendix 4).

2.3 Role of Sediments

In the water column of the reactors, a few days after set-up, particulates formed in the reactors with added organic amendments. At time, water samples were filtered through filter papers (0.45 μm pores) which were analyzed by ICAP. The data is summarised in Table 2.

Table 2: Filter analysis of laboratory reactor waters

Element ug/filter	Experiment 2 reactors		Experiment 4 reactors			
	Mean (n=6)	SD	R-2	R-3	R-4	R-5
	alfalfa/hydroseeding mulch		potato	potato	alfalfa	alfalfa
Al	72	32	235	213	132	300
As	198	196	4,727	3,250	1,125	2,769
Ca	414	175	633	1,110	5,317	27,385
Fe	790	715	2,345	1,988	1,800	9,292
Mg	116	27	360	500	1,063	3,754
Mn	20	15	65	64	160	649
Ni	78	80	6,836	2,488	890	2,108
P	387	90	942	1,186	3,400	9,723
Fe/As	4.0	3.6	0.5	0.6	1.6	3.4
Fe/Ni	10.1	8.9	0.3	0.8	2.0	4.4

100 mL reactor water column was passed through a 0.45 um cellulose acetate filter
Filters were analysed by ICAP

All filter papers contained both As and Ni, which suggests that Ni and As are formed in the water column as particulates and which will later settle to the sediment. The ratios of As, Fe and Ni these three elements on the filters showed little variation suggesting that similar precipitates were forming in the different reactors. The particulates collected on the filter papers do confirm, that indeed processes in the sediment lead to the formation of compounds, which in turn remove As and Ni from the water.

The rates of change taking place in the control jars, where organic matter was added to seepage water in the absence of sediments, indicated clearly the role of the sediment in the removal process. The rates of change of pH, Eh, phosphorus and nitrate and acidity (measured in mg.L^{-1} equivalent of $CaCO^3$) were almost identical for the jars and reactors. The changes in concentrations of As, Ni and electrical conductivity on the other hand, differed between the controls and the reactors with sediment. These declined at a much faster rate in the presence of a sediment indicating that sediment surfaces enhance the removal processes. The sediments therefore enhance the formation of organic complexes with both Ni and As.

2.4 Contaminant Removal Pattern

Overall, the BT wetland sediments in the reactors effectively removed both As and Ni from 6.11 water. In laboratory conditions, contaminant removal occurred in three phases defined by measured changes in water chemistry:

Phase 1: 0-5 days). Initially rapid changes in concentrations of ions are attributable to effects of ion exchange, complexation and precipitation on contact between 6.11 water and the sediments and associated porewater. Also dilution of 6.11 water by pore water contributes to decline in contaminant concentrations. The small changes in some contaminants (e.g. As) suggest that quantitatively this is a small factor.

Phase 2: 5-60 days During this second phase, there were dramatic changes in all parameters monitored with the exception of ammonium-N, which fluctuated with no clear pattern. Overall, pH rose from around 4 to 7 and Eh, conductivity, acidity, Ni, As, nitrate and phosphate declined. More than 90 % of the Ni and As removal due to sediments occurred within 60 days.

Phase 3: 60 days on. Changes in chemistry in this phase were slow for all parameters measured and small relative to phase 2. Phase 3 represents a near 'steady state situation. The trends observed in phase 2 continued. Concentrations of phosphate, arsenic and nickel and also conductivity continued to decline through this period and pH continued to rise. Eh and ammonium remained fairly constant. Nitrate and Fe remained below detection limits.

2.5 Ni and As Removal Capacity of Sediments

The 'sediment treatment capacity' experiment, Experiment 5 yielded valuable data on the dynamics of As and Ni removal and the treatment capacity of the B-Zone muskeg sediments. Over the initial 129 day period of observations (discussed in detail in Appendix 4), As concentrations in the water column declined from 85 $mg.L^{-1}$ to 5 $mg.L^{-1}$. In previous experiments with similar conditions, As concentration eventually declined to stable values of 0.5 $mg.L^{-1}$ to 1 $mg.L^{-1}$. In the present experiment, Ni declined from 70 $mg.L^{-1}$ to < 1 $mg.L^{-1}$.

After a standing period of 145 days, measurements and additions of stn 6.11 water to the 'exchanged' reactors resumed. Results from this 145 day period are discussed in detail in Appendix 6. Chemistry of the water column changed little during the standing period. Laboratory analysis of samples of the 'exchanged' reactors following 4 weekly changes of column water with 'fresh' stn 6.11 water, Ni removal had slowed down considerably and As removal had ceased. The limits of As removal with one 'dose' of organic amendment (potato waste) could thus be defined. At this time, a mean removal of 410 mg of As was estimated for the two reactors. The reactors had removed 466 mg of Ni. A final removal capacity for Ni from 5 g of potato waste has not yet been determined as at the time of writing Ni concentrations were still declining in the reactors. The results indicate that addition of 2 L of 6.11 water over 4 weeks, overloaded the As removal mechanisms.

3.0 FIELD ENCLOSURES

Other studies (Kalin, 1993; Wildeman, 1993) have demonstrated the capacity of wetlands to remove heavy metals from contaminated waters in a wide variety of situations. Literature on passive treatment systems and the chemistry of As and Ni in relation to potential removal processes has been reviewed and has been presented in a paper (Appendix 3). Laboratory experiments (see Section 2) have established the potential for removal and have also characterised the pattern and rate of removal when sediments are augmented with organic amendments designed to enhance removal processes. Field enclosures (Map 1) were set up in B-Zone muskeg to determine whether the laboratory observed As and Ni processes can be reproduced in the field and to assist in the development of design parameters for scale up. Early results have been published (Smith et al 1993) and were presented in the Boojum, 1992 B-Zone Report and are attached as Appendix 1.

3.1 History and Performance of the Enclosures

Each of the 6 enclosures were constructed by enclosing a 2.4 x 2.4 m area of the BT2 wetland within a Fabrene curtain which was anchored within the sediment. The chronology of activities with the enclosure set-up, the addition of amendments and the addition of seepage water and sludges is summarised in Table 3. The enclosures were constructed in July, 1992. After set-up, hydroseeding mulch and fertilizer were added to E-2 and E-5 and mulch, fertilizer and alfalfa to E-3 and E-6. E-1 and E-4 served as amendment-free controls. Station 6.11 water was added to E-4, E-5 and E-6. Data for Ni and As concentrations in the water of the 3 enclosures receiving seepage water and sludge (E-4, E-5 and E-6) since the first sampling in 1992, are shown in Figs. 1 and 2. Seepage water was added annually (a sludge was also added in 1993) and the water sampled 3 or 4 times annually including from under the ice cover in April. Samples were collected from the enclosures immediately prior to, and also 1 to 3 days after, the

Table 3: BT2 Wetland Enclosures-History

Date	Activity	Objective	Reference
July 1992	Enclosures set up 2.4 m x 2.4 m fabrene inserted into sediment E-1 No amendment E-2 0.1 m3 mulch, 2 kg NPK E-3 40 L alfalfa, 2 kg NPK E-4 800 L stn 6.11 water E-5 800 L stn 6.11 water, 0.1 m3 mulch, 2 kg NPK E-6 800 l stn 6.11 water, 40 L alfalfa, 2 kg NPK Water sampled day after setup	To determine if sediments can remove contaminants from waste rock pile seepage and whether removal rates are enhanced organic amendment (alfalfa)	1 Section 3
September 1992	Water sampled	To determine if As and Ni were removed from amended reactors over 2 month period	1 Section 3
April 1993	Water sampled under ice	To determine overwintering effects on water chemistry (sampled under ice)	Section 3
June 1993	120 L of WRP-P sludge added to E-4, E-5 and E-6 20 kg potato waste added to E-3 and E-6 Water sampled before and after amendment addition	To determine if As and Ni are released and subsequently removed by sediments To provide a fuel for anaerobic microbiological processes	Section 3
July 1993	Water sampled	To assess chemistry changes 1 month after addition of amendments	Section 3
August 1993	600 L stn 6.11 water added to E-4, E-5 and E-6 180 g of steel wool added to E-2 Water sampled before and after amendment addition	To continue to test the ability of sediments to remove As and Ni	Section 3
April 1994	Water sampled under ice	To determine overwintering effects on water chemistry	Section 3
June 1994	1154 L WRP-Q water added to E-4, E-5 and E-6 Water sampled before and after amendment addition	To determine the ability of sediments to treat a high loading of contaminants	Section 3
September 1994	Water sampled	To determine capacity of sediments to treat a h loading of contaminants over a summer	Section 3

1 CAMECO Collins Bay B-Zone Decommissioning Year 1-Proposed Target Levels, July 1993

addition of contaminated water or sludge. Water was first sampled in September 1992, on the first field trip following set-up.

In 1993, WRP-P sludge was added to determine whether contaminants were mobilised and if so, were subsequently removed by the sediments. There was little elevation in either As or Ni as shown in Figs. 1 and 2 respectively. In August of 1993, a further addition of stn 6.11 water was made to E-4, E-5 and E-6. Water was sampled the following April (under the ice) by which time most As (Fig. 1) and Ni (Fig. 2) had been removed from the water.

On each site visit in 1994, the surface water of each enclosure and the BT-2 wetland at large were sampled. A summary of water chemistry for the 6 enclosures and BT2-250 are presented in Table 4. There was little effect of the enclosure amendments on Ra226 of U concentration.

Samples were collected from under the ice cover in April 1994, 9 months after addition of stn 6.11 water in August 1993. Water chemistry in the enclosures not receiving seepage water or sludge (E-1, E-2 and E-3) were similar except for concentrations of NH_4-N and NO_3-N which were higher in E-3, the enclosure with alfalfa (Table 4a). The presence of this N-rich material augments the N cycling in this enclosure. At this time, the chemistry of water in E-6 (amended with seepage water/sludge and with alfalfa pellets added in 1992) was similar to that of the enclosures receiving no seepage water (E-1, E-2 and E-3) as shown in Table 4a. In other words, contaminant removal to background levels was complete. In E-4 and E-5 however, concentrations of dissolved Fe and Ni and overall conductivity were higher than in E-1 and E-2 both in April (Table 4a) and in June (Table 4b). As concentrations were similar to the background concentrations on both occasions. This indicates that alfalfa increases contaminant removal rates. Earlier data (Fig. 1 and 2) indicate that Ni and As removal to background concentrations is possible in the absence of alfalfa.

Fig.1: BT2 Enclosures
Dissolved As

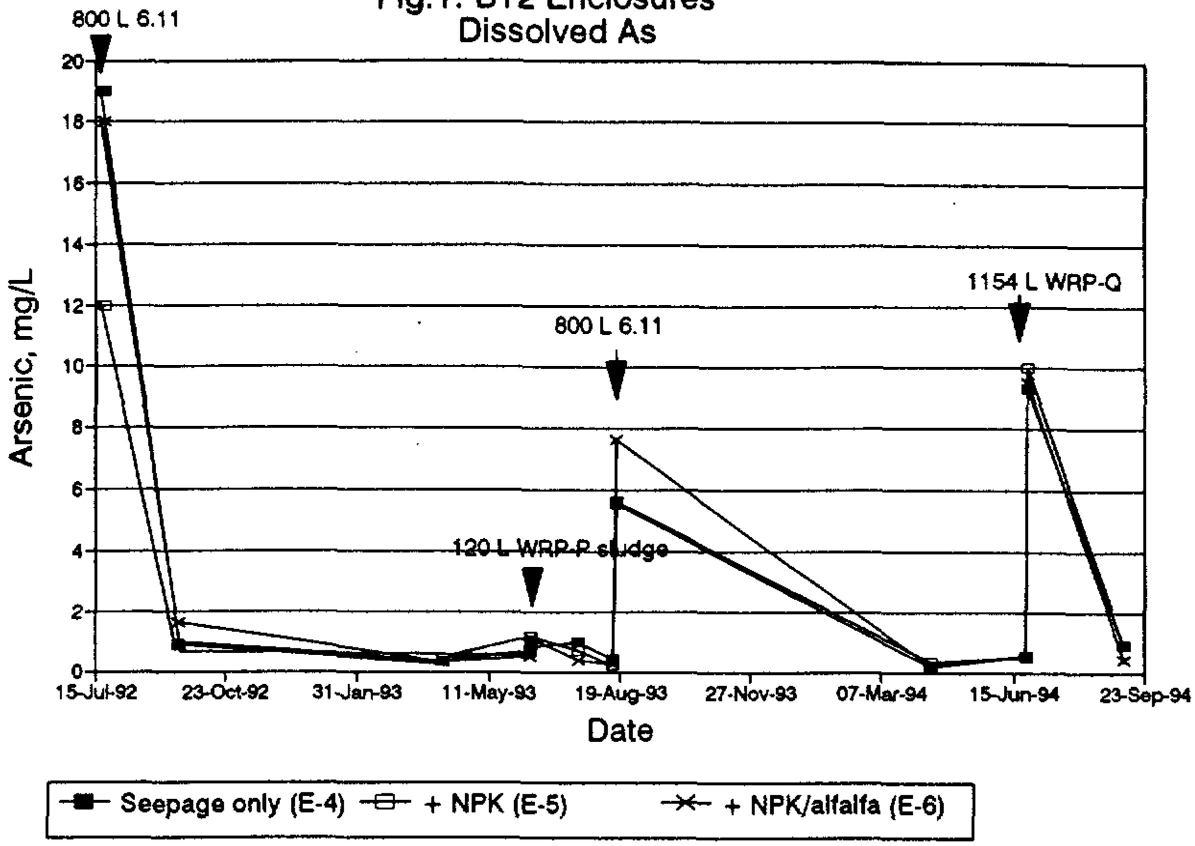


Fig.2: BT2 Enclosures
Dissolved Ni

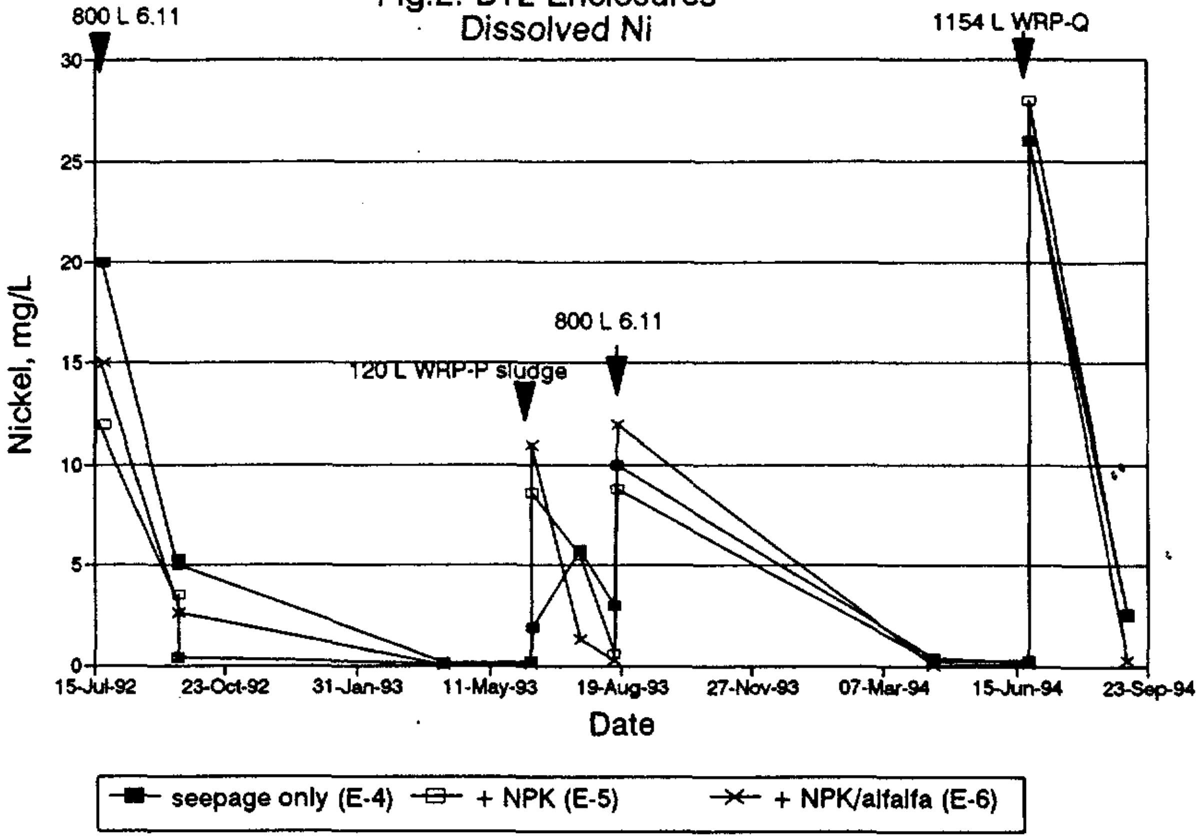


Table 4a: Enclosures-Water Chemistry, April 1994
Samples collected under ice

Description		BT2 250	No added WRP seepage/sludge			Added WRP seepage/sludge		
Enclosure			E-1	E-2	E-3	E-4	E-5	E-6
Amendments				NPK	NPK alfalfa		NPK	NPK alfalfa
pH			4.86	4.82	5.42	6.17	6.94	4.75
Conductivity	mS/cm		20	20	23	46	322	24
NH4-N	mg/L		0.11	0.12	0.35	0.13	0.17	0.12
NO3-N	mg/L		0.25	0.25	0.41	0.35	0.04	0.29
P	mg/L		0.09	0.08	0.12	0.07	0.11	0.08
SO4	mg/L		4	4	3	11	3	2
As diss	mg/L		0.21	0.13	0.13	0.2	0.35	0.21
Fe diss	mg/L		0.071	0.046	0.1	0.96	0.37	0.083
Ni diss	mg/L		0.13	0.077	0.064	0.41	0.22	0.048
Ra226 total	Bq/L		0.45	0.5	0.35	0.45	0.4	0.3

Table 4b BT2 Enclosure-Water Chemistry, June 25 and After WRP-Q water addition, June 26 1994

Description		BT2 250	No added WRP seepage/sludge			Added WRP seepage/sludge			Added WRP seepage/sludge		
Enclosure			E-1	E-2	E-3	E-4	E-5	E-6	E-4 post	E-5 post	E-6 post
Amendments				NPK	NPK alfalfa		NPK	NPK alfalfa		NPK	NPK alfalfa
pH		5.87	5.79	6.23	6.38	6.34	6.61	6.47	3.98	3.86	3.66
Conductivity	mS/cm	22	22	21	23	21	30	23	557	580	541
Em	mV	101	86	64	56	164	44	28	165	208	238
NH4-N	mg/L	0.02	0.01	0.02	0.02	<0.01	<0.01	0.01	1	0.96	0.91
NO3-N	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.4	1.2	1.1
P	mg/L	0.5	0.47	0.37	0.45	0.42	0.39	0.44	5.1	5.3	4.9
SO4	mg/L	<1	<1	<1	<1	2	7	1	264	276	267
As diss	mg/L	0.53	0.52	0.26	0.54	0.56	0.49	0.54	9.3	10	9.5
Fe diss	mg/L	0.14	0.16	0.18	0.12	0.12	0.08	0.14	2.2	1.1	0.82
Ni diss	mg/L	0.045	0.037	0.029	0.026	0.17	0.3	0.066	26	28	26
Ra226 diss	Bq/L	0.12	<0.05	<0.05	<0.05	<0.05	0.11	<0.05	1.4	1.7	1.3
U diss	ug/L	3.1	4.1	3.4	2.5	6.5	4.6	3.7	182	279	258

Table 4c BT2 Enclosures-Water Chemistry, September 8, 1994
74 days following addition of WRP-Q water to E-4, E-5 and E-6

Description		BT2 250	No added WRP seepage/sludge			Added WRP seepage/sludge		
Enclosure			E-1	E-2	E-3	E-4	E-5	E-6
Amendments				NPK	NPK alfalfa		NPK	NPK alfalfa
pH		6.01	6.16	5.89	6.29	5.68	5.33	6.16
Conductivity	mS/cm	30	29	20	30	88	204	22
Em	mV	141	50	79	88	97	72	78
NH4-N	mg/L	2.5	2.4	0.04	2.6	0.04	0.05	0.06
NO3-N	mg/L	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
P	mg/L	0.55	0.48	0.19	0.47	0.58	0.64	0.38
SO4	mg/L	<1	<1	<1	<1	40	108	2
As diss	mg/L	0.59	0.61	0.099	0.49	0.91	0.91	0.42
Fe diss	mg/L	0.41	0.39	0.34	0.31	0.062	0.047	0.48
Ni diss	mg/L	0.056	0.046	0.036	0.019	2.6	2.5	0.25
Ra226 diss	Bq/L	0.04	0.04	<0.04	0.03	0.2	0.35	0.05
U diss	ug/L	5.9	5.7	2.6	9.1	5.3	2.9	9.7

In June, 1994, 1154 L of WRP-Q was added to E-4, E-5 and E-6. This seepage has high As (45 mg.L^{-1}) and Ni (130 mg.L^{-1}). A large addition was added with the hope that by the next sampling, some Ni and As would still be present such that removal rates could be more accurately determined.

Enclosures E-4, E-5 and E-6 were sampled 24 h after addition of WRP-Q water on June 25. The chemistry of the water was similar in the 3 enclosures (Table 4b). As concentrations were in the 9.3 to 10 mg.L^{-1} range and Ni, 26-28 mg.L^{-1}. At the same time, pH declined from 6.3-6.6 prior to seepage water addition to 3.6-4.0.

At the time of the September sampling, it was 74 days since addition of WRP-P water. At this time, the water quality in E-1, E-2 and E-3, i.e. those not receiving seepage water, was similar to the background in the BT-2 muskeg (BT2-250) (Table 4c). It should be noted that E-2 had lower concentrations of NH_4-N, P, As and Ni than the other two enclosures and the wetland at large. In the enclosures amended with seepage water, concentrations of As (0.55 mg.L^{-1}), Ni (0.25 mg.L^{-1}) were substantially less in E-6 with alfalfa than in E-4 and E-5 (mean of 1.15 mg.L^{-1} for As and 2.95 mg.L^{-1} for Ni). The As concentration was similar to that in E-1, E-2 and E-3 indicating that an equilibrium concentration had been reached in the 74 days since seepage water addition. The concentration of Ni, in E-6, while much lower than in E-4 and E-5 was still higher than in E-1 to E-3 indicating that potential removal had not yet been achieved.

Overall, observed rates of Ni and As removal in the enclosures were consistent with those of the reactors where most of the As and Ni were removed from solution in a 60 to 75 day period.

4.0 THE WASTE ROCK PILE

A total of 5.6 million m^3 of waste rock was deposited at B-Zone within seven years, up to 1990. Waste rock was end-dumped and compacted by bulldozer during the mining operation. Since completion of the operation, no further measures, such as contouring, capping or revegetating have been performed. The waste rock included overburden, sandstone and basement rock excavated from the B-Zone open pit. This volume is equivalent to 12.9 million tonnes of material (average density, 2.3) placed within a 31.8 ha area, including the peripheral ditch system.

A summary of observations on seepages emerging from the waste rock pile is presented. Seepages have been collected through the ditch system at station 6.11 at the north eastern corner of the waste rock pile (Map 1). Since 1989, the water quality of samples was regularly determined at the waste rock pile seepage collection point, Station 6.11.

In 1992 and 1993, all seepages drained to a common peripheral ditch system, which directed water to the Station 6.11 seepage collection pond. High water level in this pond trigger a submersible pump, which pumps seepage water to the Rabbit Lake Mill for treatment.

In late 1993, a lined pond was constructed between the waste rock pile and the ore stock pile for retention of perimeter ditch water during periods of run-off in excess of the pumping capacity of the station 6.11 submersible pump and lines.

Upon construction of this lined pond, seepages emerging from the toe of the waste rock pile along the northeast and southeast sides no longer report to station 6.11 and, instead, pool in the ditch at Station WRP-Q. A submersible pump is situated at WRP-Q for pumping of this water during periods of high run-off.

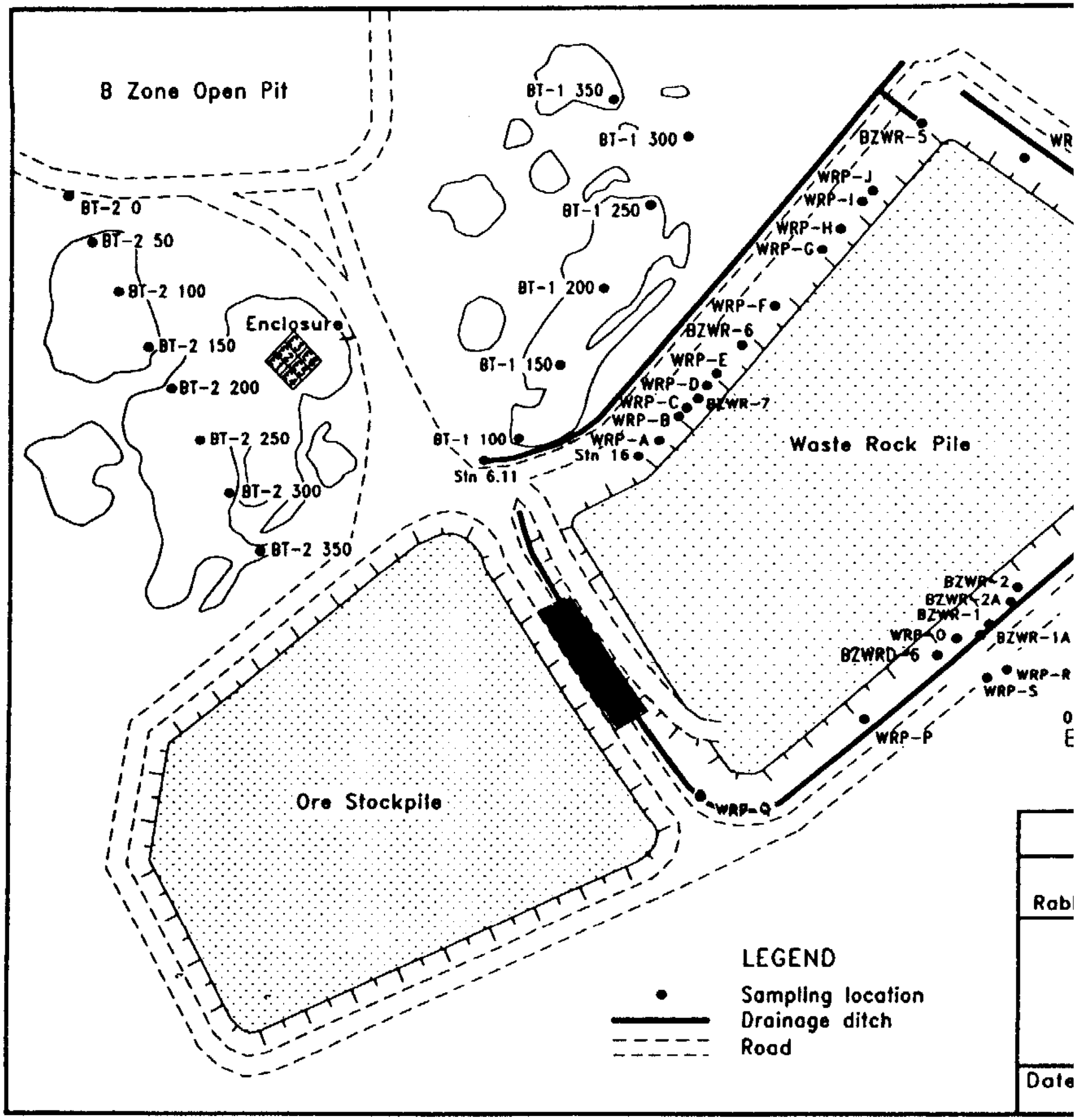

B Zone Open Pit
BT-1 350
BT-1 300
BT-1 250
BT-1 200
BT-1 150
BT-1 100
Stn 6.11
BT-2 0
BT-2 50
BT-2 100
BT-2 150
BT-2 200
BT-2 250
BT-2 300
BT-2 350
Enclosure
BZWR-5
WR
WRP-J
WRP-I
WRP-H
WRP-G
WRP-F
BZWR-6
WRP-E
WRP-D
WRP-C
BZWR-7
WRP-B
WRP-A
Stn 16
Waste Rock Pile
BZWR-2
BZWR-2A
BZWR-1
WRP-O
BZWR-1A
BZWRD-6
WRP-R
WRP-S
WRP-P
WRP-Q
0
E
Ore Stockpile
LEGEND
Sampling location
Drainage ditch
Road
Rab
Date

Table 5: Water Quality of B-Zone WRP Seepages, 1992-1994

	Average	STD	Max	Min	N
FIELD					
Temp. (C)	9	5	20	0.70	73
pH	3.53	2.89	6.00	1.94	110
[H+], mM/L	2.93E-04	1.28E-03	1.00E-06	1.15E-02	110
Cond. (uS/cm)	1463	771	4550	273	73
Eh (mV)	217	64	454	111	72
Flow, L/s	0.053	0.065	0.250	0.002	61
LAB					
Cond. (uS/cm)	1311	538	2140	160	22
Acidity (mg/l)	147	269	1723	5	70
In mg/L: Diss Al	5	13	56	0.11	19
Diss As	46	54	221	0.06	84
Total As	48	62	235	0.09	39
Diss Ca	164	61	292	43	61
Diss Fe	8	36	220	<0.0001	49
Total Fe	8	22	85	0.06	14
Diss K	28	10	56	6	61
Diss Mg	81	43	253	19	57
Diss Mn	7	4	18	2	49
Total Mn	11	0	11	11	1
Diss Na	27	11	70	5	61
Diss. Ni	80	82	400	2	86
Total Ni	63	64	320	2	39
Diss Si	17	6	30	5	18
Bq/L Diss Ra 226	3	2	8	0.25	39
Bq/L Total Ra 226	5	3	20	1	39
Diss U	1	4	27	<0.00005	39
Total U	2	5	28	0.01	39
In mg/L: Chloride	3	1	7	1	61
Bicarbonate	1	1	6	<1	64
Sulphate	806	549	3590	108	80
Nitrate (as N)	21	15	70	1	61
Ammonia (as N)	7	5	21	1	43
Total Kjeld., N	10	6	16	5	2
Total P	25	35	178	0.03	43
T.D.S.	1234	592	2700	327	56
T.S.S.	264	610	2300	<1	15
Total Hardness	672	169	903	292	12

Fig. 3: WRP, Station 6.11
Average, Minimum and Maximum pH by Year

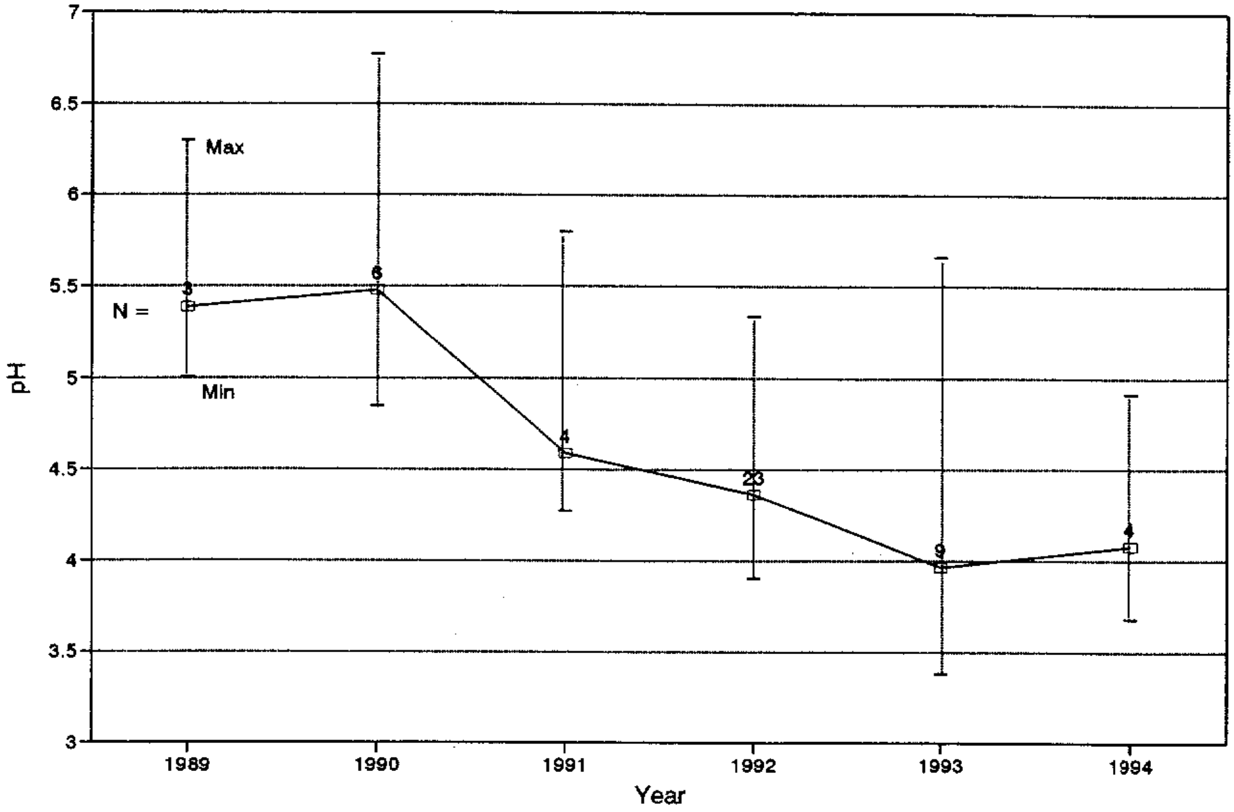
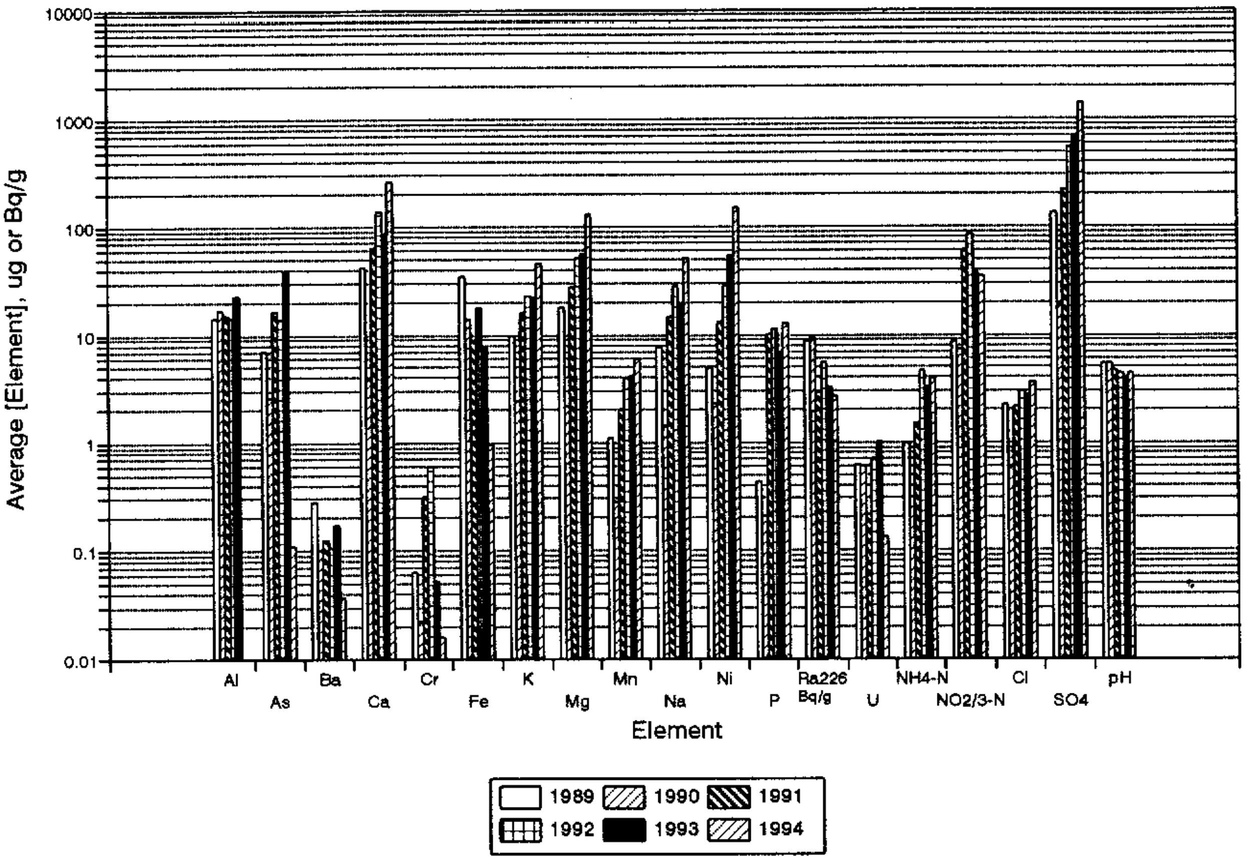


Fig. 4: Stn 6.11, 1989 - 1994



Shallow piezometers have been installed in the wetland areas around the waste rock pile and water quality is monitored periodically. The hydrology of the waste rock pile is summarized, leading to estimations of contaminant loadings from the waste rock pile to the ditch collection system.

4.1 Waste Rock Seepage Characteristics

Waste rock pile run-off water quality has been regularly assessed since 1989 at Station 6.11 and is summarized in Table 5.

From 1989 to 1994, the pH of Stn 6.11 water has overall declined from an average pH of 5.4 in 1989, to an average pH of 4.1 in 1994 (Figure 3). Between 1989 and 1993, the annual average arsenic concentration overall increased (6.1 to 40 $mg.L^{-1}$), but in 1994, the annual average arsenic decreased to 14 $mg.L^{-1}$ (n=4; Figure 4). Annual average nickel concentrations have increased in each year since 1989 (4.9 $mg.L^{-1}$) to an average of 137 $mg.L^{-1}$ in 1994 (n=4; Figure 4).

4.1.1 Waste Rock Pile Toe Seepages

In 1992, 1993 and 1994, water quality and flow rates have been determined for small seepages emerging from the toe of the waste rock pile on the northwest, northeast and southeast sides (Map 1). Seepages have not been observed along the southwest side adjacent to the ore stockpile area.

Seepage samples were collected on May 21, 1992, August 11, 1992, September 18, 1992, May 10, 1993, August 3, 1993, August 17, 1993, August 28, 1993, June 13, 1994, June 26, 1994, July 6, 1994 and September 8, 1994. In Table 5 the data are presented for all toe seepages, describing the average value min max and the standard deviation. The individual samples and their characteristics are given in Appendix 7. The data are discussed, describing the ranges of the concentrations reported for the sampling dates considering all three years.

The pH of the seepages has ranged from pH 1.94 to pH 6.0, averaging pH 3.53 (n=110). The conductivity has ranged from 273 to 4,550 μS.cm^{-1}, averaging 1,463 μS.cm^{-1} (n=73).

The arsenic concentrations have ranged from 0.09 to 235 mg.L^{-1}, averaging 47 mg.L^{-1} (n=86). Nickel concentrations have ranged from 1.8 to 400 mg.L^{-1}, averaging 81 mg.L^{-1} (n=86).

Sulphate concentrations have ranged from 108 to 3590 mg.L^{-1}, averaging 806 mg.L^{-1} (n=90). Iron concentrations have ranged from 0.001 to 229 mg.L^{-1}, averaging 7.4 mg.L^{-1} (n=61).

4.1.2 Toe Seepage Drainage Trends

During the 1994 ice-free season, seepages WRP-A through WRP-J, Stn 16, and BZWR-5 through BZWR-7 (northwest side) drained to Station 6.11 (Map 1). Seepages

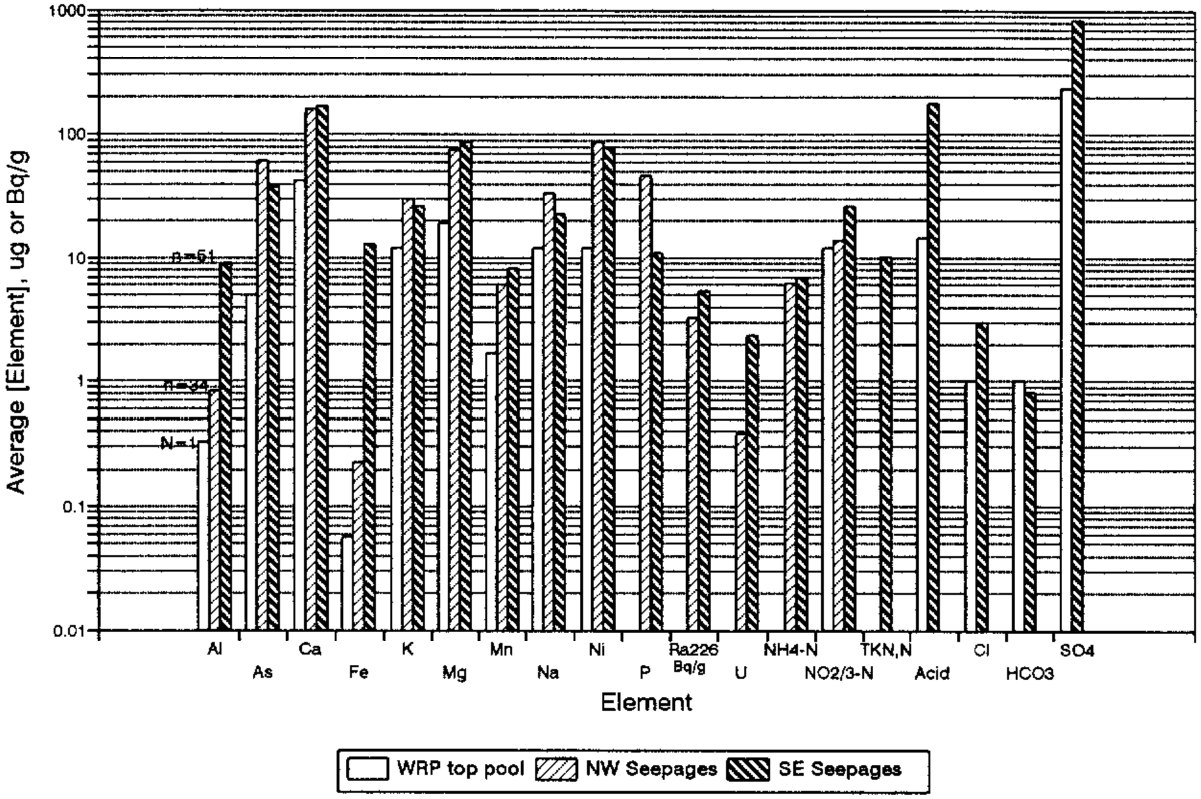
WRP-K through WRP-P, BZWR-1 through BZWR-4, and the seepage at BZWRD-6 report to the peripheral ditch at pool at station WRP-Q (Map 1). The drainage pattern to determine differences in the seepage characteristics are used to group the seepages.

In Figure 5, the average concentrations of elements in the seepages between 1992 and 1994 are presented in three groups. The first group is a single water sample (WRP-T) collected from a pool on top of the northeast end of the waste rock pile on August 19, 1993. The second group is comprised of the northwest seepages which have always reported to station 6.11. The third group is comprised of seepages which, in 1994, drained to station WRP-Q.

As expected, the WRP-T sample (Figure 5: WRP Top Pool) contained, overall, lower concentrations of elements than the seepages which had passed over/through the waste rock pile (NW, SE Seepages). However, as water drained over the waste rock pile surface to the WRP-T pond, it still gained 5.1 $mg.L^{-1}$ As and 12 $mg.L^{-1}$ Ni.

The northwest seepages contain, on average, higher concentrations of As (61 $mg.L^{-1}$) and Ni (87 $mg.L^{-1}$) than the southeast seepages (38 and 78 $mg.L^{-1}$, respectively; Figure 8).

Fig. 5: WRP Seepages, 1992 - 1994
N-W Seepages, SE Seepages; WRP Top Pool



4.2 Whole Rock Analysis and Leach Tests

Whole rock analysis, leach test results and metal concentrations are presented as a preliminary attempt to identify the sources and the processes leading the seepage characteristics. Whole rock analyses were performed on waste rock pile samples collected during a coring program conducted in November, 1993. In addition, 24 hour leach tests were performed on selected samples collected during the coring program.

4.2.1 Results of Whole Rock Analyses

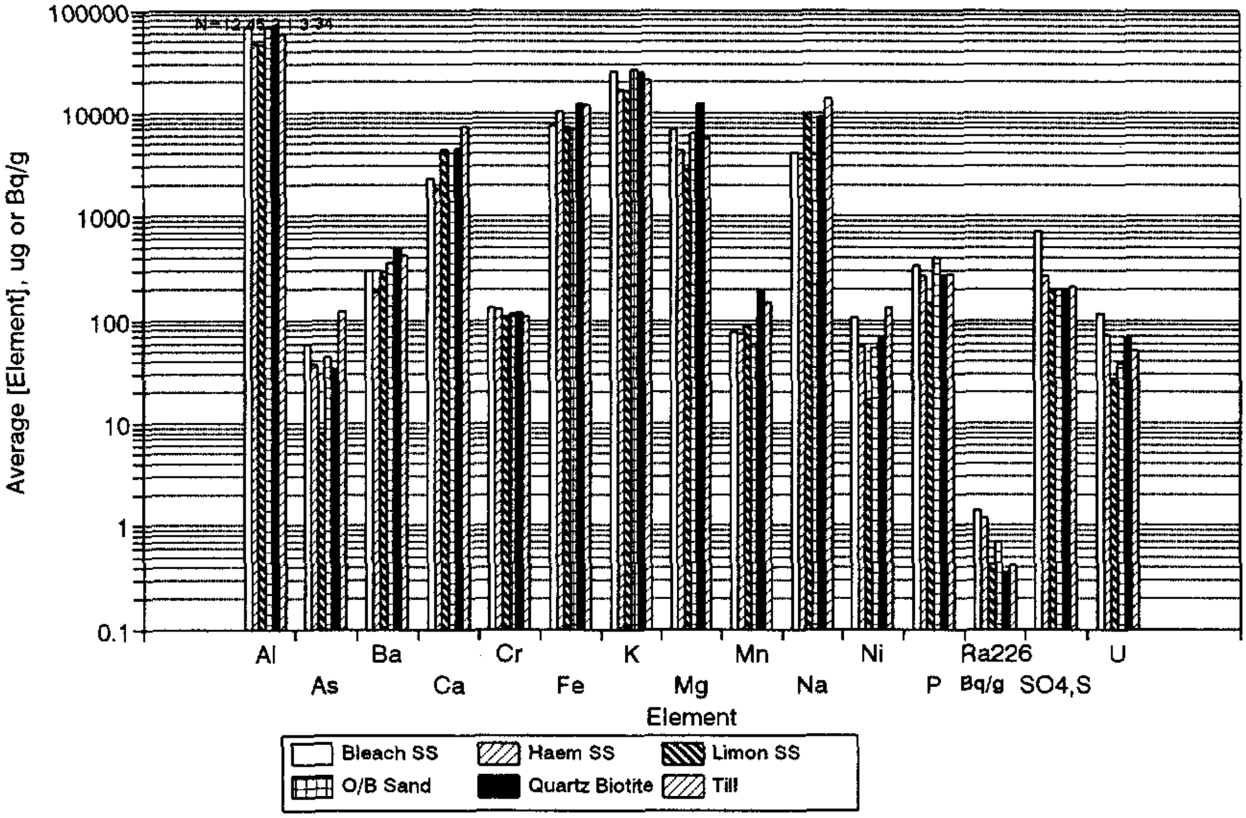
The elemental composition of a total of 95 solid samples was determined. Sandstone (bleached, hematized, limonized) was the primary constituent of 59 of these samples, while 34 samples were comprised primarily of till, and 1 sample of overburden sand, and the remaining 2 samples contained mainly quartz biotite gneiss.

In Figure 6, the average concentrations of elements in the six categories of rock are shown (note log scale). Elements which either comprise a large fraction of the samples (Al, Ca, Fe, K, Mg, Mn, Na, S) or are of environmental concern (As, Ni, ^{226}Ra, U) are presented.

The till is not free of arsenic or nickel, compared to the sandstone or quartz biotite gneiss samples, but actually contained, on average, higher concentrations of these elements than the other five categories. The till also contained, on average, more Ca and Na than the other rock types.

Compared to the sandstone, overburden sand and quartz biotite gneiss, the till contained a similar content of Al, Cr, Fe, K, Mg, P, S and U. The till contained relatively little ^{226}Ra. Overall, arsenic and nickel seems to be more associated with the till component of the waste rock pile, compared to other components, including sandstone, overburden sand and quartz biotite. This suggests, that till containing likely

Fig. 6: WRP Whole Rock Analyses
Grouped by Type of Waste Rock Sample



a significant component of clays, which would adsorb both Ni and As serves as a collector material of the elements.

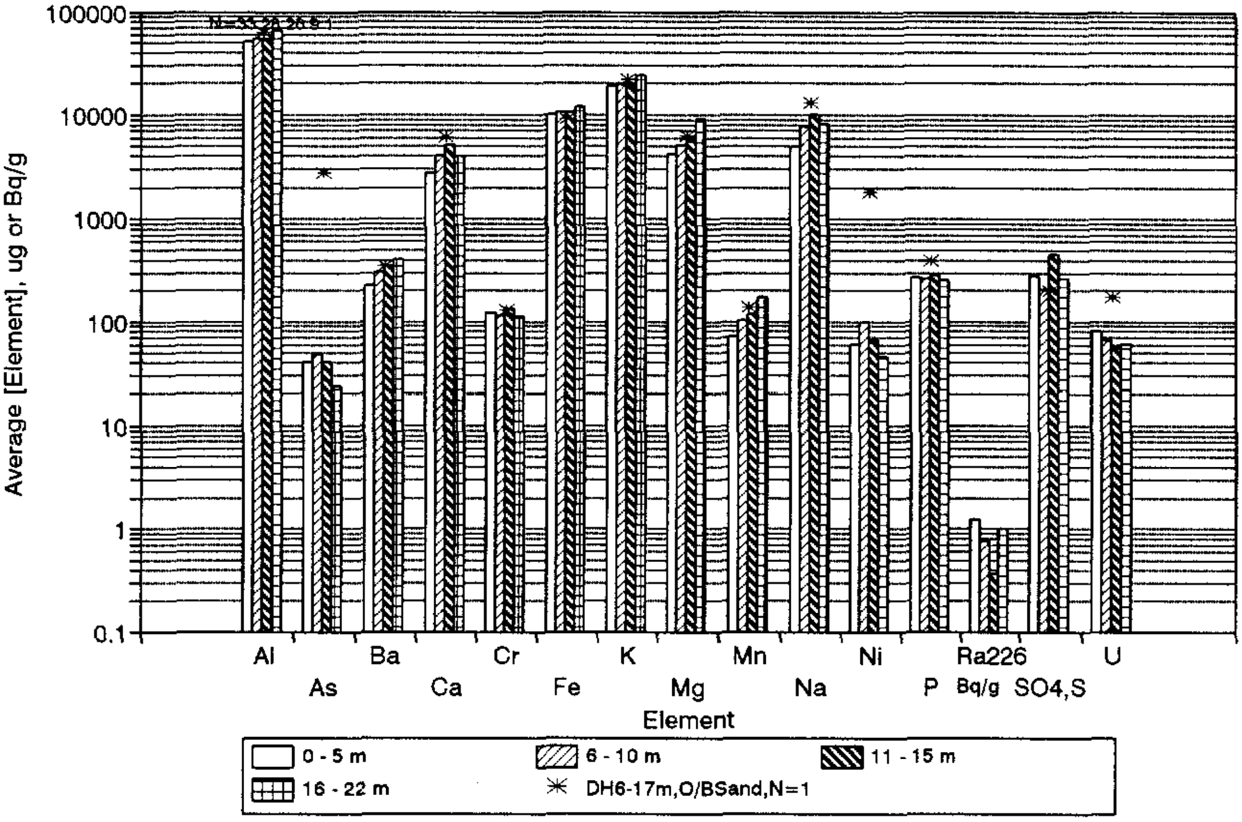
Having identified, that till contains the highest fraction of As and Ni an analysis of the concentrations with respect to their distribution with depth in the waste rock pile, might reveal that the metals are accumulated at a particular depth. In Figure 7, the distribution of elements with depth of sampling, regardless of rock type (sandstone, overburden, combination), is presented. One sample of overburden sand has an extremely high As and Ni content, collected at a depth of 17 m from drill hole 6, and it is presented separately in the graph.

No relationship between the depth of sample and the concentration of any element can be discerned. As and Ni concentrations are somewhat higher, on average, in samples taken at depth between 6 and 10 m, compared to samples taken above and below these depths. There is some suggestion that average Al, Ba, Mg and Mn concentrations slightly increase with depth.

As stated above, the overburden-sand sample collected at a depth of 17 m from drill hole 6 exceptionally high As and Ni. The As concentration in this sample was 2,760 $\mu g.g^{-1}$, compared to average arsenic concentrations in the four depth ranges which were between 20 and 50 $\mu g.g^{-1}$. The Ni concentration in this sample was 1,844 μg.g-1, compared to average concentrations in the four depth ranges of 40 to 100 $\mu g.g^{-1}$.

Overall, no clear trends in the distribution of arsenic and nickel according to depth within the pile, can be discerned. This absence of variation in arsenic and nickel concentrations with depth suggests that As and Ni leaching from the upper layer of waste rock is not enriching, the lower layer of the waste rock pile. Instead, leached arsenic and nickel is likely moving out of the pile via run-off and seepages. It remains possible that enrichment of the till component with arsenic and nickel may be occurring within the waste rock pile at the same time.

Fig. 7: WRP Whole Rock Analyses
Grouped by Depth of Sample



4.2.2 Results of 24 Hour Leach Tests

If the leach conditions during testing for acid generation potential are those which lead to the liberation of metals in the waste rock pile, then a relations ship should be found between the rock type with the highest metals content and its leachate. This furthermore assumes, that indeed the rock type with the highest concentrations of metals, is indeed that type, which liberates most of the metals.

Bleached sandstone, hematized sandstone and till samples collected during the November 1993 drilling program were subjected to a 24 hour leach test in order to determine which elements are solubilized from the waste rock during this procedure. In Figure 8, the results of analyses of leachates, grouped by primary rock type (bleached sandstone, hematized sandstone and till) are shown.

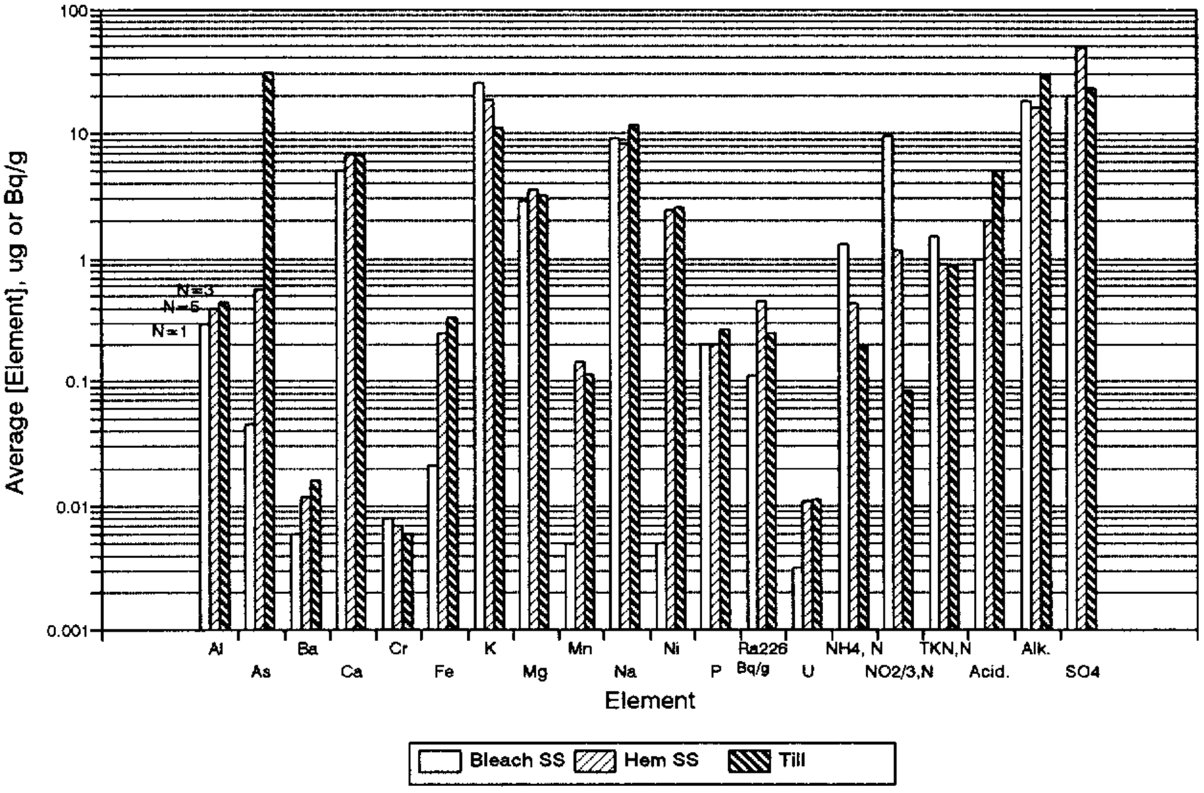
Overall, the average concentrations, for at least one of the three groups of waste rock, of As, Ca, K, Mg, Na, Ni, NH_4-N, NO_2+NO_3-N, TKN-N, acidity, alkalinity and SO_4 exceeded 1 mg.L^{-1}.

The As concentrations of leachates was highest in the till samples, reaching 30 mg.L^{-1} on average (n=3). The leachate from the single sample (n=1) of bleached sandstone contained only 0.05 mg.L^{-1} As, while the hematized sandstone samples' leachates averaged 0.6 mg.L^{-1} As (n=5). This corroborates with the whole rock analyses, where the till samples contained the highest As concentrations.

The Ni concentrations in the leachates from the hematized sandstone and the till samples were similar, at 2.4 and 2.5 mg.L^{-1} , respectively. The bleached sandstone leachate contained <0.005 mg.L^{-1} Ni.

^{226}Ra concentrations in the bleached sandstone leachate was only 0.11 Bq.L^{-1} , while in the hematized sandstone and till leachates, ^{226}Ra concentrations were 0.45 and 0.25 Bq.L^{-1}, respectively. Uranium concentrations were less than 0.01 mg.L^{-1} on

Fig. 8: 24 Hr Leach Test
Grouped by Waste Rock Type



average in all three types of waste rock. Therefore, uranium was not leaching from these samples during this test.

This preliminary analysis of rock types and leachates suggests, that indeed concentrations of As and Ni in the till are mobile and likely contributing to the metal loadings in the seepages. If geological records could be used to evaluate the total quantity of till in the waste rock pile, it could lead to an estimate of the total long term loading of these two contaminants which can be expected to emerge from the waste rock pile. This could be confirmed with further leach tests which could also address the source of the acidity in the seepages.

4.3 Water in the Vicinity of the Waste Rock Pile

Surface water samples have been periodically sampled from at station BT-3 100 and 125, stations 6.9.44. 6.9.4, 6.9.3, a stream flowing into the Ivison Bay wetland and from within the Ivison Bay wetland (see Map 2).

In Figure 9, arsenic concentrations at these stations are plotted. At the BT-3 100 station, As concentrations have been typically elevated and above 1 mg.L^{-1}. At station 6.9.4.4, the point where a surface stream (Stream 1) begins, As concentrations have remained below 0.09 mg.L^{-1}. Downstream, at Stn 6.9.4, As concentrations have remained below 0.03 mg.L^{-1}. At Stn 6.9.3, a point on a second stream (Stream 2) to the west of station 6.9.4, As concentrations were less than 0.09 mg.L^{-1} on the two occasions. At both the Stream 1 location near the Ivison wetland, and in the Ivison wetland, As concentrations have been less than 0.09 mg.L^{-1}.

In Figure 10, nickel concentrations are presented for surface waters between the WRP and the Ivison wetland. Some WRP seepage water has recently entered the BT-3 area, indicated by the high Ni concentration in this surface water. There is some indication that BT-3 water is moving to Stn 6.9.44, as Ni concentrations have overall increased to 0.33 mg.L^{-1}, in 1994, compared to <0.001 mg.L^{-1}in 1991. Ni concentrations at other locations are less than 0.06 mg.L^{-1}.

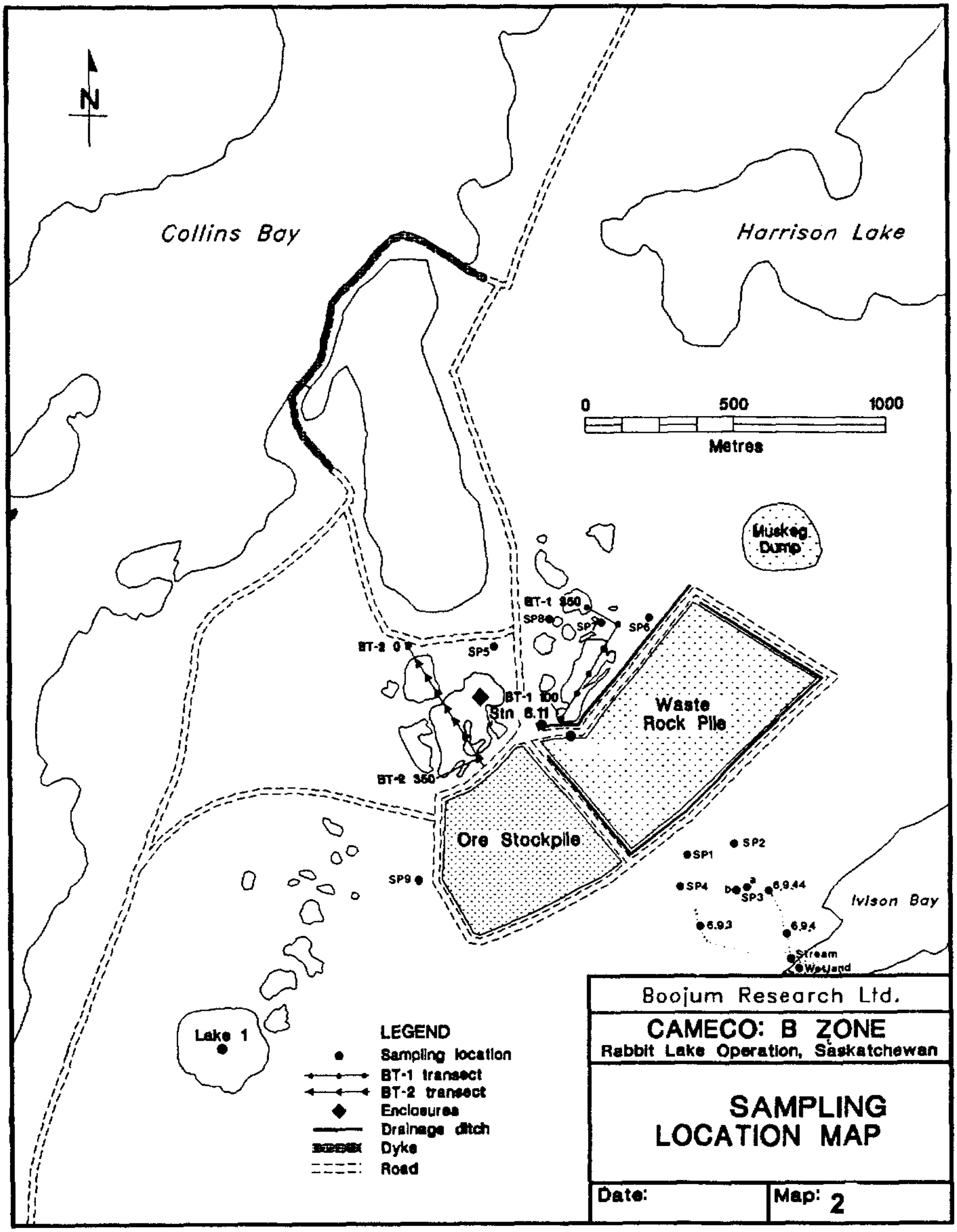

N
Collins Bay
Harrison Lake
0
500
1000
Metres
Muskeg Dump
BT-1 350
SP8
SP7
SP6
BT-2 0
SP5
BT-1 100
Stn 6.11
Waste Rock Pile
BT-2 350
Ore Stockpile
SP9
SP1
SP2
SP4
SP3
6.9.44
6.9.3
6.9.4
Stream
Wetland
Ivison Bay
Lake 1
LEGEND
Sampling location
BT-1 transect
BT-2 transect
Enclosures
Drainage ditch
Dyke
Road
Boojum Research Ltd.
CAMECO: B ZONE
Rabbit Lake Operation, Saskatchewan
SAMPLING LOCATION MAP
Date:
Map: 2

Fig. 9: Run-off Southeast of WRP
As Concentrations in Surface Water

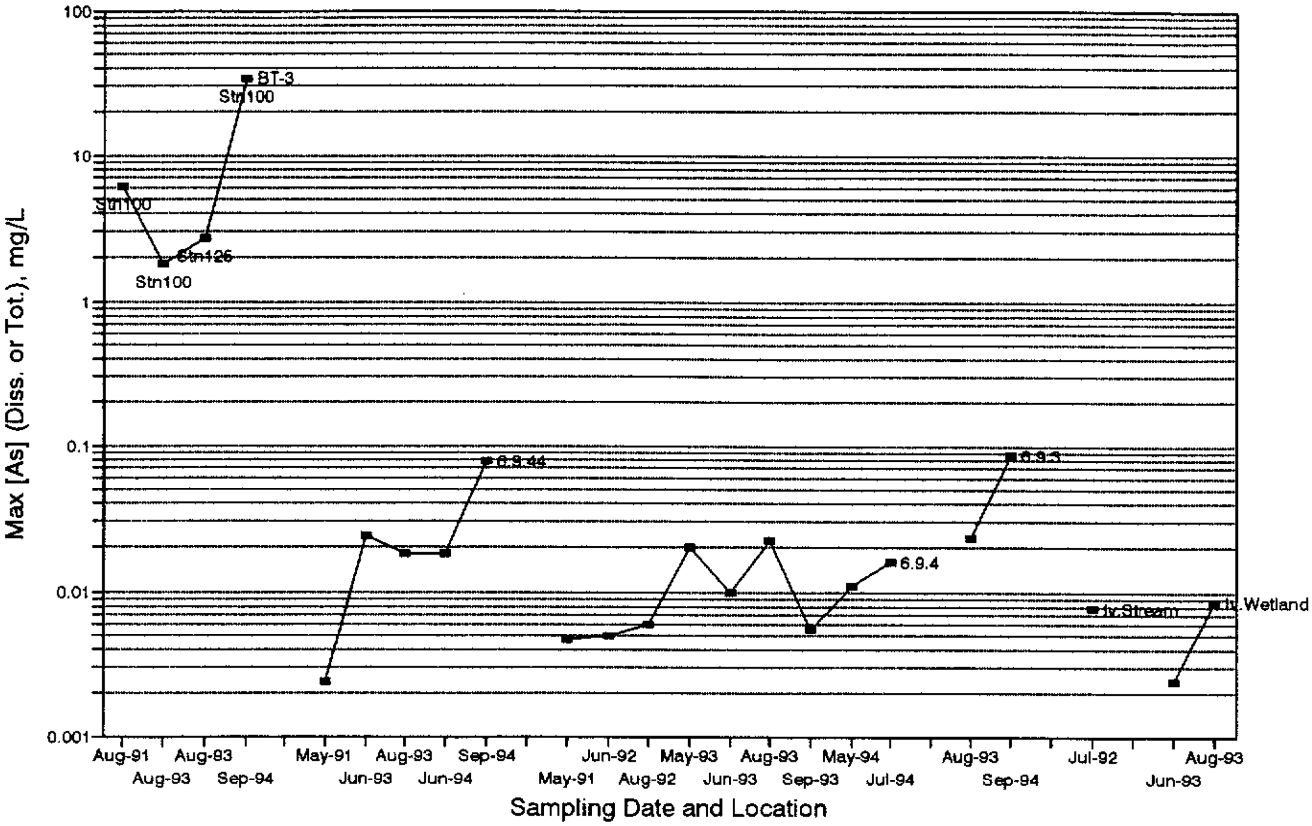
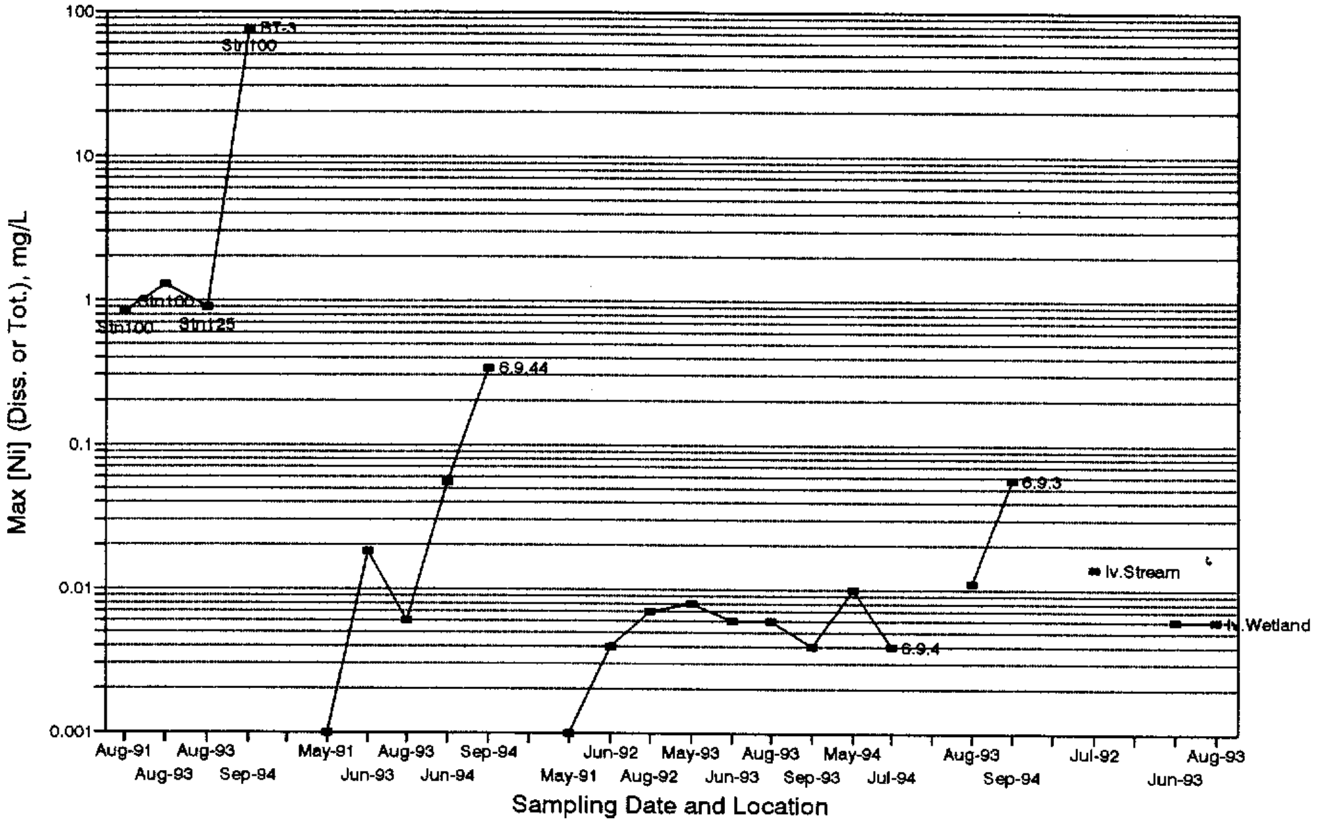


Fig. 10: Run-off Southeast of WRP
Ni Concentrations in Surface Water



4.4 Shallow Groundwater piezometers

Shallow piezometers were installed at nine locations in the vicinity of the B-Zone waste rock pile in 1993 indicated as SP in Map 2. Installation records are provided in the CAMECO B-Zone l993 Decommissioning report, Appendix 2B.

Water samples were collected from the shallow piezometers in June, 1993, June 1994 and September, 1994. As, Ni, Cl and Na concentrations are presented in Figure 11.

Only 3 or 4 samples have been collected to date. Overall, As concentrations have remained less than 0.6 $mg.L^{-1}$. There is some indication that the As and possible Ni concentrations in subsurface waters at SP-3A and 3B might be increasing, but with the scarcity of the samplings the suggestion is very tentative. As and Ni concentrations do not appear to be increasing at all other locations.

Water levels in the shallow piezometers are presented in Figure 12 although there are very few water level measurements the general assumption that the BT-2 wetlands represent a perched water table appear to be confirmed, given the small fluctuations in the piezometers.

Fig. 11: B-Zone Shallow Piezometers
Subsurface Water Quality, 1993-1994

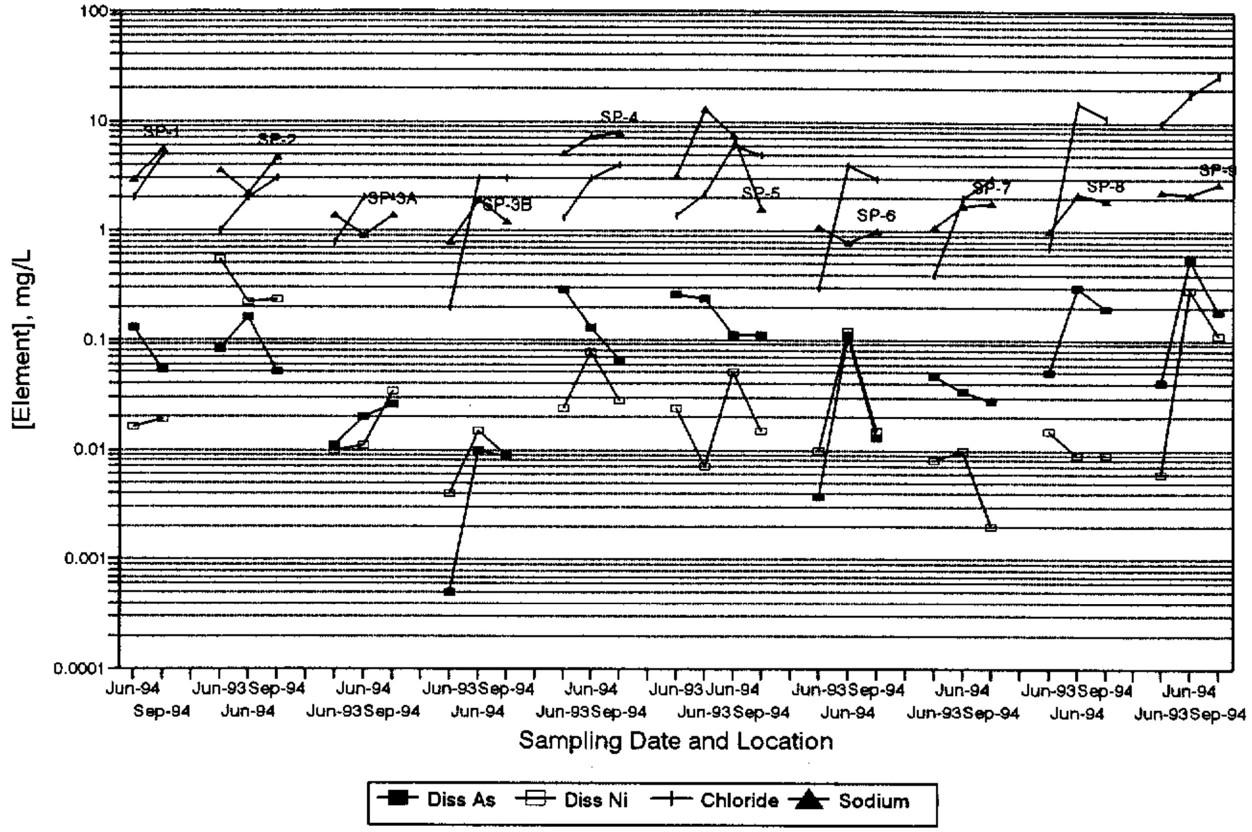
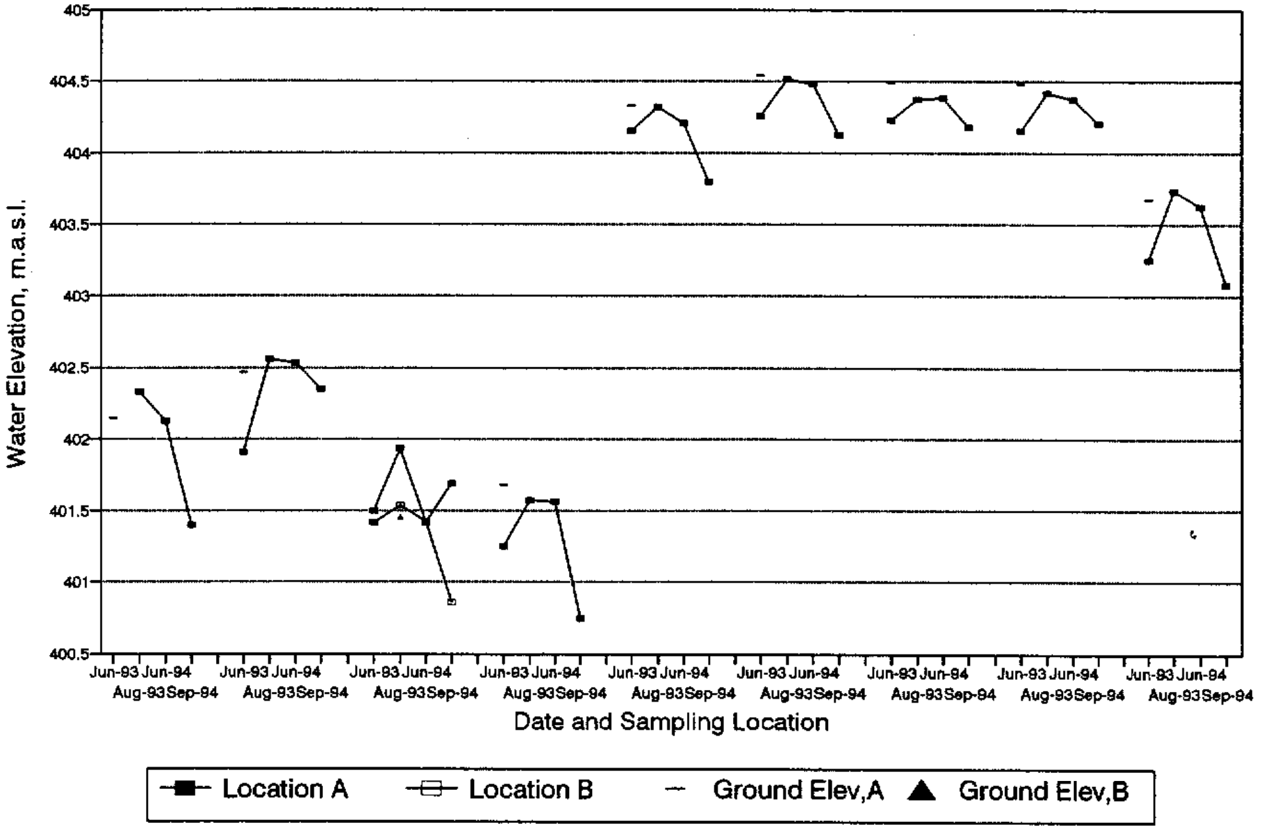


Fig. 12: B-Zone Shallow Piezometers
Water Level, m.a.s.l.



4.5 Waste Rock Pile Hydrology and Contaminant Loadings

Daily precipitation data can be compared to daily pumped volumes in 1992 and 1993 (Figure 13, Table 6).

In 1992, an estimated 73,402 m^3 of precipitation fell on the 26.2 ha WRP area between May 7 and October 10 (Table 6). During this period, 5,085 m^3 of water was pumped out of the Stn 6.11 pond. Therefore, 6.9 % of precipitation reported to Stn 6.11 as run-off (Figure 13). In 1993, an estimated 63,886 m^3 of precipitation fell on the WRP area between May 1 and October 10 (Table 6). During this period, 8,466 m^3 of water was pumped out of the Stn 6.11 pond. Therefore, 13.3 % of precipitation reported to Stn 6.11 as run-off (Figure 13).

These run-off percentages (6.9%, 13.3%) are in the same range of the estimated run-off value of 7 % derived from HELP modelling of the waste rock pile in its current configuration (bare rock, no contouring, capping or revegetation; Table 6).

Annual average arsenic and nickel concentrations in Stn 6.11 water are shown in Table 6. These average concentrations, multiplied by the pumped water volumes, give the arsenic and nickel loads for the May to October period for 1992, 1993 and 1994. Using the pumped volume data in these three years, it appears that the arsenic load to Stn 6.11 is variable, while the nickel load is increasing (Table 6).

The arsenic and nickel load at Stn 6.11 are also calculated using the 7 % run-off value (HELP modelling) and the 16 year annual average precipitation for Collins Bay for the entire year. This run-off estimate is considerably higher than the 3 % run-off estimate calculated in 1992, and estimated As and Ni loads are accordingly higher.

Fig. 13: WRP Measured Cumulative Prec. and Cumulative Pumped Run-off, 1992-93

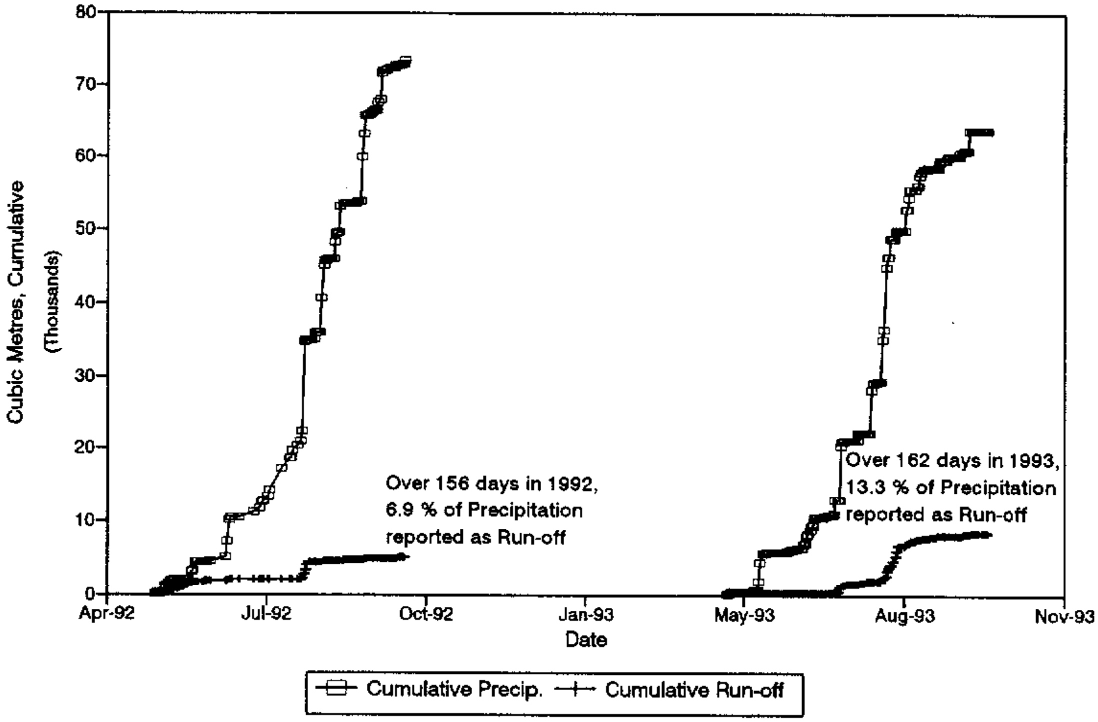


Table 6: Estimated Arsenic and Nickel Loads in Run-off from the B-Zone Waste Rock Pile, 1992-1994

	1992 May 7 - October 10	1993 May 1 - October 10	1994 May - October
Days in Period	156	162	
Area of WRP including peripheral ditch, m2	262,000	262,000	262,000
Measured Prec. x Area, m3 in period	73,402	63,886	
Measured Pumped Volume, m3 in period	5,085	8,466	8,100
Calculated % Run-off	6.9%	13.3%	
Stn 6.11 Annual Avg Tot [As], mg/L	36	39	15
Stn 6.11 Annual Avg Tot [Ni], mg/L	80	54	137
As Load in period, kg	183	330	122
Ni Load in period, kg	407	457	1110
Total volume on WRP, based on 16 year precipitation average, 0.556 m/yr, m3/yr	145,672	145,672	145,672
At est. 7% of Precip. reporting as run-off, m3/yr	10,197	10,197	10,197
As Load, kg/yr	367	398	153
Ni Load, kg/yr	816	551	1,397

5.0 DESIGN PARAMETERS: ARSENIC AND NICKEL REMOVAL BY MUSKEG

The capacity of muskeg sediments to remove Ni and As from WRP seepage water has been demonstrate both in the laboratory (Section 2) and in the field (Section 3). Removal rates both in field and laboratory conditions can be calculated. The total estimated capacity of 1 m^2 of sediment with additions of 637 g of potato waste are assessed at 52.2 g for As and a minimum of 59.3 g for Ni based on reactor Experiment 5. The field enclosures should continued to be charged with seepage, in order to determine a final carrying capacity for both contaminants. These results demonstrate that a low maintenance treatment option exists for the waste rock pile seepages.

The estimates of annual Ni and As loadings from WRP seepages were to range for the years l992 to l994 between 150 kg and 400 kg of As and 0.5 to 1.4 tonnes of Ni. From these expected loadings, areas required for seepage treatment can be derived using estimates presented in Table 7. The highest rates were not surprisingly found for the reactors with frequent changes of seepage water (0.36 $g.m.^{-2}day^{-1}$ for Ni and 0.245 $g.m.^{-2}day^{-1}$ for As, Experiment 5). The rates for the field enclosures are of the same order of magnitude as in the laboratory reactors. It should be noted, that these rates are determined by the sampling interval and not by the removal process. As the sampling intervals for the enclosures are long, the rates are low. By the time the enclosures are sampled after the addition of seepage, all Ni and As has been removed, but this may have occurred within a shorter period.

The removal rate data has been combined with the estimated WRP loadings for 1992, 1993 and 1994 in Table 8 to provide estimates of the area required to treat the total annual loadings of As and Ni. Each of the 3 years for which total annual loadings have been calculated, are considered separately as the loadings show considerable annual variation. Using the 'conservative' enclosure removal rates (0.135 $g.m.^{-2}day^{-1}$ for As and 0.11 $g.m.^{-1}day^{-1}$ for Ni), areas required for As removal range from 0.31 ha (with 1994 loadings) to 0.81 ha (with 1993 loadings).

Table 7: B-Zone enclosures and laboratory reactors-As and Ni removal rates

A Arsenic

Treatment	Source of rate	Removal rate (mg/m2/min)	Removal rate (g/m2/day)	Note
Weekly pumping of seepage water	Recharged reactors (Expt.5)	0.17	0.245	1
Rates with 1 annual loading of seepage water	Unchanged reactors (Expt.5)	0.08	0.115	2
Rates in field with annual C addition and annual addition of seepage water	Enclosures (1992 data for stn 6.11 water)	0.093	0.046 (5)	3
Rates in field with annual C addition and annual addition of seepage water	Enclosures (1994 data for WRP-P water)	0.042	0.059	4

B Nickel

Treatment	Source of rate	Removal rate (mg/m2/min)	Removal rate (g/m2/day)	Note
Weekly pumping of seepage water	Recharged reactors (Expt.5)	0.25	0.360	1
Rates with 1 annual loading of seepage water	Unchanged reactors (Expt.5)	0.05	0.075	2
Rates in field with annual C addition and annual addition of seepage water	Enclosures (1992 data for stn 6.11 water)	0.077	0.123 (5)	3
Rates in field with annual C addition and annual addition of seepage water	Enclosures (1994 data for WRP-P water)	0.107	0.165	4

1 Based on removal from day 12 to day 91 in R-1, R-2 and R-3 in Expt.5

2 Based on removal from day 12 to day 56 in Expt. 5

3 Based on removal from addition of 6.11 water on 22 July to sampling on 17 September 1992

4 Based on mean removal in E4, E5 and E6 from 25 June to 8 September 1994

5 From 1992 Report

Table 8: Areas of wetland required to remove As and Ni from seepages
Based on estimated contaminant removal rates from field enclosure and Laboratory reactor experiment 5
Area available is 2.4 ha in BT-1, 6.1 ha in BT-2 and 5.6 ha in Lake 1

Arsenic

Year	Estimated l kg/yr (1) 7% runoff	Estimated l g/day (1) 7% runoff	Area required (ha) Enclosure rates 1992 0.046 g/m2/day (2) At 3 % runoff	At 7 % runoff	Enclosure rates 1994 0.059 g/m2/day (4)	Weekly chang 0.245 g/m
1992	367	1005	0.9	2.2 (3)	1.7	0.4
1993	398	1090	1	2.4 (3)	1.8	0.4
1994	153	419	0.4	0.9 (3)	0.7	0.1

Nickel

Year	Estimated l kg/yr (1) 7% runoff	Estimated l g/day (1) 7% runoff	Area required (ha) Enclosure rates 1992 0.123 g/m2/day (2) At 3 % runoff	At 7 % runoff	Enclosure rates 1994 0.165 g/m2/day (4)	Weekly chang 0.36 g/m2
1992	816	2236	0.8	1.8 (3)	1.4	0.6
1993	551	1506	0.5	1.2 (3)	0.9	0.4
1994	1397	3827	1.3	3.1 (3)	2.3	1.0

(1) Estimated loadings based on stn 6.11 pump volumes and water quality data for year in question
(2) From 1992 report
(3) Based on rates in 1992 report and recalculated loadings
(4) Based on mean change in concentration from June 25 to September 8, 1994
Removal rates for reactors are based on Experiment 5 data
(5) Rates for 'weekly changed reactors' based on change in mean [As] or [Ni] in reactors 4-6 from 12 to 91 days
(6) Rates for unchanged reactors are based on change in mean [As] or [Ni] in Reactor 1-3 water column from 1

Areas required for Ni removal are larger and range from 1.37 ha (1993 loadings) to 3.48 ha (1994 loadings). The BT-1 wetland with an area of 2.4 ha would be large enough to remove the As and large enough to remove the Ni for two of the three years.

It is therefore suggested, that the removal process be scaled-up in one of the selected muskeg areas along with the continued additions of seepage to the old enclosures.

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CAMECO Collins Bay, B-Zone Commissioning Year 1: Proposed Target Levels, July 1993

SECTION 3.1 Investigative studies 1992-Ecological Engineering

Appendix 4b Decommissioning of B-Zone Area Using Ecological Engineering

ARSENIC AND NICKEL REMOVAL FROM WASTE ROCK SEEPAGES USING MUSKEG SEDIMENT

FINAL REPORT

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada

DSS FILE #: 015SQ.23440-3-9275
DSS CONTRACT SERIAL #: 23440-3-9275/01-SQ
SCIENTIFIC AUTHORITY: Dr. G. Bechard
Date: April 20, 1994

EXECUTIVE SUMMARY

Passive treatment systems for mine waste water have, over the past 10 years, received increasing attention from the research community. These types of treatment options are particularly attractive for decommissioning in situations where effluent loadings are low and flows seasonal. The effluent-cleansing processes are natural in passive systems, and are biologically-mediated. Wetland sediments are the most important aspect of these natural treatment systems.

The use of sediments for passive treatment in ponds within a muskeg area surrounding a waste rock pile is being investigated. Acidic seepage from that waste rock pile requires treatment, specifically for the removal of As and Ni. Microbial activity is stimulated in the sediment with additions of degradable carbon. Field enclosures set up in the muskeg ponds have removed As and Ni from seepage water and the pH has been increased. Detailed laboratory studies confirmed the removal at similar rates in batch conditions.

A literature review on As and Ni in sediments indicates that adsorption/desorption are the main processes which control both metals' chemistry in the sediment; these processes are affected by Eh and pH. Arsenic can be precipitated as ferrous-arsenate and Ni as nickel sulphide. Both precipitates can be microbially mediated in the lower parts of the sediment.

Sediments were spiked with these precipitates and recovered using sequential extractions. The sequential extractions identify the exchangeable forms of the precipitates, those which are organically bound, the carbonate forms of the precipitates, and finally with a nitric acid extraction, the mineralized forms of the precipitates. Arsenic was extracted mainly in the organically-bound fraction, ranging from 86 % to 98 % of the spike. Nickel was partitioned between the exchangeable fraction and the organic fraction. In the presence of sulphide, a significant shift was noted in that more Ni was extracted as exchangeable (86 %) and less remained in the pore water (1.3 %). This suggests indirectly that the sediment adsorption properties change in the presence of sulphide reduction, which increases the stability of the sediment as a Ni sink.

The laboratory reactor sediments, which facilitated the removal of As and Ni from the seepage, were sampled destructively to determine pore water chemistry and the chemical forms of As and Ni which had accumulated in the top 1 cm of the sediment.

The pore water chemistry indicated that in reactors where microbial sulphate reduction took place, the lowest Ni concentrations (0.43 mg/L) were detected in the pore water. In the control reactor, the concentrations were 7.8 mg/L. The highest As concentrations were reported in the control reactors, at 11 mg/L, which was reduced to 3 mg/L when carbon amendments were added to the sediment. The original seepage water concentrations were 39 mg/L and 61 mg/L of As and Ni respectively.

The As in the top layer of the sediment is present either as organically bound or extractable with the carbonate fraction. Through carbon additions, a shift takes place to the carbonate form. None of the As is present in the mineral fraction of the sediments. The distribution of the precipitated Ni is different from As in that about 43 % to 84 % is present in the exchangeable form, 42 % to 69 % as organically bound, and the remainder as either carbonate (3 % to 8 %) or in the mineral form (6.8 % to 16 %).

A final mass balance on the reactors suggests that, overall, only a small fraction of the As and Ni is available in the pore water. In the reactors where organic matter was added to the sediment, generally higher fractions are retained in the sediment.

Experiments were carried out in 2 L column reactors to repeat the previously noted removal capacity of muskeg sediments to treat seepage high in As (85 mg/L) and Ni (74 mg/L). The results were repeated and effective removal (> 90 %) was achieved for both elements within 56 days. Organic amendments (potato waste) stimulated microbial activity and generated reducing conditions.

Further work will be required to compare the laboratory results to the field results. To date however, the stimulation of microbial activity in muskeg sediments appears to be a promising option for decommissioning.

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1.0 INTRODUCTION

Wetlands have been employed for the mitigation of acid mine drainage. Most of these wetlands are for the treatment of coal drainage and function by precipitation of iron as iron(III) hydroxides in aerobic conditions (Brodie 1990). Treatment of base-metal-rich mine drainage has been less extensively investigated. Emphasis has been placed on anaerobic microbial treatment where, in sediments, alkalinity generation takes place through iron and sulphate reducing bacteria. The pH is elevated as a result of the microbial activity which, in turn, facilitates the precipitation of metals as either sulphides and/or hydroxides (Bell et al 1989, Kalin 1993, Wildeman 1992). These processes take place in wetland and lake sediments and might be utilized as a decommissioning option for seepage treatment.

A waste rock pile of a uranium operation in northern Saskatchewan generates acidic seepages with elevated concentrations of arsenic, nickel, phosphate, sulphate and nitrate. The quantity of seepage from the waste rock pile is not extremely large and only emerges seasonally. The waste rock pile is surrounded by muskeg, which has several open shallow ponds; the ponds have been assessed as to their usage as seepage treatment areas. The muskeg/wetland is a perched water body, supplied only by atmospheric precipitation with diffuse inflow and outflow.

The feasibility of using the open water ponds in the muskeg has been addressed through a series of field and laboratory experiments. It has been proposed that if microbial activity can be stimulated in the muskeg sediments through additions of carbon to generate alkalinity, then the production of reducing conditions would lead to the precipitation of contaminants. As the concentrations of nutrients in the seepage are relatively high, the biomass expected to be produced in the ponds could utilize both phosphate and nitrate present in the seepage. This biomass, in turn, could provide a continuous source of carbon for the microbial activity in the sediments. Since 1992, seepage water has been introduced to field enclosures and laboratory reactors in which the rates of removal of both As and Ni have been determined.

Results are summarized in Smith et al (1993), and Fyson et al (1994). The field enclosures and the laboratory reactor experiments established that, under reducing conditions and in the presence of potato waste or alfalfa pellets, the sediment from the wetland was able to remove As and Ni from seepage water in batch conditions.

Prior to large-scale treatment in the field, it is essential to assess the treatment capacity of the muskeg sediment and the stability of the removed contaminants in the sediments, with particular reference to the possibility that the pond water chemistry could change over the season (e.g. an influx of spring runoff water could result in dilution of the pond seepage water).

The objective of the work carried out jointly with CANMET and CAMECO seeks to characterize the chemical forms of As and Ni removed from the seepage water to the sediments. Laboratory reactor experiments will be initiated to determine the capacity of sediments to remove As and Ni under flow conditions. The sediments from the laboratory reactors, from which the initial data were collected on the removal of As and Ni, will be used to determine the stability of the precipitates formed in the sediments. Sequential extractions are used to determine the chemical form of the precipitates, either as an organocomplex or in an adsorbed form.

A literature review on both arsenic and nickel biogeochemistry is used to identify the main chemical factors controlling the water-sediment interface, as this is the driving force of the proposed seepage treatment system.

2.0 ARSENIC AND NICKEL IN THE AQUATIC ENVIRONMENT - A LITERATURE REVIEW

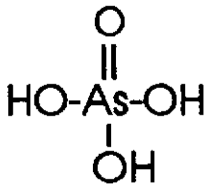
2.1 Species of Arsenic

The average concentrations of arsenic in shales, igneous rocks and sandstones is 13, 1.8 and 1.0 mg/kg respectively (Onishi and Sandell 1955, Lemmo et al 1983). Arsenic is an element of multiple oxidation states. The common species of arsenic found in water, sediment and soil systems are arsenate(+5), arsenite(+3), monomethylarsonate (MMAA +3) and dimethylarsonite (DMAA +1) (Andreae 1979, 1983). Their respective chemical structures are presented in Figure 1. Most of the natural arsenic pool in water exists in the inorganic forms of arsenite (As+3) and arsenate (As+5). The organic forms MMAA and DMAA are very small components of the total As pool, representing up to 5% in water or sediments (Faust et al 1987a).

The inorganic As species are primarily controlled by Eh and pH. Figure 2 is a pH - Eh diagram of As which shows the interchange between As(+5) and As(+3). The thermodynamic data are from Kotz and Purcell (1987) and Stumm and Morgan (1981).

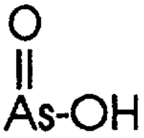
Generally, As(+5) dominates in surface waters, sediment surfaces and aerobic environments. In some sandy sediments, even under anaerobic conditions, As(+5) is the dominant species. This is probably due to the absence of electron donors (i.e. organic matter in the sandy sediments) (Faust et al 1987a), or due to the presence of oxidizing material in the sediments (Oscarson et al 1980). As(+3) exists in the deep sediments and pore water under anaerobic conditions.

Figure 1. The Major Arsenic Species In Nature


$\mathrm{HO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}{-}OH}$

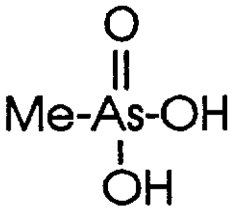
H_3AsO_4 (+5)

Arsenic acid


$\mathrm{\overset{\overset{O}{\|}}{As}{-}OH}$

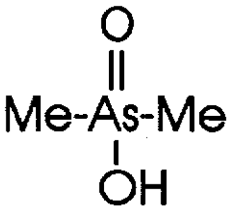
$HAsO_2$ (+3)

Arsenious acid


$\mathrm{Me{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}{-}OH}$

MMAA (+3)

Monomethylarsonic acid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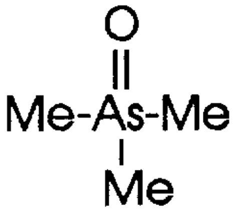
DMAA (+1)

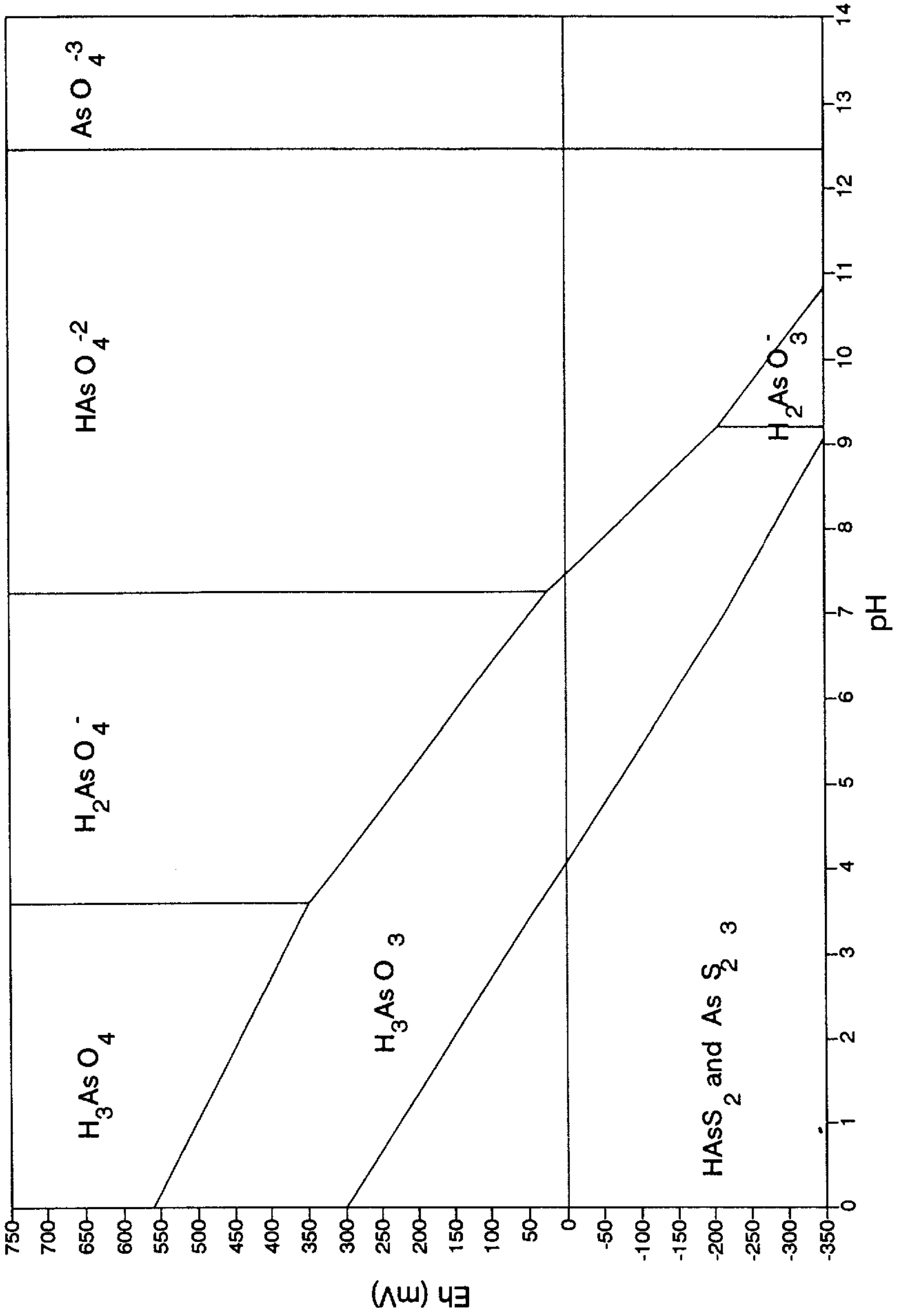
Dimethylarsinic acid


$\mathrm{Me{-}\underset{\underset{Me}{|}}{\overset{\overset{O}{\|}}{As}}{-}Me}$

TMAO (-1)

Trimethylarsine oxide

Figure 2. Eh-pH Diagram of Arsenic



2.1.1 Biological Cycling of Arsenic

Arsenic can enter a biological system similar to the phosphorus cycle in the environment; the As cycle and balance in nature are important. Arsenic is toxic due to its ability to form covalent bonds with sulphur, and As(+3) has a high affinity for thiol groups of proteins. This reaction inactivates many enzymes, making this radical more toxic than As(+5) (Tamaki and Frankenberger 1992).

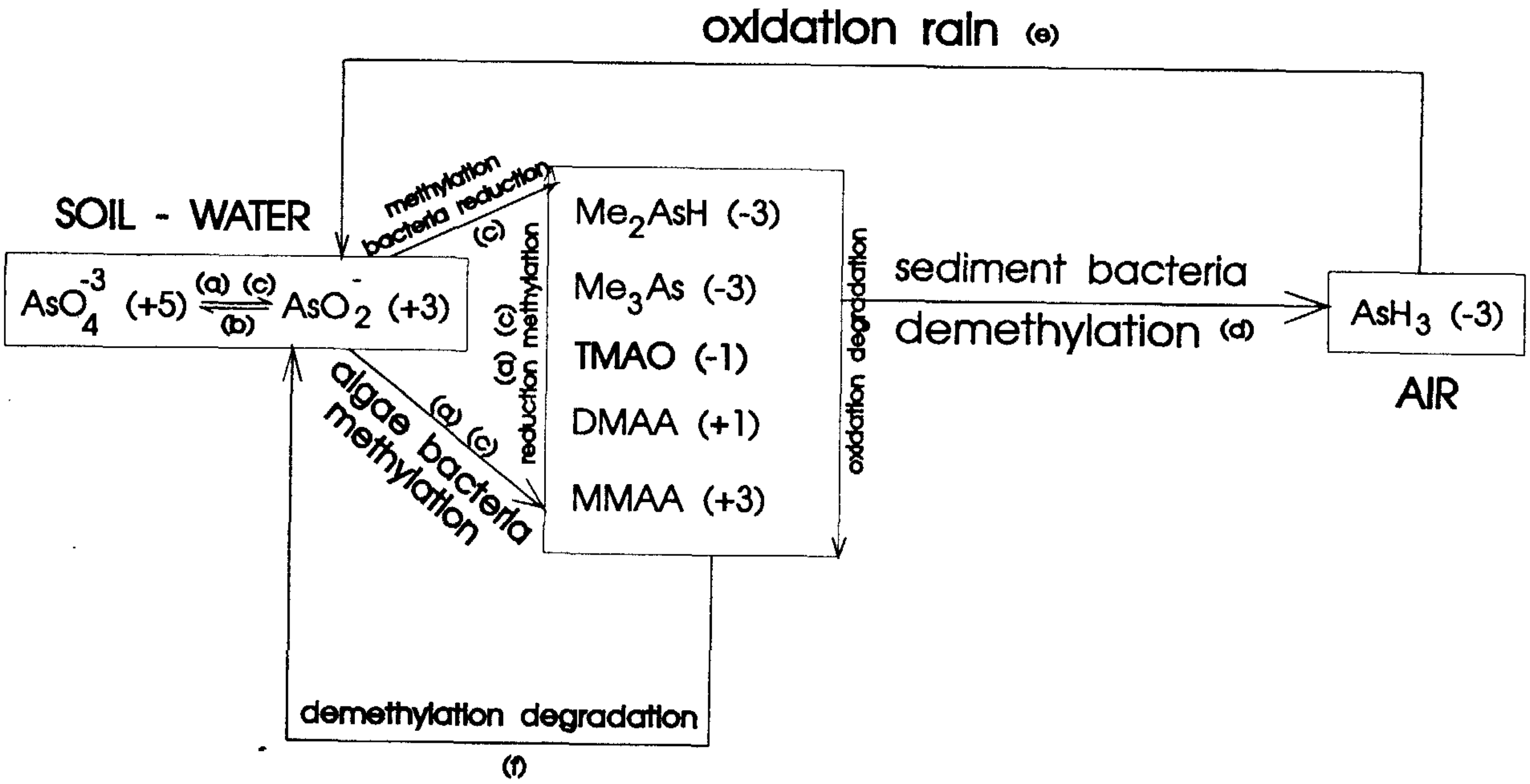
In highly productive ecosystems in the water, up to 80% of the total As pool may undergo reduction and methylation by algae (Sanders 1983). Arsenic uptake is not influenced by external phosphate (Budd and Craig 1981), however the presence of As may depress the uptake of phosphorus by algae (Brunskill et al 1980).

In aerobic conditions algae can reduce As(+5) to As(+3), and methylate As(+3) to the non-volatile compounds (Baker et al 1983) monomethylarsonic acid (MMAA +3), dimethylarsinic acid (DMAA +1) or trimethylarsine oxide (TMAO -1) (Johnson and Burke 1978, Andreae 1983). Methylation is equivalent to a biological detoxification process for As. In Figure 3 all biological reactions for As are summarized and lettered, starting with "(a)" for the algal reduction and methylation.

Bacteria are approximately 10-fold more resistant to As(+5) than to As(+3) (Osborne and Ehrlich 1976). Under aerobic conditions, bacteria catalyse 78-96% of the As(+3) oxidation into As(+5) (Wakao et al 1988) (see Figure 3(b)).

Under anaerobic conditions, bacteria reduce As(+5) to As(+3) and methylate As(+3) into MMAA (+3), DMAA (+1) and further into dimethylarsine (see Figure 3(c)). Some fungi generate trimethylarsine (Tamaki and Frankenberger 1992).

Figure 3. Arsenic Cycle in Nature



Soil and sediment bacteria can demethylate dimethylarsine and trimethylarsine into arsine; this is the primary mechanism for As loss to the atmosphere (see Figure 3(d)). Arsine in the air can be oxidized into As(+3) and As(+5) forms, and fall down to the ground with rain (Figure 3(e)).

Since As can enter the food chain, microbial metabolism is another facet of its biological cycling. The end product of As in the higher trophic levels (e.g. shrimps) is arsenobetaine (Norin and Christakopoulos 1982). Such organic forms of As can be broken down by bacteria to As(+5) and carbon dioxide. The general degradation process follows the direction below (Kaise et al 1987, Hanaoka 1987):

arsenobetaine → trimethylarsine oxide → DMAA →
→ MMAA → $AsO_2^-(+3)$ → $AsO_4^{-3}(+5)$ (see Figure 3(f))

2.1.2 Stability of Arsenic Species

The residence times of arsenic in various environmental components are listed below (Mackenzie et al 1979, Woolson 1983):

Environment	Residence Time (years)
Sediments	99,800,000
Ocean (dissolved)	9,400
Land	2,400
Terrestrial Biota	17
Oceanic Biota	0.07
Air (total)	0.03

Overall, organic fractions comprise only about 5% of the total As. These organic forms are chemically less stable than inorganic arsenate and arsenite - the more desirable forms of arsenic - which can remain in the sediments as stable precipitates.

2.1.3 Arsenic Adsorption Processes

Arsenic chemistry in soils and sediments is believed to be mainly controlled by adsorption-desorption mechanisms; both As(+3) and As(+5) can be adsorbed. The adsorption process is controlled by Eh and pH (Goldberg and Glaubig 1988) which are the same factors controlling the chemical species of the inorganic As forms.

Elkhatib et al (1984) used a modified Freundlich equation to describe the kinetics of the As(+3) adsorption process in soil. They found that Fe(+3) oxides and Eh are the main soil properties controlling the As adsorption rate.

Pierce and Moore (1982) studied the adsorption of As(+5) and As(+3) on amorphous iron hydroxide. Their conclusion was that As(+5) adsorbs more readily than As(+3); the optimum pH condition for As(+5) adsorption is pH 4, and for As(+3) pH 7.

The adsorption of As to oxides (Fe, Al, and Mn), clays and sediments has been studied. Strong linear correlations exist between total As concentrations and both Fe and Mn concentrations (all elements are determined by neutron activation analysis) in the surface sediments of Lake Washington. A poor linear correlation of total As concentration with organic carbon concentration (oven-dried sediment treated with HCl and then with a LECO carbon analyzer) was observed in the same sediments (Crecelius 1975).

Although adsorption of As occurs on the surfaces of both Fe(+3) and Mn(+4) oxides, the situation is different. The surface of Mn(+4) oxide is mostly negatively charged. When Mn(+4) oxide is reduced to Mn(+2) in the deeper sediment, it dissolves and diffuses into the porewater. Mn(+2) may then be adsorbed by the surface of Mn(+4) oxide. This changes the sediment-bound Mn(+4) oxide's surface charge from negative to positive, which then adsorbs the negatively charged As(+5) anions (Takamatsu et al 1985). These oxidation/reduction processes can be affected by microbial activity in the sediment.

Mn(+4) oxide can oxidize As(+3) into As(+5) (Takamatsu et al 1985). For example, As(+3) is observed to be oxidized by Mn(+4) in fresh sediments from a southern Saskatchewan lake into As(+5) through an abiotic process. The reaction activation energy is only 3.3-8.5 kcal/mole. This low activation energy required for the reaction indicates that the oxidation process is very fast and mainly diffusion-controlled (Huang et al 1982). It has been shown that under N_2 gas flow, As(+3) is oxidized by Mn(+4) and Fe(+3) in the sediments. These oxidations can take place according to the following reactions:

$$HAsO_2 + MnO_2 + 2H^+ = H_3AsO_4 + Mn^{+2}$$
$$HAsO_2 + 2Fe^{+3} + 2H_2O = H_3AsO_4 + 2Fe^{+2} + 2H^+$$

Sorption of As is occurring simultaneously with the oxidation of As(+3) to As(+5) (Oscarson et al 1980).

The Fe(+3) oxide surface is mostly positively charged, hence it readily adsorbs the negatively charged As(+5) anions. However, the adsorption is only favoured by a low pH. At a higher pH (> 5.5 - 6), the Fe(+3) hydroxide surface becomes negatively charged and this makes the adsorbed As unstable (Dzombak et al 1990, Brewster preprint).

There is disagreement in the findings about the relationship between As and Al(+3) oxide components in the sediments. Some reports showed a positive correlation effect between them (Huang 1975, Livesey and Huang 1981), whereas a poor correlation was indicated by others (Crecelius 1975).

Phosphate (P+5) and sulphate (S+6) sometimes compete with As in the adsorption process. Addition of phosphate or sulphate after As(+5) or As(+3) had been adsorbed had very little affect on the adsorption of As. A significant effect on the adsorption of As at low concentrations was evident after phosphate or sulphate had already been adsorbed (Pierce and Moore 1982). Barrow (1974) found that high concentrations of

As(+5) solution (As(+5) = 37.5 g/L) can displace phosphate (200 μg phosphate per g of soil) from soil. Livesey and Huang (1981) examined the influence of anions (nitrate (N+5), chloride (Cl-1), sulphate, and phosphate) on the adsorption of As by active soil components. The molar ratio of anions to As(+5) ranged from 100 to 10000 (As(+5) = 0.10 mg/L to 2.15 mg/L). Nevertheless, other anions, which were tested in relation to affecting the adsorption of As by the soils, did not vary significantly with increased concentrations of chloride, nitrate and sulphate. Only phosphate substantially suppressed the adsorption of As.

As mentioned above, adsorption-desorption equilibria with sediments are considered to dominate the As concentrations in the aqueous phase. Part of the adsorbed As is related with Fe(+3) oxide and may be extracted by oxalate solution, while the remainder is complexed with organic molecules and, hence, is not oxalate-extractable.

Faust et al (1987a, b, and c) did a series of experiments to test the stability of As in sediments of the Maurice River, Blackwater Branch, and Union Lake. They found that both sandy and organic sediments have 43% to 81% As non-extractable by distilled water or 1 N HCl solutions (Faust et al, 1987a). Among the extractable As, less than 1% is released from organic sediments while 28-48% is released from sandy sediments. This indicates that organic sediments have a stronger affinity and a greater capacity for sorption of As than sandy sediments (Faust et al, 1987b).

As(+3) is more mobile than As(+5). Under reducing conditions therefore, where this form will predominate, As concentration increases greatly (Masscheleyn et al 1991). The As release is strongly dependent on the oxidation states and the surface charge of Fe(+3) hydroxide in sediments. Under anaerobic conditions, 10 times as much As is released from sediment than in aerobic conditions (Clement and Faust, 1981). Arsenic is not released within the aerobic range of 10% to 100% oxygen saturation in the sediment.

2.1.4 Arsenic Precipitation Processes

Besides adsorption to the sediments, arsenic may also precipitate or coprecipitate in the sediments. Various metal ions can form precipitates with arsenate (As+5). Hess and Blanchar (1976) used ion products of Al, Ca, Fe, Mn, and Pb arsenate compounds to study the equilibrium states of As in some soil samples. They found that Pb arsenate and Mn arsenate are more stable than Fe, Al, Pb and Ca arsenate precipitates in their soil samples, and both Mn and Pb concentrations control the level of As in solution. Under reducing conditions, As can react with sulphur to form the stable sulphides As_4S_4 (realgar) and As_2S_3 (orpiment).

Overall, adsorption of As in sediments with Fe(+3) and Mn(+4), Al(+3), and precipitation of As with sulphide (S-2) and other metal ions are the major mechanisms for arsenic removal from aqueous environments.

2.2 Species of Nickel

Most nickel is produced from sulphide ores, such as pentlandite ($(Fe,Ni)_9S_8$), the arsenide ores, such as niccolite (NiAs), chloanthite ($NiAs_2$) and nickel glance (NiAsS) (Nicholls 1973). Nickel can form compounds in a series of valence states from -1 to +4; the most common state is Ni(+2). Additionally, nickel can form organometallic compounds (Nicholls 1973), while free nickel ions can form a large number of complexes with organic phosphorus and nitrogen compounds. Nickel also has quite a high adsorption ability (Weider, 1990).

In a study of the Yukon and Amazon rivers, 2.2% to 2.7% of the total nickel was found in solution as free ions and complexes. The rest was found adsorbed on suspended materials in metallic coatings, or incorporated in solid biological materials, or in crystalline structures (Gibbs 1973).

The mobility of nickel in soil and sediment pore water is low. In Sudbury, nickel and copper concentrations in surface samples of soil and sediment were found to be elevated (Hutchinson et al 1975). However, the elevated concentrations were confined to the top 15 cm. This indicates that the nickel does not move vertically downward through the sediment or soil profile.

2.2.1 Biological Cycling of Nickel

Nickel is one of the essential trace elements for living organisms (Mertz 1974, Nielsen 1971). It is an essential component of bacterial enzymes such as hydrogenases (Hausinger 1987), but it is also very toxic to most bacteria (>5.87 mg/L).

Bacteria with high nickel resistance have been isolated from heavy-metal-rich sites. Four hundred nickel tolerant "isolates" have been collected (Schmidt et al 1991) and some were able to grow in the presence of 2.35 mg/L $NiCl_2$.

Nickel resistance is determined by the presence of genes on a DNA plasmid which can be transferred between bacteria and can, therefore, potentially spread within heavy-metal-polluted ecosystems. The plasmids carrying nickel resistance may show resistance to other heavy metallic ions such as cobalt, chromate, and mercury (Mergeay et al 1985, Schmidt et al 1991).

Algae (*Scenedesmus acutiformis* var *altemans*) isolated from heavy-metal-polluted lakes near Sudbury, Ontario are tolerant to nickel (Stokes et al 1973). This study found that growth rates were sub-maximal in solutions containing 1.5 mg/L nickel; some algal growth occurred at 3 mg/L nickel. In the laboratory, 0.25 mg/L nickel solutions had no effect on the growth of the cultured isolate (Stokes et al 1973).

Stokes et al (1973) established a positive correlation between nickel concentrations in water and algae, and between sediment and roots of the water lily *Nymphaea*. The highest concentrations of nickel were found in the algal periphyton which had 20,000 times more nickel than in the water. In the vegetation, nickel concentrations uniformly exceeded both copper and zinc levels at the contaminated sites.

A few flowering plants, termed nickel-hyperaccumulators, can survive in heavily contaminated soils and may accumulate 1% dry weight as nickel (Schlegel et al 1991). The oral toxicity of nickel to man is very low. Nickel does not accumulate in human tissues and is eliminated via the faeces and urine.

2.2.2 Stability of Nickel Species

In aquatic ecosystems, the biogeochemical processes that may contribute to the removal of nickel from polluted waters include: (1) uptake by vegetation; (2) binding to organic matter as organic complexes; (3) adsorption to sediment by cation exchange or coprecipitation; (4) the formation of insoluble metal oxides/oxyhydroxides; (5) insoluble metal sulphides; and (6), other insoluble metal precipitates. The ability to form organic complexes assists nickel removal and retention by organic sediments.

An experiment to measure the maximum binding capacities for ten cations to sphagnum peat and sawdust showed that Ni^{+2} was one of the more strongly bound ions (Weider 1990) . The ions are listed below in decreasing order of binding capacity:

$$Al^{+3} = Zn^{+2} > Fe^{+3} > Ni^{+2} = Cd^{+2} > Na^{+} = Mn^{+2} > K^{+} > Ca^{+2} > Mg^{+2}$$

Eger and Lapakko (1989) and Lapakko and Eger (1988) showed that, at a neutral pH, peat could remove up to 20 mg Ni per g peat (dry weight). Removal rates were reduced at lower pH.

2.2.3 Nickel Adsorption Processes

The removal of nickel from the aquatic environment is mainly a result of adsorption on other metal oxide surfaces (Theis and Richter 1980). Sediments rich in iron hydroxide (goethite) and manganese oxide are effective scavengers of heavy metals in the aquatic environment (Singh and Subramanian 1984). The adsorption of Ni on goethite has been studied under different conditions - pH 4 to 8, concentration of Ni from $5.87*10^{-2}$ mg/L to 5.87 mg/L, and temperature from 5°C to 35°C (Bruemmer et al 1988). Ni adsorption on MnO_2 solid has also been studied (Laitinen and Zhou 1988). The adsorption was in agreement with the Langmuir equation and it was found that the adsorption increased with pH, reaction time and temperature.

2.2.4 Nickel Precipitation Processes

Precipitation as sulphides under reducing conditions is a further common mechanism by which nickel is precipitated in the sediment. Reactor studies (Hammack and Edenborn 1992, Dvorak et al 1992) have shown that nickel is effectively removed from solutions in batch-reactor conditions into sulphide precipitates. The resulting sulphide precipitates are stable over a wide range of pH's and can be expected to trap the nickel as long as reducing conditions prevail.

The nickel sulphide formation may be closely linked to the presence of nickel organic complexes since, in nature, metal sulphides commonly exhibit a close association with high-molecular-weight organics in fine-grained sediments (Kirchner 1985), and several studies suggest that organo-metallic complexes which form *in situ* play an important role in the transfer of metallic ions to sulphide phases (Nissenbaum and Swaine 1976, Lett and Fletcher 1980).

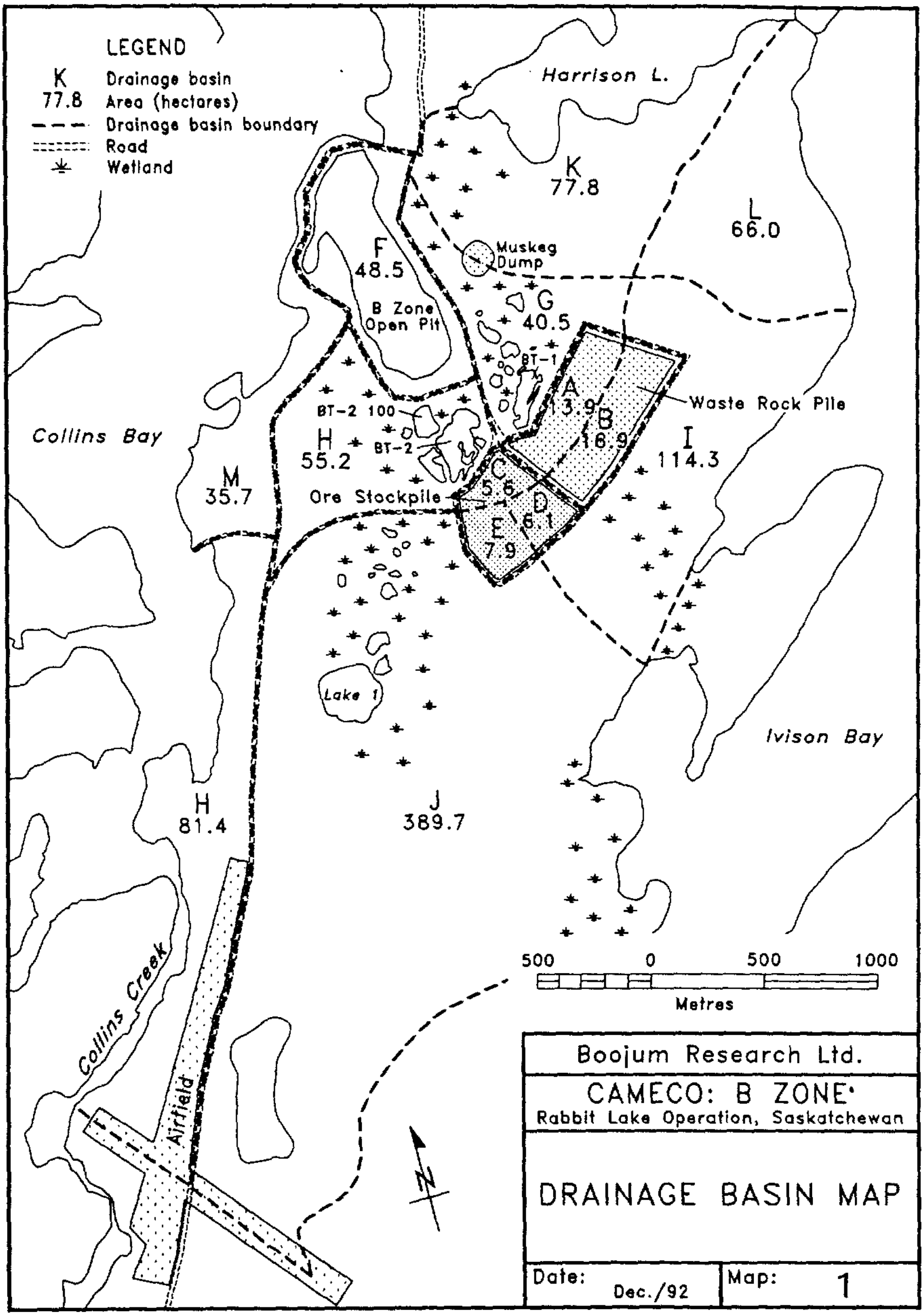
Nickel may form organic complexes at the bacterial cell surface, then further react with microbially produced S^{-2}. Ferris et al (1987) found microcrystalline millerite (NiS) associated with bacterial surfaces in a lake sediment contaminated from mine drainage near Sudbury, Ontario. Ferris et al (1989) also showed that bacterial biofilms formed on slides suspended in lakes accumulated more Ni in neutral conditions than in acidic conditions, indicating that an increase in pH may be important in determining Ni removal rates.

3.0 MATERIALS AND METHODS

3.1 Site description

The study was conducted at CAMECO's Rabbit Lake uranium operation in northeastern Saskatchewan (Collins Bay, Wollaston Lake). Located northwest of the waste rock pile in the B-Zone area is the BT-1 wetland which covers 40.5 hectares, and drains primarily towards the flooded B-Zone open pit (Map 1). The BT-2 wetland is immediately adjacent to the northwest side of the ore stockpile, and covers 55.2 hectares; water from this wetland also drains towards the flooded pit. A series of ponds, with an average depth of 0.5 m and underlain by 1 m of sediment primarily composed of peat particles, is located in the northeast section of the BT-2 wetland. An overview of the BT-2 wetland is depicted in Plate 1.

Plate 1: Overview of the BT-2 Wetland


LEGEND
K Drainage basin
77.8 Area (hectares)
Drainage basin boundary
Road
Wetland
Harrison L.
K 77.8
L 66.0
Muskeg Dump
F 48.5
B Zone Open Pit
G 40.5
BT-1
A 13.9
B 16.9
Waste Rock Pile
BT-2 100
H 55.2
BT-2
I 114.3
Collins Bay
M 35.7
Ore Stockpile
C 5.6
D 6.1
E 7.9
Lake 1
Ivison Bay
H 81.4
J 389.7
Collins Creek
Airfield
500 0 500 1000
Metres
N
Boojum Research Ltd.
CAMECO: B ZONE
Rabbit Lake Operation, Saskatchewan
DRAINAGE BASIN MAP
Date: Dec./92
Map: 1

3.2 Preparation and Operation of Reactors

3.2.1 1993 Laboratory Reactors

Six acrylic cylinders (9.5 cm internal diameter and 42 cm high) were used as "reactors" for the water column experiment, as well as two 2 L glass jars. They were cleaned and rinsed with distilled water. The reactors are shown in Plate 2.

The experiment was set up on May 3, 1993 and terminated on January 10th 1994. To each reactor, 500 mL of original BT-2 station 250 muskeg sediment was added and left to settle for 24 hours. Then 760 mL of 6.11 water from the Waste Rock Seepage was carefully added to the top of the sediment in each reactor. Reactor R1 was the control without organic amendments, reactors R2 and R3 were used for the potato waste anaerobic treatment, and reactors R4 and R5 were used for the alfalfa anaerobic treatment.

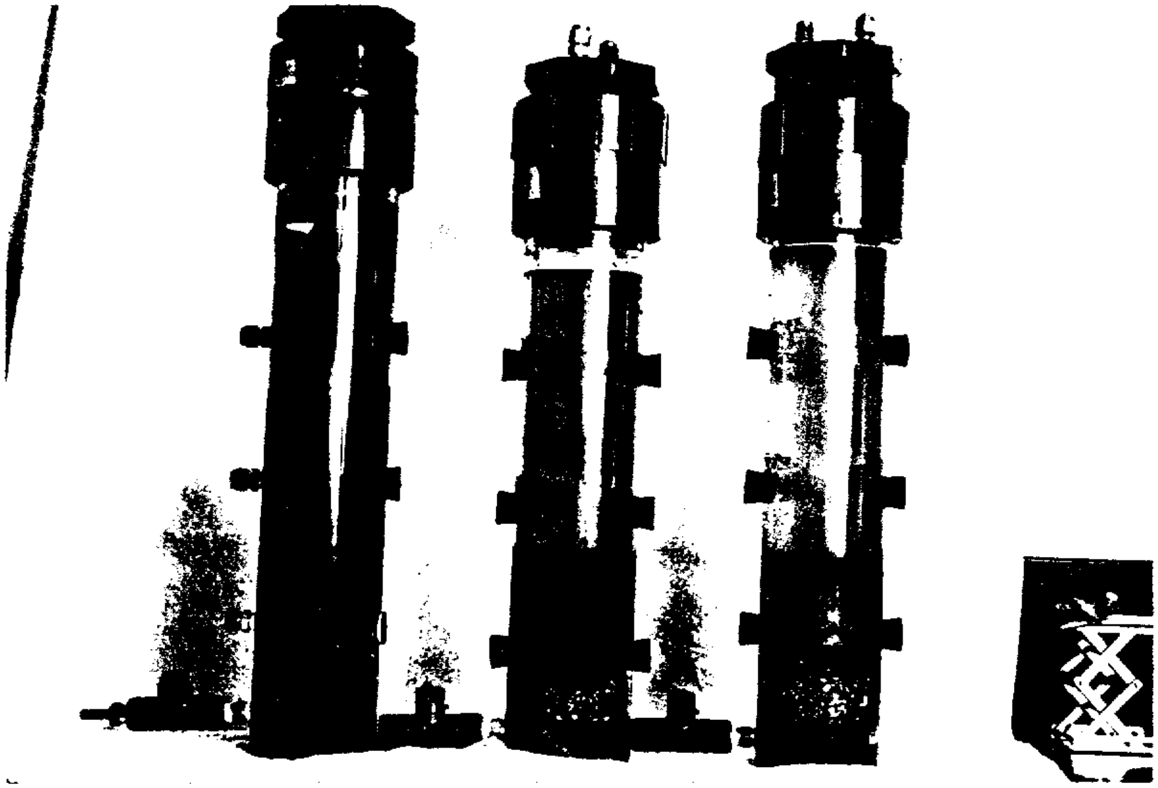


Plate 2: 1993 Laboratory reactors used to study biological arsenic removal

Six days after adding the 6.11 water (May 10, 1993), 5 g of potato waste was added to R2 and R3, and alfalfa pellets (55 mL or 31.5 g) were added to R4 and R5. At the same time, glass jars 1 and 2 were set up as controls with 760 mL 6.11 water and no sediment. Jar 1 was amended with 5 g potato waste and Jar 2 was amended with 55 mL alfalfa pellets. All the reactor cylinders and jars were tightly sealed.

3.2.2 1994 Laboratory Reactors

The sediment contained in the 1993 reactors was used in sequential extractions to determine the form of the As and Ni which had accumulated in the sediment. The same reactors were washed and reused to set up the 1994 experiment; the set-up of the reactors was identical to the experiments carried out in 1993.

900 mL of sediment collected at the BT-2 250 m section of the transect, and 900 mL of 6.11 seepage water was added carefully by siphoning to minimize sediment disturbance. Glass jars were set up with 6.11 water (900 mL) to which no sediment was added. The slightly milky appearance of the seepage water in the reactor is depicted in Plate 3; the reactor shown is following set-up with 5 g of potato waste (McCain Foods) after a 24 h settling period. Potato waste was added to the top of the water and reached the sediment surface within 1 hour.

The sediment in the reactors received the following treatments:

A. Reactors 1,2,3,7,8 & 9 - no further treatment
B. Reactors 4,5,& 6 - replace 500 mL of the water column weekly, simulating continuous flow of the seepage in the "field"
C. Jar 1 & 3 - no further treatment
D. Jar 2 - replace 500 mL of the water column weekly

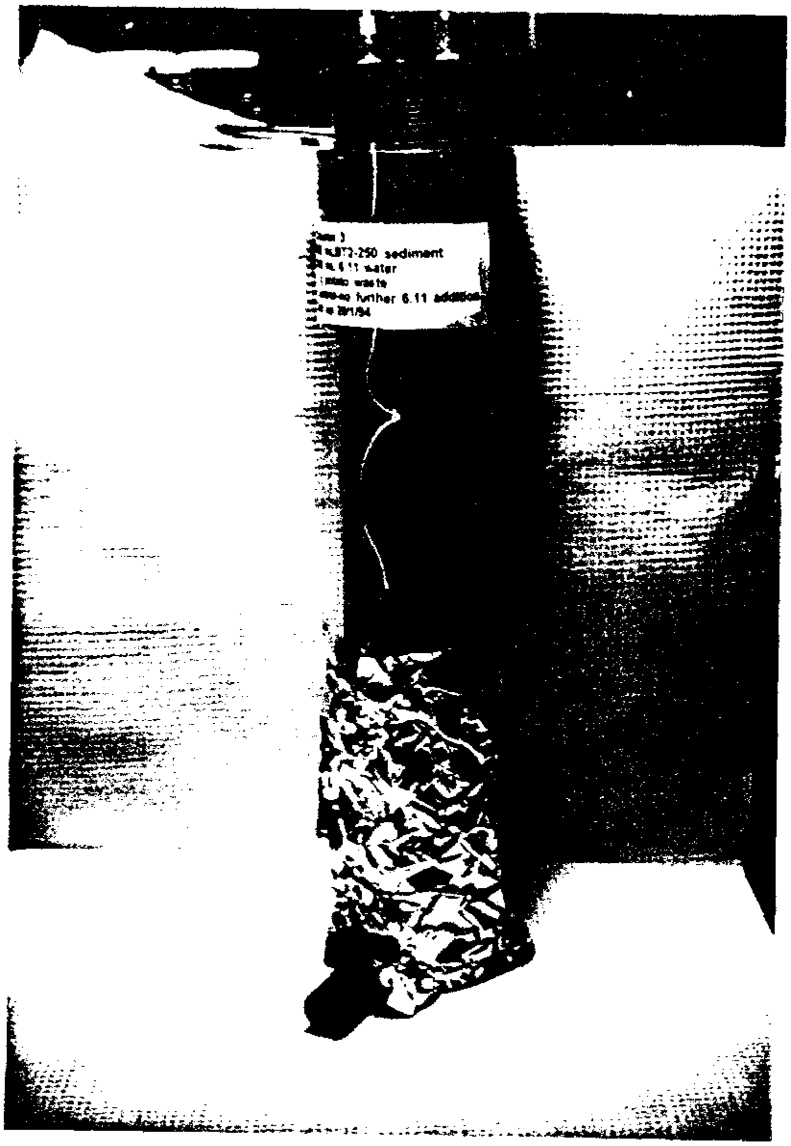


Plate 3: 1994 Laboratory reactor at set-up

3.3 Monitoring and Analytical Methods

Water was drawn from the sediment with a syringe while seepage water was carefully replaced from above to minimize or avoid sediment disturbance. The following parameters were monitored:

pH
Em
conductivity
acidity
alkalinity
NO_3
Ni
As
Fe

The pH was measured with a Canlab probe and Jenco meter, Em with Fisher probes and Corning Model 103 meter, and conductivity with an Orion 140 meter and probe. Em values were converted to Eh values by means of the formula:

$$Eh\ (mV) = Em\ (mV) + (241 - 0.66(T-25))$$

where T is the measured temperature (°C). Acidity was determined by titration against NaOH with a Metrohm 702 SM Titrino autotitrator. Nickel was determined with a colorimetric test (Rollet's dimethylglyoxime complexation) and reading absorbance at 445 nm. Arsenic was measured with the Merck Merckoquant strip test which measures the reaction between hydrogen arsenide gas and mercury(+2) bromide. Iron was determined by a phenanthroline test (absorbance at 510 nm) and NO_3-N with a Hach cadmium reduction (absorbance at 545 nm). For the colorimetric tests, a Bausch and Lomb Spectronic 70 spectrophotometer was employed.

The colorimetrically-determined concentrations were compared to those determined by ICP (Inductively Coupled Plasma Spectrophotometry). These analyses are carried out by a certified laboratory in Toronto; the laboratory's QA/QC procedures are given in Appendix 7. For the seepage water which was treated, the agreement between the colorimetric concentrations and those determined by ICP were reasonable, but nickel concentrations in the solutions derived from the sequential sediment extraction were unacceptable due to interference. Therefore, all Ni concentrations in solutions from the sequential sediment extractions were determined by ICP.

3.4 Sediment Sampling in the 1993 Reactors

After 35 weeks (January 10, 1994) of operation the sediments were sampled. The water overlying the sediments in the reactors was syphoned carefully not to disturb the sediment. The seepage water overlying the sediments in the reactors was referred to as the **Top** water sample. Water filtered from the top and middle layers of the sediments was referred to as the **Middle** water sample. Water filtered from the bottom sediments was referred to as the **Bottom** water sample.

Sediments in the reactors were divided into three layers - the top 1 cm was referred to as the top sediment sample of the reactors while the 5 cm section of sediment immediately below it was referred to as the middle sediment sample. The remaining sediment below this was referred to as the bottom sediment sample.

Each layer of sediment was collected with a spoon and filtered immediately. The pore water derived in this manner was used to quickly measure Em, pH and electrical conductivity.

All of the pore water samples were purged with N_2 gas, sealed in plastic bottles and refrigerated (4°C). ICP analysis was carried out within 48 h of removal from the sediment. Concentrations of sulphide and sulphate were determined in the pore water.

Each of the sediment layers were well mixed and then separated into two portions. One portion was sealed under nitrogen gas and kept in the refrigerator (4°C) for sequential extraction analysis. One portion was used for measurement of wet volume, dry weight and loss on ignition (LOI), a measure of the organic content of the material.

The sequential analysis of sediment is designed to determine: (1) the form of metal deposit in the sediment, and (2) the stability of the various As and Ni precipitates.

The sequential extractants are referred to in previous metal extraction studies (Salomons and Forstner 1984, Bupp and Ghosh 1991, Henrot and Wieder 1990). The extraction steps are:

(1) 1M KNO_3 solution for exchangeable metals, solid/solution ratio 1:50, 2 hours shaking.
(2) 0.1M $Na_4P_2O_7$ + 0.01N EDTA solution for organically-bound metals, solid/solution ratio 1:50, 24 hours shaking.
(3) 1M ammonium acetate solution (pH=5) for metal carbonate, solid/solution ratio 1:50, 5 hours shaking.
(4) concentrated HNO_3 solution for other metal precipitates (arsenates, hydroxides and sulphides), solid/solution ratio 1:50, 2 hours heating at 120°C.

3.5 Sequential Extraction of 'Spiked' Sediments

To test the applicability of the sequential extraction method to the sediments and determine the reliability of the colorimetric tests as monitoring tools for the experiment, extractions were carried out with sediments spiked with precipitates. The proposed As and Ni precipitates were synthesized as described below and mixed with the sediment; this allowed for an assessment of the effectiveness of the extraction method with respect to the relevant elements which were removed from the seepage water in the reactors.

BT-2 250 sediment (collected in 1993) was used to adsorb all the precipitates in the spike experiment. The sediment moisture was measured by drying the sediments at 104°C in an oven for 24 hours (Clesceri et al 1989).

In the reactors, to which seepage water was added, the concentrations of As and Ni were reported as 50 mg/L and 82 mg/L respectively. The total volume of seepage water added to the reactors was 700 mL which resulted in a total quantity of As and Ni (precipitated or adsorbed onto the sediments) of about 35 mg and 57.4 mg respectively.

To precipitate the total loading of As and Ni added to the reactors, it required 26 mg of Fe and 121.3 mg $Na_2CO_3{\cdot}H_2O$ or 234.7 mg $Na_2S{\cdot}9H_2O$.

In order to run the spike experiment within a similar concentration range, precipitate was produced in solutions which considered concentrations of reagents in stoichiometric proportions to achieve the desired concentration range of total As and Ni.

Sediment was prepared once to produce a combination of iron arsenate precipitate and nickel carbonate, referred to as sample #2, while a second combination produced a sediment spiked with iron arsenate and nickel sulphide, referred to as sample #3 . For each preparation 20 g of the wet sediments were used. Sample #1 sediment was used as a control with no precipitates added.

To make precipitates of $FeAsO_4$ and $NiCO_3$, a solution consisting of 98.6 mg Na_3AsO_4 (22.2 mg As) and 260 mg $NiSO_4{\cdot}6H_2O$ (58 mg Ni) was prepared and added to the sediments in 20 mL distilled water. A second solution containing 167 mg $FeCl_3{\cdot}6H_2O$ and 119 mg Na_2CO_3 solutions was prepared in 10 mL distilled water and slowly dropped into the slurry of the sediment. Thus in the sediment, the respective precipitates were expected to form (sample #2). Finally, the pH was adjusted to 6.35 by dilute NaOH or H_2SO_4 solutions, and the slurry was allowed to settle for 1 hour.

To form the combination of $FeAsO_4$ and NiS precipitates (sample #3), solutions of 93 mg Na_3AsO_4 (20.5 mg As) and 266 mg $NiSO_4{\cdot}6H_2O$ (59.4 mg Ni) were dissolved in 20 mL distilled water and added to the sediments. This was followed by adding a solution of 158 mg $FeCl_3$ and 205 mg Na_2S dissolved in 10 ml of distilled water to the sediment. The sediment changed colour to a dark black and the pH was adjusted with 1N NaOH to 6.30.

After the sediments and their respective precipitates settled for one hour, the sediments were filtered with a 0.45 μm filter paper. Before each extraction, the sediments were rinsed twice with 50 mL distilled water to wash away the remaining extractants. The washing water was combined with the extraction solutions to give a total volume of 150 mL. The sequential extractions, as described above, were carried out on the washed sediments.

Solutions derived from each extraction were assayed using the colorimetric methods to determine the concentrations of iron, arsenic and nickel which were released from the sediment during the extractions.

4.0 RESULTS

4.1 1993 Experiment - Arsenic and Nickel Forms in Sediments

In the 1993 reactors, where arsenic and nickel was removed from the seepage water to the sediment, a known amount of both contaminants can be expected when the sediments are extracted. Through (a) destructive sampling of these reactors, (b) analysis of the pore water collected from different depths, and (c) analysis of the sediment in the reactors, estimates can be derived as to the fraction of the contaminants removed by the sediments. The pore water concentrations are those which are potentially available to diffuse throughout the sediment layers and to the water column. The results from the pore water analysis are presented in Section 4.1.1.

The chemical form in which the contaminants are present in the sediment can be determined through their extractability using sequential extractions; exchangeable metals are recovered in the first extraction with potassium nitrate, followed by the extraction of organically-bound metals with a sodium diphosphate and EDTA solution in the second step. The third extraction is carried out with ammonium acetate, which recovers carbonate precipitates formed in the sediment, and finally a hot nitric acid extraction is employed to recover all remaining metals not bound in a silicate matrix.

Although the sequential extraction steps will provide good estimates as to the form of metals bound to the sediment, it can not be expected that a complete recovery of all precipitates formed in the sediments is possible with such an extraction process. Each extraction step will have its own methodological error as well as an analytical error. Thus, in order to assess the ability of the procedure to allow for accurate quantification of the extracted fractions, a spiked sediment extraction was carried out.

The results of the spiked sediment extraction are presented in Section 4.1.2., and the sequential extractions carried out on the top 1 cm layer of the sediments in the reactors are presented in Section 4.1.3.

4.1.1 Seepage Water and Sediment Pore Water Analysis

Laboratory measurements of pH, Eh and conductivity of the reactor seepage water overlying the sediments, and pore water derived from filtrations of the sediments are summarized in Table 1. The **Top** layer refers to the treated seepage water overlying the sediments, the **Middle** layer to the pore water derived from a combination of the top and middle layers of the sediment, and the **Bottom** layer to the pore water derived from the lower part of the sediment. Also included in Table 1 are the concentrations of As, Ni, Fe, P, sulphate and hydrogen determined by the assay laboratory.

Table 1: 1993 Reactor Experiment - Chemistry of Water Overlying Sediment & Sediment Pore Water after 35 Weeks of Operation, Jan. 10, 1994

REACTOR	Layers	pH	Eh (mV)	Cond. (umhos/cm)	As (mg/L)	Fe (mg/L)	Ni (mg/L)	P (mg/L)	HS (mg/L)	SO4 (mg/L)
R-1	Top	4.31	518	474	11	0.034	7.85	0.25	<0.01	235
Control	Middle	5.17	402	477	7	0.038	5.17	0.15	<0.01	242
	Bottom	5.32	201	393	3.5	0.056	1.82	0.1	<0.01	199
R-2	Top	6.44	221	470	3	0.266	0.66	1.56	<0.01	84.4
Potato	Middle	6.53	173	393	6	0.177	1.41	1.19	<0.01	44.9
Waste	Bottom	6.43	152	268	3	0.581	0.18	0.68	<0.01	12.5
R-3	Top	6.35	223	376	0.7	0.094	0.28	0.78	<0.01	47.8
Potato	Middle	6.42	123	328	6	0.161	1.36	0.76	0.01	21.9
Waste	Bottom	6.16	111	318	3	1.45	0.37	1	<0.01	12.4
R-4	Top	7.48	2	3650	3	0.488	0.46	6.97	0.17	4.93
Alfalfa	Middle	7.48	131	3860	4.5	0.778	0.43	7.47	0.05	4.62
Pellets	Bottom	7.02	106	4030	5.5	1.21	0.53	7.66	<0.01	5.81
R-5	Top	7.33	167	3890	3	0.176	0.33	6.01	<0.01	70
Alfalfa	Middle	7.47	96	3910	3	0.132	0.6	7.31	<0.01	23.9
Pellets	Bottom	7.16	101	4100	3.5	0.368	0.63	2.49	<0.01	4.08
6.11 Water*		4.41	208	1541	39.6	0.48	61.0	20	n.d.	22

* assayed by SRC on Aug. 14, 1993

n.d. = not determined

Note: all parameters measured at room temperature (20-21 C)

To determine the fractionation of the contaminants between pore water (mobile fractions) and sediments, the calculations have to be based on the pore water concentrations. This is the potentially mobile fraction which can move out of the sediment and become available for release into the water column. The results obtained from the analysis of the seepage water overlying the sediment and the pore water are briefly discussed for each reactor below.

R1 (no organic amendment to sediment): It is evident that pH values for R1 (6.11 seepage water and E-6 sediment) were lower than those of the other reactors. However, they were much higher than the seepage water added at the start of the experiment (pH 4.41). In this reactor, redox potential (Eh) was much higher in the top samples (+518 mV) than in the middle (+402 mV) or bottom samples (+201 mV) where more reducing conditions prevailed. The pH was higher at the bottom of the reactor (pH 5.32) than in the middle (pH 5.17) or top (pH 4.31) indicating that alkalinity generating processes, such as denitrification, iron reduction and sulphate reduction have taken place. The lower conductivity in the bottom sample (393 µmhos/cm compared to 477 µmhos/cm in the middle and 474 µmhos/cm at the top) suggests that precipitation or other ion removal processes have occurred or that ions have been removed from the seepage water before it reaches this zone. The chemistry data (Table 1) indicates that concentrations of As and Ni were substantially lower at the bottom (3.5 mg/L and 1.82 mg/L) than at the surface (11 mg/L and 7.85 mg/L). In contrast, iron concentrations were highest in the bottom sample (0.056 mg/L compared to 0.034 mg/L for the surface sample).

R2 and R3 (with potato waste): The water from these reactors had a higher pH (6.44 and 6.35 for surface samples) and lower Eh (221 mV and 223 mV for surface samples) than the control reactor (pH 4.31 and Eh 518 mV). The fermentation of the potato waste can result in development of more reducing conditions than with the sediment alone. This in turn results in promotion of alkalinity generating anaerobic processes. There was no clear difference in pH between top and bottom samples but as observed for R1, the Eh and conductivity were lower at the bottom of the reactors. There were no substantial differences in top and bottom samples for As and Ni. Iron concentrations were higher in the bottom samples (0.58 mg/L and 1.45 mg/L for R2 and R3 respectively) than the top samples (0.27 mg/L and 0.09 mg/L for R2 and R3 respectively) indicating that iron (III) reduction and dissolution may have taken place here in reducing conditions. Overall, conductivity was lower than in the control reactor (R1) indicating the enhancement of metal removal processes by the potato waste.

R4 and R5 (with alfalfa pellets): The pH of reactors with alfalfa pellets was higher and the Eh lower in the top, middle and bottom layers of R4 and R5 than both that of the control (R1) and the potato waste reactors (R2 and R3). The conductivity was an order of magnitude higher than in the other reactors (approximately 4000 µmhos/cm compared to approximately 400 µmhos/cm). In R4, arsenic concentrations were higher at the bottom (5.5 mg/L) than at the top (3 mg/L) whereas in R5 they were consistent throughout (3 mg/L to 3.5 mg/L). Iron concentrations increased with depth from 0.49 mg/L (R4) and 0.18 mg/L (R5) at the surface to 1.21 mg/L (R4) and 0.37 mg/L (R5) at the bottom. Sulphide was detected in R4 sediments but not in any of the other reactors. This sulphide was associated with the lowest Eh values and may indicate the occurrence of sulphate reduction and subsequent precipitation of metal sulphides. Very high phosphate concentrations (2.5 to 7.3 mg/L) were found in the alfalfa pellet reactors.

Comparison of the pore water concentrations of all the reported elements clearly indicates that changes have taken place. For example, the highest concentration of As in the pore water was reported as 11 mg/L in the control reactor (R1), but the seepage water contained 39.6 mg/L of As. In all other reactors, where organic amendments were added to stimulate microbial activity, the concentrations of As in the pore water were lower ranging between 3 mg/L to 5 mg/L. Similar trends are seen for Ni in that the control reactors had the highest pore water concentrations with 7.8 mg/L in the surface water, but considerably lower concentrations were noted (0.3 mg/L to 1.4 mg/L) in sediments of reactors with organic amendments.

For the nutrient phosphate, the conditions were reversed as expected, since no additions of phosphate-rich organic amendments were made to the control reactors. Here the control had the lowest concentration of P at 0.25 mg/L (top sample), followed by the potato waste reactors (R2 and R3) with concentrations of 0.8 mg/L to 1.6 mg/L in the surface layer. The alfalfa-pellet amended reactors (R4 and R5) had the highest P concentrations with 6.0 mg/L to 7.0 mg/L in the surface layer.

The fact that sulphide reduction can take place in the presence of alfalfa pellets is indicated by the presence of sulphide in R4 and also the reduced concentrations of sulphate in sediments at the bottom of reactors. The highest sulphate concentrations are present in the control reactor sediments with 235 mg/L in the surface sample. In the potato waste amended reactors (R2 and R3) a reduction to 47.8 mg/L and 84.4 mg/L at the surface and lower in the lower layers of the reactors was observed. In R4 (alfalfa-pellet amended) the lowest sulphate concentrations are reported with 4.9 mg/L at the surface where concurrently HS concentrations are noted. In order to detect hydrogen sulphide in the pore water, the availability of metals to react with the sulphide must be low. This is suggested by the relatively low Ni concentrations in R4, where the highest hydrogen sulphide concentrations are reported. The pore water data strongly indicate, that the sediments are instrumental in changing the chemical composition of the seepage water.

4.1.2 Sequential Extraction Effectiveness and Specificity

Sediments were spiked with precipitates of $FeAsO_4$ and $NiCO_3$ to produce one combination, called sample #2, and a second combination was made by spiking sediment with $FeAsO_4$ and NiS, called sample #3. Sample #1 was the original sediment without a spike.

The results from the spike sequential extractions are summarized in Table 2a for As, Table 2b for Ni, and Table 2c for Fe. All data determined in the experiment, including data required for the calculations to arrive at summary Table 2 are given in Appendix Table A1.

Metal concentrations in the original solution and in each extraction were measured. The total extracted metal values in each solution were calculated by multiplying the assays by the solution volume. The percentages of extracted metals in each extraction were determined by comparison with the total extracted metal value. In Table 2, the final column "total measured %" is the sum of all the measured amounts divided by the original added amount.

The As present in the original sediment is bound mainly as organic complexes, as this was the only extraction in which As was detected (Table 2a). For Ni, fractions are present in the sediment as exchangeable Ni, organically-bound Ni, and Ni in a mineral form, while no Ni is present as a carbonate (Table 2b). For Fe, the original sediment does not contain exchangeable iron. A large fraction of Fe is organically-bound, followed by mineral forms (Table 2c); no other forms of Fe exist in the sediment.

Sample #2 was spiked with iron arsenate and nickel carbonate to concentrations of known amounts. With these extractions it is possible to examine the behaviour of these precipitates in the selective extractions. Sample #2 for As indicates that the largest fraction is organically-bound, followed by some recovery as a carbonate but none in the exchangeable form or the mineral phase. For Ni, the results are different as a large

Table 2: Spike Extraction Data

a.

		original solution		1M KNO3 solution		1M Na4P2O7 + EDTA sol'n		1M HN4 acetate sol'n		conc. HNO3 solution		total measured As %
sample No	added As(mg)	tot.As mg	%	tot.As mg	%	tot.As mg	%	tot.As mg	%	tot.As mg	%	
#1	0	0	0	0	0	0.04	100	0	0	0	0	
#2	22.2	0.23	1.30	0	0	15.0	85.8	2.3	12.9	0	0	78.6
#3	20.9	0.05	0.31	0	0	15.0	98.3	0.2	1.4	0	0	72.9

b.

		original solution		1M KNO3 solution		1M Na4P2O7 + EDTA sol'n		1M HN4 acetate sol'n		conc. HNO3 solution		total measured Ni %
sample No	added Ni(mg)	tot.Ni mg	%	tot.Ni mg	%	tot.Ni mg	%	tot.Ni mg	%	tot.Ni mg	%	
#1	0	0	0	0.1	4.7	0.2	6.6	0	0	2.1	88.7	
#2	58	16.1	40.8	5.6	14.2	17.5	44.4	0.3	0.6	0	0	68.1
#3	59.4	0.1	1.3	9.8	86.2	1.4	12.5	0	0	0	0	19.1

c.

		original solution		1M KNO3 solution		1M Na4P2O7 + EDTA sol'n		1M HN4 acetate sol'n		conc. HNO3 solution		total measured Fe %
sample No	added Fe(mg)	tot.Fe mg	%	tot.Fe mg	%	tot.Fe mg	%	tot.Fe mg	%	tot.Fe mg	%	
#1	0	0	0	0	0	4	64.7	0.2	0	2.0	32.0	
#2	34.6	0.04	0.1	0	0	23	79.5	1.3	4.5	4.6	15.9	83.5
#3	32.7	4.7	14.7	0	0	26.9	84.3	1.2	3.7	-0.9	0	100.3

Note: tot.M(mg) = [M](mg/L) * vol.(mL)/1000

% M extracted = tot.M/tot.M(extract orig. + extract1 + extract2 + extract3 + extract4)

where: M = As, Ni, Fe

fraction remained in the pore water, not bound in any form to the sediment. The second largest fraction was the organically- bound, while some fraction was present in the exchangeable phase; none of the Ni was extracted in the mineral form. The Fe results were very comparable to the original sediment in that most was organic, none exchangeable, and some present as carbonates and in the mineral form.

Sample #3 contained iron arsenate together with nickel sulphide. For arsenic, one would expect very similar results to sediment sample #2 unless the formation of nickel sulphide changes surface charges in the sediment thereby facilitating different adsorptions for the arsenic forms. This indeed seems to be the case, as lower recoveries were reported in the pore water solutions than in sample #2; this was also the case for the carbonate extractions which reported lower "% recoveries" than in sample #1. In the presence of nickel sulphide, the largest fraction of As is organically-bound in the sediment while none is present in the mineral extraction.

For Ni, the distribution of the forms changes drastically, in that very low fractions remain in the original pore water. The largest fraction is present as extractable Ni followed by organically-bound Ni in the sediment. The two last extractions - carbonate and mineral forms - yielded no nickel.

Nickel concentrations in sample #'s 2 and 3 display a different distribution in five solutions. Sample #2 contains synthesized $NiCO_3$ precipitates. Sample #3 contains synthesized NiS precipitates. The sequential extraction analysis shows that, for $NiCO_3$, almost 40 % of Ni remained in solution, while for sample #3 only 1.3 % was measured in the original solution. Most of the nickel was adsorbed as organic complexes onto the sediment in both samples. For NiS, 3.6 % and 1.2 % of the measured Ni was present in the 3rd and 4th extractions respectively; these are the weak-acid-soluble or mineral-stable precipitates (most likely NiS).

In the presence of nickel sulphide, Fe concentrations in the original pore water were the highest of all three samples, which might suggest that some FeS had also been formed in the sediment. None of the iron was in the exchangeable form, which was consistent with all the previous extractions. The largest fraction was, again, organically-bound Fe followed by extracted fractions as carbonate an in the mineral phase (although very little).

In summary, the spiked sediment extractions suggest that, for As, the presence of sulphide reduction produces a larger fraction of organically-bound As, while for Ni the presence of sulphide suggests a shift towards exchangeable Ni forms. Iron is mainly present in the organically-bound form, which is essential to the microbially-driven sediment contaminant removal process.

In Table 3, the concentrations of As , Ni and Fe determined colorimetrically in the laboratory are compared to concentrations determined by ICP in the same solutions recovered from the sequential extractions. In-house colorimetric determinations were required due to time limitationss (given the large set of analyses required to complete the examination of the reactors) and economic constraints.

Table 3: Comparison of Boojum and EPL Data

		original solution		1M KNO3 solution		1M Na4P2O7 +EDTA solution		1M NH4 acetate solution		conc. HNO3 solution		total measured %
	added (mg)	mg/L	total mg	mg/L	total mg	mg/L	total mg	mg/L	total mg	mg/L	total mg	
Lab As	20.9	0.4	0.0	0.0	0.0	100.0	15.0	1.4	0.2	0.0	0.0	72.9
EPL	20.9	0.2	0.0	0.5	0.1	124.0	18.6	6.9	1.0	0.3	0.1	94.6
Sample #2												
Lab Ni	58.0	121.0	16.1	38.2	5.6	117.9	17.5	1.7	0.3	0.0	0.0	68.1
EPL	58.0	123.0	16.4	50.1	7.4	322.0	48.1	61.8	9.3	31.4	5.7	149.7
Sample #3												
Lab Ni	59.4	1.3	0.1	65.8	9.8	10.5	1.4	0.0	0.0	0.0	0.0	19.1
EPL	59.4	100.0	11.8	68.7	10.2	183.0	27.3	12.1	1.8	3.6	0.6	86.0
Lab Fe	32.7	39.9	4.7	0.0	0.0	206.4	27.0	9.3	1.2	6.5	-0.9	100.3
EPL	32.7	39.5	4.7	0.05	0.01	158.0	19.7	14.0	1.9	14.7	0.5	80.3

Comparing the reported elements for both analyses with respect to concentrations and total measured %, it is evident that the results for iron and arsenic are in good agreement and acceptable. However, the nickel determinations show large deviations in concentrations between the two laboratories.

In summary, the laboratory measurements of arsenic and iron are similar to those determined by ICP. For higher concentrations, the differences between the analyses are somewhat larger, as the colorimetric determinations have to go through several dilution factors.

With respect to the effectiveness of the sequential extractions, it can be concluded, based on the summary of the total measured concentrations from the spiked sediment extractions, that As can be accounted for in the range of 73 % to 95 %. Nickel determined by ICP is accounted for between 86% and >100 % (some of the Ni was extracted from the original sediment in addition to the spiked concentrations added). The methods yield reliable results on which conclusions can be based with respect to the sediment's capacity to act as an environmental sink for both Ni and As.

4.1.3 1993 Reactor Sediment Extraction Test

The first series of sequential extractions on the reactors were carried out on the top samples of the sediments. The top layer of the sediments (about 1 cm thick) can be expected to have the largest component of accumulated As and Ni from the treated seepage water. The summary results for As, Ni, and Fe are given in Table 4. All analytical results are presented in Appendix Tables A3a and A3b with a detailed explanation of the calculations for the approach taken. Table 5 presents a summary of the mass balance in the reactors.

Arsenic

The sum of all measured As amounts (last column in Table 5) are low; they are only 22 % to 38 % of the total As content in the R2 to R5 columns. However in R1, the control column, the measured As amount is 117% of total estimated original As. The difference is probably caused by the distribution of As in the reactor sediments.

Table 4: Extraction of As, Ni, and Fe in top 1 cm of Sediment in Reactors

	1M KNO3 solution			1M Na4P2O7+EDTA sol'n			1M NH4 acetate sol'n			conc. HNO3 solution		
sample	% As	% Ni	% Fe	% As	% Ni	% Fe	% As	% Ni	% Fe	% As	% Ni	% Fe
R1	0	45.9	0	84.3	42.0	87.8	2.3	0	3.9	0	0	8.3
R2	0	28.6	0.8	57.1	58.0	69.8	23.1	6.4	16.2	0	6.8	12.9
R3	0	32.6	0	73.5	47.9	24.1	8.8	3.2	5.9	0	15.8	69.4
R4	0	3.8	0	43.2	68.9	48.7	15	8.1	13.5	0	18	36.9
R5	0	2.2	0	51.8	79.1	57.5	26.9	8.1	16.2	0	9.9	26.1

Table 5: Mass Balance of As, Ni, and Fe in Reactors

		measured			measured to total
sample		total (mg)	sediment %	pore water %	%
R1	As	31.9	86.6	13.4	117.3
	Ni	24.2	88	12	52.5
	Fe	79.1	100	0	
R2	As	10.5	80.1	19.9	38.7
	Ni	136.0	99.7	0.3	306.1
	Fe	88.8	99.8	0.2	
R3	As	8.1	82.3	17.7	30.2
	Ni	60.4	99.5	0.5	132.8
	Fe	50.0	99.4	0.6	
R4	As	6.4	58.2	41.8	22.1
	Ni	23.6	98.8	1.2	47.1
	Fe	62.5	99.2	0.8	
R5	As	9.2	78.7	21.3	33.4
	Ni	49.6	99.3	0.7	98.9
	Fe	109.5	99.9	0.1	

The pore water data show that As is mostly concentrated in the top water in R1, therefore the surface sediment should contain more as. In the pore water of the R2 to R5 reactors, the As concentrations increased with depth. This indicates that As may be more concentrated in lower layers of sediments.

Since only the top layers of sediments were used in the extraction experiment, and the calculated total As amounts in the sediments were based on the top sediment values, the measured As amounts are lower than the real values. In most reactors As was concentrated in the sediments (78.7 % to 86.6 %). Reactor R4 sediment only contained 58.2 % of the total As, the reason probably being that most As in the lower layers was not detected.

In all reactors, none of assayed As in the sediments was in the ion-exchangeable form (1st extraction) or in the least soluble form (4th extraction), as shown in Figure 4. All the As found was in the form of organic complexes and weak-acid-soluble forms.

In R1 sediment, 84.3 % of As (Table 4) was adsorbed as organic complexes, while the rest was extracted as weak-acid-soluble precipitates. In reactors R2 to R5, the As organic complexes ranged from 73.5 % to 43.2 % in the sediments. The weak-acid-soluble form increased from 8.8 % to 26.9 %. This indicates that the as has moved into relatively stable precipitate forms.

Nickel

The final Ni "accounted for" amounted to about 50 % to 100 % of the feed Ni in reactors R1, R4, and R5. In reactors R2 and R3 (potato waste as substrate) the "accounted for" Ni was higher than the original content. The Ni was concentrated in the sediments, especially in the R2 to R5 reactors (Figure 5).

Fig 4: Reactor sediments
As in sequential extractions

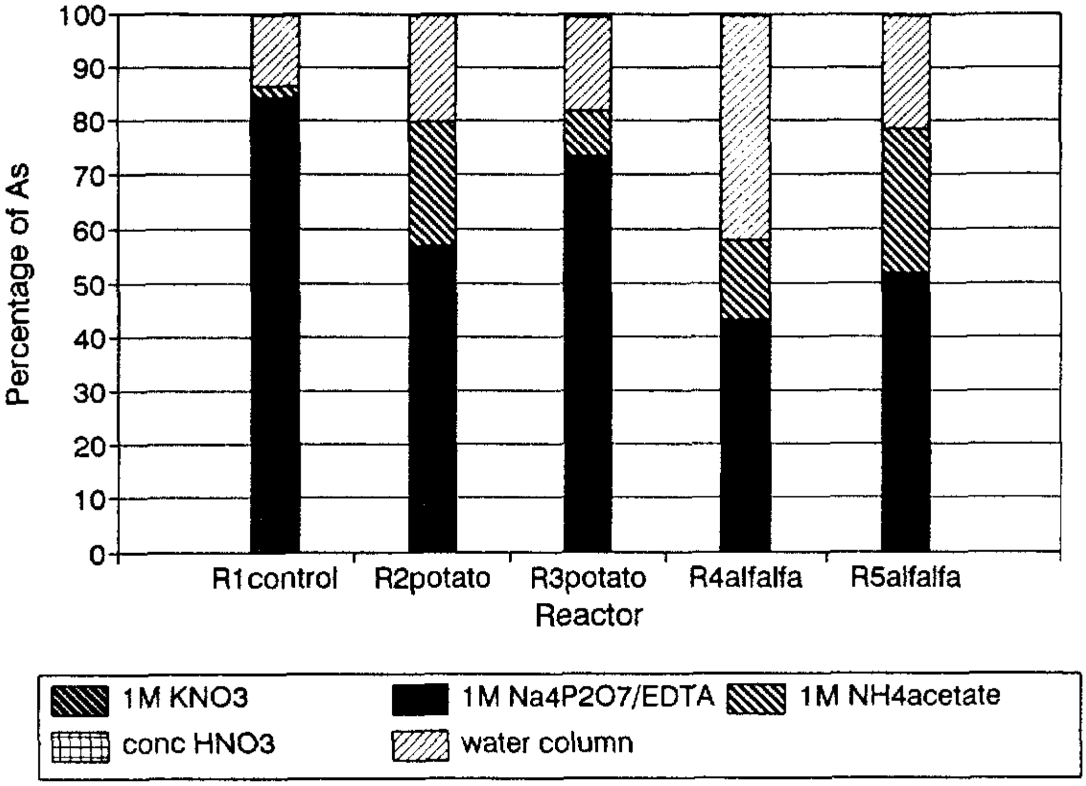
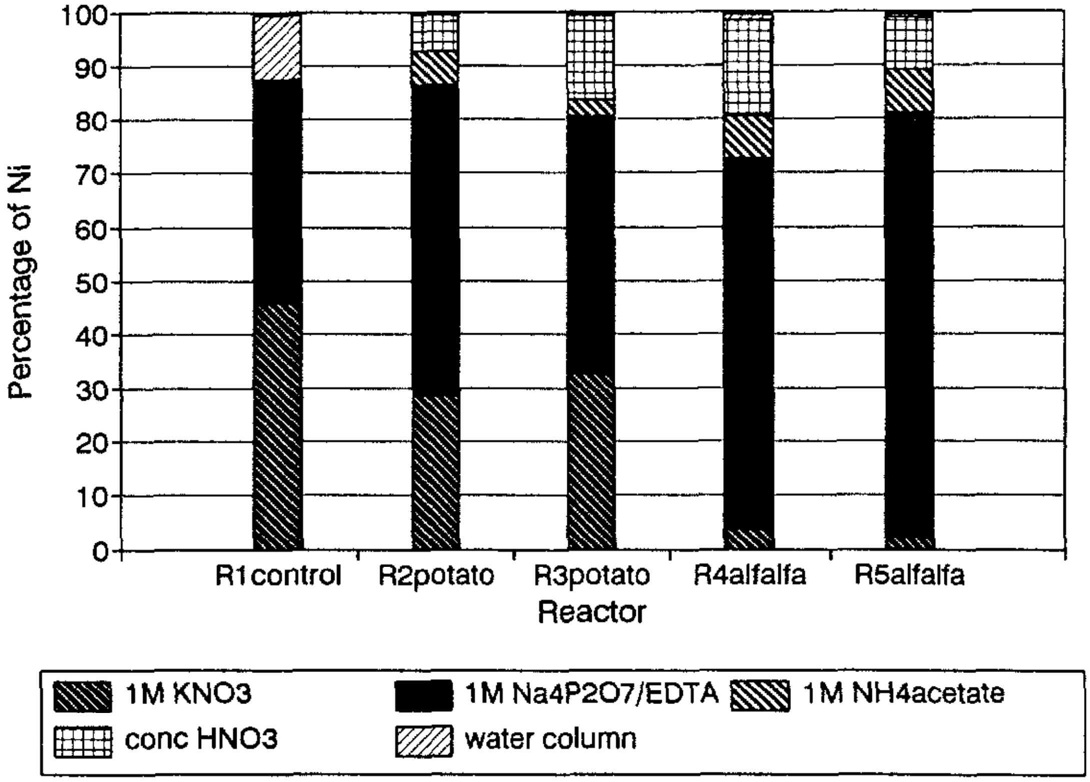


Fig 5: Reactor sediments
Ni in sequential extractions



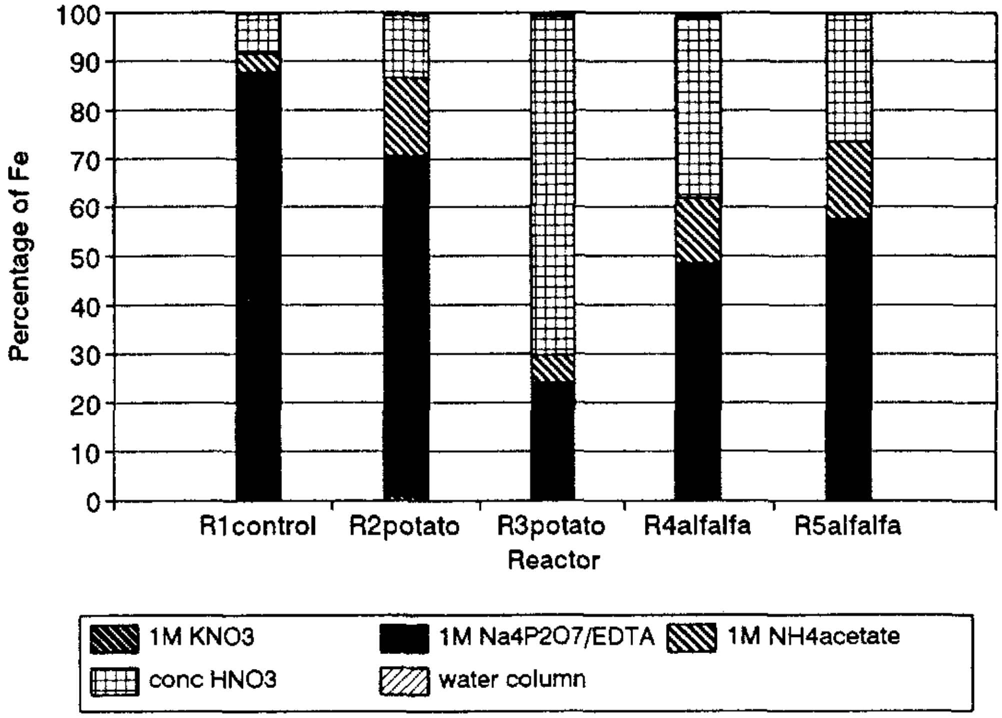
Nickel was detected in all four extraction fractions. The adsorbed Ni indicated by the first extraction fraction was less in R4 and R5 reactors (alfalfa as substrate). The percentage of Ni in organic complexes was similar in all reactors (Figure 5). Nickel formed weak-acid-soluble and strong-stable precipitates only in reactors R2 to R5.

Iron

As the initial Fe concentration in 6.11 water was very low, most of the extracted Fe was from the original sediments therefore no original amount of Fe was estimated. In Table A3b, the "accounted for" Fe contents are listed. The values from reactors R1, R2 and R5 are very close and indicate that the calculations are rational. The R3 and R4 bottom pore water samples had relatively high Fe concentrations, therefore it was expected that the bottom sediment samples would have the highest Fe concentrations. This, however, was not the case.

The extraction data showed that over 99 % of the Fe was in the sediment, and almost none was ion-exchangeable. In R1, 87.8 % of the Fe was organically-complexed and about 12.2 % was in the form of weak-or-strong-acid-soluble precipitates (Figure 6). This is consistent with the spike experiment.

Fig 6: Reactor sediments
Fe in sequential extractions



In the R2 to R5 reactors, the amount of organically-complexed Fe decreased to 24 % to 70 %, while the acid-extractable precipitates increased to 29 % to 75 %. Most of the Fe precipitates were in the stable form and only concentrated nitric acid could dissolve it (Figure 6).

4.2 1994 Experiment - As and Ni Removal Capacity of Sediments

This experiment was designed to test the capacity of muskeg sediment to treat a seasonal seepage from the waste rock pile.

Measurements made on the water columns of the reactors after set-up but prior to addition of potato waste are shown in Table 6. The initial readings for the columns indicate that the water chemistry is similar to that of the seepage water. Mixing with sediment pore water results in an elevated pH (4.3 to 5.0 compared to 3.85 for 6.11 water) and reduced conductivity (1155 µmhos/cm to 1262 µmhos/cm compared to 1386 µmhos/cm for the seepage water) and Eh (367 mV to 445 mV for column water and 522 mV for the seepage water).

After 4 to 5 days of incubation with potato waste, samples from all reactors and jars were analyzed together with the added seepage water and sediment pore water. The data is shown in Table 7. By this time, dramatic changes in the Eh had occurred in some of the columns due to the hydrolysis and fermentation of potato waste. In 5 of the 9 reactors, reducing conditions had established negative Eh values. The fermentation of potato waste was reflected in the increased acidity in the reactors with low Eh values. Under these conditions, denitrification had commenced as indicated by lower NO_3-N concentrations compared to the seepage water. Also, the reducing conditions were responsible for the appearance of dissolved iron in solution. There was no detectable dissolved iron in 6.11 water. In general, the lower the Eh value for the reactor column, the higher the iron concentration. Arsenic concentrations were consistently lower in the reactor columns than in the seepage water. Nickel concentrations were somewhat lower in the reactors than in the seepage water. The lower values in the reactors with the lowest Eh values indicates that some precipitation may already be occurring in reducing conditions.

The chemistry of water samples from the controls (seepage water and potato waste) was very similar to that of 6.11 water. There was no clear indication that hydrolysis

Table 6: Sediment Treatment Capacity Reactors, Chemistry after 24 h.

Reactor	pH	Eh (mV)	Cond. (umhos/cm)	Temp. (C)
1	4.97	432	1155	21.3
2	4.68	435	1197	21.5
3	4.55	389	1207	20.2
4	4.49	445	1195	21.5
5	4.39	430	1221	21.7
6	4.44	414	1237	20.1
7	4.36	432	1237	21.7
8	4.5	368	1163	20.3
9	4.36	409	1262	20

Table 7: Sediment Treatment Capacity Reactors, Chemistry after 96 h.

Reactor	pH	Eh (mV)	Cond. (umhos/cm)	Temp. (C)	As (mg/L)	Fe (mg/L)	Ni (mg/L)	NO3-N (mg/L)	Acidity (mg/L)*
1	4.81	278	1255	20.9	56	2.6	51.8	26.3	171.4
2	4.87	257	1301	20.8	50	2.8	61.3	23.9	150.3
3	4.69	-272	1313	20.6	50	4.99	48.4	11.7	234.5
4	4.76	299	1269	20.8	56	2.8	56.1	20	172.2
5	4.59	319	1306	20.8	62	2.6	77	31.1	154.5
6	4.62	-272	1291	20.8	50	5.44	37.2	10.4	241.1
7	4.54	146	1334	20.7	50	2.3	59.6	24.7	154.4
8	4.49	-72	1291	20.7	45	4.28	35	23.9	178.8
9	4.41	-243	1384	20.9	50	3.83	58.7	16.8	214.7
jar 1	4.04	469	1570	20.1	85	0.37	48.4	26.3	165.1
jar 2	4.03	471	1568	20.3	85	0.38	62.2	33.4	152.8
jar 3	3.98	469	1587	20.5	85	0.24	69.9	27.1	168.7
6.11	3.85	522	1386	21.6	85	0.08	72.5	27.1	106.7

Sediment 5.68 173 196 20.9
BT 2 Stn 250

*(mg/L) equivalent of CaCO3

at day 40. By this time, 250-300 mg/L of acidity had been consumed in both unchanged reactors and unchanged jars.

pH

The seepage water had a pH of 3.95. The first readings at 10 days showed little change (pH 4.31 to 4.87 in reactors and pH 4.75 to 5.55 in jars). There was a steady rise in pH from the second sample onwards for all reactors to around pH 6-6.5 by day 40 (Figure 9). In other words, the 'recharge' reactors exhibited the same pH rise as the 'unchanged' reactors. There was a similar pH rise in the jars.

Conductivity

For reactors not receiving 'fresh' seepage water, there was a fairly steady decline in conductivity through the course of the experiment from around 1300 μmhos/cm to around 960 μmhos/cm (Figure 10). This decrease was not apparent in the control jars. Initially, the conductivity was considerably higher in these jars compared to the reactors (around 1600 μmhos/cm). Thereafter, values were steady at around 1300 μmhos/cm. The reactors receiving 'fresh' seepage water weekly exhibited an initial decline in conductivity between the first two readings, comparable to that observed for the other reactors. Thereafter, values were steady at around 1150 μmhos/cm.

Nickel

The nickel concentration in the reactors was generally lower (25-61 mg/L) than the control jars (60-70 mg/L) at the first sampling (4 to 5 days), attributable to dilution by sediment water in the reactors (Figure 11). In contrast, in the reactors with no further additions of seepage water, there was a decline to approximately 20 mg/L at day 26 after which the concentration remained steady. Nickel concentration in the control jars remained more or less constant throughout the course of the experiment.

Fig. 9: Reactor water column
pH

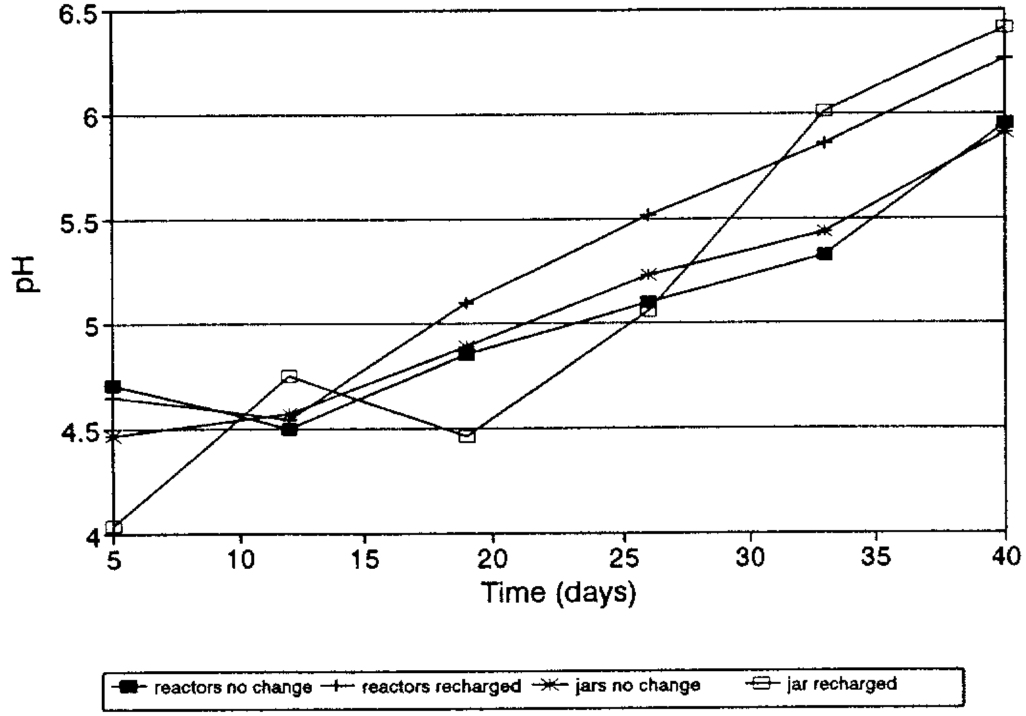


Fig 10: Reactor water column
Conductivity

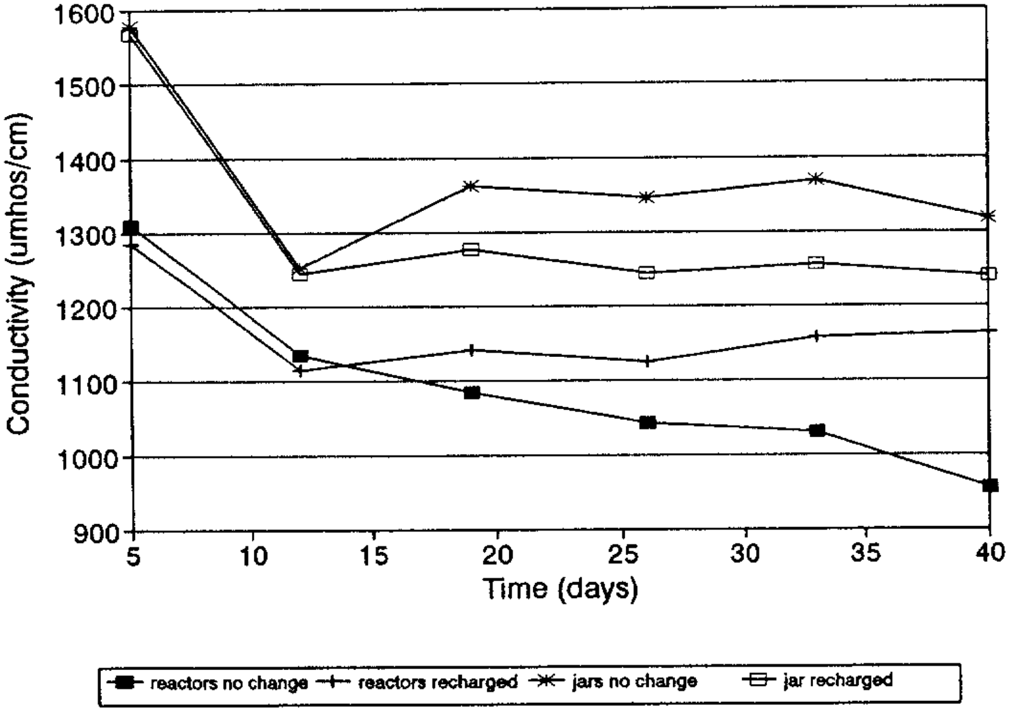


Fig. 11: Reactor water column
Nickel

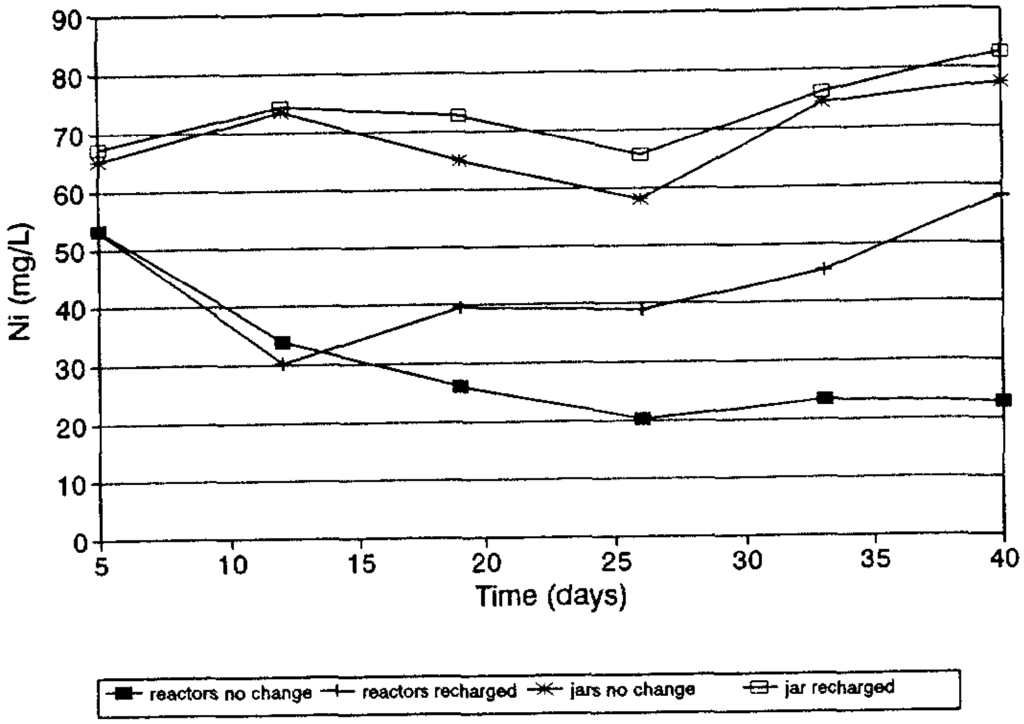
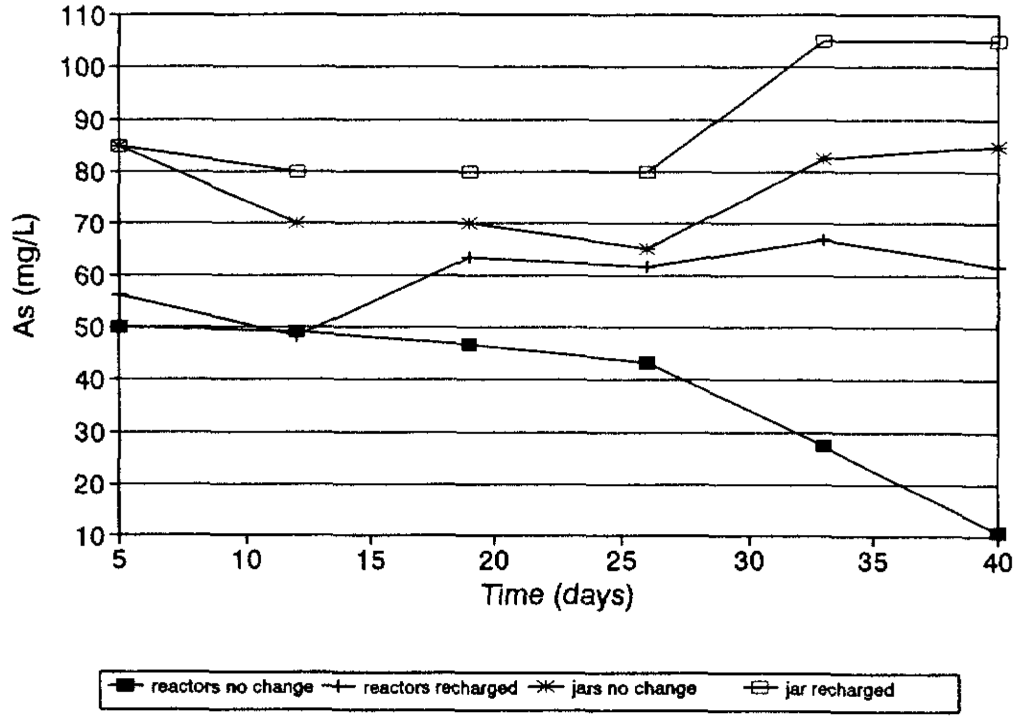


Fig 12: Reactor water column
Arsenic



Arsenic

The seepage water contained 90 mg/L dissolved arsenic (Figure 12). By the first reading (10 days), the As concentration had dropped to 50 mg/L. Much of this change is attributable to dilution by water in the sediment, although removal by other means cannot be discounted.

In the jars, there was no decline in As concentration over the course of the measurements. After this time, the As concentration in the reactors without water change declined to a mean value of 10 mg/L by 40 days from 50 mg/L at 4 to 5 days.

Iron

There was an increase in iron in both jars and reactors (Figure 13). The Fe in the jars is released from the potato waste as it decomposes. The maximum concentration observed was around 4 mg/L. The concentration was lower in the 'recharged' jar due to removal at the time of water change. In the 'no change' reactors, Fe concentration rose to a mean of 16.5 mg/L. The dramatic dip at 33 days may be due to settling of weakly-suspended solids. Iron in the reactors came both from the potato waste and the sediments.

Nitrate-N

There was a dramatic decline in nitrate-N concentrations in all reactors and jars from day 5 to day 12 (Figure 14). Thereafter, the decline continued in reactors until day 40 when concentrations were 0.13 mg/L or less for the 'unchanged' reactors and 0.49 mg/L or less for the 'recharged' reactors. For the 'unchanged' jars, there was a substantial increase in nitrate-N from day 12 to day 19 followed by a decline to < 0.5 mg/L by day 40.

Ammonium-N

There was a steady decline in ammonium-N in all reactors and jars to day 26, after which values recovered to near initial values (Figure 15). There was no clear effect of 'recharging' with 6.11 water on the ammonium-N concentration.

Phosphate

Phosphate-P concentrations were higher in reactors than in jars up to 26 days, presumably due to release from the sediments (Figure 16). Overall there was a steady decline in phosphate-P concentrations in all reactors to 4-6 mg/L and control jars until day 33. From this time to day 40, concentrations were steady in both reactors and control jars.

Overall

The data for the unchanged control jars shows the effects of potato waste on seepage water. The early decline in Eh and establishment of reducing conditions is associated with the decomposition of potato waste and probable release of volatile fatty acids which contributes to the increase in acidity. The reducing conditions thus established support the reduction of nitrate (denitrification) and iron. The removal of phosphate and ammonium may be due in part to uptake by microorganisms. The lack of arsenic and nickel removal are attributable to a lack of ferric and sulphide ions respectively for precipitation and/or surface sites for adsorption processes. The steady conductivity in the jars suggests little overall removal of ions from solution.

In contrast to the jars, there was a steady reduction in conductivity in the reactors indicating a net removal of ions from solution. The drop in Eh and rise in acidity exhibited a similar pattern to that of the jars. The removal of nitrate, ammonium and phosphate was also similar. Iron concentrations were much higher in the reactors, undoubtedly due to reduction and dissolution of iron from the sediments. Iron reduction inhibits sulphate reduction if ferrous iron is present (Lovley and Phillips 1987). Therefore sulphate reduction may not have occurred. In some reactors, Eh values were lower at the initial reading (4-5 days) than the theoretical maximum value (-220 mV) at the initial reading at which sulphate reduction occurs (Zehnder and Stumm 1988). The removal of approximately 70 % of the Ni from solution before a steady state was achieved is interesting. If nickel is removed as a sulphide precipitate, sulphate reduction must occur for generation of sulphide. This may have occurred early on. Some removal by adsorption processes is possible. However, the available sites would likely be filled within hours of set-up as indicated by the data of Eger and

Lapakko (1989). The steady decline in Ni is more suggestive of a precipitation process. The steady decline in As is also indicative of precipitation. The low Eh and release of ferrous iron from the sediments suggests that precipitation of ferrous arsenate may be occurring.

Weekly changing of 500 mL of water with 'fresh' seepage water resulted in concentrations of Ni and As similar to the original values after 2 weeks for As. This suggests that for As, the net removal ceases. For Ni, on the other hand, some removal continued. It is possible to estimate the total Ni removed from the water column in these reactors during the period of observations. The estimated total removal (mean of 3 reactors) together with the total Ni in the reactors is summarized in Figure 17.

It is assumed that the volume of water in the reactors being treated is 0.9 L. The data indicate that by day 40, a total of 93 mg of Ni had been removed from a total of 145 mg added to the reactors. This is nearly double that removed from the 'unchanged' reactors. However by the end of the observations the amount of Ni removed with each addition of seepage water was small. Clearly the system is approaching saturation.

Calculations of As removal form the 'recharged' reactors 4, 5 and 6 have also been made (Figure 18). With additions of seepage water, the As concentration in the water column remains fairly constant (Figure 11) but is considerably lower than in the seepage water (85 mg/L), therefore the As is being removed from the reactor water throughout the period of observations. Figure 18 shows that by day 40, a total of 83 mg had been removed. The rate of removal remained constant over the observation period. In other words there is no indication that the removal process(es) is nearing full capacity.

Since the As concentration in the 'unchanged' reactors was still declining at the end of the observation period, the water column in reactors 7, 8 and 9 was not changed. It is planned to run these reactors until there is no longer any net removal of As and Ni at which point, 500 mL of the water column will be replaced with 'fresh' seepage water.

Fig. 17: Recharged reactors
Nickel removal

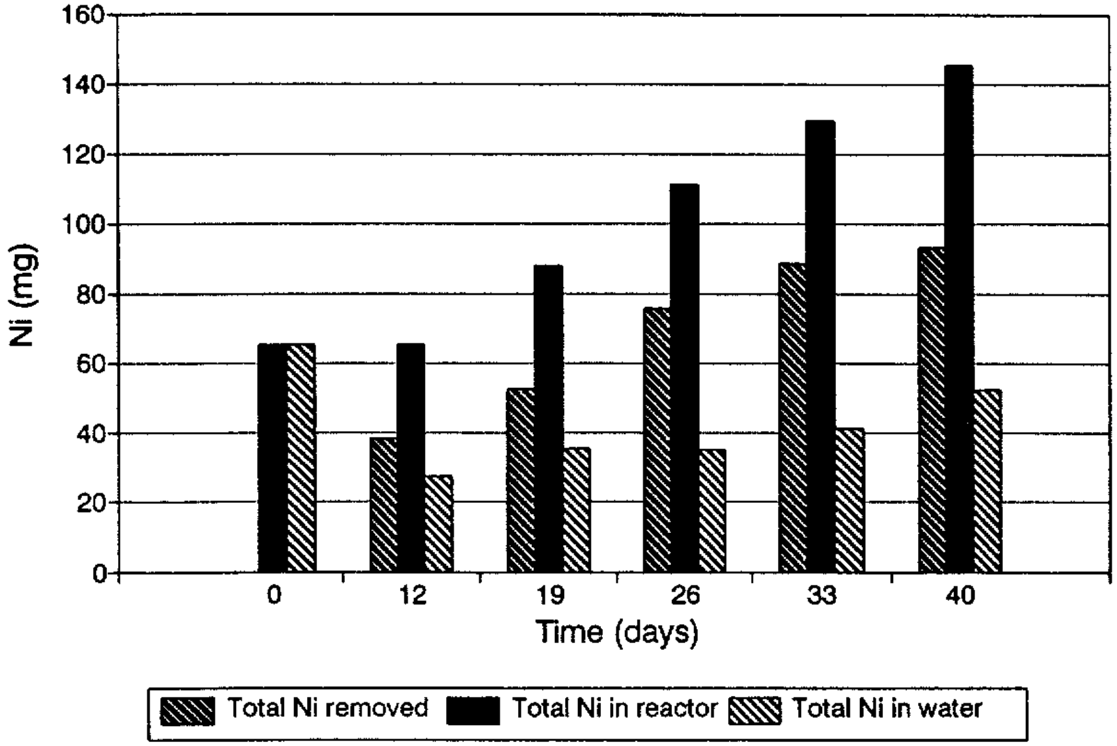
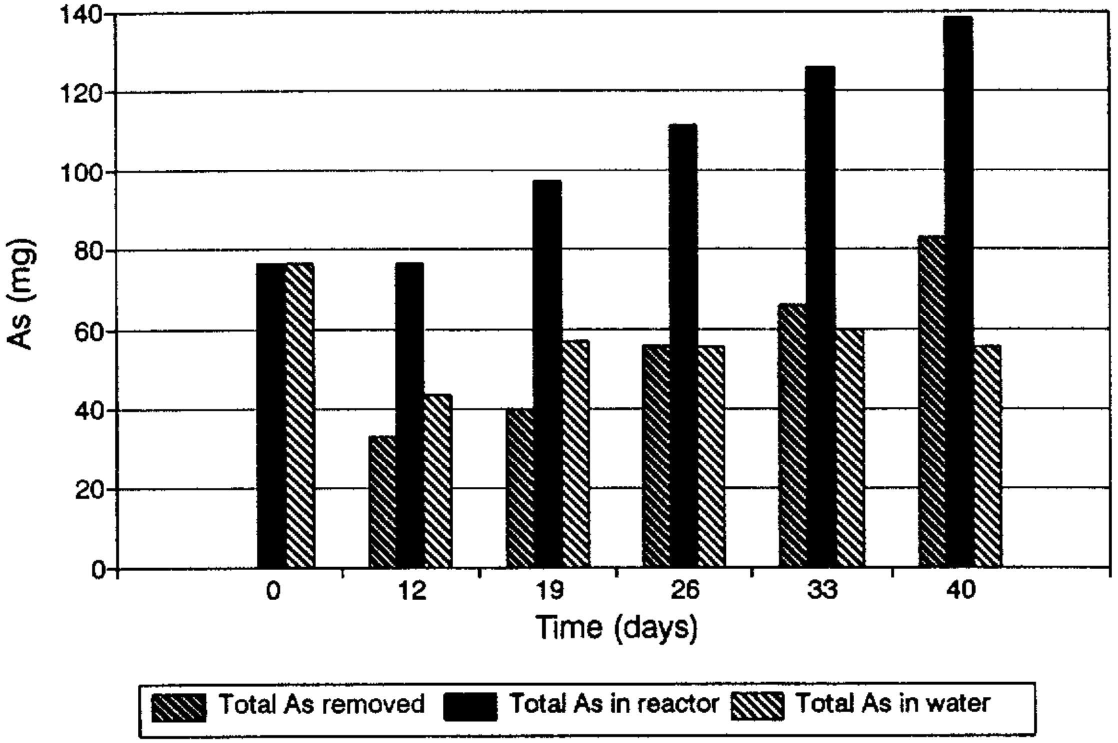


Fig. 18: Recharged reactors
Arsenic removal



5.0 DISCUSSION AND CONCLUSIONS

To date, analyses have demonstrated that the muskeg sediment was effective in removal of Ni and As from added acid mine drainage, especially when organic supplements (potato waste, alfalfa pellets) were added.

Analysis of the 1993 reactors provided a test for sequential extraction techniques for determination of amounts and forms of As and Ni held in sediments. The method was found to be reproducible for As and Fe but yielded highly variable results for Ni.

The sequential analysis suggests that much As is held by the sediment in organic complexes. In the presence of organic amendments in the reactors, a substantial amount of precipitate was present. This indicates that reducing conditions, established through addition of potato waste or alfalfa pellets, can lead to removal of arsenic as precipitates. The Eh/pH diagram suggests that the conditions found soon after addition of the organic amendments were favourable for formation of arsenite. This form of As has recently been detected in anaerobic soils contaminated by waste waters from a gold mine (Bowell et al, 1994). Although reducing conditions were no longer present in the water column at the time of sampling for the sediment analysis, pre-formed precipitates would be expected to be stable in the conditions observed. In the absence of organic amendments, less As was removed. The As removed was entirely as organic complexes. These are likely to be less stable than inorganic precipitates when conditions change.

The Ni data from the sequential analysis is too variable for quantitative estimation of forms removed. However it is clear that precipitates are formed only when organic amendments (potato waste or alfalfa) have been added to the reactors. As for arsenic, reducing conditions produced through decomposition of organic matter can lead to precipitation of nickel salts which will be more stable in sediments than complexed forms.

The 'sediment treatment capacity' experiment yielded valuable data on the dynamics of As and Ni removal and began to examine the treatment capacity of the B-Zone muskeg sediments. Over the 40 day period of observations, As concentrations in the water column declined from 85 mg/L to 10 mg/L. In previous experiments with similar conditions, dissolved As concentration eventually declined to stable values of 0.5 mg/L to 1 mg/L. In the present experiment, Ni declined from 70 mg/L to 20 mg/L. Further decline was likely inhibited by the high Fe in solution (reduced Fe released under reducing conditions). This will inhibit sulphate reduction (Lovley and Phillips 1991) so sulphide ions would not be present for precipitation of nickel sulphides.

Exchange of 6.11 water in the water column of reactors determined that the sediment can remove considerably more Ni and As than present in a 'single dose.' Arsenic removal continued at a linear rate through 5 changes of water. Nickel removal rates declined towards the end of the observations. The third treatment, where 6.11 is exchanged when a steady state concentration of As and Ni prevails in the water column, has not yet commenced.

To summarize, both As and Ni can be removed from 6.11 water as potentially stable precipitates if exposed to reducing conditions induced through decomposition of organic amendment and the sediment environment.

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Table A1. Spike Extraction Data

		original solution				1M KNO3 solution				1M Na4P2O7+EDTA solution				1M HN4 acetate solution				conc.HNO3 solution				total
sample	added	vol.	[As]	tot.As	%	vol.	[As]	tot.As	%	vol.	[As]	tot.As	%	vol.	[As]	tot.As	%	vol.	[As]	tot.As	%	measured
No	As(mg	mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		As %
#1	0	0	0	0	0	150	0	0	0	150	0.3	0.04	100	150	0	0	0	150	0	0	0	
#2	22.2	133	1.7	0.23	1.30	150	0	0	0	150	100	15.0	85.8	150	15	2.3	12.9	180	0	0	0	78.6
#3	20.9	118	0.4	0.05	0.31	150	0	0	0	150	100	15.0	98.3	150	1.4	0.2	1.4	170	0	0	0	72.9

		original solution				1M KNO3 solution				1m Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution				total
sample	added	vol.	[Ni]	tot.Ni	%	vol.	[Ni]	tot.Ni	%	vol.	[Ni]	tot.Ni	%	vol.	[Ni]	tot.Ni	%	vol.	[Ni]	tot.Ni	%	measured
No	Ni(mg)	mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		Ni %
#1	0	0	0	0	0	150	0.8	0.1	4.7	150	1.1	0.2	6.6	150	0	0	0	150	14	2.1	88.7	
#2	58	133	121	16.1	40.8	150	38.2	5.6	14.2	150	117.9	17.5	44.4	150	1.7	0.3	0.6	180	0	0	0	68.1
#3	59.4	118	1.3	0.1	1.3	150	65.8	9.8	86.2	150	10.5	1.4	12.5	150	0	0	0	170	0	0	0	19.1

		original solution				1M KNO3 solution				1M Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution				total
sample	added	vol.	[Fe]	tot.Fe	%	vol.	[Fe]	tot.Fe	%	vol.	[Fe]	tot.Fe	%	vol.	[Fe]	tot.Fe	%	vol.	[Fe]	tot.Fe	%	measured
No	Fe(mg	mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		Fe %
#1	0	0	0	0	0	150	0	0	0	150	26.6	4	64.7	150	1.4	0.2	0	150	13	2.0	32.0	
#2	34.6	133	0.3	0.04	0.1	150	0	0	0	150	179.7	23	79.5	150	10.0	1.3	4.5	180	37	4.6	15.9	83.5
#3	32.7	118	39.9	4.7	14.7	150	0	0	0	150	206	26.9	84.3	150	9.3	1.2	3.7	170	6.5	-0.9	0	100.3

Table A2. Comparison of Boojum and EPL Data

		original solution				1M KNO3 solution				1M Na4P2O7+EDTA solution				1M NH4 acetate solution				conc. HNO3 solution				total
	added	vol.		total	%	vol.		total	%	vol.		total	%	vol.		total	%	vol.		total	%	measured
	(mg)	mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		mL	mg/L	mg		%
Lab As	20.9	118	0.4	0.05	0.3	150	0	0	0	150	100	15.0	98.3	150	1.4	0.2	1.4	170	0	0	0	72.9
EPL	20.9	118	0.2	0.02	0.1	150	0.5	0.1	0.4	150	124	18.6	94.0	150	6.9	1.0	5.2	170	0.3	0.06	0.3	94.6
Lab Ni	58	133	121	16.1	40.8	150	38.2	5.6	14.2	150	117.9	17.5	44.4	150	1.7	0.3	0.6	180	0	0	0	68.1
EPL	58	133	123	16.4	18.8	150	50.1	7.4	8.5	150	322	48.1	55.4	150	61.8	9.3	10.7	180	31	5.7	6.5	149.7
Lab Ni	59.4	118	1.3	0.1	1.3	150	65.8	9.8	86.2	150	10.5	1.4	12.5	150	0	0	0	170	0	0	0	19.1
EPL	59.4	118	100	11.8	23.1	150	68.7	10.2	19.9	150	183	27.3	53.4	150	12.1	1.8	3.6	170	3.6	0.6	1.2	86.0
Lab Fe	32.7	118	39.9	4.7	14.4	150	0	0	0	150	206.4	27.0	82.5	150	9.3	1.2	3.6	170	6.5	-0.9	0	100.3
EPL	32.7	118	39.5	4.7	14.2	150	0.05	0.01	0.02	150	158	19.7	60.3	150	14	1.9	5.8	170	15	0.5	0	80.3

Appendix 3. Explanation of Sequential Extraction Calculations

In Table A3a the second column gives the metal loadings which have been added with the seepage to the reactors, and represents the mg/L multiplied by the volume of seepage added. In the third column, the accumulated As and Ni losses due to the weekly sampling where water is withdrawn from the reactors is presented.

The fourth column represents the amount of As and Ni which remained in the reactors for removal by sediments. The sediment ratios represented in the fifth column are the ratios of the dry weight of the total sediment in the reactors to the dry weight of the sediment used in the extractions.

For each of type of sequential extraction, the extracted metal concentrations and the volumes of the extraction solutions were measured, from which the total quantity of metal extracted (representing the respective form of the metal present in the sediment) was calculated. The percentage of each fraction is referenced back to the original amount present in the reactor sediments.

The concentrations of each metal in the reactors' water columns are shown in Table A3b. The waters are divided into three layers; the "top" solution is the water above the sediment (the treated seepage in the reactors), the "middle" solution is the pore water from sediment layers 1 and 2, and the "bottom" solution is the pore water from sediment layer 3. The metal content and percentages were calculated. The "pore water %" is the sum of the dissolved metals in the three solutions, and the "sediment %" is the total extracted.

The percentage comparison of the amounts of metal in the sediment and those in the water body, assessed by analysis, is listed in the three columns under the "measured" section of Table A3b. The last column in Table A3b shows the comparison of the "head" less the "sampling loss" (the 3rd column in Table A3a) with the total metal analyzed in the pore water and the sediment.

Table A4. Chemistry of Laboratory Reactors

Reactor	pH	Eh (mV)	Cond. umhos/cm)	T-C (C)	Ni (mg/L)	As (mg/L)	Fe (mg/L)	N03-N (mg/L)	NH4-N (mg/L)	PO4-P (mg/L)	Acidity (mg/L)*
February 1/94											
1	4.41	-246	1105	20.4	26.0	45	5.0	7.8	44.4	16	368.6
2	4.37	-215	1150	20.5	29.5	50	9.5	10.0	19.7	19	436.8
3	4.87	75	1110	20.7	31.2	55	11.3	7.6	16.2	13	230
4	4.44	-231	1111	20.6	27.8	50	11.8	9.2	12.7	15	374.4
5	4.49	-232	1165	20.7	29.5	45	6.8	9.2	26.8	22	320.6
6	4.73	209	1068	20.6	32.9	50	14.5	2.8	9.2	14	415
7	4.37	-188	1160	20.6	39.8	50	11.2	6.8	5.6	17	508.1
8	4.76	196	1135	20.7	31.2	45	13.0	6.0	19.7	14	284.2
9	4.68	-191	1144	20.5	45.0	50	13.8	10.8	16.2	13	357.7
jar-1	4.75	-204	1264	20.4	72.6	75	4.2	4.4	12.7	9.5	269.5
jar-2	5.17	-193	1245	20.4	74.3	80	4.0	6.8	12.7	8.7	237.4
jar-3	5.55	-275	1241	20.5	74.3	65	3.8	6.0	16.2	10	183
February 8/94											
1	4.78	222	1055	20.2	22.6	45	12.3	6.0	12.7	13	195
2	4.77	210	1091	20.3	24.3	45	14.2	9.2	16.2	15	258
3	5.05	155	1065	20.3	29.5	45	12.8	5.2	16.2	9	154.8
4	5.33	234	1140	20.4	39.8	65	7.8	9.2	2.1	8	117.7
5	4.89	280	1176	20.3	39.8	65	11.2	8.4	12.7	19	217.8
6	5.21	226	1108	20.4	38.1	60	6.5	13.2	2.1	22	130.7
7	4.72	-114	1098	20.4	27.8	50	14.2	6.0	5.6	12	296.9
8	5.08	113	1062	20.3	26.0	45	14.3	5.2	12.7	10	158.6
9	4.93	226	1135	20.4	34.7	50	14.7	2.8	16.2	9	233.6
jar-1	4.46	-197	1365	20.2	65.7	75	3.7	4.4	12.7	6	367.1
jar-2	5.05	-177	1278	20.1	72.6	80	2.8	18.7	9.2	16	121.5
jar-3	4.43	-203	1361	20.1	64.0	65	3.7	5.2	19.7	10	418.5
February 15/94											
1	5.03	248	1063	20.4	19.1	40	15.7	2.8	5.6	10	171.2
2	5.06	257	1032	20.5	19.1	40	16.7	3.6	2.1	12	186.6
3	5.22	233	1038	20.6	22.6	45	16.3	1.2	5.6	9	137.3
4	5.54	220	1108	20.6	36.1	60	10.7	3.6	2.1	9	94.5
5	5.41	229	1126	20.6	41.6	55	11.0	2.8	2.1	13	136.9
6	5.67	202	1142	20.6	36.4	70	11.3	9.2	2.1	14	78.4
7	5.17	236	1035	20.7	17.4	45	14.7	1.2	2.1	11	171.5
8	5.29	230	1011	20.6	19.1	45	16.3	2.8	5.6	10	142.8
9	5.25	232	1076	20.6	24.3	45	19.7	2.0	5.6	8	194.8
jar-1	5.06	66	1356	20.4	58.8	60	4.0	2.8	9.2	6	168.2
jar-2	5.18	-48	1245	20.3	65.7	80	2.7	15.5	12.7	15	92.2
jar-3	4.56	-13	1336	20.4	57.1	70	4.3	3.6	5.6	13	310.7
February 22/94											
1	5.26	151	1017	21.5	17.4	25	0.2	0.1	10.3	3.5	137.3
2	5.31	180	1031	21.4	20.9	30	0.1	0.1	13.1	3.8	129.1
3	5.43	152	1011	21.6	19.1	25	0.7	0.1	12.4	4.2	111.2
4	5.81	161	1156	21.5	45.0	60	0.1	0.5	17.3	2.5	92.6
5	5.83	171	1175	21.6	48.4	70	0.1	0.6	19.4	2.1	86.9
6	5.94	144	1144	21.5	43.3	70	0.3	0.6	18.0	4.5	86.4
7	5.43	175	1059	21.6	19.1	20	0.2	0.1	12.4	4.8	162.2
8	5.51	108	987	21.5	24.3	20	0.3	0.1	10.3	4.9	159.9
9	5.38	171	1078	21.6	39.8	45	0.7	0.1	14.5	4.3	169.6
jar-1	6.01	138	1388	21.4	76.0	85	0.3	0.3	25.1	4.6	108.2
jar-2	5.52	206	1257	21.3	76.0	105	0.1	0.7	22.3	4.8	77.4
jar-3	5.31	186	1353	21.2	72.6	80	0.6	0.3	20.8	4.7	138.3
March 2/94											
1	5.91	-88	985	21.5	24.0	10	10.5	0.1	0.6	3	77.7
2	5.89	-84	928	21.4	23.1	10	9.2	0.1	0.3	3.5	62.7
3	6.08	-93	940	21.3	21.4	10	11.2	0.1	0.2	4	71.3
4	6.19	10	1155	21.5	58.5	60	3.5	0.5	0.5	6	56.2
5	6.27	8	1185	21.6	63.6	65	4.5	0.6	0.7	5.5	56.9
6	6.34	9	1150	21.6	51.6	60	3.0	0.7	0.3	5	53.1
7	5.92	-69	1010	21.6	16.1	5	16.3	0.1	0.1	4.1	79.3
8	6.08	-89	820	21.5	18.3	10	9.7	0.1	0.1	4.3	59
9	5.77	-15	1050	21.4	34.3	20	18.7	0.1	0.7	3.8	96.5
jar-1	6.41	56	1310	21.1	75.7	80	1.5	0.3	1.0	4.6	45.4
jar-2	6.39	92	1240	21.2	82.6	105	0.16	0.9	1.0	5.2	30.8
jar-3	6.45	79	1325	21.1	79.2	90	1.2	0.6	1.0	4.7	59.9
6.11 water	3.95	528	1398	21.5	87.6	90	0.16	21.5	20.8	58	89.5

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ARSENIC AND NICKEL REMOVAL BY WETLAND SEDIMENTS[1]

Andrew Fyson[2], Margarete Kalin[2], and Les W. Adrian[3]

Abstract: Laboratory experiments were carried out to test the capacity of sediments from muskeg ponds to treat waste rock seepages with mean concentrations of As and Ni of 36 mg/L and 79 mg/L, respectively (1992 data). Seepage water was added to column reactors containing muskeg sediment, and additions of organic matter (alfalfa, potato waste and hydroseeding mulch) were made to the sediments to stimulate microbial activity. In the first experiment, arsenic concentrations in the water column of the reactors decreased to less than 1 mg/L from 50 mg/L, and Ni to less than 0.1 mg/L from 74 mg/L in 112 days. A second experiment established that the results are reproducible. More than 90% of As and Ni present at start-up is removed within 43 days. A third experiment indicated that alfalfa and potato waste increased the rate at which reducing conditions were established, which in turn resulted in increasing the rate of arsenic and nickel removal from the seepage water. The addition of alfalfa resulted in greater metal removal than when potato waste was used. These experiments have shown that muskeg sediments have the capacity to remove As and Ni from a waste rock seepage water through providing conditions that facilitate precipitation and adsorption with or without the addition of organic amendments.

Additional Key Words: acid mine drainage, passive treatment, sulfate reduction, iron reduction.

Introduction

Waste rock piles from metal mining operations often generate seepages with low pH and high concentrations of heavy metals. Depending on decommissioning methods chosen, contaminated seepage waters may emerge from waste rock piles for a long time. Treatment may therefore be required in perpetuity. Passive treatment systems, utilizing natural processes driven by bacteria, are attractive treatment alternatives, as opposed to maintaining a chemical treatment plant. Such systems would provide a low maintenance option and are environmentally sustainable.

Research on the utilization of wetlands for the treatment of a variety of wastewaters has been carried out in the past decade, including constructed wetlands treating acid mine drainage (AMD) from coal operations (Brodie 1988, Hammer 1989). Wetlands are considered passive treatment systems, since they have the capacity to regenerate themselves through continued growth.

Microbially-driven sulfate and iron reduction are processes occurring naturally in wetland sediments which facilitate the removal of metals from the AMD through increasing the pH, which in turn results in precipitation of the metals either as hydroxides or as sulfides (Wildeman 1993, Kalin 1993). Adsorption processes, which assist in metal removal, can also be active in wetlands. Wieder (1992) has provided some estimates quantifying different metal removal mechanisms in wetlands. Eger and Lapakko (1989) utilized peat in constructed wetlands to treat AMD with Ni concentrations up to 15 mg/L, following laboratory studies where peat was observed to adsorb up to 20 g Ni/kg dry weight.

Kalin (1993) reported Ni concentration reductions in an AMD tailings seepage from an initial concentration of 25 mg/L originally to less than 1 mg/L. The microbially-driven treatment system removes Ni likely by co-

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[2] Andrew Fyson, Microbiologist and Margarete Kalin, Ecologist, Boojum Research Ltd., Toronto, Ont, Canada.

[3] Les W. Adrian, Environmental Engineer, CAMECO Corp., Saskatoon, Saskatchewan, Canada.

precipitation with iron. When reducing conditions are established in the treatment system, Ni also potentially precipitates as a sulfide. Through additions of organic matter to the sediments, it should be possible to stimulate microbial activity and thereby maintain the capacity of the sediment to remove metals from water. If reducing conditions can be achieved in the sediment, a biological treatment system, for seepage waters which contact sediments in muskeg ponds, would be developed.

This paper presents the results of laboratory reactor experiments in which waste rock seepage water was added to sediments from muskeg ponds. The objective of this study was to determine the chemical and microbial processes which take place in the sediment and define the specific conditions necessary for metal removal.

Materials and Methods

Laboratory reactors were set up, constructed from acrylic columns with a diameter of 10 cm and a total volume of 2.5 L. The reactors were gas-tight and fitted with rubber stoppers as sampling ports. In the first set of experiments, sediment samples were supplemented with an amendment consisting of 10 % w/w of ground alfalfa and 90 % w/w of weathered hydroseeding mulch. Prior to addition to each column, 100 cm^3 of the amendment blend were mixed into 300 cm^3 of the sediment sample. The reactors were then filled with 1.0 to 1.5 L of test water, leaving approximately 0.5 litres of headspace in each reactor. The test water (station 6.11) is from a seepage collection pond next to the waste rock pile of a uranium mining operation in northern Saskatchewan, Canada. Three types of sediments from three different locations in two muskeg ponds in the same drainage basin of the waste rock pile were used in the first experiment. Water for the reactors was prepared by diluting waste rock pile seepage water with water to 20% of the original seepage concentration, since it was expected that, upon scale-up in the muskeg ponds, a dilution of the concentrations of most ions in the seepage would take place. To increase the arsenic concentrations in the seepage, the water was spiked with KH_2AsO_4 to a concentration of 50 mg/L arsenic to test the ability of the ecosystem to remove As at the maximum concentration likely to be encountered in the field.

A second experiment was set up using sediment from a single location. In this experiment, the same conditions were provided as in the first experiment, including the mixing of organic amendments into the sediment and using diluted (20%) seepage. This experiment was performed in order to establish whether the results obtained in the first experiment were reproducible.

During set-up of the third experiment, new samples of muskeg pond sediments without additions of organic matter (Control) and undiluted waste rock seepage water were added to the reactors. The sediments in the reactors were left for 6 days prior to addition of seepage water (760 mL), thereby allowing them to equilibrate. Those reactors receiving organic matter were treated with a surface layer of potato waste (5 g) or alfalfa (37.5 g). Application of a surface layer to the sediment surface was considered a realistic approach to simulating application of organic matter in field conditions.

To verify the function of sediments in the treatment process, 2 L glass jars with organic material but without sediment at the same ratio as used in the reactors were set up, using 760 mL of seepage water and 5 g potato waste or 37.5 g alfalfa. The quantities of organic matter added to the sediment were based on related work in base metal AMD (Kalin 1993).

Measurements of redox potential, electrical conductivity and pH were made using standard methods. The potential (Em), measured in the reactors, was converted to redox potential (Eh) by the following formula: Eh (mV) = Em (mV) + (241 - 0.66(T°C - 25)) to adjust for the potential of the reference electrode (Hem 1985). Water samples from above the sediment-water interface were extracted from the reactors through the sampling ports with a syringe. Samples were then filtered through 0.45 µm cellulose-acetate filters, acidified with concentrated HNO_3 and stored under ice or at 4°C until required for further analyses. Acidity and alkalinity were determined by titration with 0.01<u>N</u> NaOH (to pH 8.3) and 0.01<u>N</u> H_2SO_4 (to pH 4.5) respectively. Concentrations of Ni and As were determined by inductively coupled plasma spectrophotometry (ICAP) analysis and total Fe, PO_4, NH_4 and NO_3 were determined by colorimetric methods (Hach). Nickel was determined by the diacetyldioxamine colorimetric method (Merck). Arsenic was determined by the Merck test strip method. Sulfate was determined by the $BaSO_4$ turbidometric method (ASTM 4500-SO_4^{2-}).

Adenosine triphosphate (ATP) concentration, a measure of biomass, was determined with a firefly luciferase test. Cells were lysed with ethanol, filtered, further lysed with acetone, filtered and then ATP was extracted in trisodium phosphate buffer containing Mg-EDTA to prevent inhibition of the luciferase enzyme by heavy metal ions. Sulfate reducers were enumerated with Rapidchek II tests (Conoco, Houston, Texas) which detect the presence of adenosine phosphosulfate (APS) reductase by a colour-linked immunological assay.

Results

The water chemistry of the seepage used in the experiments for 1991 and 1992 is summarized in table 1. The average pH of this water was 4.28. This water is characterized by high concentrations of Ni and As. The seepage water also contains very high nutrient concentrations (ammonium, nitrate and phosphate). The sample used for the laboratory experiments had a Ni concentration of 74 mg/L, an As concentration of 50 mg/L and pH of 3.85.

Table 1. Major chemical parameters in waste rock seepage pumping pond water, 1992.

Parameter		Mean	Standard deviation	Minimum	Maximum	Number of samples
pH....................................	units	4.28	4.38	3.94	5.20	6
Conductivity......................	uS/cm	1,433	569	259	2,120	6
Total dissolved solids.......	mg/L	774	524	210	1,360	4
Chloride............................	mg/L	3.0	1.8	0.8	6.0	6
Bicarbonate.......................	mg/L	2.7	2.1	0.0	5.0	3
Sulfate..............................	mg/L	546	376	86	1,060	5
Calcium.............................	mg/L	137	68	24	210	8
Iron....................................	mg/L	3.3	4.4	0.1	9.6	3
Potassium.........................	mg/L	23	11.9	5.0	46	8
Magnesium........................	mg/L	51	28	7	92	8
Manganese........................	mg/L	3.9	1.8	0.9	6.5	6
Sodium..............................	mg/L	28	18.8	3.0	61	5
Ammonia-N.......................	mg/L	4.6	2.4	0.8	7.2	6
Nitrate-N...........................	mg/L	87	39	12.0	128	6
Phosphate.........................	mg/L	34	30	1.0	89	5
Total arsenic.....................	mg/L	36	32	5.4	97	5
Total nickel........................	mg/L	80	74	4.8	220	5
Aluminum..........................	mg/L	14	27	0.1	68	5

The characteristics of the sediments are given in table 2. The sediments have a diverse microbial population. In two of the sediments, sulfate reducing bacteria could be quantified (1 to 50 x 10^4 cells/mL). Fine particulates plugged equipment which prevented quantification of sulfate reducing bacteria in the third sediment. The ATP values indicate the presence of active microbial populations in all 3 reactors at the time the reactors were set up.

The Ni and As concentrations after 87, 112 and 229 days in the first experiment are given in table 3 for each of the three sediment types used. Nickel concentrations declined in all three reactors to less than 0.12 mg/L by day 87. Thereafter, low Ni concentrations were maintained until the experiment was terminated after 237 days. Arsenic concentrations decreased substantially, in the presence of all three sediments, to 0.4 to 0.7 mg/L.

he results of the first experiment were ncouraging. A second experiment ·as set up to determine the ·eproducibility of the results obtained. he data collected 115 days after set p are summarized in table 4. Eh alues remained positive, but were ıfficiently low that denitrification and issimilatory nitrate reduction could roceed in the water column. These rocesses, which reduce nitrate to $_2$O/N$_2$ and NH$_4$, respectively, can enerate alkalinity and help establish onditions for further precipitation actions, through lowering Eh and ising pH. The low NO$_3$ oncentrations (0.41 to 1.94 mg/L) ter 115 days also suggest that one or oth of these processes has taken place. ulfate reduction is indicated by the lour of H$_2$S and decline in the SO$_4$ oncentration. As and Ni oncentrations showed a rapid decline all reactors. More than 90 % of oth elements was removed within 44 ays. After 115 days, As oncentrations were in the range 0.1 to 3 mg/L and Ni concentrations were the range of 0.05 to 0.14 mg/L. hese 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

ND[1] Not determined

Table 3. Arsenic and nickel removal by sediments.

	As, mg/L			Ni, mg/L		
Sediment	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						
		E6-1	E6-2	E6-3	E6-4	E6-5	E6-6	Mean
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).

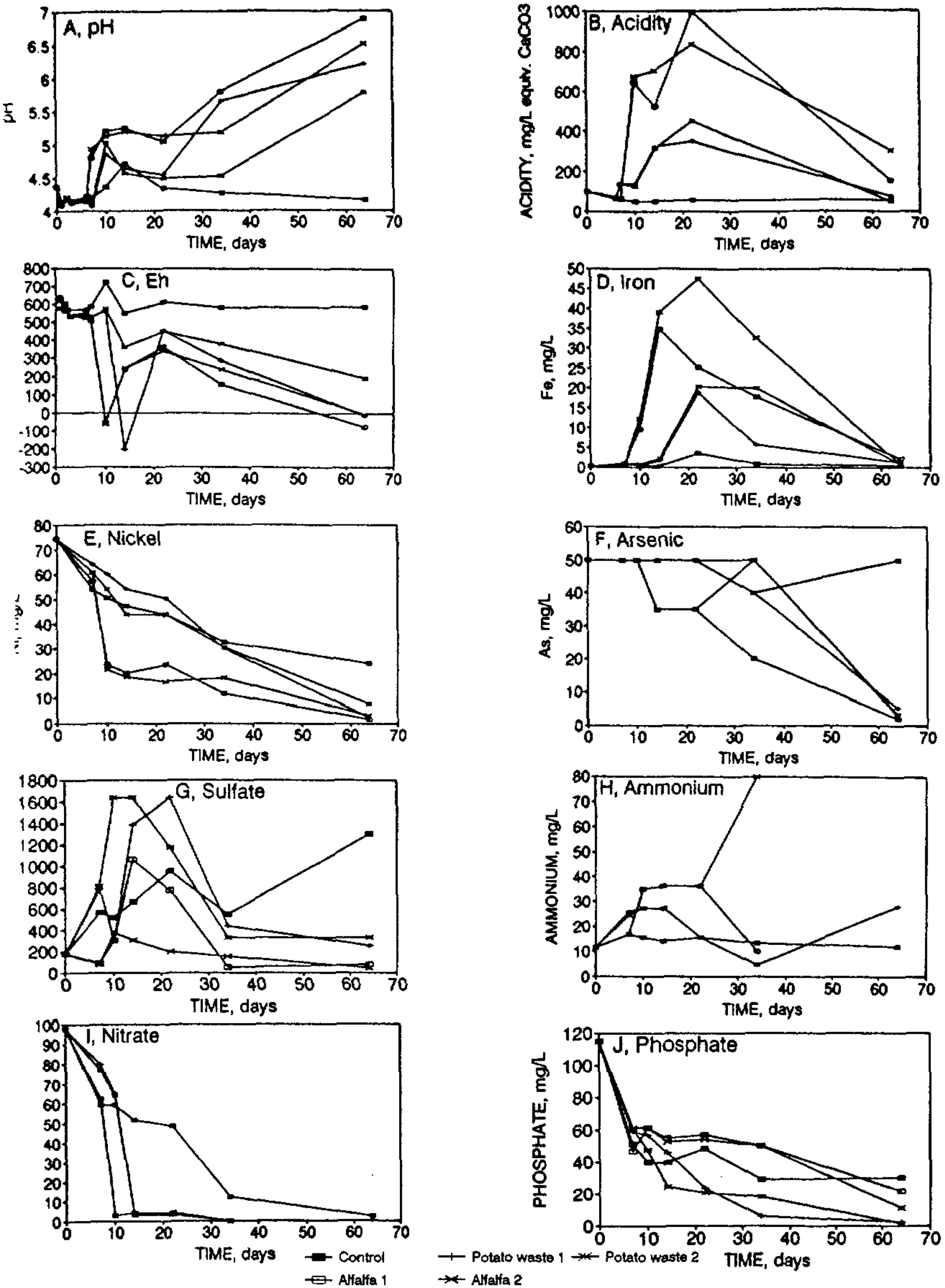
Table 5. Chemistry of control jars without sediments.

Treatment	Days	pH	Eh, mV	Cond, uS/cm	Temp, C	Fe, mg/L	Ni, mg/L	As, mg/L[2]	SO4, mg/L	NH4, mg/L	NO3, mg/L	PO4, 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

ND[1]Not determined.

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

[3] mg/L CaCO3 equivalent.



re 1. Changes in concentrations of major parameters over 64 days in third reactor experiment.

Ni concentrations decreased in the potato waste reactors over the course of the experiment at rates similar to those observed in the control reactor up to 30 days (fig. 1e). Arsenic concentrations held constant over the first 16 days (fig. 1f). From samples collected 63 days after set up, As concentrations had declined, averaging 4.1 mg/L. Sulfate concentrations increased in the reactors (fig. 1g). Sulfate was likely being released from both the potato waste and the sediments to the overlying water.

Alfalfa Reactors

Most trends of concentration changes in the reactors with added alfalfa were similar to those in the reactors with potato waste, except that concentration changes were more pronounced and changes occurred earlier in the experiment. The Eh decreased, within 2 to 3 days following set-up, to values much lower than in the potato waste reactors (fig. 1c). Greater NO_3 concentration decreases were observed (fig. 1i), more NH_4 was generated (fig. 1h) and higher pH's were reached (fig. 1a) than in the potato waste reactors. Phosphate concentrations declined more slowly than in the potato waste or control reactors, possibly due to release of phosphate from the decomposing alfalfa at a faster rate than precipitation (fig. 1j).

The measured iron concentrations increased (fig. 1d) and, according to the low Eh (fig. 1c), iron was likely in the reduced form, due to iron reduction by bacteria in the presence of alfalfa as a nutrient source. The nickel concentration decreases (fig. 1e) are likely related to production of large quantities of CO_2, with subsequent precipitation of Ni as $NiCO_3$. A consistent decrease in arsenic concentrations was not observed during the first 35 days of the experiment (fig. 1f). By 63 days however, the concentrations in the reactors had decreased to 2.49 mg/L As (mean of 2 reactors) with the exception of the control reactor. These decreases are likely related to the rate of microbial arsenate reduction and arsine production, which require low redox conditions for relatively long periods compared to precipitation reactions.

To determine the effects of the sediments in the metal removal process, and that of the organic material added to the sediment in the reactors, seepage water was tested in 1 L jars with additions of organic matter only. The results are summarized in table 5. After 51 days the organic matter had decomposed, the pH had increased and the concentrations of As, sulfate, nitrate, and phosphate, particularly in the jar with potato waste, had increased in the water. The possibility exists that interferences during colorimetric tests may account for the higher concentrations of As at this time.

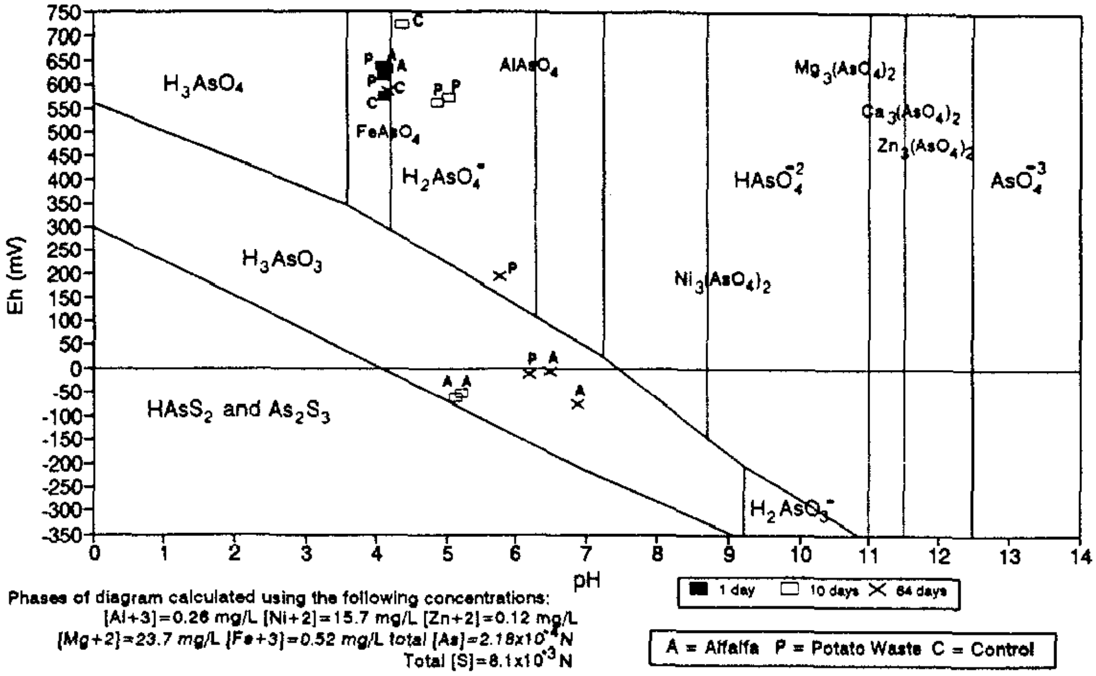
Discussion

Arsenic Removal Processes

Arsenic may exist in natural systems as many chemical species, owing to the fact that it two major oxidation states: +V and +III. The oxidation state of arsenic is dependent on the pH and the redox potential (Eh) of the system. A pH-Eh diagram was constructed to show possible forms of arsenic in particular chemical conditions (fig. 2).

At high Eh and low pH, arsenic +V exists as arsenic acid (H_3AsO_4). At higher pH, the As +V species, hydrogen arsenate ions ($H_2AsO_4^-$, $HAsO_4^{-2}$, AsO_4^{-3}) predominate in water. Also, at higher pH, these As +V ions are predominant over an increasingly wide range of Eh; at pH greater than 11, hydrogen arsenate ions are the only arsenic species in a system at Eh between -350 mV and +750 mV (Kotz and Purcell 1987, Stumm and Morgan 1981). Different metals can precipitate with arsenate ions above specific pH's. The average concentrations of metals and arsenic in three field enclosures are taken to calculate the pH of precipitation for these various compounds, including Fe, Al, Ni, Mg, Ca and Zn. They are shown as dotted vertical lines in the diagram.

The Eh values from the reactor experiments are plotted as they were changing over the period of the experiment, from the time at set-up (day 1), on day 10 and on day 64. On day 1, all the reactors lay within the



Phases of diagram calculated using the following concentrations:
[Al+3]=0.26 mg/L [Ni+2]=15.7 mg/L [Zn+2]=0.12 mg/L
[Mg+2]=23.7 mg/L [Fe+3]=0.52 mg/L total [As]=2.18×10^{-4}N
Total [S]=8.1×10^{-3}N

Figure 2. Redox-pH arsenic species phase diagram. Experiment 3 reactors' pH and redox on day 1, 10 and 64 are plotted.

zone where As occurs as $H_2AsO_4^-$. By day 10, the reactors which received organic material had changed considerably; the control and potato waste reactors were still in the $H_2AsO_4^-$ zone, whereas the alfalfa reactors were in the zone where the predominant form is H_3AsO_3. By day 64, one of the potato waste reactors had moved near to the AsO_3 zone, the zone where precipitation of As as sulfides is possible. The control reactor remained in the $H_2AsO_4^-$ zone for the entire 64 days.

Nickel Removal Processes

In aquatic ecosystems, the chemistry of nickel is less complex than arsenic, owing to its predominant oxidation state of +II. Therefore, there is both a more limited variety of chemical species of nickel, and fewer pathways by which dissolved nickel is removed from solution. Nickel is very mobile in acidic, high Eh water, while in high pH, reducing (low Eh) conditions, nickel sulfides can form. In addition, nickel is relatively amenable to adsorption onto iron and manganese hydroxides, clay particles and organic surfaces. Because of these properties, nickel removal can be anticipated in wetland environments with microbially active, reducing, organic sediments.

Summary and Conclusions

The reductions in arsenic and nickel concentrations observed in laboratory column experiments were also demonstrated in field enclosures installed in some of the same wetlands from which the reactor sediments were collected (Smith et al. 1993). Overall, field and laboratory estimates all fall within the same order of magnitude.

The laboratory experiments have established that muskeg sediments represent an effective micro-environment for removal of As and Ni from waste rock seepage water. The metal removal is associated with reducing conditions and is accelerated by the addition of readily degradable organic amendments which feed microbial processes.

The rate of arsenic removal was augmented by the presence of alfalfa, but not by potato waste. Both amendments reduced the Eh and augmented the supply of nutrients for anaerobic, alkalinity-generating microbial processes. This microbial community was active, as suggested by the decline in sulfate, the H_2S odour indicating sulfate reduction, the increases in dissolved iron (Fe III reduction), the dramatic decline in nitrate (denitrification) and the rise in pH. The removal of Ni in the reactors without amendments indicates that the processes involved were already present in the sediment. The addition of alfalfa increased the rates of As and Ni removal, compared to the other treatments. The rapid decline in Ni can be attributed to precipitation of $NiCO_3$ and/or NiS following the rise in pH generated by anaerobic microbial processes, including denitrification, iron reduction and sulfate reduction. Addition of alfalfa, both in the reactors and in the field, increased rates of Ni and As removal.

As a first approximation, the experimental results can be used to estimate the muskeg pond treatment capacity. A decrease of 49 mg in As concentration in the columns with a surface area of 0.005 m^2 in 65 to 110 days is equivalent to 151 $mg/m^2/day$ and 89 $mg/m^2/day$, respectively. For Ni, in all three reactors of the first experiment, nickel concentrations decreased from 12.9 mg/L to 0.2 mg/L in 40 days, equivalent to 64 $mg/m^2/day$. The rates for the third experiment range from 154 to 253 $mg/m^2/day$ for Ni and for As, 196 to 211 $mg/m^2/day$.

The data presented here, together with results from a field experiment (Smith et al. 1993), indicate that long-term exposure of seepage water to wetland sediments is a very promising approach to treatment of this wastewater. Ongoing experiments will determine the long-term stability of precipitates or other forms of the heavy metals held in the ecosystem.

Acknowledgment

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NICKEL AND ARSENIC REMOVAL FROM MINE WASTEWATER BY MUSKEG SEDIMENTS

A. FYSON, M. KALIN and M.P. SMITH

Boojum Research Limited, Toronto, ON

ABSTRACT

Experiments were carried out in 2.5 L column reactors to assess the capacity of muskeg sediment to treat an arsenic (97 $mg.L^{-1}$) and nickel (72 $mg.L^{-1}$) rich seepage from a wasterock pile of a Saskatchewan mining operation. When degradable organic material (potato waste) is added, effective removal (> 90 %) of both elements was achieved within 60 days and was associated with reducing conditions and an increase in pH from 4 to > 7. Frequent replacement of seepage water in the column above the sediment has shown that sediments can remove at least 3.8 $g.L^{-1}$ sediment for both nickel and arsenic. Analysis of sediments established that most of the arsenic and nickel is in the surface layer of the sediment. Removal rates of 50 $\mu g.m^{-2}.min^{-1}$ for nickel and 80 $\mu g.m^{-2}.min^{-1}$ for arsenic were estimated for the reactors receiving one dose of seepage waters. For the reactors recharged every 1 to 2 weeks, rates of 170 $\mu g.m^{-2}.min^{-1}$ for nickel and 250 $\mu g.m^{-2}.min^{-1}$ for arsenic were obtained. Microbially-active muskeg sediments have a capacity to remove substantial quantities of both nickel and arsenic from the seepage water.

ÉLIMINATION DE L'ARSENIC ET DU NICKEL PAR DES SÉDIMENTS DE TOURBIÈRE.

A. FYSON, M. KALIN et M.P. SMITH

Boojum Research Limited, Toronto, ON

RÉSUMÉ

Des expériences ont été faites en réacteurs (colonnes) de 2.5 L pour vérifier le potentiel de sédiments de tourbière à traiter des eaux d'infiltration de terrils d'une mine en exploitation de Saskatchewan, riche en arsenic (97 $mg.L^{-1}$) et nickel (72 $mg.L^{-1}$). Lorsque de la matière organique dégradable comme des déchets de pommes de terre est ajoutée, un taux d'élimination de plus de 90 % des deux éléments est obtenu en 60 jours et est associé à des conditions réductrices et à une augmentation du pH de 4 à > 7. Le remplacement fréquent de l'eau d'infiltration au dessus des sédiments a montré que les sédiments peuvent éliminer au moins 3.8 $g.L^{-1}$ de nickel et d'arsenic. L'analyse des sédiments a permis d'établir que la majorité de l'arsenic et du nickel se retrouve dans une couche à la surface des sédiments. Des taux d'élimination de 50 $\mu g.m^{-2}.min^{-1}$ pour le nickel et de 80 $\mu g.m^{-2}.min^{-1}$ pour l'arsenic ont été estimés pour les réacteurs ne recevant qu'un seul ajout d'eau d'infiltation. Pour les réacteurs recevant de l'eau à chaque 1 ou 2 semaines, des taux d'élimination de 170 $\mu g.m^{-2}.min^{-1}$ pour le nickel et de 250 $\mu g.m^{-2}.min^{-1}$ pour l'arsenic étaient obtenus. Des sédiments de tourbière microbiologiquement actifs peuvent éliminer des quantités appréciables de nickel et d'arsenic des eaux d'infiltation.

INTRODUCTION

Wasterock piles from metal mining operations often generate seepages with low pH and high concentrations of heavy metals in perpetuity. Passive treatment systems, utilizing natural processes driven by bacteria, are an attractive alternative to continued operation of a chemical treatment plant, as passive treatment systems require little maintenance and are environmentally sustainable.

Microbial sulfate and iron reduction occur naturally in wetland sediments. These processes, which take place in reducing conditions, facilitate the removal of metals from acid mine drainage through an increase in pH and precipitation of metal ions as sulfides or hydroxides (1, 2) or co-precipitation. In oxidizing conditions and $pH > 3$, iron(III) is hydrolysed and will precipitate as iron(III) hydroxides with co-precipitation of other metal ions (1). Metals may also be removed through adsorption processes to sediment surfaces (3).

Kalin (1) reported nickel concentration reductions from 25 to 1 $mg.L^{-1}$ in a passive treatment system through enhancement of microbial activity and generation of reducing conditions.

Run-off and seepages from a wasterock pile in northern Saskatchewan contain high concentrations of nickel and arsenic. The possibility of using sediments of muskegs surrounding the pile to passively treat this water is being investigated. This paper presents the results of laboratory reactor experiments in which wasterock seepage water is added to muskeg sediments in laboratory reactors. Previously published results (4) established that both arsenic and nickel could be effectively removed and that removal was enhanced in reducing conditions, established through addition of microbially-degradable organic material (potato waste or alfalfa).

Decomposition of these amendments generates reducing conditions and supports microbially-mediated processes (denitrification, iron(III) reduction and sulfate reduction (5)) which generate alkalinity, raise the pH and lead to removal of metals from solution. The present study was designed to further define the rates of contaminant removal and the removal capacity of sediments to help establish design criteria for scale-up in the field.

MATERIALS AND METHODS

Reactor Set-up

2.5 L reactors of acrylic tubing with an internal diameter of 100 mm were set up. Muskeg sediment (500 mL) was placed in the reactors followed by the addition of 900 mL of wasterock pile seepage water. After a 24 h settling period, 5 g of potato waste (McCain Foods) was sprinkled on the water surface (to minimise sediment disturbance). This material sank to the sediment surface within 10 min. 2 L wide-mouthed glass jars, containing seepage water and potato waste only, provided sediment-free controls to facilitate interpretation of the role of the sediment materials in contaminant removal processes.

For some reactors and jars, 500 mL of water from the water column was removed (by syphoning), and the reactor or jar was 'recharged' with 'fresh' seepage water to assist in determination of arsenic and nickel removal capacity of a particular sediment material.

The experiment investigated nickel and arsenic removal in recharged reactors and 'unchanged reactors' with sediments, and 'recharged jars' and 'unchanged jars', the controls.

Water Chemistry

The seepage water (station 6.11) used in the present study is characterized by high concentrations of both nickel (72 $mg.L^{-1}$) and arsenic (97 $mg.L^{-1}$) as determined by ICAP analysis. This water also has high concentrations of sulfate and nutrients (21 $mg.L^{-1}$ nitrate-N, 21 $mg.L^{-1}$ ammonium-N and 29 $mg.L^{-1}$ phosphorus) and a pH of 3.9. The unusually high nutrient concentrations make this water very suitable for passive biological treatment.

Measurements of redox potential, electrical conductivity and pH were made using standard methods (5). The measured potential (E_m) was converted to E_h to adjust for the potential of the reference electrode by means of the following formula:

$$E_h \quad = \quad E_m + (241 - (0.66*(T^\circ - 25)))$$

where E_m and E_h are in mV and T° in degrees Celsius.

Water samples from 5 cm above the sediment-water interface were extracted with a syringe. Acidity and alkalinity were determined by titration against 0.01 N NaOH (to pH 8.3) and 0.01 N H_2SO_4 (to pH 4.5) respectively (6) with a Metrohm 702M Titrino autotitrator. Nickel was determined with a colorimetric test (Rollet's dimethylglyoxime complexation) and reading absorbance at 445 nm. Arsenic was measured with the Merck Merckoquant strip test which measures the reaction between hydrogen arsenide gas and mercury(+2) bromide. Iron was determined by a phenanthroline test (absorbance at 510 nm) and nitrate-N with a Hach cadmium reduction test (absorbance at 545 nm). For the colorimetric tests, a Bausch and Lomb Spectronic 70 spectrophotometer was employed.

Sediment samples from the reactors were sent to the Saskatchewan Research Council Analytical Chemistry Laboratory for more detailed chemical analysis. From inductively coupled plasma spectrophotometry (ICAP) data, a mass balance for arsenic, nickel and iron in the reactors was made.

RESULTS and DISCUSSION

Laboratory chemistry measurements, collected over 129 days, are summarized in Figures 1a to 1j. The data for the unchanged jars shows the effects of potato waste on seepage water. The early decline in E_h (Figure 1a) and establishment of reducing conditions is associated with the decomposition of potato waste and release of volatile fatty acids. These acids contribute to the observed increase in acidity (Figure 1d). The reducing conditions supported the reduction in concentrations of nitrate (denitrification; Figure 1h) and of iron (Figure 1g). The removal of phosphate (Figure 1j) and ammonium (Figure 1i) may be due in part to uptake by microorganisms. Minor arsenic and nickel removal are attributable to a lack of iron and sulfide ions, respectively. Also, in the absence of sediment, there are fewer sites for adsorption. The steady conductivity values in the control jars (Figure 1c) suggests little overall removal of ions from solution. Overall, despite the presence of reducing conditions in the jars, conditions were not favourable for arsenic and nickel removal when sediment was absent.

In the reactors, in contrast to the control jars, there was a steady reduction in conductivity (Figure 1c), indicating a net removal of ions from solution. The decrease in E_h (Figure 1a) and rise in pH (Figure 1b) and acidity (Figure 1d) follows a similar pattern to that of the jars. The removal pattern in the reactors for nitrate, ammonium and phosphate (Figures 1h to 1j) was also similar to the jars. However, nickel and arsenic were effectively removed (Figures 1e and 1f) in the reactors. Clearly, the sediments appear to be essential for substantial nickel and arsenic removal. Removal of arsenic in the reactors may be related to the higher iron concentrations compared to the jars (Figure 1g). This iron is probably released from sediments following reduction and dissolution.

The low E_h and release of ferrous iron from the sediments suggests that precipitation of ferrous arsenate may be occurring. In addition, the E_h/pH diagram (Figure 3b) suggests that the conditions found soon after addition of the organic amendments were also favourable for formation of arsenite (AsO_3). This form of arsenic has recently been detected in anaerobic soils contaminated by waste waters from a gold mine (7). Finally, the sequential analysis of sediments from a previous experiment (data not shown) suggests that much arsenic is held by the sediment in organic complexes. Overall, arsenic removal in the reactors could be due to several processes.

The removal of most of the nickel from solution in the reactors before a fairly constant concentration of 3 $mg.L^{-1}$ was achieved (Figure 1e) is interesting. The experimental data was fitted to an E_h/pH phase diagram for nickel (Figure 3a). Most data points fit in the zone where equilibria favour Ni^{+2} in solution. Early on, when short lived, very low E_h values were coupled to low pHs (4-5), the data points clearly fit into the zone where sulfide formation is favoured (Figure 3a). If nickel is removed as a sulfide precipitate, sulfate reduction must occur for generation of sulfide. NiS formed during this period early in the experiment will not likely redissolve in the conditions prevailing later, *i.e.*, stable NiS precipitates may have formed.

Some removal of Ni by adsorption processes, such as ion-exchange and complexation to organic molecules, undoubtedly occurred too. However, the available sites for cation exchange would likely be filled within hours of set-up as indicated by the data of Eger and Lapakko (8). In fact, sequential analysis of sediments in a previous experiment indicated that much of the Ni was complexed to organic matter.

Frequent 'recharging' of the water column of three reactors with 'fresh' seepage water was carried out. The estimated total nickel removed is shown in Figure 2a. The data indicate that during the first 91 days, 264 mg of nickel, of a total of 271 mg added, had been removed from 'recharged' reactors water columns. This is nearly double that removed from the 'unchanged' reactors. There is no indication that the 'recharged' reactors are approaching nickel saturation.

Calculations of arsenic removal form the 'recharged' reactors have also been made. With additions of seepage water, the arsenic concentration in the water column remained fairly constant (Figure 2b), but is considerably lower than in the seepage water (97 $mg.L^{-1}$). This indicates that the rate of removal remained constant over the observation period. Figure 2b shows that by day 91, 184 mg of arsenic, of a total of 236 mg added, had been removed in the 'recharged' reactors. As for nickel, there is no indication that the 'recharged' reactors are approaching saturation.

Table 1 summarizes the distribution, in mmol of nickel, arsenic, sulphur and iron in the top 2 cm (surface), 2 to 7 cm (middle) and 7 to 12 cm (bottom) layers of the sediments in an 'unchanged' reactor. The content of these elements in sediments is the sum of pore water and solids. These solids include fractions removed by precipitation, ion-exchange and complexation as well as the amount originally present in the sediments. The surface layer of sediment had a higher nickel and arsenic content, while the bottom layer contained the highest iron content. This indicates that nickel and arsenic have accumulated, following precipitation/adsorption, in the top layer of the unchanged reactors. In contrast, the bottom layer of sediment serves as an iron sink, possibly due to sulfate reduction and iron sulfide precipitation in this zone.

According to E_h/pH diagrams (Figures 3a and 3b), the conditions in the reactors were, at times, favourable for sulfate reduction (9). Based on the total sulphur content, in mmol, in the sediment, it is plausible that all nickel and arsenic could be bound in the sediments as sulfides.

In Table 2, the total nickel and arsenic content of the water column and the three sediment layers are expressed as in total mg and as percentages of the total amount added to the reactors. Most of the nickel (87 %) and arsenic (73 %) added to the reactors was recovered, and almost all was present in the sediments. The nickel and arsenic unaccounted for in this mass balance may reside on acrylic reactor walls, or the disparity may be due to analytical error.

From the experimental data, rates of contaminant removal have been calculated in terms of both water volume and sediment area. This data can help determine optimum rates of addition of contaminant water. Calculations were based both on 'recharged' reactors (Table 3) and 'unchanged' reactors (Table 4).

The data for 'unchanged' reactors gives rates of arsenic removal of 0.71 $mg.m^{-3}$ $water.min^{-1}$

or 0.08 $mg.m^{-2}$ $sediment.min^{-1}$ (Table 3). The 'recharged' reactors give higher figures of 1.47 $mg.m^{-3}$ $water.min^{-1}$ and 0.17 $mg.m^{-2}$ $sediment.min^{-1}$, respectively. For nickel, the 'unchanged' reactors give removal rates of 0.39 $mg.m^{-3}.min^{-1}$ and 0.05 $mg.m^{-2}.min^{-1}$. The 'recharged' reactors yield values of 2.21 $mg.m^{-3}.min^{-1}$ and 0.25 $mg.m^{-2}.min^{-1}$. For both arsenic and nickel, recharging the reactors enabled the sediments to attain high removal rates. This is likely due to the additional supply of nutrients in the seepage water (N and P).

CONCLUSIONS

The results of this study indicate that in laboratory conditions and in the presence of organic amendment, muskeg sediments have a considerable capacity for removal of both nickel and arsenic from a wasterock pile seepage water.

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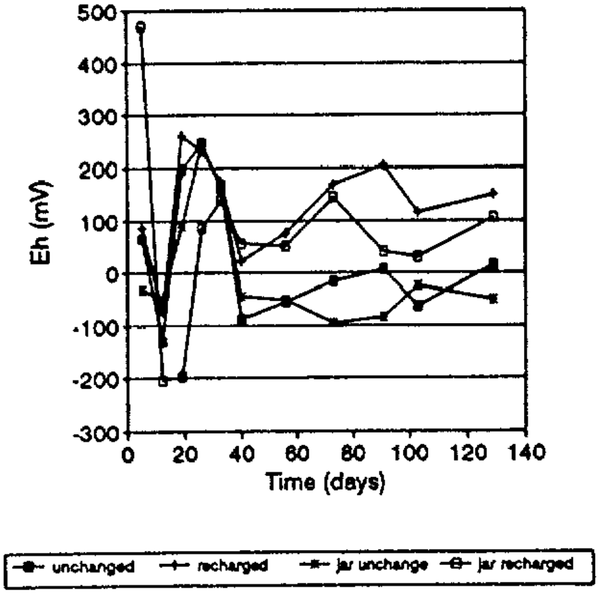


Fig. 1a: Reactor water column
Redox potential (Eh)

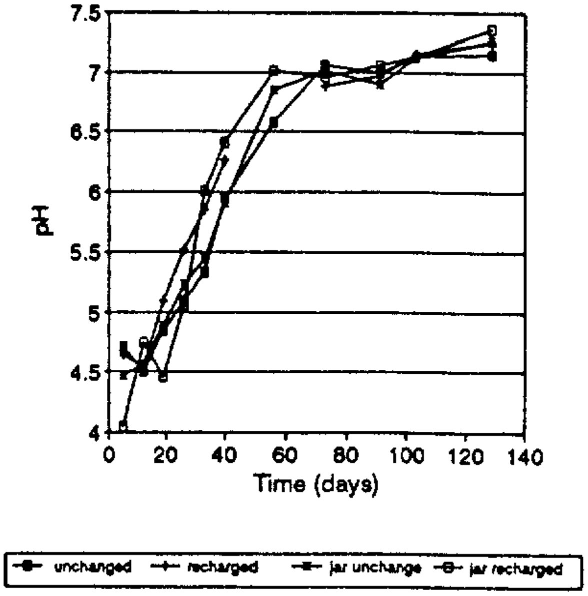


Fig. 1b: Reactor water column
pH

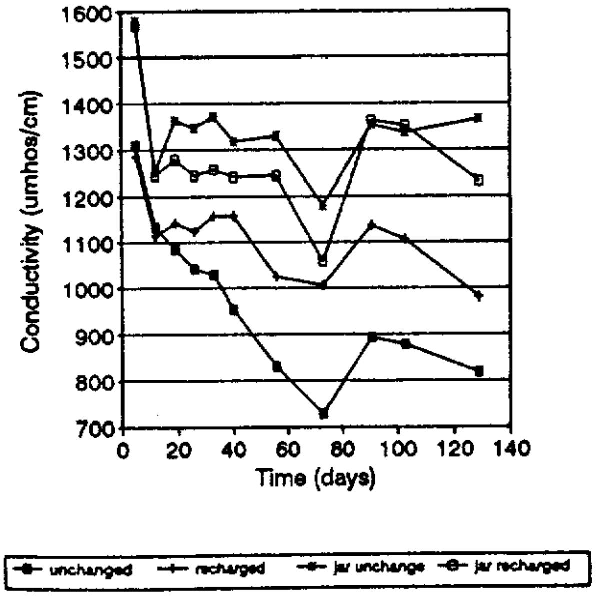


Fig 1c: Reactor water column
Conductivity

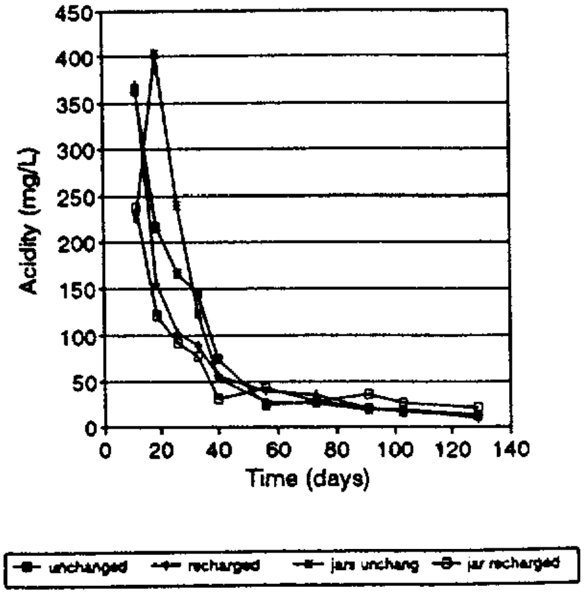


Fig 1d: Reactor water column
Acidity

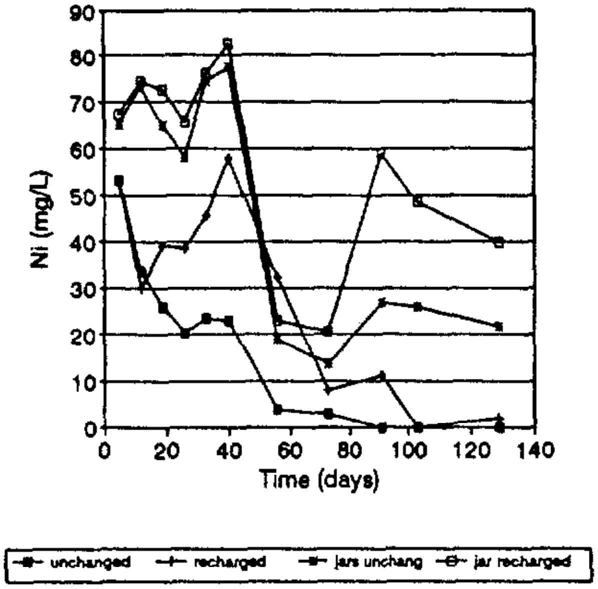


Fig. 1e: Reactor water column
Nickel

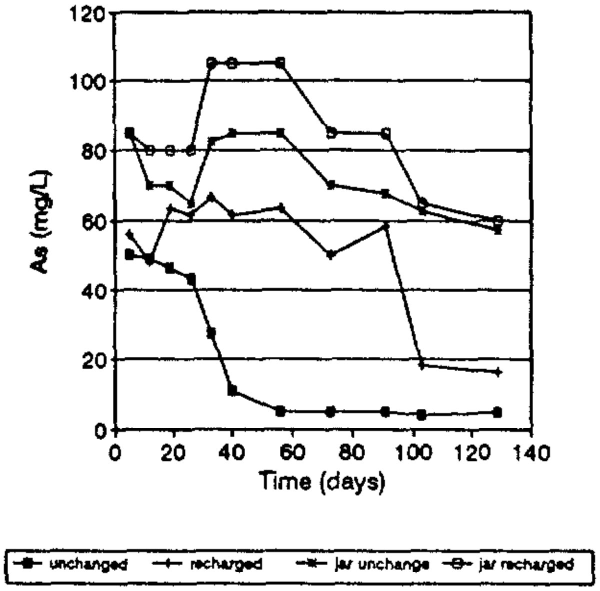


Fig 1f: Reactor water column
Arsenic

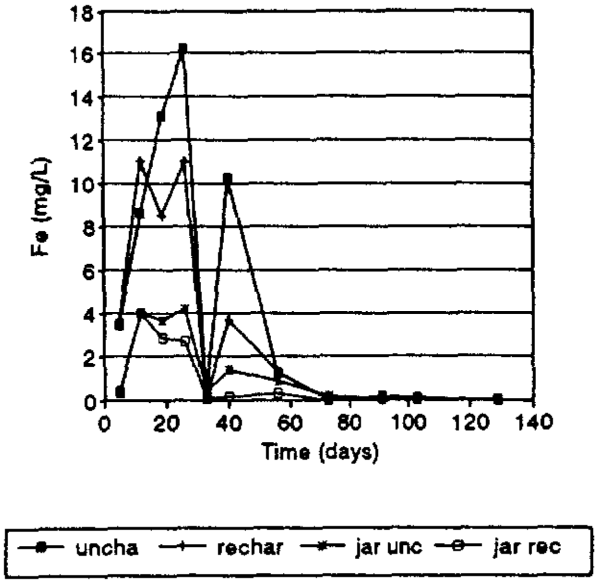


Fig 1g: Reactor water column
Iron

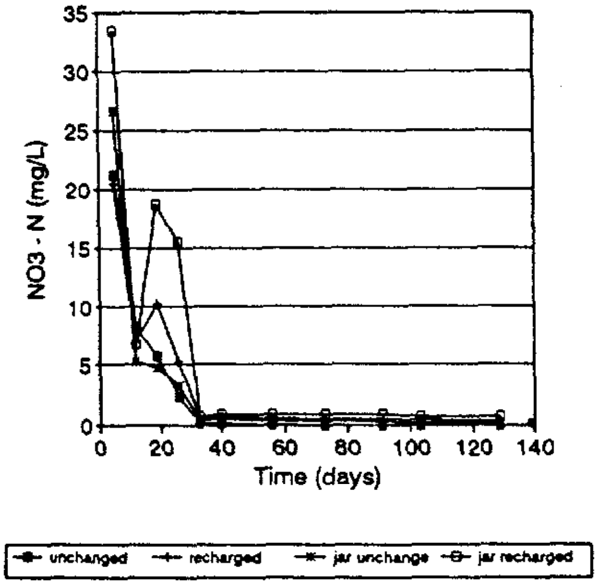


Fig. 1h: Reactor water column
Nitrate-N

Fig. 1i: Reactor water column
Ammonium-N

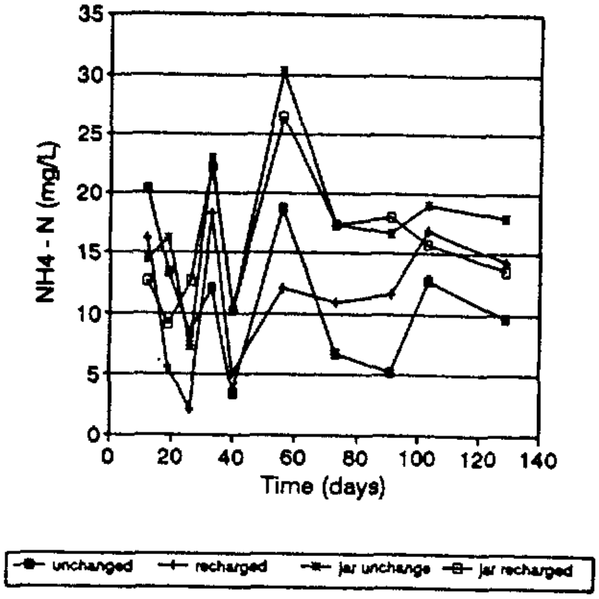


Fig. 1j: Reactor water column
Phosphate-P

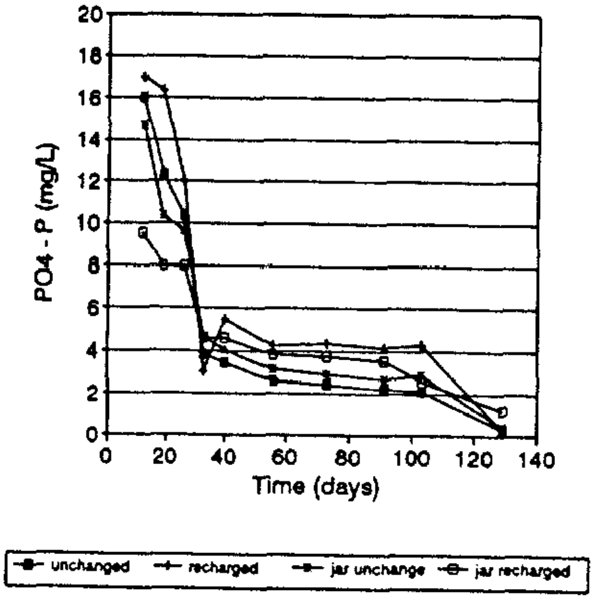


Fig. 2a: Recharged reactors
Nickel removed

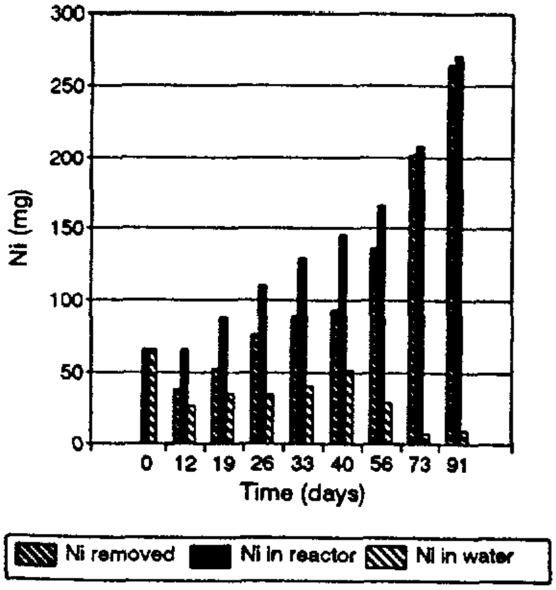


Fig 2b: Recharged reactors
Arsenic removal

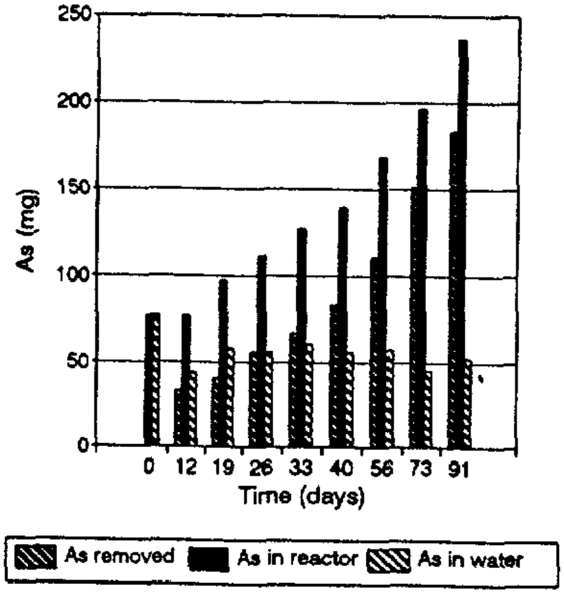


Fig. 3a: Eh-pH phase diagram for Ni

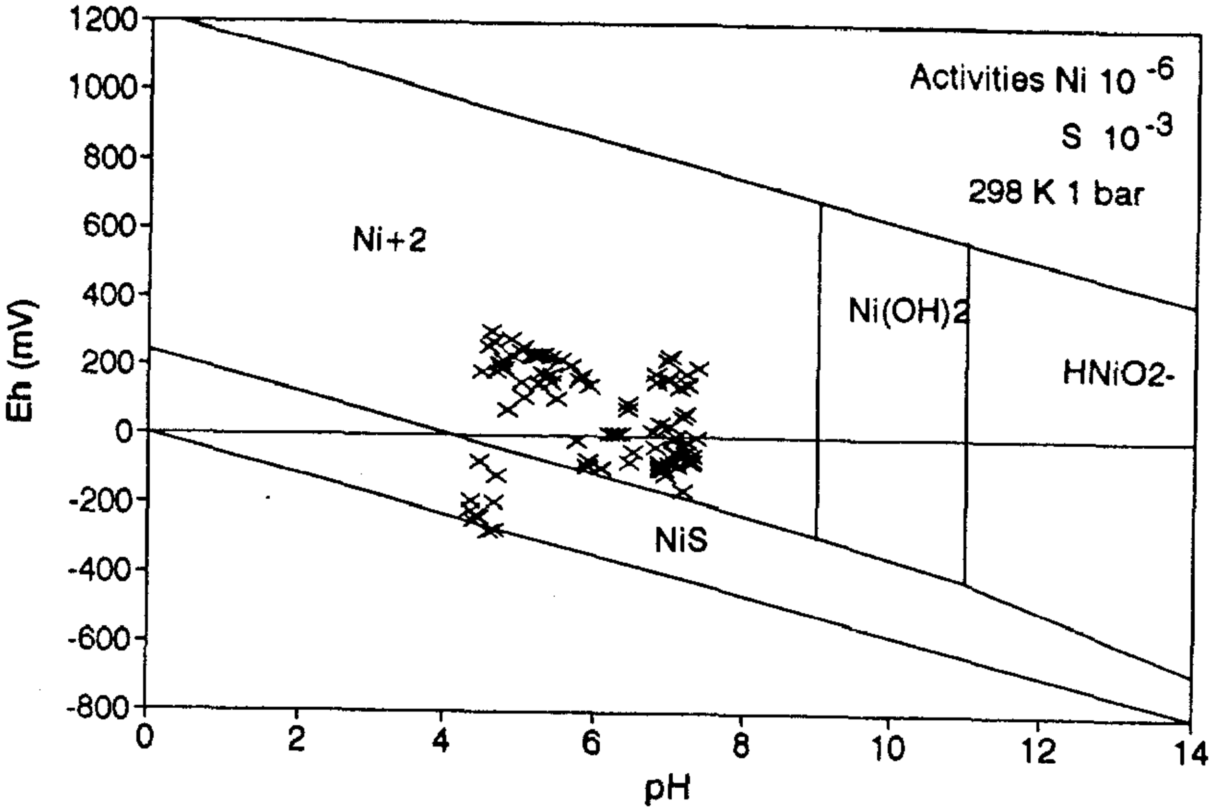


Fig 3b: Eh/pH Phase Diagram for As

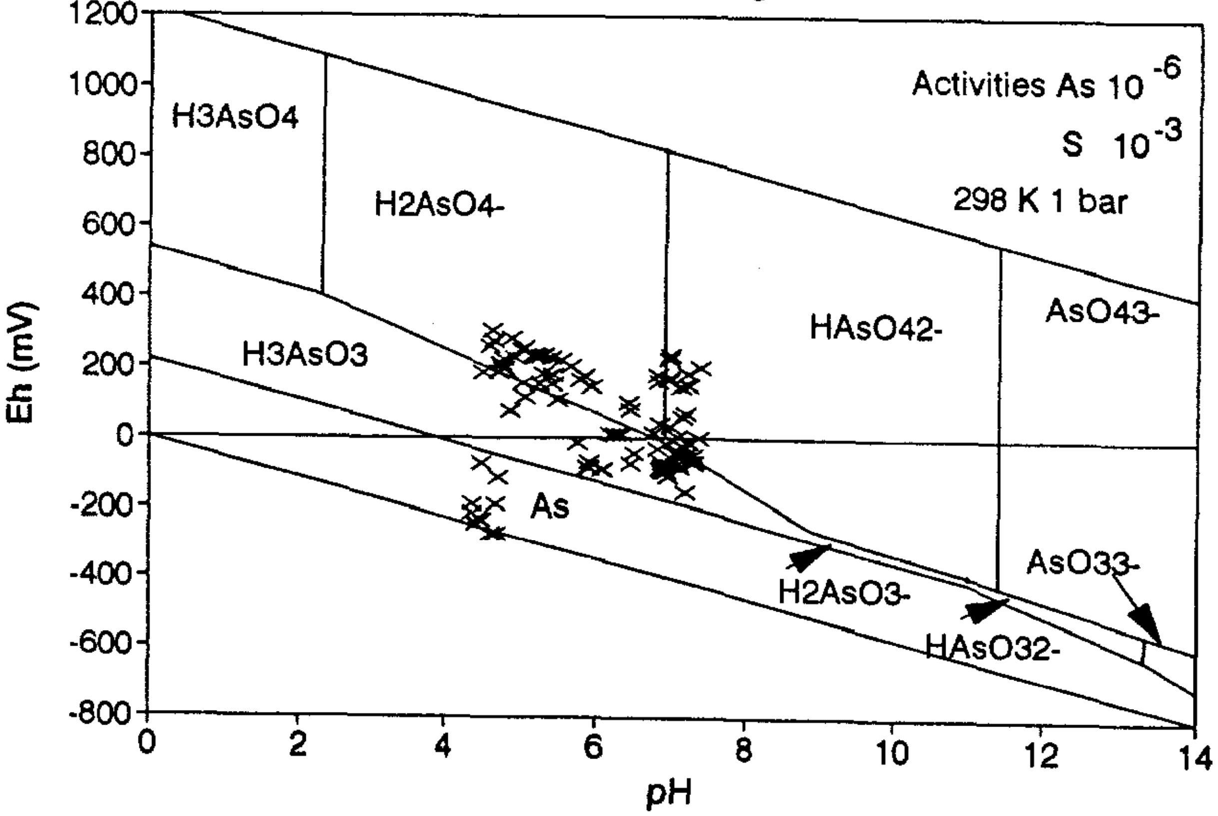


Table 1: S, Ni, As and Fe Content in Unchanged Reactor Sediments.

	Unchanged (900 mL 6.11 added)		
	surface (0-2cm) sediment	middle(2-7cm) sediment	bottom(7-12 cm) sediment
S mmol	1.19	1.58	1.03
Ni mmol	0.35	0.29	0.14
As mmol	0.29	0.17	0.11
Fe mmol	0.39	0.84	0.99

Table 2: Distribution of Ni and As in Water Column and Sediment Fractions of Unchanged Reactors.

	Unchanged (900mL 6.11 added)			
	Ni mg	Ni % of total added	As mg	As % of total added
Total added to reactor (mg)	53.1		61.2	
Mass / % in water column	0.4	0.8	2.6	4.2
Mass / % in top 1 cm of sediment	20.6	39	21.6	35
Mass / % in middle of sediment	16.9	32	13.0	21
Mass / % in bottom of sediment	8.2	15	8.0	13
Total accounted for (mg or %)	46.1	87	45.2	73

Table 3: Rates of Removal of Ni and As, Based on Recharged Reactors.

	Ni	As
Quantity in sediment on day 12 (mg)	38.2	33
Quantity in sediment on day 91 (mg)	264.4	183.5
Rate (mg/day/reactor)	2.86	1.91
Rate per volume of water (mg/m3/min)	2.21	1.47
Area of sediment in reactor = 78.6 cm2 Rate per area of sediment (mg/m2/min)	0.25	0.17
Volume of sediment in reactor = 500 mL Rate per volume of sediment (mg/m3/min)	3.98	2.65

Table 4: Rates of Ni and As Removal Based on Uncharged Reactor Data.

	Ni	As
Concentration in water column day 12 (mg/L)	28.9	50
Concentration in water column day 56 (mg/L)	4	5
Removal rate (mg/L/day)	0.57	1.02
Removal rate per volume of water (mg/m3/min)	0.39	0.71
Rate per area of sediment (mg/m2/min)	0.05	0.08
Rate per volume of sediment (mg/m3/min)	0.71	1.28

DECOMMISSIONING OF B-ZONE AREA
USING
ECOLOGICAL ENGINEERING

Progress Report No. 2
for
CAMECO

April 1993

B-Zone Progress Report

April 7, 1993

1.0 E6 enclosure laboratory reactors-Experiment 1

It was decided on completion of the I992 work, that we should repeat the reactor experiment to obtain confirmation on reproducibility of the removal rates observed. The 3 reactors were set up at the Dearborn laboratory originally and transferred to Boojum in February 1993.

The first, E6-enclosure sediment reactor experiment was described in the first progress report and samples were sent for ICAP analysis. Results are summarised in Fig.1 -3.

The pH of all 6 reactors remained in the 6 to 7 range. Arsenic and Ni concentrations showed the same rapid decline in all 6 reactors (Fig.2 and Fig.3). More than 90 % of both elements was removed within 44 days, which represented the first time Dearborn had been sampling the reactors, but unfortunately they did not analyze for either Ni or As during the intervening period.

On arrival at Boojum laboratory the experiment was terminated after 121 days since low, steady concentrations of As and Ni were maintained in all reactors. This experiment established that E6 enclosure sediment with added alfalfa and mulch material could effectively remove As, Ni and other measured elements from B-Zone seepage water. A second experiment was established adding additional seepage water to determine the capacity of the sediment to improve water quality.

2.0 E6 enclosure laboratory reactors - Experiment 2 (recharged reactors)

The 6 reactors were set up as described in the previous report (March, 1993 Section 2.3), reactors E6-1 and E6-2 receiving WRP-P water, reactors E6-3 and E6-6 receiving undiluted 6.11 water and reactors E6-4 and E6-5 receiving 5 x diluted 6.11 water. The chemistry of the two seepage waters added is summarised in Table 1. The chemistry of the water overlying the sediment was assayed for As, Fe, Ni, NO_3, NH_4, SO_4, PO_4, E_m, pH and titratable acidity 1 day, 11 days and 21 days after set up. Analytical methods were as described previously (see March, 1993 progress report). The results are summarised in Figures 4 to 13.

2.1 WRP-P reactors (E6-1 and E6-2)

The pH rose in the WRP-P reactors (E6-1, E6-2) from around 4 to around 5.5 (Fig. 4). This change was associated with a drop in acidity from 282 to 17 mg/L equivalent of $CaCO_3$ in E6-1 and 255 to 10 mg/L equivalent of $CaCO_3$ in E6-2 (Fig. 5). In E6-1 the acidity loss was linear over the study period at a rate of 12 mg/L /day.

The E_m in E6-1 declined from an initial +270 mV to -111 mV (Fig. 6). In contrast, the E_m in E6-2 remained fairly steady at around +150 mV. In other words, reducing conditions were established in the water column above the sediment in one reactor (E6-1) but not in the other.

Dissolved As concentrations (Fig. 7) declined in both reactors from 2 mg/L to below detection limits (1 mg/L). Iron concentrations declined linearly in both reactors at a rate of 1.4 to 1.6 mg/L/day (Fig. 8). Nickel concentrations declined 20-30 % during the course of the observations (Fig. 9). Ammonium concentrations (Fig. 10) declined at first in both reactors. However in E6-1 there was a dramatic rise between 11 and 21 days from 9 to 29 mg/L. Nitrate was depleted rapidly (Fig. 11). The rise in ammonium in E6-1 may be due to reduction of some of the nitrate by anaerobic bacteria (dissimilatory nitrate reduction).
The rest of the nitrate loss is attributable to denitrification to N_2 and N_2O gases. This process carried out by bacteria generates alkalinity and may in part at least account for the observed rise in pH and decline in titratable acidity. The high concentrations of PO_4 in the water were rapidly depleted from >50 mg/L at day one to <1 mg/L at 11 days (Fig. 12). Sulphate concentrations were erratic (Fig. 13) but overall showed a decline indicating the probability of sulphate reduction occurring. This is another alkalinity generating bacterial process which may contribute to the observed increase in pH and decline in acidity.

2.2 6.11 reactors

Acidity declined in the 6.11 reactors with both full strength and dilute seepage added (Fig. 5). This was associated with a rise in pH in the two reactors. In the others, pH stayed steady. All pH readings were in the 6-7 range (Fig. 4). Negative E_m values (reducing conditions) were established in all reactors within 24 h (Fig. 6).

In the undiluted reactors, initial As concentrations (1 day after set up) were much higher (70-80 mg/L) than in the diluted reactors (1.7 mg/L) indicating that some process was already removing As in the diluted reactors (Fig. 7). In the undiluted reactors (E6-3 and E6-6), As was removed at a linear rate of approximately 3.7 mg/L/day. By 21 days, more than 80 % of the dissolved As had been removed. Iron concentrations (Fig. 8) were higher in the undiluted reactors. Concentrations of Fe remained fairly steady during the observation period. Nickel concentrations (Fig. 9) declined in the undiluted reactors from 21-22 mg/L at 1 day to 6.1-6.7 mg/L at 21 days, or approximately 0.7 mg/L/day. In the undiluted reactors, ammonium declined by 50 % from 7.8 mg/L to 3.9 mg/L (Fig. 10). In contrast, there was a slight increase in the diluted reactors. Nitrate concentration declined dramatically in the undiluted reactors from approximately 50 mg/L at day one to 3-4 mg/L after 11 days. This decline is attributable to denitrification in the reducing conditions prevailing. Phosphate declined rapidly within the first 11 days (Fig. 12) and remained steady thereafter. Sulphate concentrations were erratic but exhibited an overall decline between day 1 and day 21 (Fig. 13).

2.3 Summary

Overall, within 21 days, substantial changes have occurred in the water chemistry of all reactors. Negative E_m values, indicative of reducing conditions have been established in the water column of 5 reactors. Substantial declines in As, Fe, Ni, PO_4, NO_3, SO_4 and acidity and a rise in pH are apparent in most reactors. In the WRP-P reactors (E6-1 and E6-2), the high concentrations of Fe, PO_4 and NO_3 were nearly all removed within 21 days of experimental set up. In the 6.11 reactors, approximately 70 mg/L of As was removed from solution. Ni concentrations declined with both seepage waters but it will clearly take a much longer period to remove this metal than the As.

3.0 NEXT STEPS

The analytical data which are presented in the graphs included with this progress report were received last week. Chemical reactions from these experiments which might account for the removal of both Arsenic and Nickel will be derived. The initial decreases in arsenic for example are certainly due to precipitation of ferric arsenate.

Although this may be revised after the chemistry of the reactors is interpreted, we envisage at present the following experiments to be completed before the field season starts.

Four reactors from experiment 2 will be used to replace the water above the sediment with WRP seepage full strength and 6.11 seepages (second recharge). Measurements of removal rates are obtained in weekly intervals up to 40 days to determine the rates indicated between day 0 and 40 figure 2 and 3. This would give us the real removal rate in laboratory conditions for the worst case that all of the B-zone seepage is turning acid.

From the results obtained in the field enclosures, we know that amendment in the form of alfalfa was required. Fertilizer additions were not needed, as the seepages themselves contain both phosphorus and nitrogen.

However we should consider the differences in sediments which might be encountered in the B-zone wetland with the material collected on the last field trip and with the same application rate for alfalfa and mulch. Reactors will be set up with different sediments with the addition of 6.11 to be able to compare with the field situations between the different enclosures.

Furthermore, the addition of alfalfa without sediment and its effect on the chemistry should be evaluated, for both the field application rate (enclosure 7L/ m2 and the reactor rate which is 1.4 L/ m2). Alfalfa reactors are run with 6.11 seepage.

This will conclude the experimental phase and we should have conclusions on the removal process by the beginning of the field season.

Fig. 1: B-Zone reactors, Expt. 1 -pH

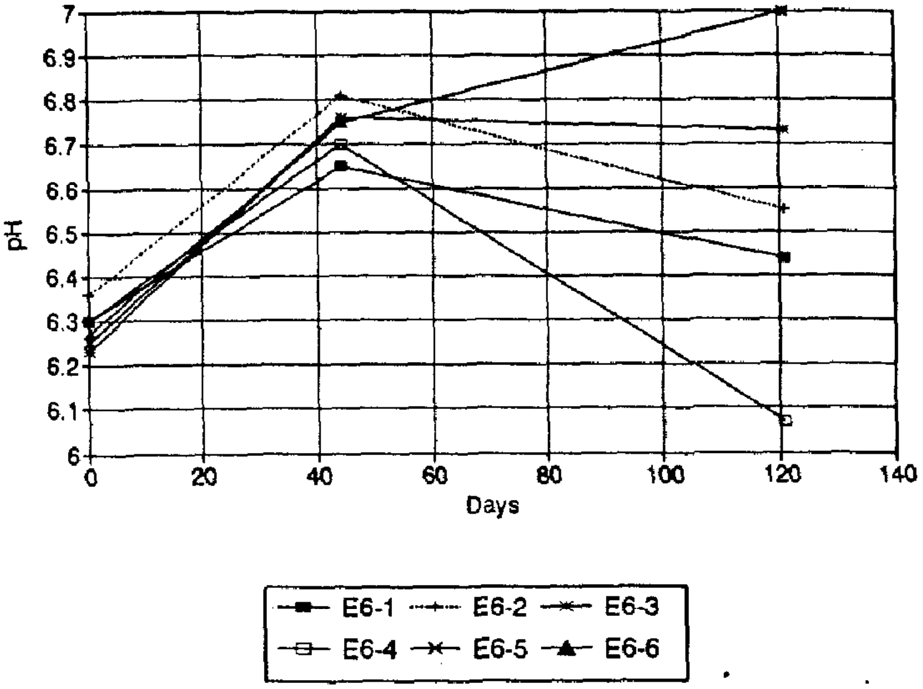


Fig. 2: B-Zone reactors, Expt. 1 -As

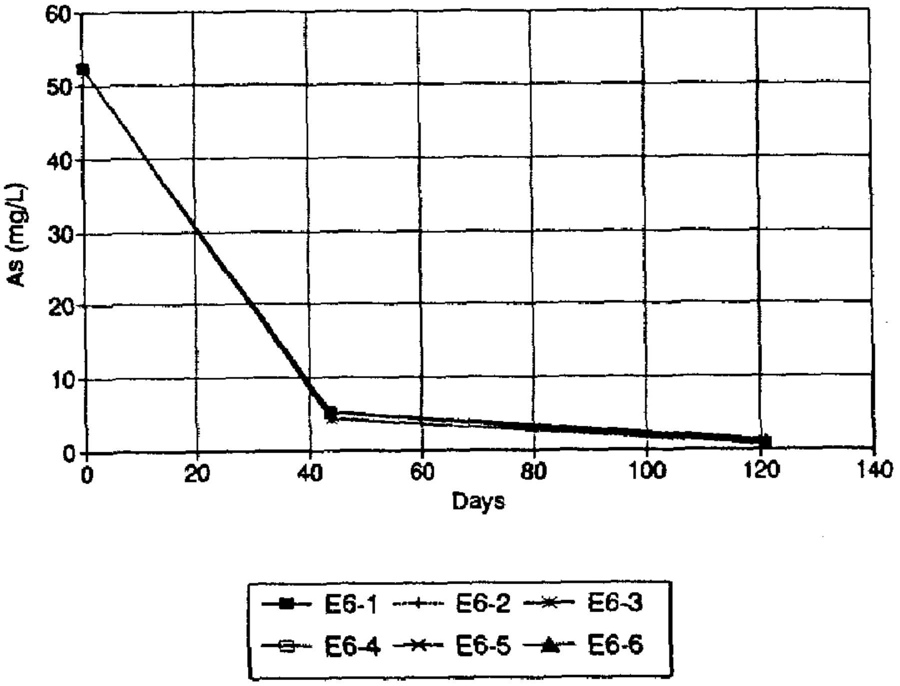


Fig.3: B-Zone reactors, Expt. 1 - Ni

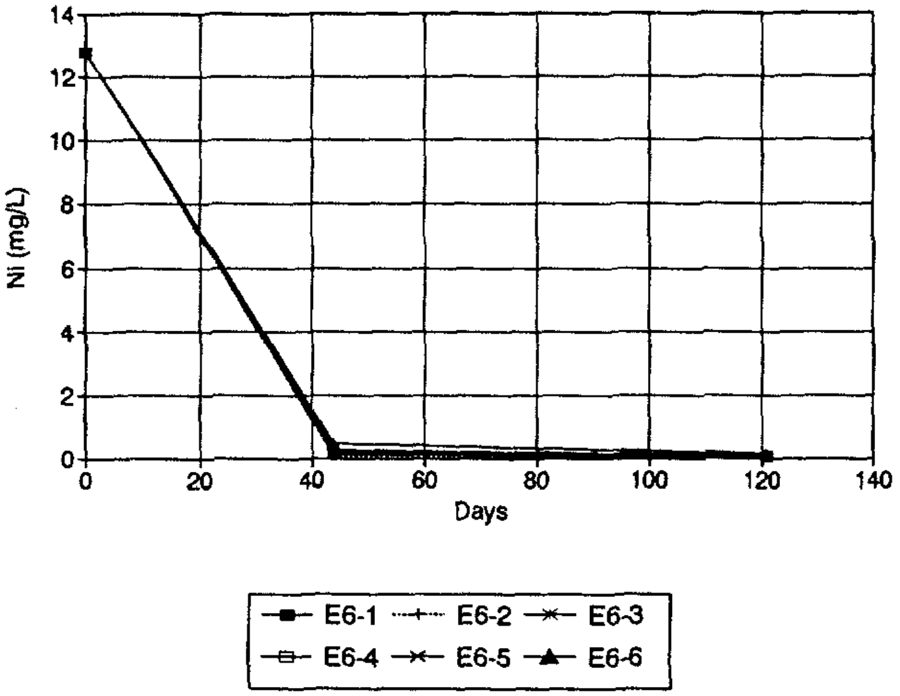


Table 1: Chemistry of B-Zone seepage waters as added to reactors for second experiment (recharge of reactors from first E-6 experiment)

	WRP-P	6.11
pH	3.86	2.67
acidity (mg/L CaCO3)	95.5	809.5
As (mg/L)	6	75
Fe (mg/L)	83.1	2.2
Ni (mg/L)	24.9	162.8
NH4 (mg/L)	27.3	7.8
NO3 (mg/L)	146.3	126.8
PO4 (mg/L)	2.45	88.1
SO4 (mg/L)	1369	506

Fig. 4: B-Zone reactors -pH

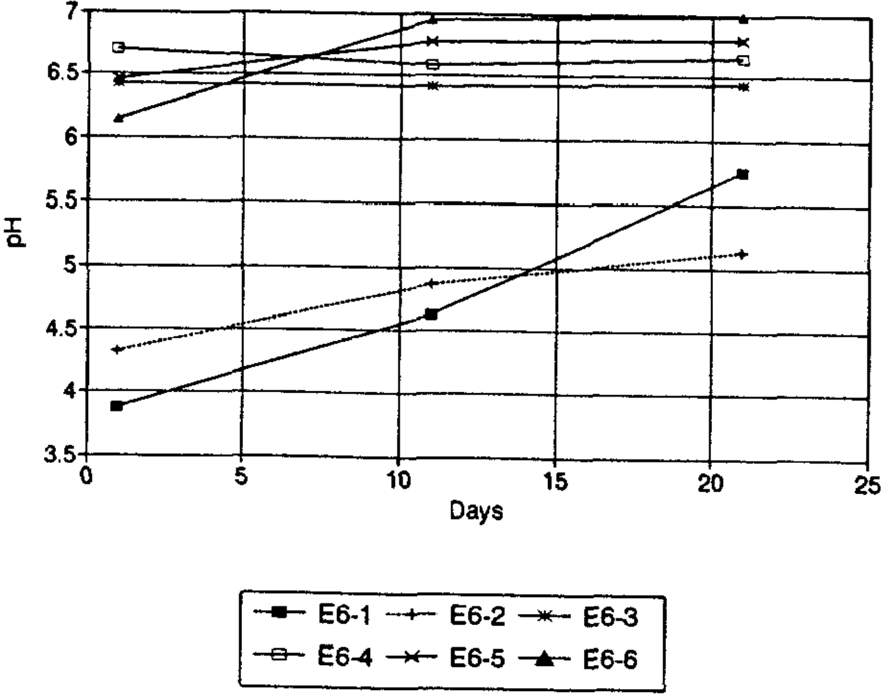


Fig. 5: B-Zone reactors -acidity

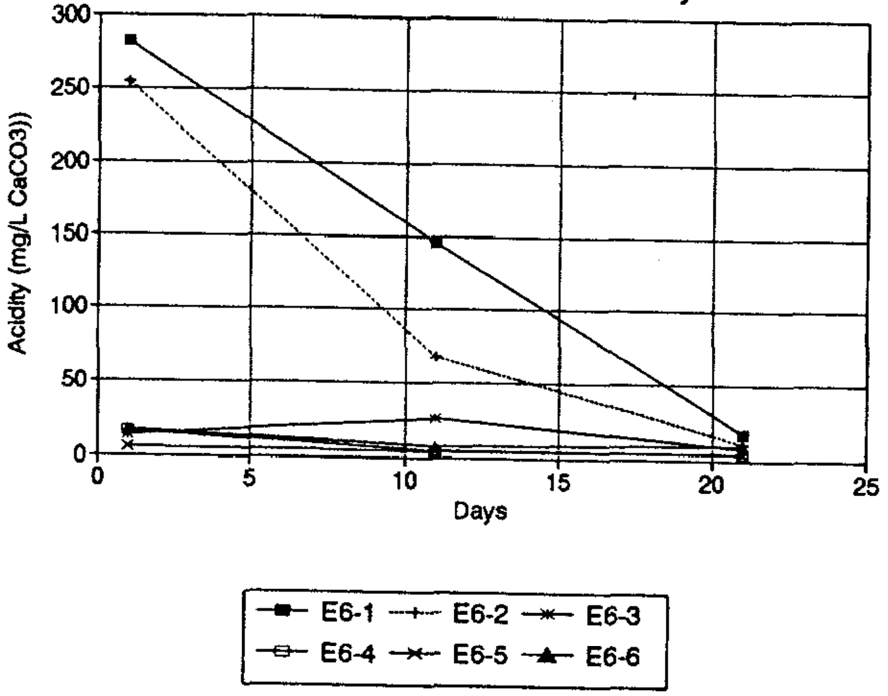


Fig. 6: B-Zone reactors -Em

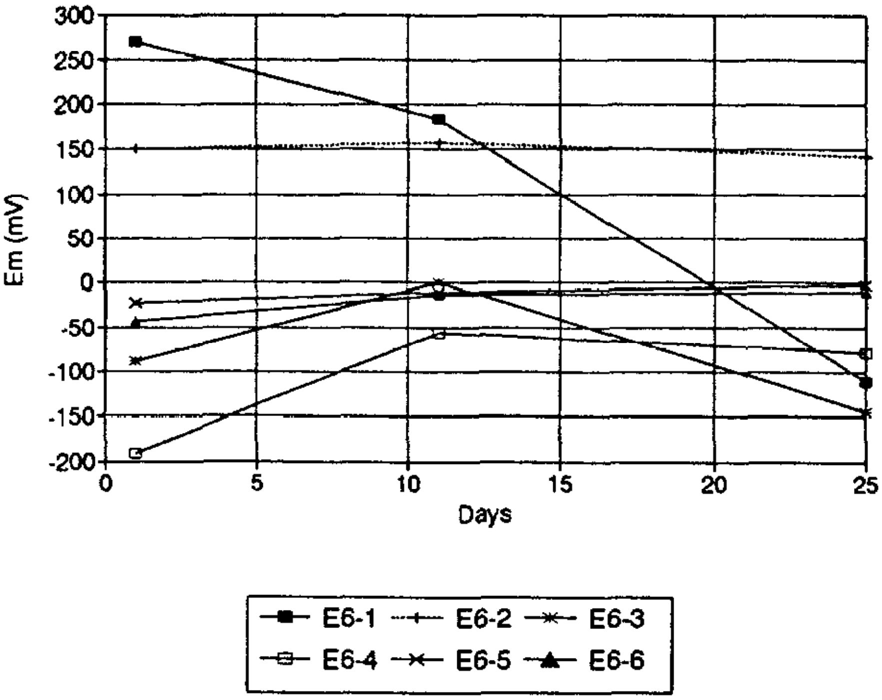


Fig. 7: B-Zone reactors -arsenic

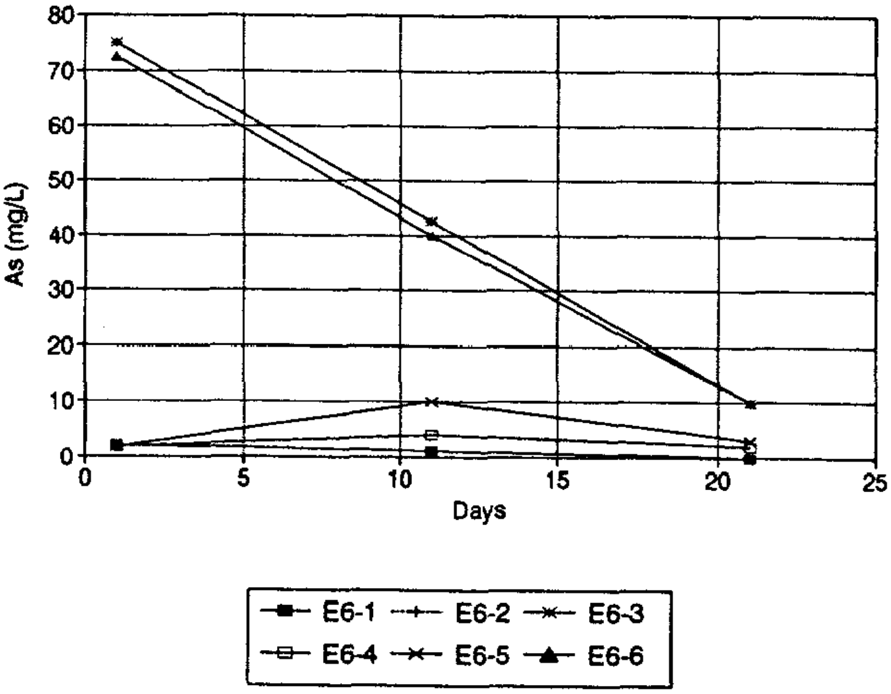


Fig. 8: B-Zone reactors -iron

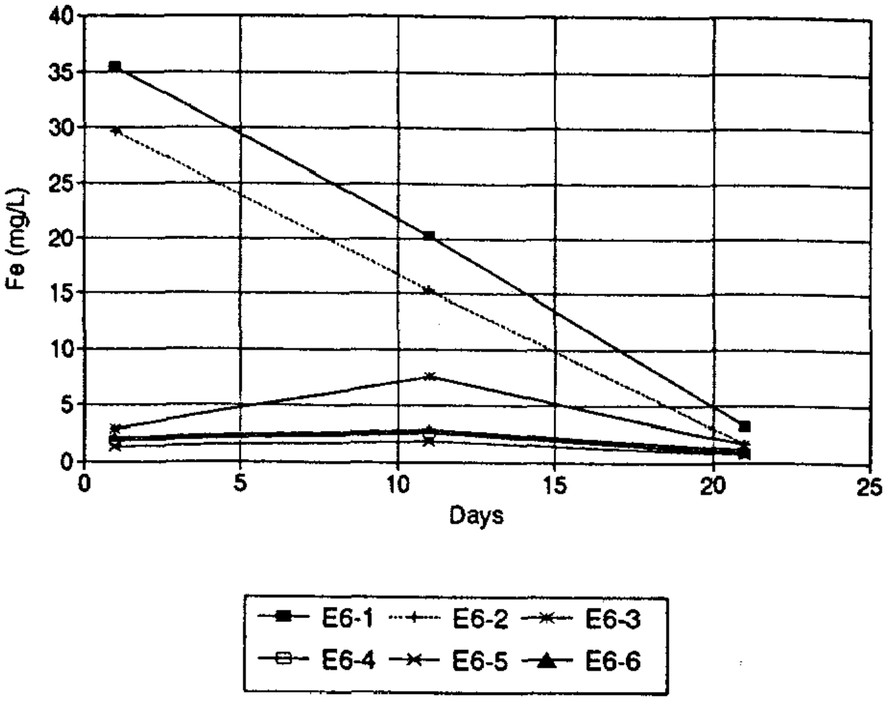


Fig. 9: B-Zone reactors -nickel

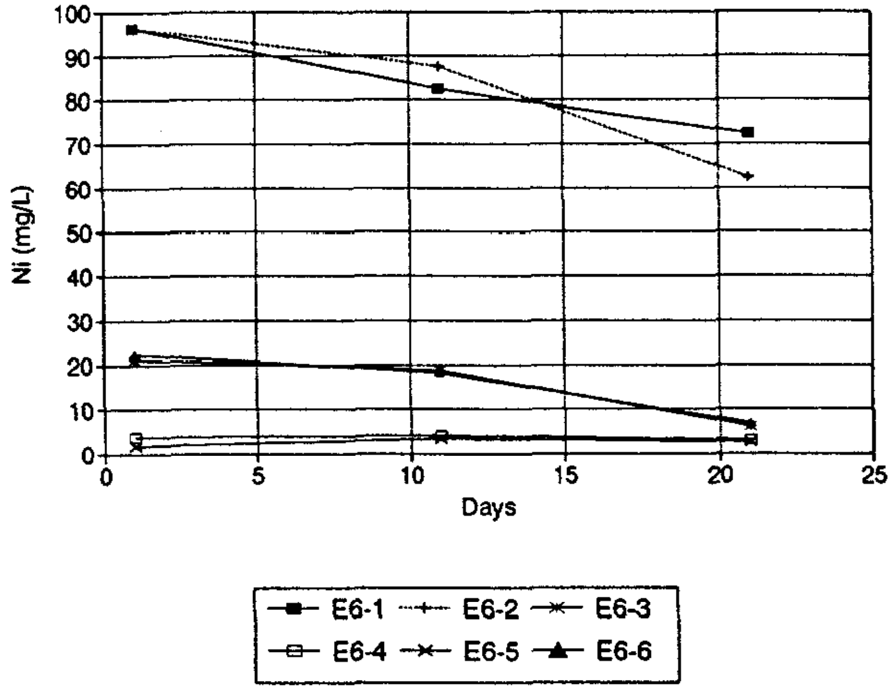


Fig. 10: B-Zone reactors -ammonium

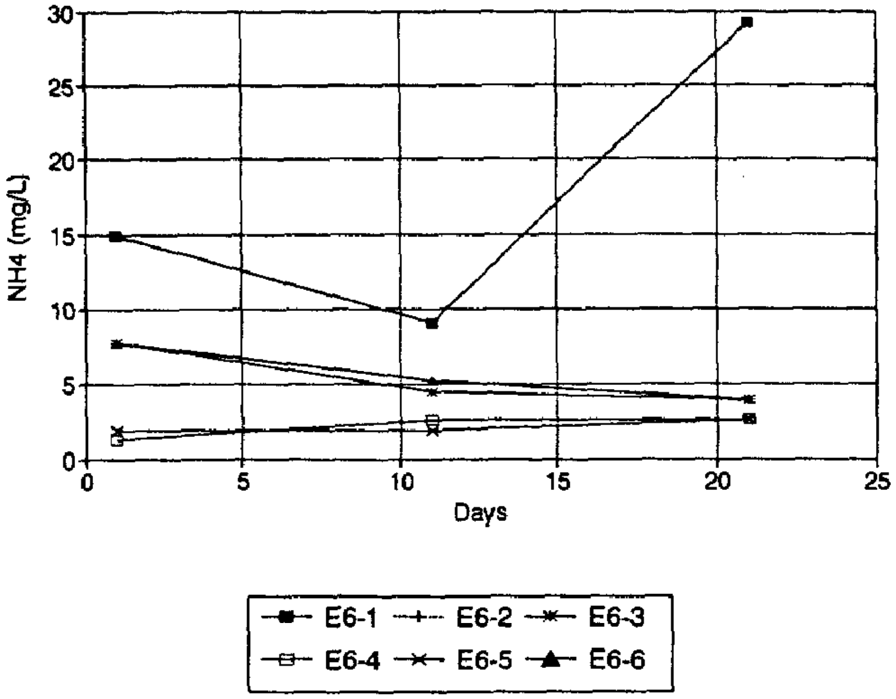


Fig. 11: B-Zone reactors -nitrate

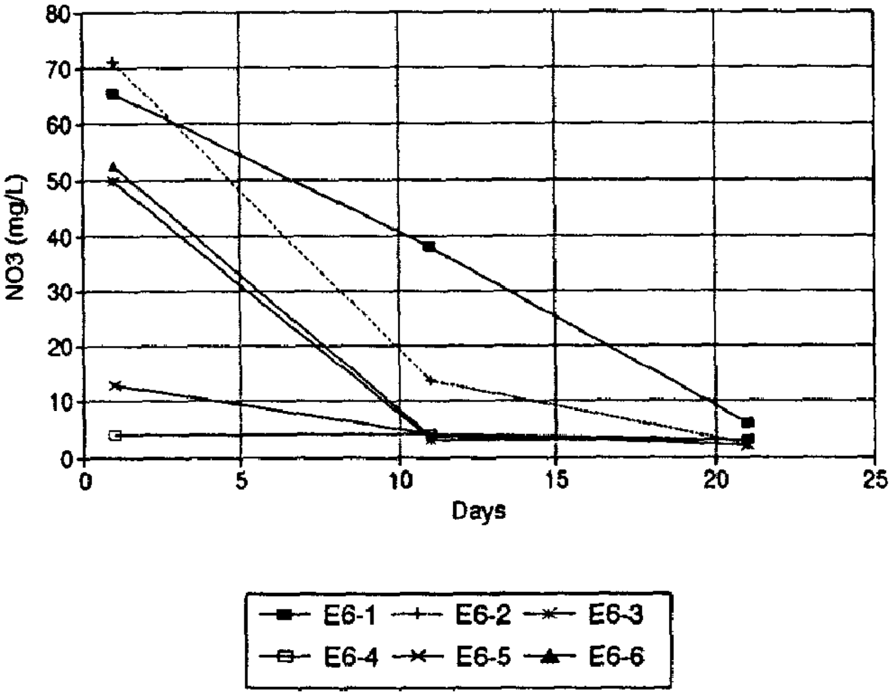


Fig. 12: B-Zone reactors -phosphate

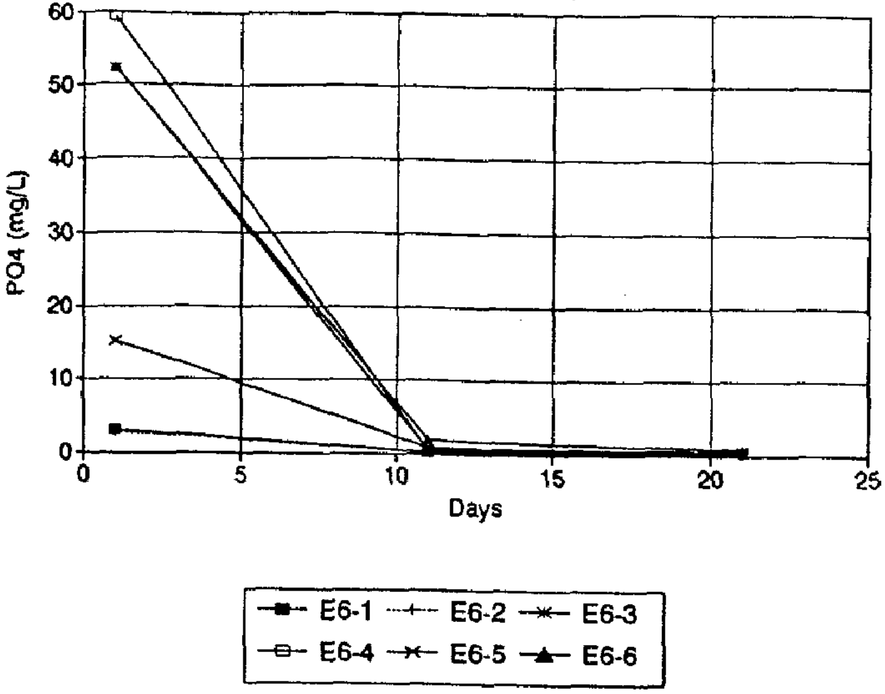
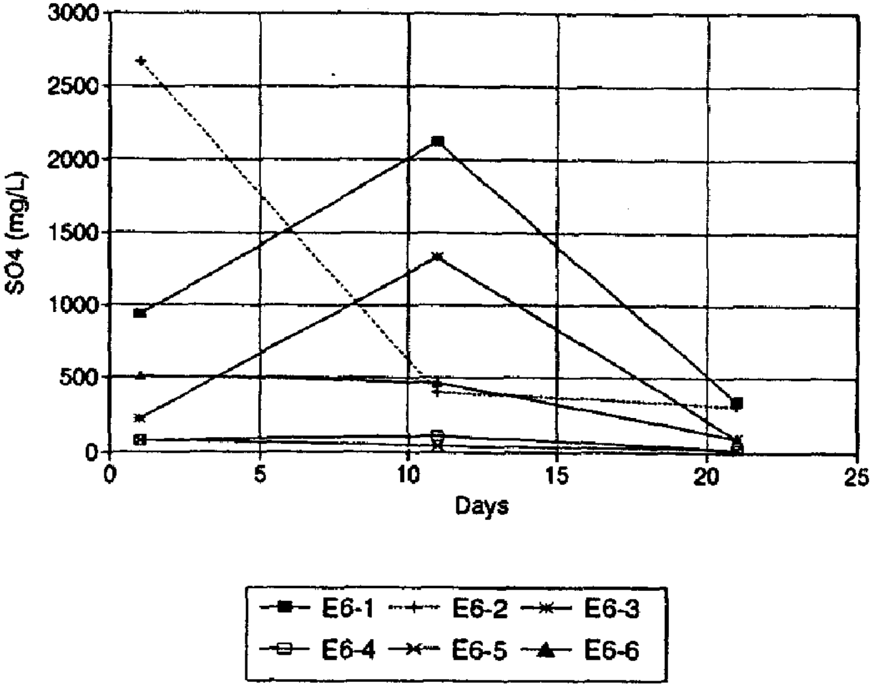


Fig. 13: B-Zone reactors -sulphate



Appendix 6 Experiment 5: Total removal capacity continued.

The results for the first 129 days of this experiment are summarised and discussed in Appendix 4. Later observations are discussed below.

Following the sampling at 129 days, the reactors were left standing for 145 days. Two 'unchanged' reactors (R-1 and R-2) and two 'recharged' reactors (R-4 and R-5) were sampled further from 274 days to 367 days from set up. 500 mL of water column water of the recharged reactors R-4 and R-5 was exchanged for stn 6.11 water (as used previously) weekly from 274 days to 305 days. From 306 days, no further stn 6.11 water was added. The reactors were sampled at 274 days, prior to the new water changes, after 4 exchanges (305 days, prior to last water change) and at 345 and 367 days from set up. The results are summarised in Fig. A1 to A10.

Following the 145 days of standing without any changes, the chemistry of the reactor water was little changed from the 129 day sampling. Conductivity showed a decline (Fig. A3 indicating that the sediment is was still removing ions from solution during this period. Little change in pH was observed (Fig A1. Eh increased in all 4 reactors (Fig. A2), In R-1 and R-2, this is probably as a consequence of exhaustion of potato waste for decomposition and a consequent reduction in oxygen consumption. In R-4 and R-5 the dilution of potato decomposition products in solution would also have an effect. Arsenic (Fig. A5), Ni (Fig. A6) and Fe (Fig. A7) concentrations remained low. NO_3-N remained undetectable (Fig. A8). Ammonium-N (Fig. A9) and phosphate-P (Fig. A10)concentrations were similar to those at 129 days.

Following 4 changes of water in R-4 and R-5, there were substantial changes in the water chemistry. In contrast at day 305, the chemistry of the water column of R-1 and R-2 was little changed from that of day 274. Data for R-4 will be considered. Numbers for R-5 showed the same trends. There was a decline in pH in R-4 from 7.64 to 6.65 (Fig. A1), a decrease in Eh from 333 V to 177 mV (Fig. A2) and an increase in conductivity from 620 umhos.cm^{-1} to 1110 umhos.cm-1 (Fig A3). The changes in pH and conductivity suggest that contaminated water is being added faster than it can be treated. Arsenic concentration increased dramatically from 3 mg.L^{-1} at day 274 to 80 mg.L^{-1} at day 306 (Fig. A5). There was no net removal of As in this period (stn 6.11 water added contains 85 mg.L^{-1} As). Ni concentration also increased from <0.1 mg.L^{-1} to 58 mg.L^{-1} (Fig. A6). Ammonium-N, NO_3-N and PO_4-P concentrations (Fig. A9, A8 and A10 respectively) remained low (much lower than in stn 6.11 water) suggesting that these ions were being treated in the columns. The low NO_3-N concentration, together with the decline in Eh, suggests that reducing conditions were still present in the sediment. Iron concentration (Fig. A7) and acidity (Fig.A4) also remained low.

One exchange of water was carried out immediately following the 305 day sampling. Thereafter the reactors were sampled at 345 and 367 days to determine if Ni and As removal processes continued to operate in the 'exchanged' columns R-4 and R-5. The trends noted for the 305 day sampling continued. The chemistry of R-1 and R-2 changed a little with slight increases in Eh (Fig. A2) and acidity (Fig. A4). The pH remained high and concentrations of As and Ni low (Fig. A5 and A6 respectively) indicating that with one dose of potato waste, Ni and As can be stably held within the sedient for a full year. In R-4 and R-5, there was a continuation in decline in pH (Fig. A1). Conductivity remained more or less constant (Fig. A3) indicating no net overall removal of dissolved species from the water column. Acidity (Fig. A4) increased along with phosphate-P (Fig. A10), the release of which may be related to the drop in pH. There was no increase in NO_3-N (Fig. A8) and Eh (Fig. A2) was still favourable for denitrification. Nickel (Fig. A6) and As (Fig.A5) concentrations remained high. There was a decline in Ni concentration (Fig A6). For example, concentration in R-4 declined from 58 mg.L^{-1} at day 305 to 26.5 mg.L^{-1} at day 367 indicating that net removal by the sediment is continuing.

Results of alkalinity titrations (carried out with the Metrohm Titrino autotitrator with 5 mL samples titrated against 0.01 N H_2SO_4) for 274 days (after 145 day standing), 305 days (after 4 water exchanges in R-4 and R-5) and after 367 days are shown in Fig A11 to A13.

The estimated accumulated removal of Ni and As by the changed reactors are shown in Fig. A14 and Fig. A15 respectively. The data indicate that by the last sampling (367 days), there was a small net release of As from the sediment into the water column. Sediment removal processes are now equalled or exceeded in rate by release processes. Total As removed is estimated at 410 mg per reactor (mean of R-4 and R-5) at day 305. Net Ni removal by sediments was still taking place at day 367 as indicated above. Total estimated Ni removed by day 305 was 466 mg per reactor (mean of R-4 and R-5).

Overall, Experiment 5 showed that the reactors with one dose of potato waste could remove all the Ni and As from at least 5 L of stn 6.11 water. Eventually, the potato waste is exhausted through decomposition and dilution. This slows down sediment removal processes and with a decline in pH and rise in Eh, conditions are less favourable for Ni and As removal.

Fig. A1: B-Zone Reactors Expt. 5
pH

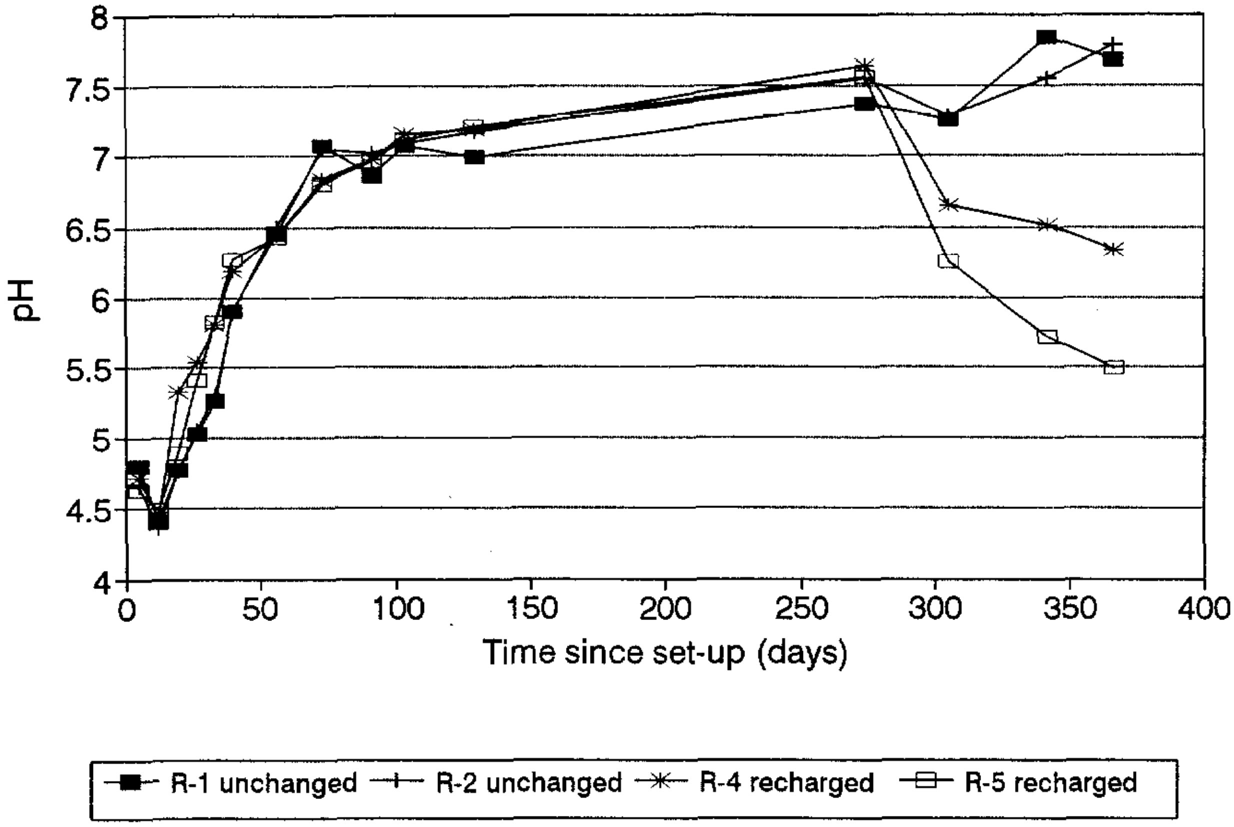


Fig. A2: B-Zone Reactors Expt. 5
Eh

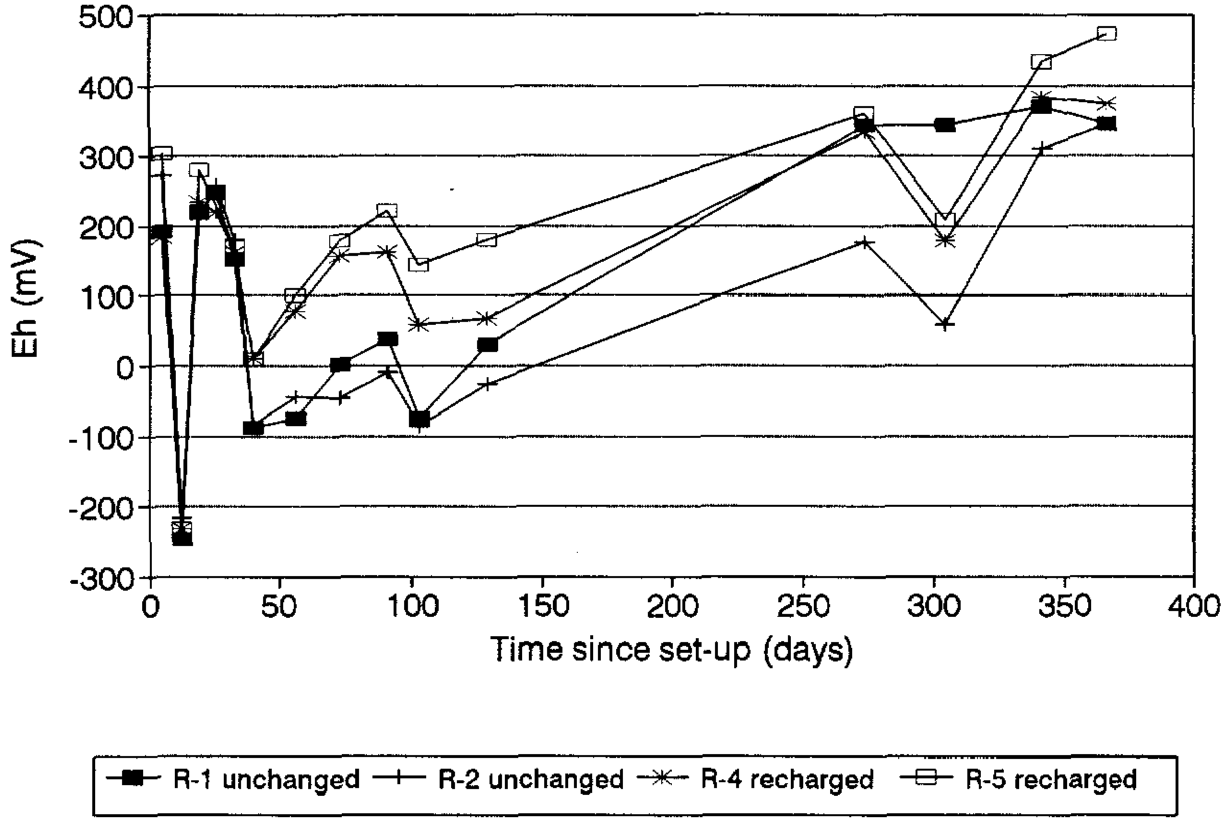


Fig. A3: B-Zone Reactors Expt. 5
Conductivity

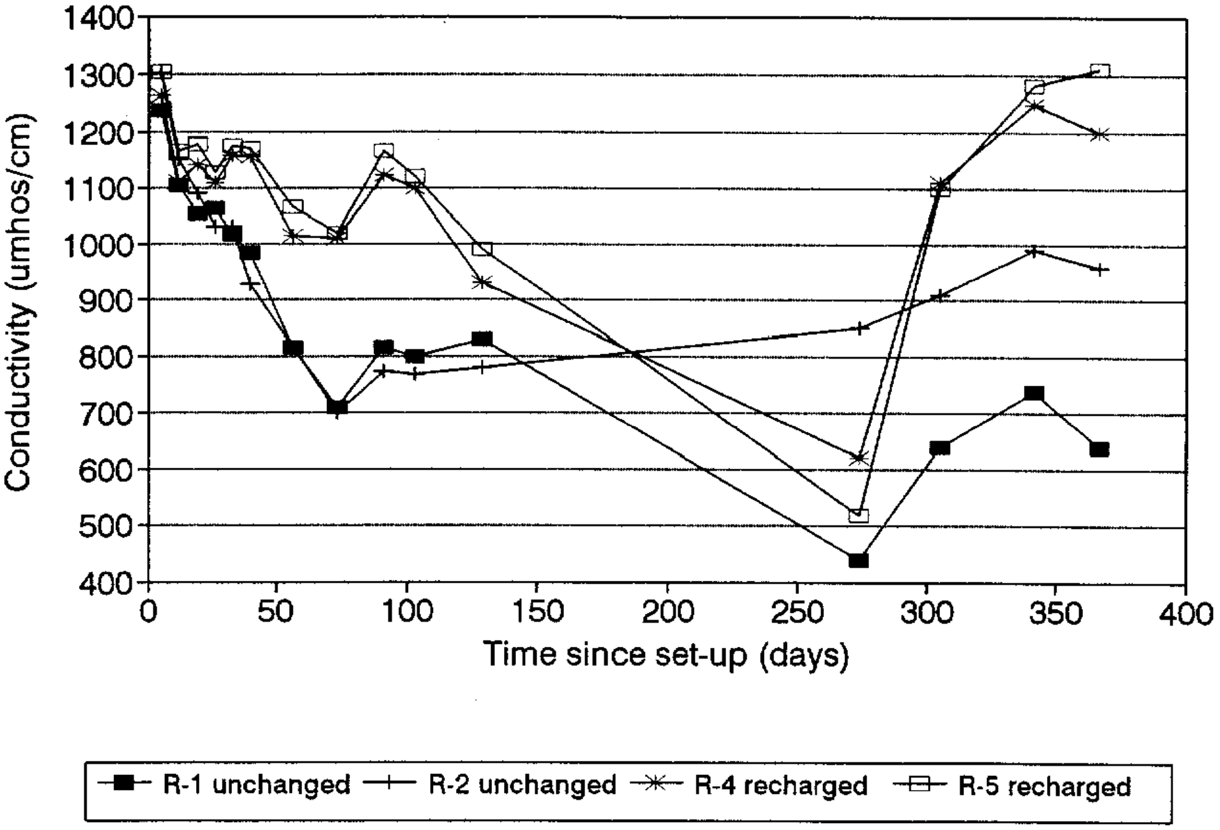


Fig A4: B-Zone Reactors Expt. 5Acidity
Acidity

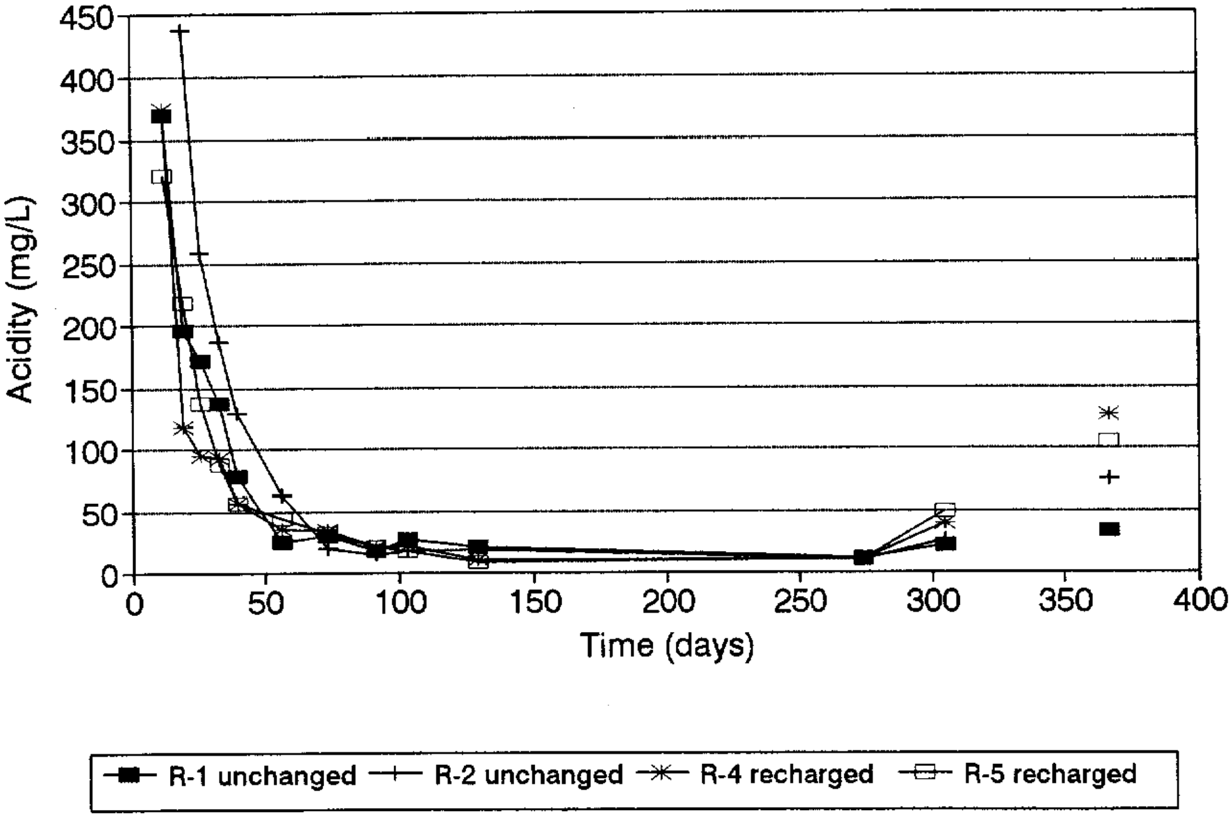


Fig A5: B-Zone Reactors Expt. 5
Arsenic

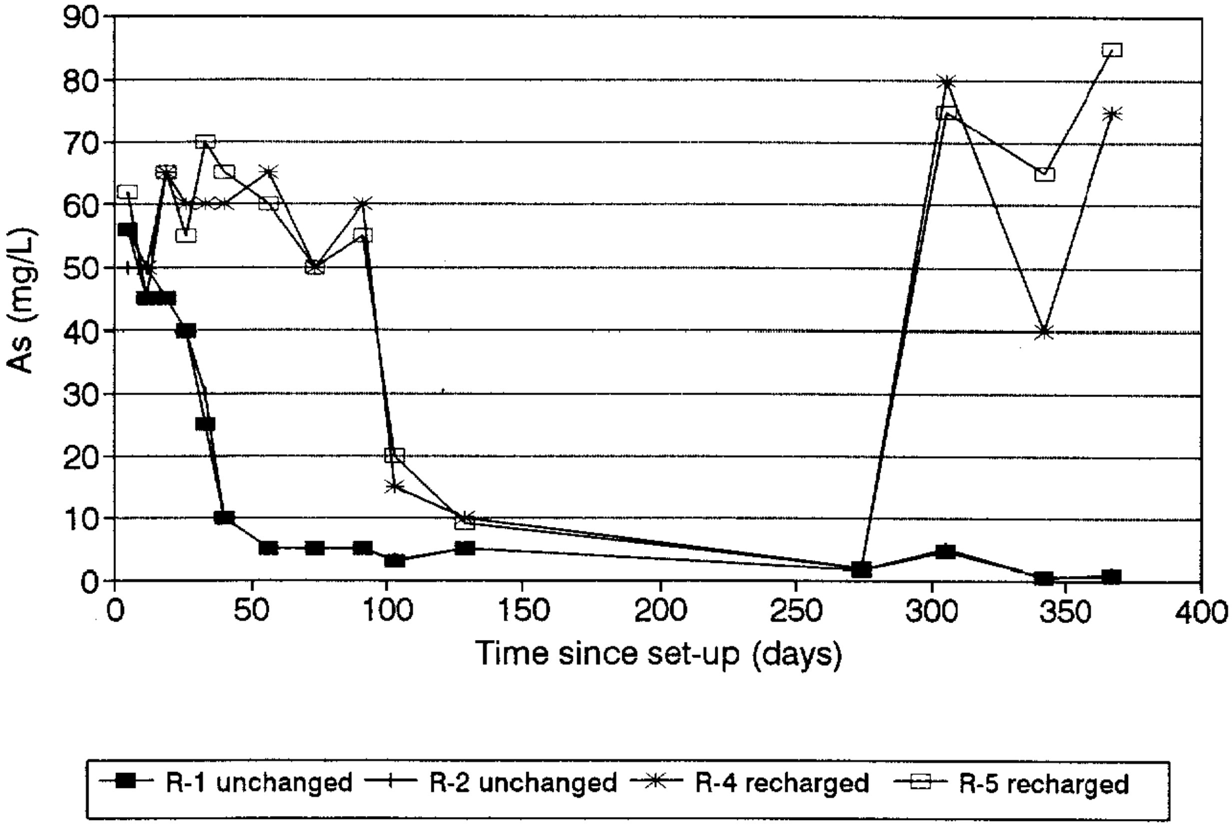


Fig. A6: B-Zone Reactors Expt. 5
Nickel

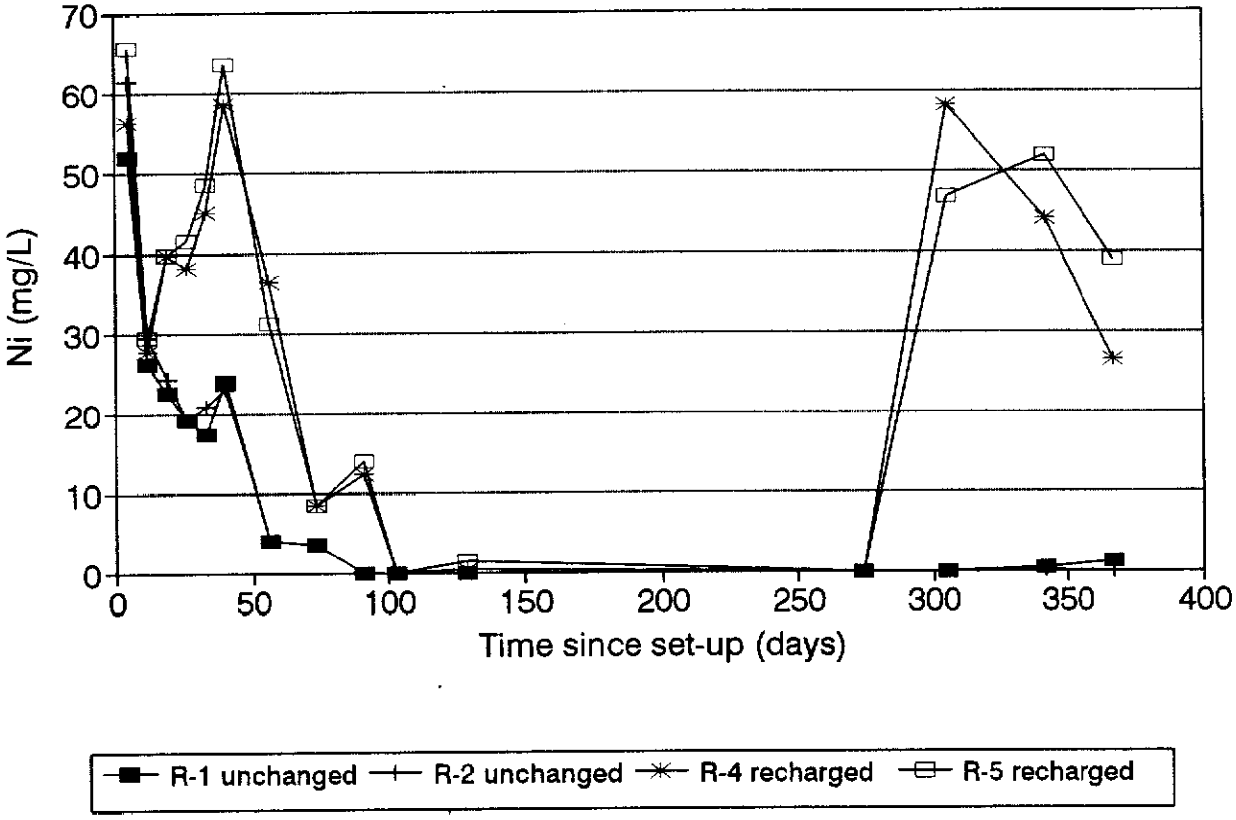


Fig. A7: B-Zone Reactors Expt. 5
Iron

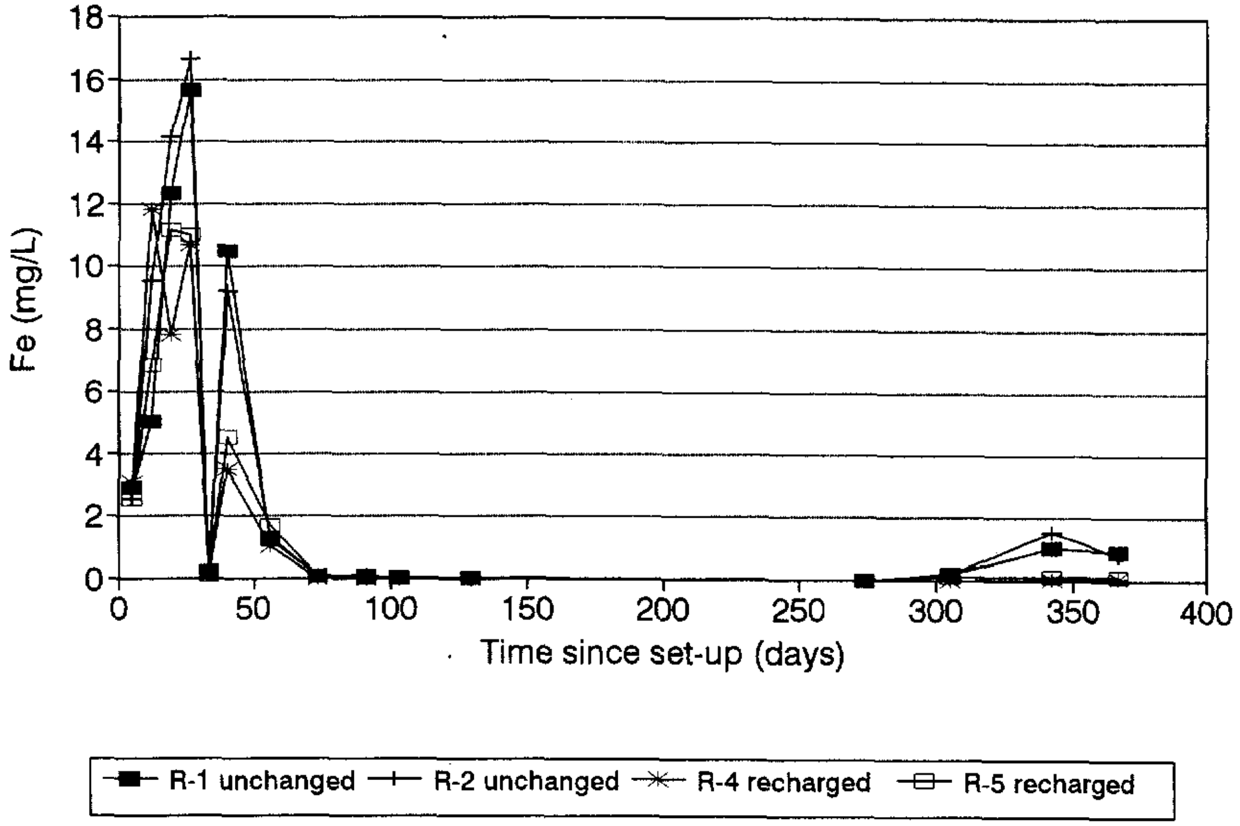


Fig. A8: B-Zone Reactors Expt. 5
Nitrate-N

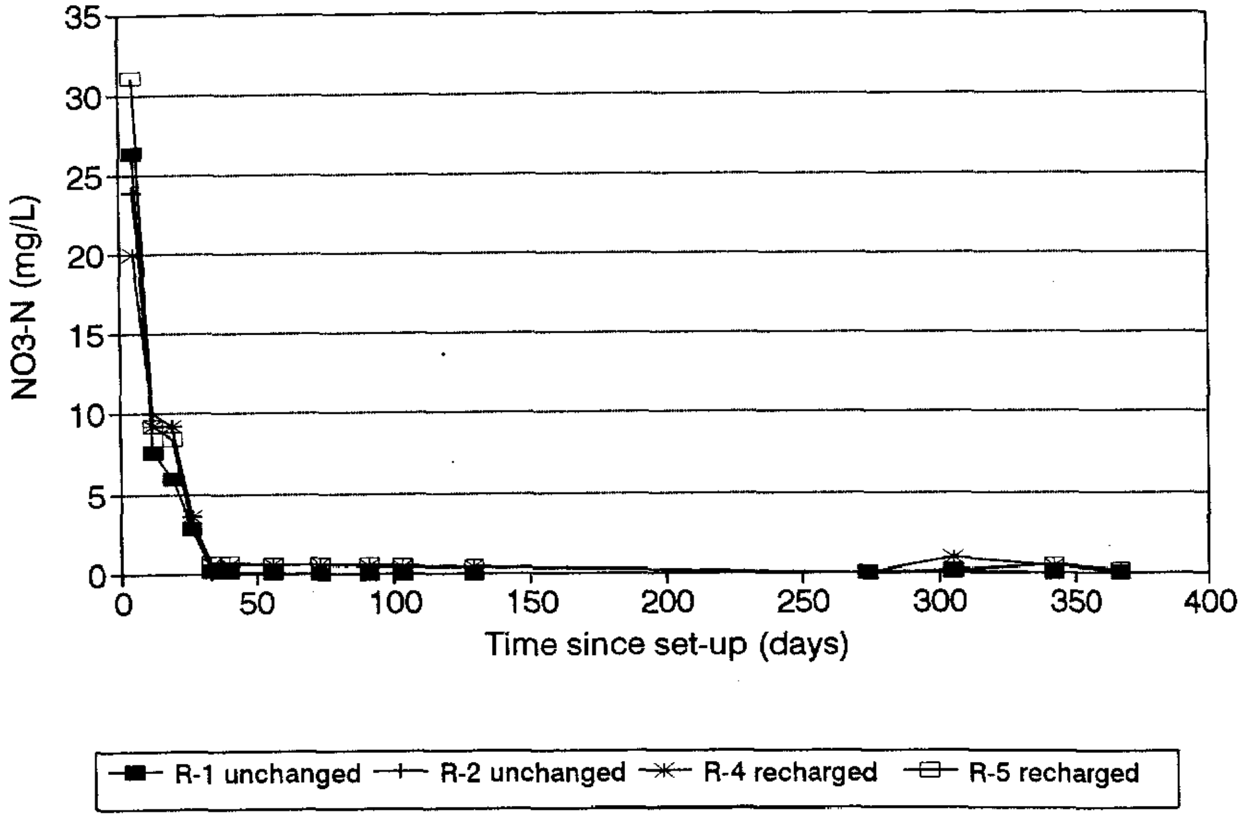


Fig. A9: B-Zone Reactors Expt. 5
Ammonium-N

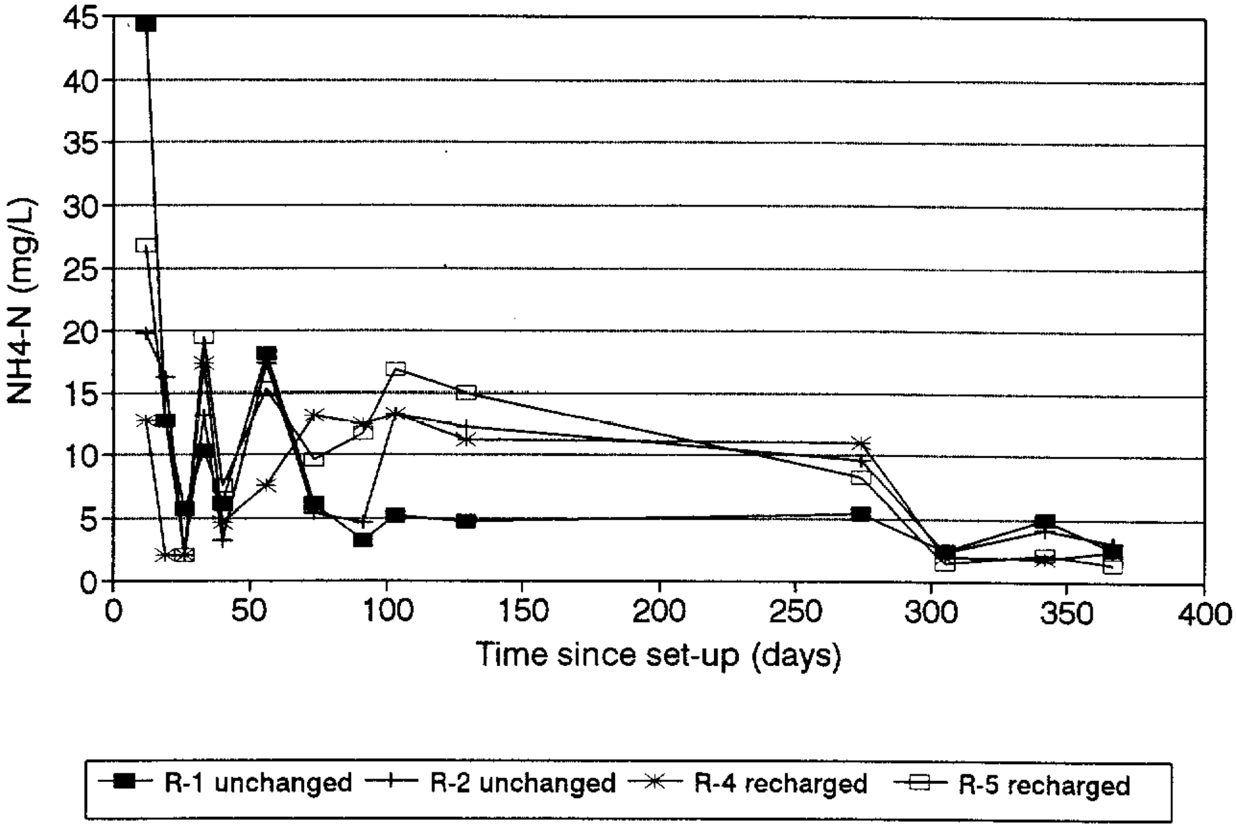


Fig. A10: B-Zone Reactors Expt. 5
Phosphate-P

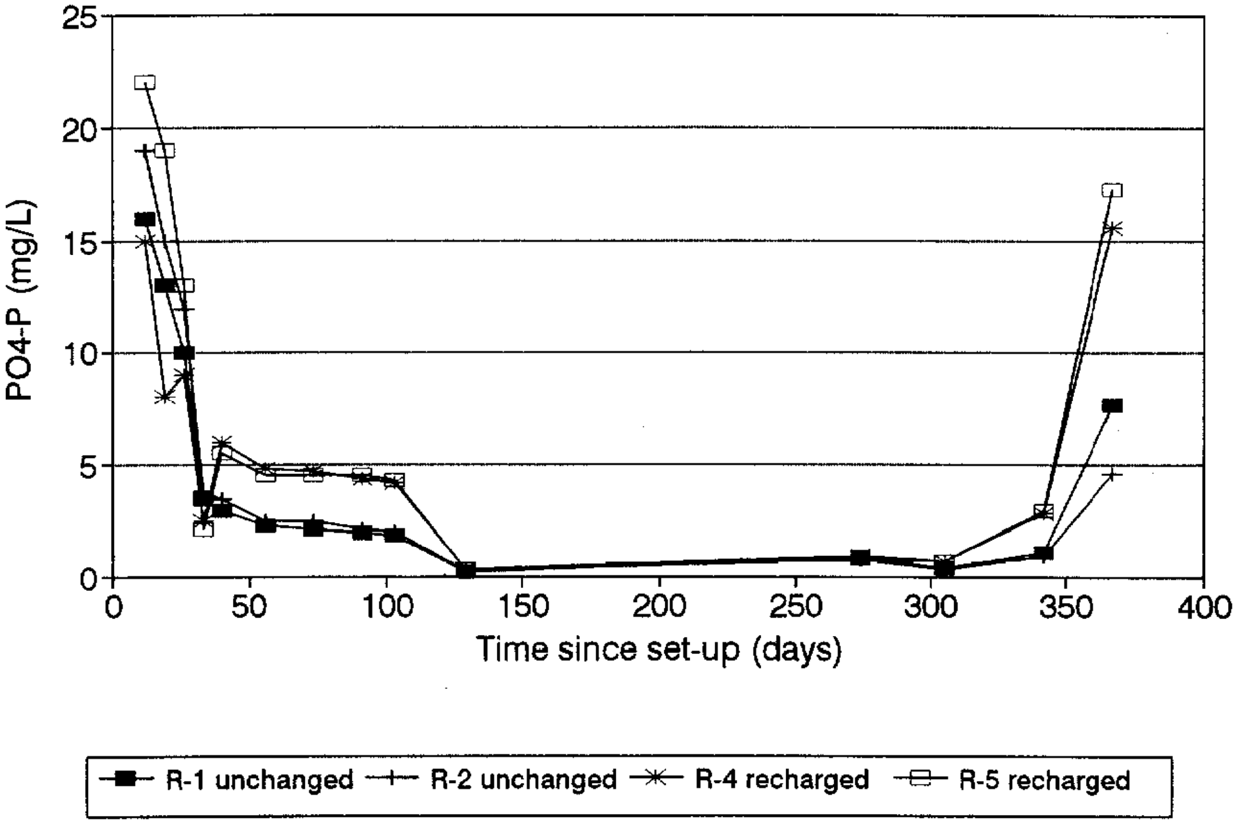


Fig. A11: B-Zone Reactors Titrations
274 days

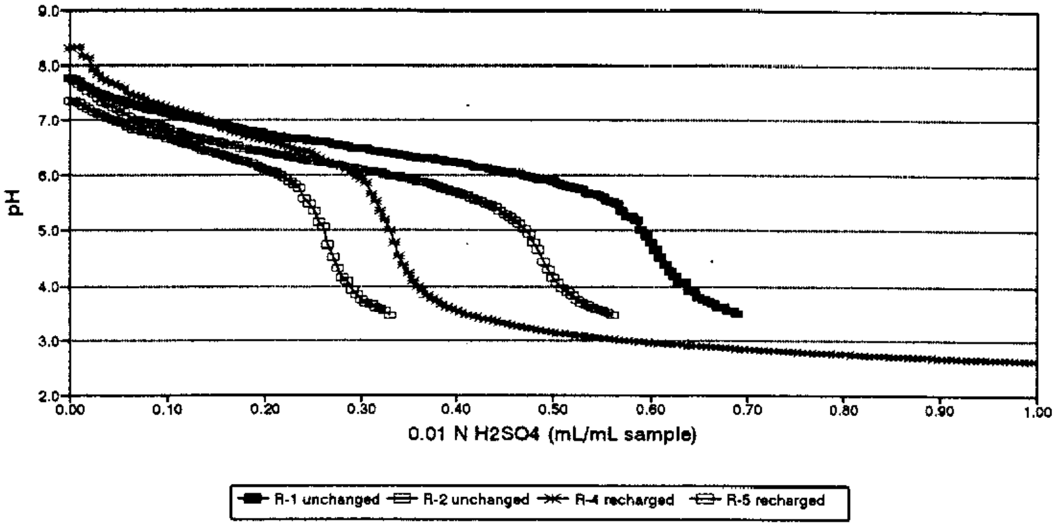


Fig. A12: B-Zone Reactors Titrations
305 days

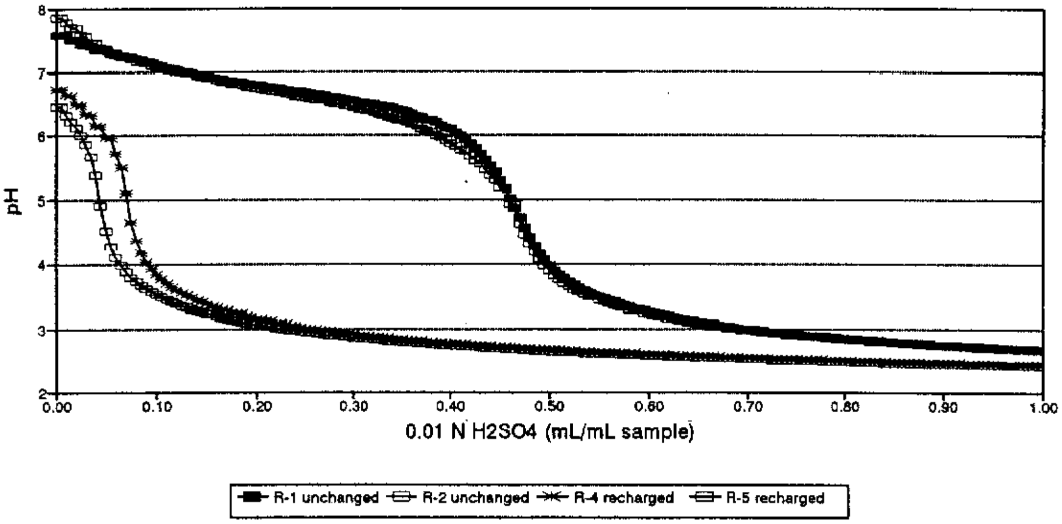


Fig. A13: B-Zone Reactors Titrations
367 days

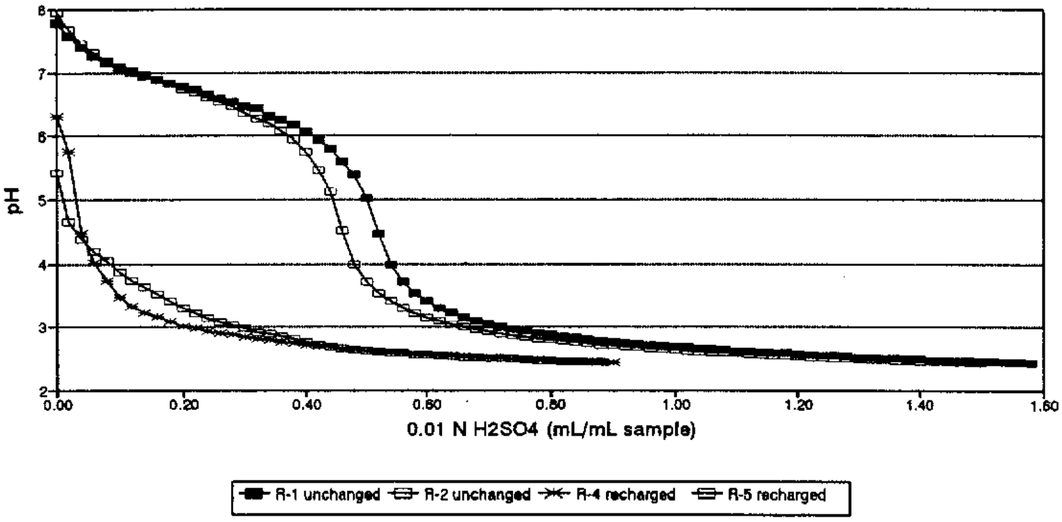
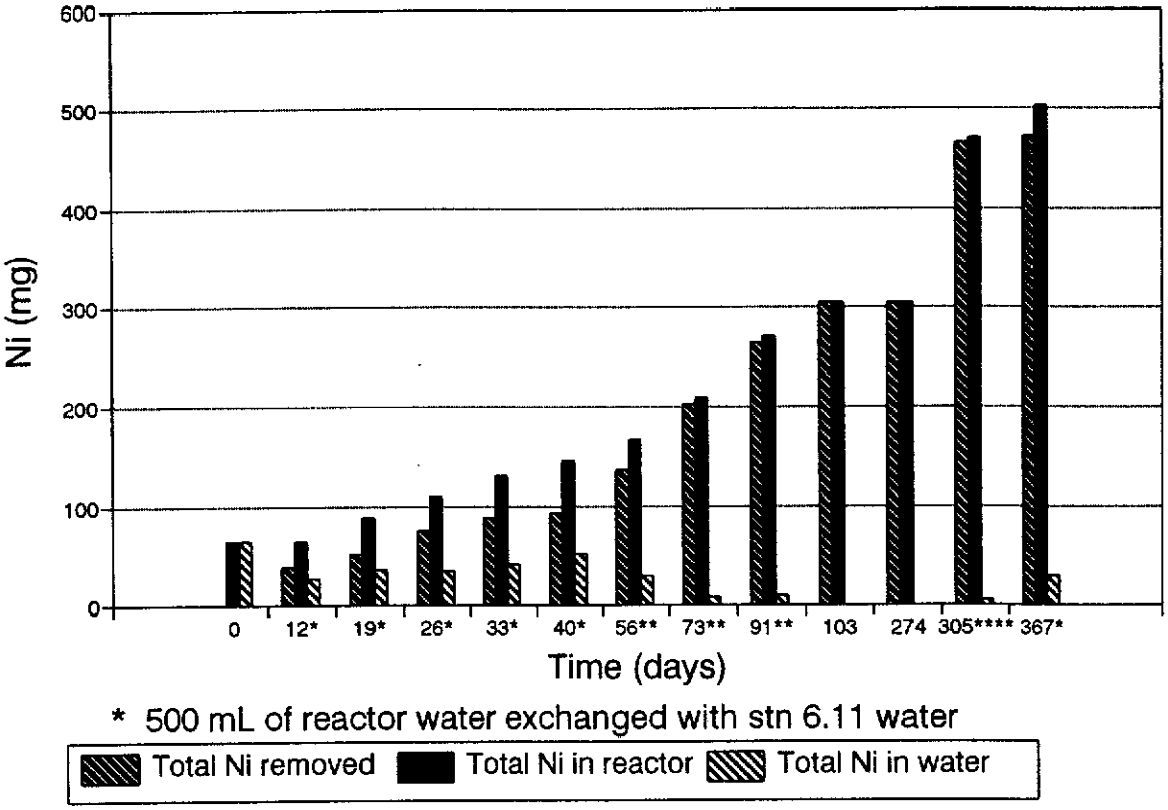
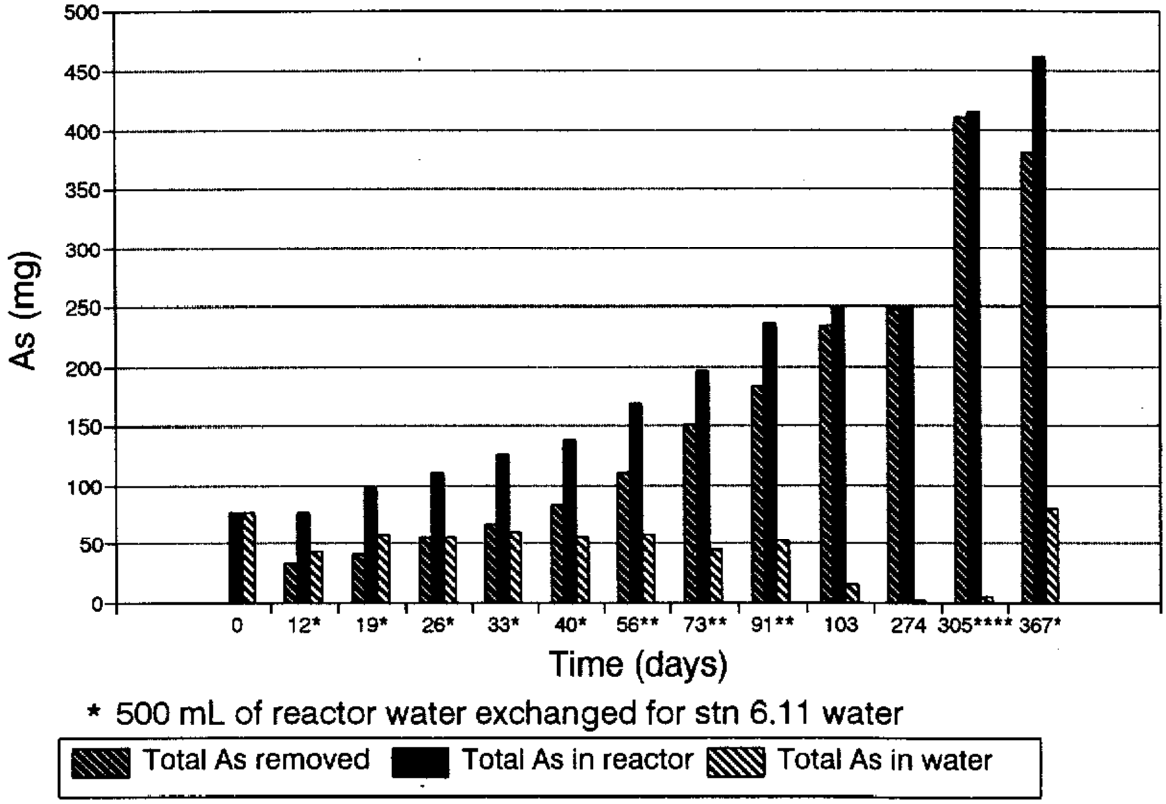


Fig. A14: Expt. 5 - Recharged reactors
Nickel removed by sediment



* 500 mL of reactor water exchanged with stn 6.11 water

Fig A15: Expt. 5 - Recharged reactors
Arsenic removal by sediments



* 500 mL of reactor water exchanged for stn 6.11 water

Appendix 7: Stati

			1994				
	Max	N	Mean	Std	Min	Max	N
	5.66	9	4.07	4.13	3.68	4.92	4
Em	260	3	236				1
TDS (	1910	6	2965	1205	1760	4170	2
TSS (	770	6	47	37	10	84	2
T-Hard (	748	2	1390	640	750	2030	2
Lab/Field Cond., u	2230	9	2157	894	1097	3540	4
Cl (	4.0	5	3.7	1.7	2.0	6.0	3
		1	0.23	0.02	0.21	0.24	2
H	4.0	4	1.3	1.9	0.0	4.0	3
N	6.10	5	3.97	1.22	2.30	5.20	3
N	97.00	4	35.00	34.56	3.00	83.00	3
	1080	8	1319	581	902	2320	4
T	52.00	5	39.67	9.18	30.00	52.00	3
	5.30	3	5.20				1
Pb210 (	6.50	2	1.38	1.13	0.25	2.50	2
Po210 (	5.50	2	0.12	0.04	0.08	0.16	2
Diss Ra226(	3.50	4	0.00				1
Tot Ra226(	5.00	8	3.25	1.03	2.50	5.00	4
Th230 (	3.50	2	0.13	0.07	0.06	0.20	2
Diss U(	2.22	5	1.17	1.05	0.12	2.22	2
Tot U(	2.87	8	0.66	0.91	0.04	2.23	4
Ag (	0.00	2					0
	58.00	3					0
Di	120.00	7	29.06	28.94	0.12	58.00	2
T	130.00	9	14.58	25.07	0.08	58.00	4
	0.42	2	0.97	0.34	0.63	1.30	2
	0.31	2	0.04	0.01	0.03	0.05	2
	178	5	264	125	172	441	3
	0.32	2	0.27	0.08	0.19	0.35	2
T	1.40	2					0
Di		0	2.25	0.25	2.00	2.50	2
	0.09	2	0.02	0.00	0.01	0.02	2
	0.28	2					0
Di		0	0.05	0.03	0.01	0.08	2
Di	0.48	3	0.10				1
T	30.00	3	0.59	0.51	0.16	1.30	3
	36.0	5	45.3	16.1	32.0	68.0	3
	85	5	130	69	78	227	3
	6.80	5	6.03	0.90	5.40	7.30	3
	0.14	2	0.65	0.08	0.56	0.73	2
	36.0	5	51.7	25.8	31.0	88.0	3
D	120.0	7	109.0	11.0	98.0	120.0	2
T	120.0	9	136.8	43.3	97.0	210.0	4
	0.06	2	0.01	0.00	0.01	0.01	2
	0.01	2	0.01	0.00	0.01	0.01	2
	0.14	2	0.04	0.01	0.03	0.04	2
	0.63	2	0.99	0.21	0.78	1.20	2
Acidity		0	158				1
Alkalinity		0					0