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Boojum RESEARCH LIMITED

BIOLOGICAL POLISHING

PHASE IV: MODEL VERIFICATION AND SCALE-UP

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 #: 15SQ.23440-3-9213

DSS CONTRACT SERIAL #: 23440-3-9213/01-SQ

SCIENTIFIC AUTHORITY: Dr. D. Koren

July 30, 1994

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EXECUTIVE SUMMARY

Four years of research on the utilisation of attached algae in polishing ponds has resulted in the formulation of a biological polishing model. A preliminary model was completed in early l993. The design parameters were used to scale-up the application of the biological polishing process from ponds with a volume of about 300 m^3 to ponds with a volume of 6,000 m^3.

Predictions on the performance of the process were made, relating retention time to percent zinc removal. During winter conditions, a 2.2 % decrease in zinc concentrations was predicted for each additional day of retention and, therefore, a 45 day retention time is required for 100 % removal. In summer months, a 5.2 % decrease in zinc was predicted for each additional day of retention time. By the end of l993, the scaled-up ponds were operating with low retention times of 1 to 3 days. The % zinc decrease for the months of October to November, 1993, ranged from 2 % to 27 %. In the summer of l994, the system was performing as predicted, with 70 % zinc removal during a retention time of 22 days.

The preliminary biological polishing model was refined with the intention to identify the key operating parameters of the process. The box model considers bioaccumulation of the contaminants by algae the only contaminant sink. Field measurements for two systems, the scaled-up ponds with a circumneutral pH and zinc concentrations of about 20 $mg.l^{-1}$, and an acidic lake (1,000,000 m^3) with 10 $mg.l^{-1}$ of zinc, are evaluated using the box model. The box model predicts for the circumneutral ponds that other sinks for zinc are present. For the acidic lake, an increase in zinc concentrations is predicted, if bioaccumulation of zinc in the algae is the only zinc removal mechanism.

A second approach to modelling considers metal cycling and evaluates the two systems as continuous time reactors. Inputs for the model are measured and quantified as rates of cycling of contaminant species, in tonnes per year. With this refinement, iron cycling is identified as a key factor which can affect the water quality and, therefore, the zinc removal processes. This refined model does describe the process better, but requires the quantification of growth rates, sedimentation rates, recycling rates in addition to contaminant loading rates.

Sedimentation rates have been quantified in order to produce input parameters for modelling the biological polishing process as a continuous time reactor. Sedimentation rates ($g.m^{-2}.d^{-1}$) of precipitates, primarily comprised of iron hydroxide are in the same order of magnitude for both the acidic and circumneutral ponds, with 1 to 4 $g.m^{-2}.d^{-1}$, and 0.5 to 8 $g.m^{-2}.d^{-1}$, respectively. Zinc removal, through co-precipitation of with iron hydroxide, is an important factor in the biological polishing process. The amount of zinc co-precipitated appears to be related to the conditions under which the iron hydroxide is formed.

A literature review, presented in this report, focuses on the oxidation and reduction of iron, the redox boundary, and adsorption and complexation of iron in sediments. Some

of the most important findings with respect to the biological polishing process are summarized. Due to seasonally changing redox boundary in the sediment, the flux of reduced iron from sediment to overlying water might be significant. Iron reduction is microbially-mediated, and iron oxyhydroxides accumulated on the sediment surface are an abundant source of iron for iron reduction. Iron oxidation and iron reduction are important processes controlling the water characteristics, as iron oxidation is associated with the production of H^+, and reduction with the production of OH^- ions. Bacteria are able to couple the oxidation of organic substrates to the reduction of iron. Organic-rich, chemically reducing (low Eh) sediments will produce those substrates sustaining microbial iron reduction in polishing pond sediments.

The sediments from the acidic lake and the circumneutral polishing ponds were assessed both in the laboratory and in the field. Concentrations of elements in sediment pore waters were determined using pore water peepers. Reduced iron concentrations in sediment pore water ranged from 10.5 $mg.l^{-1}$ to as high as 115 $mg.l^{-1}$ for both systems. The highest iron concentration measure exceed pore water iron concentrations of 70 $mg.l^{-1}$ reported for non iron-enriched sediments.

Phosphate availability and iron cycling in sediment are closely coupled and, hence, phosphate can be the limiting nutrient in biological polishing systems. Phosphate additions to the sediments in the acidic lake were made using natural phosphate rock, a type of fertilizer suitable for acidic soils. It was proposed that, through addition of phosphate rock to the sediment, several objectives could be achieved which would, collectively, prevent deterioration of this lake currently receiving acidic seepage from the mine site and tailings.

Most importantly, the cycling of iron at the sediment-water interface may be curtailed following the formation of iron-phosphate colloids. If these colloids dissolve in the deeper portion of the sediment, some phosphate may be released. Upon supplying phosphate at the sediment surface, both bacterial activity and, possibly, periphytic algal growth, could be induced at the sediment-water interface. If the sediment-water interface could be covered by aquatic vegetation, an interface would be created between the sediment and the oxygenated water. A vegetation cover could be beneficial with respect to the recycling of iron hydroxides from the surface of the sediments.

The results of these additions are difficult to assess, although it is suspected that both microbial activity in the sediment and periphytic algal growth over the sediment have been stimulated. The acidic lake sediment characteristics are spatially heterogenous, with iron concentrations as high as 45 % in those areas where seepages enter the lake. Organic-rich sediments with high zinc concentrations are located in those areas where substrates were provided of periphytic algal growth. Although the continuous time reactor model indicates an trend of increasing zinc concentrations each year, this trend has not been observed in these areas where biological polishing has been implemented. Studies are under way to expand the area of biological polishing in the 1,000,000 m^3 acidic lake.

SUMMAIRE

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

LIST OF MAPS

LIST OF SCHEMATICS

LIST OF APPENDICES

1.0 INTRODUCTION

Decommissioning of inactive mine sites presents an economic and environmental challenge. Ecological Engineering processes are being developed to assist the mining industry in finding solutions to the decommissioning challenge.

Biological Polishing, one of the Ecological Engineering processes, has been quantified with data collected from three different acid-generating mine sites as follows: (1) an abandoned coal seepage in Cape Breton, N.S.; (2) the Buchans Mine in central Newfoundland; and (3) effluents from acid-generating tailings at the South Bay Mine in northwestern Ontario.

Biological polishing can assist in the improvement of AMD seepages by the following processes:

(1) the provision of nucleation/precipitation sites for metals on attached algae, or periphyton, surfaces;
(2) the provision of living covers over metal-laden sediments; and
(3) the provision of extracellular polysaccharides for complexation of metals.

Process development started in 1990 with a literature review on periphyton growth conditions and geochemical considerations of the contaminant removal process. It was concluded that species of the order *Ulothrichales* dominated algal complexes in acid conditions, and *Oscillatoria* species dominated complexes in neutral or alkaline conditions. These algal complexes represent the surfaces on which biological polishing takes place and are referred to as polishing agents. The algal complexes have the ability to create conditions on their surfaces which facilitate metal precipitation, adsorption and absorption.

A report, entitled "Periphyton Communities as Biological Polishing Agents in Mine Waste Waters and The Precipitation Process in Tailings. Final Report." (CANMET DSS Contract # 23440-0-9182/01SQ, 1991), was issued focusing on the approach for developing the process.

In 1991, field work was carried out at three different sites where the algal complexes were growing, covering acid to circumneutral pH mine effluents. Photosynthetic rates were determined both in controlled laboratory experiments and in field conditions. Metal concentrations were quantified in the algal biomass, and the algal communities' overall growth rates were determined, taking seasonal variations into account. The results of this work facilitated the determination of biological polishing capacity, or contaminant removal effectiveness, which is summarized in a report entitled, "Algal Bio-polishing of Zinc. Final Report." (CANMET DSS Contract # 23440-1-9009/01SQ).

In 1992, field experiments of various scales were carried out. At the old Buchans Mine in central Newfoundland, circumneutral effluent with elevated zinc levels leaving an open pit was diverted through six pools constructed in series. A mass balance of zinc entering and leaving the pools, along with the amount of zinc concentrated in the algal biomass, was determined. Algal growth and sloughing were quantified using peritraps. Peritraps are devices where growth substrate branches are held in nylon netting frames, to which slow release fertilizer can be added. The algal biomass growing on the branches is sampled periodically.

Peritraps were also installed to quantify growth and determine the effects of fertilization in acidic water at the South Bay site in northwestern Ontario. Tailings from this base metal mine have acidified a lake, which is used as a polishing pond. Boomerang Lake (1,000,000 m^3) received 41 truck loads of cut brush in 1992, based on biological polishing measurements made on brush cuttings placed in the lake since 1989. The brush cuttings provide surface area for algal biomass growth. In Boomerang Lake, *Ulothrix* spp. dominated algal complexes represent the polishing agents. Biological polishing was quantified in the same manner in the old Decant Pond (pH 6) on the South Bay tailings using *Oscillatoria* spp. as the polishing agent for zinc removal.

An acidic seepage emerging from a coal dump in Cape Breton was included in the research program to determine the capacity of biological polishing in coal seepage. Geochemical conditions of the waste water which allow for the formation of iron-precipitates were identified as a very important factor in the biological polishing process. Slow-release fertilizer was found to be useful in increasing growth rates of the algae. A report, entitled "A Study of Algae-Precipitate Interactions." (DSS Contract # 23440-1-9011/SQ, 1992), gives the details of the work.

In 1992, a site-specific application model was developed based on the data which had been derived from data for the six experimental ponds in operation at Buchans. A model was also developed for biological polishing at the coal seepage in Cape Breton and for the acidified lake receiving tailings seepage at South Bay. In field experiments, it was found that part of the biological polishing process was due to collection of precipitates on algal biomass which formed in the water bodies. The precipitate formation was, therefore, considered an essential component of the contaminant removal process. Sedimentation of precipitates was quantified in the open pit at Buchans and in Boomerang Lake at South Bay. The results of this phase of the research are summarized in a report, entitled "Biological Polishing In Acid Mine Drainage: Contaminant Removal Capacity and Application Model. Final Report." (DSS Contract # 23440-2-9216).

This report summarizes improvements to the model and elucidates on relevant factors which affect the biological polishing process.

In 1993, it was possible to test the model predictions in large ponds constructed at Buchans, covering about 1.3 ha with a volume of 5,951 m^3. The ponds are operated based on the performance data generated from the model. Critical model parameters are evaluated and are presented in Section 2 along with a refinement of the application model.

The biological polishing capacity of these polishing ponds, filled with brush cuttings, is quantified based on growth per "unit brush". Alternative algal growth measurement units were tested in 1993. The growth results using these alternative units are incorporated into the biological polishing model presented in Section 2.

Sedimentation rates of iron hydroxide, measured since l992 in both Buchans and South Bay, were found to be high. It was concluded that sediment iron chemistry needed to be evaluated in detail. The oxidation of reduced iron is a significant factor in acidification of water and, in turn, water pH is an important factor affecting the biological polishing process. A literature review on iron cycling in sediments is presented in Section 3.

A possible avenue to curtail acidification, caused by the hydrolysis of ferric iron, is to reduce the quantity of iron available for cycling between the water (ferric ions, ferric hydroxide) and the sediments (ferrous ions). If phosphate, released from natural phosphate rock added to the sediments, is available at the sediment-water interface, it might facilitate the formation of iron phosphate, a compound much less soluble than iron hydroxide. This compound would fix iron in the sediments, thereby reducing the amount of iron available for cycling. Surplus phosphate released from the sediments would serve as a fertilizer for the biological polishing process. Finally, through additions of natural phosphate rock to the lake sediments, it might be possible to establish a vegetation cover over the sediments which would further reduce contact of sediments with oxygenated lake water.

Laboratory and field tests were initiated to further address iron cycling between water and sediments. This included determination of iron hydroxide precipitation/ sedimentation rates and examination of natural phosphate rock as a means to fix iron in sediments. In Section 4, the results of the field and laboratory experiments are presented.

2.0 BIOLOGICAL POLISHING SCALE-UP AT BUCHANS

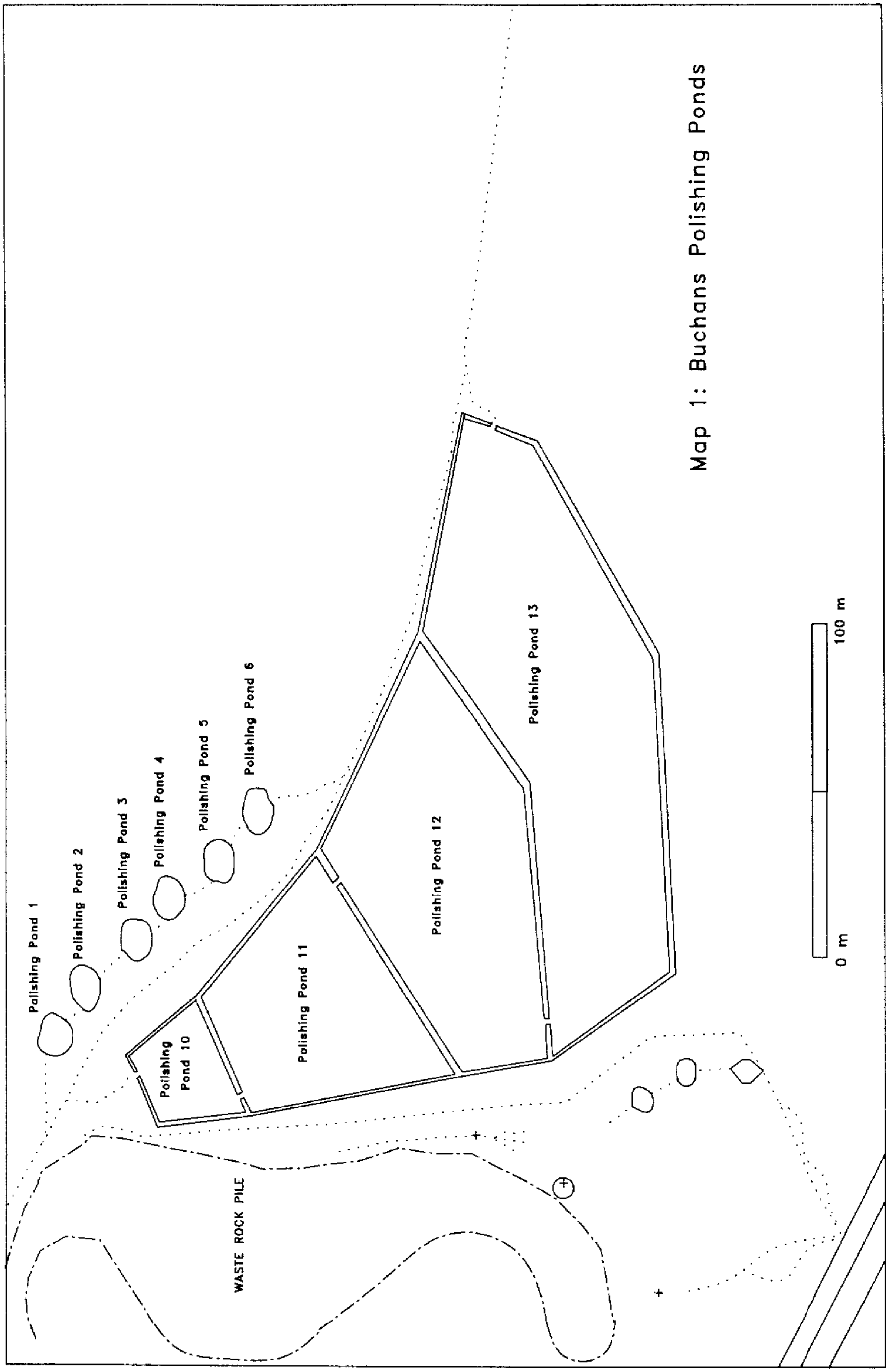
In 1989, six ponds were constructed in series at the Buchans mine site in Newfoundland (Map 1). A fraction of discharge from the Oriental East Gloryhole, a flooded pit, was directed through the ponds and the flow was quantified. Brush was placed as a growth substrate for the algae, and performance (% zinc removal per day retention time) of the system was derived. Fertilizer was found to increase algal growth and hence, improve the zinc removal. The summer season of 1993 represented the fourth year when samples were collected, to describe the biological polishing capacity of the system.

In l992, Polishing Pond 10 was constructed, with a volume, 319 m^3, very similar to Polishing Ponds 1 to 6 (243 m^3). Based on the performance of this pond, construction of Polishing Ponds 11, 12 and 13 proceeded, creating a total polishing pond volume of 6,000 m^3. Construction of the large Polishing Ponds (PP) was completed by the end of l993.

2.1 Overall Performance of Polishing Ponds 1 To 6

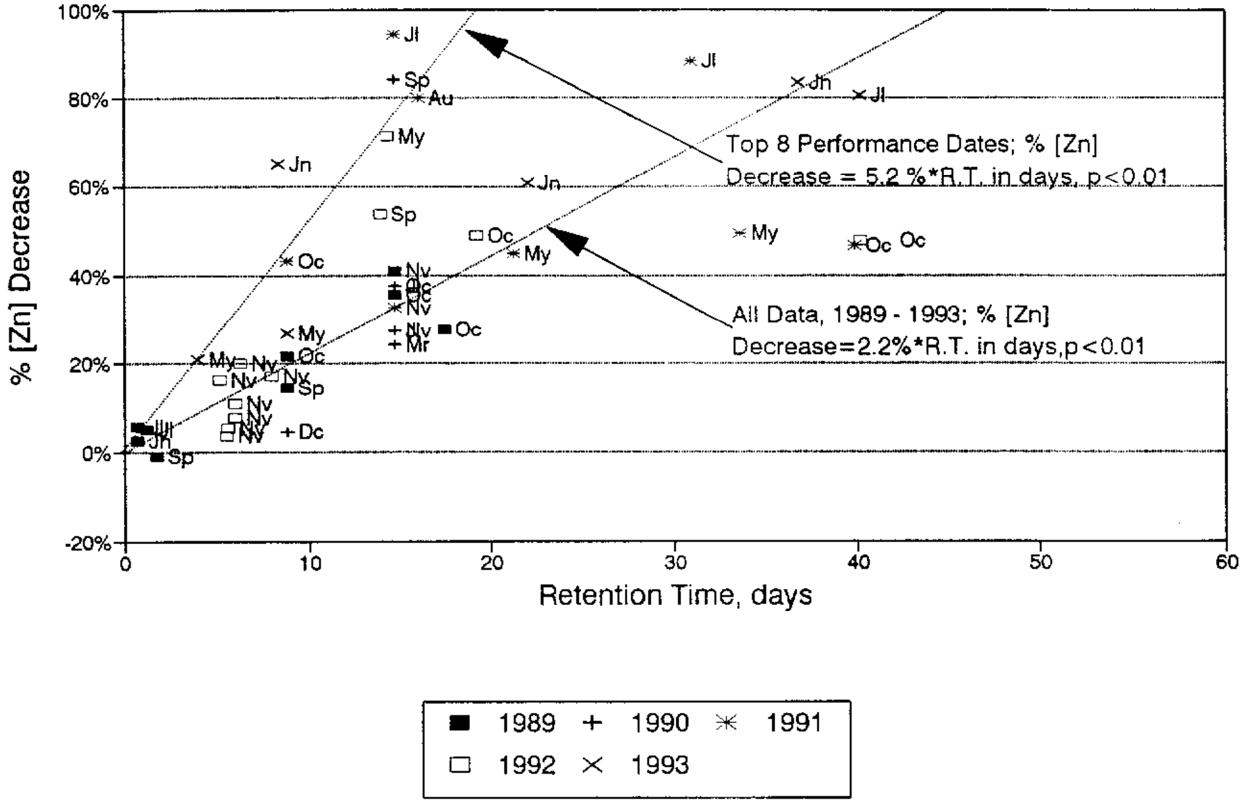
Using all data available from PP1 to PP6, the percentage zinc removal is plotted against retention time (in days) in the pond system. Retention time can be used as a design criterion to evaluate PP10, a pond which has the same volume, but not configured as a series of ponds as are PP1 to PP6.

From a regression analysis, a zinc concentration decrease of 2.2 % can be expected with each additional day of retention time. To achieve 100 % zinc removal, a projected retention time of 45 days would be required. For PP1 to PP6, this retention time is achieved if the inflow is maintained at 0.06 $L.s^{-1}$. A flow of 0.08 $L.s^{-1}$ for PP10 would provide the same retention time.



Map 1: Buchans Polishing Ponds

Fig.1: % [Zn] Decrease in PP 1 to 6
with Retention Time



In Figure 1, each data point is differentiated according to year and month (e.g. Jn = June) of collection. Data for 1989, the first year of test system operation, are included in the calculation of the regression line. In the first year, zinc removal has to be considered to be mainly as non-biological, as virtually no algal growth was then present. In the years following 1989, all % zinc removal data are well above the 2.2 % regression line. As expected, good zinc removal performance occurs in the summer months when the algal population was actively growing. In contrast, the many data points below the regression line are mostly November and December data. Therefore, percent zinc concentration decreases represented by the 2.2 % regression line are either winter performance or non-biological removal processes.

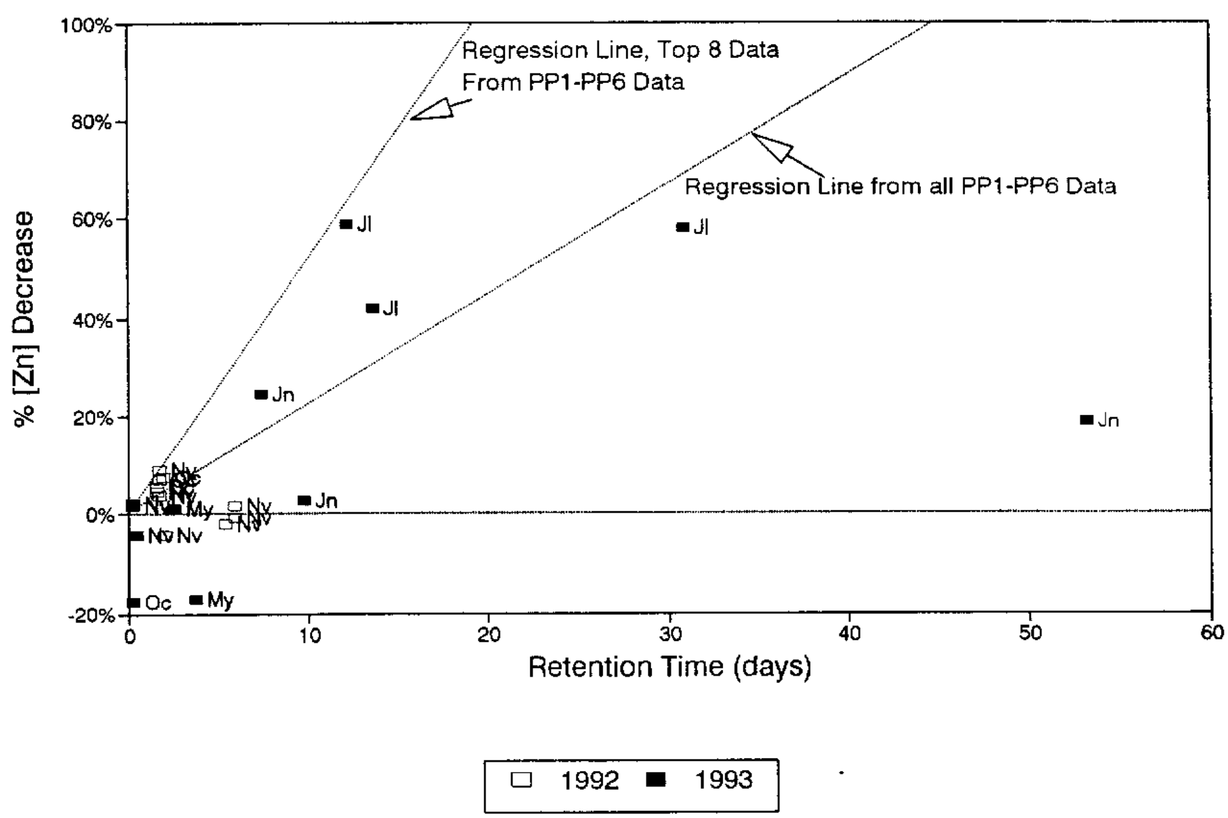
A second regression line, using the top 8 performance period data, is given in Figure 1. The slope of top performance regression line represents a 5.2 % zinc concentration decrease for each day of retention time.

Based on the performance of PP1 to PP6, it can be concluded that winter performance will be a function of the 2.2 % regression line, where zinc removal is primarily due to non-biological processes limited by retention time. Summer performance will be a function of the 5.2% regression line, where zinc removal is enhanced by algal growth and zinc uptake.

PP10 data for l992 and l993 are plotted in Figure 2, and the 2.2% and 5.2% regression lines, derived from PP1 to PP6, are included so to provide the framework for performance evaluation.

Since construction of PP10 was completed in late 1992, good performance was expected in 1993. Very little data was collected in 1992, the period before algae had colonized the substrate. Also, in this period the flow rate through the pond was initially set high in order to test the stability of the berms. Therefore, with little algae present and the low retention time, zinc removal was negligible.

Fig. 2: % [Zn] Decrease in PP 10
1st Yr Performance:6-10-92 to 28-11-93



The zinc removal data collected in the summer of 1993 fall between the regression lines, indicating that the larger pond performs in the same manner as the PP1 to PP6 arranged in series. These were encouraging data, supporting the scale-up of the biological polishing system. Construction of Polishing Ponds 11, 12 and 13 during 1993 increased to system's volume to 6,000 m^3.

2.2 Projected Performance of Polishing Ponds

The mechanisms responsible for the observed zinc removal in the biological polishing process have been identified to involve: 1) settling of zinc-bearing suspended solids; 2) adhesion of suspended solids onto algal biomass surfaces; 3) adsorption of dissolved zinc onto algal cell walls; and 4) photosynthetically induced pH increases, with subsequent precipitation of zinc carbonates.

Given these different mechanisms which can take place simultaneously, the evaluation of the most important factor controlling process performance is very complex as several physical, chemical and biological variables are involved.

Removal of zinc by algal biomass via filtration and adsorption are only two of four main mechanisms which are operating. It was estimated that 70 % of zinc removal in the biological polishing ponds may occur as the result of co-precipitation followed by collection of the precipitate onto algal biomass.

Precipitate formation is, however, also mediated by algal photosynthesis which promotes the precipitation of zinc carbonates with increased pH. This can be demonstrated when changes in acidity and alkalinity take place in the water passing through the experimental pools. Data from pools 1 to 6 evidence such changes both in 1992 and 1993 (Figures 3a to d). The same process takes place in Polishing Ponds 10 through 13.

Fig. 3a: Polishing Ponds Acidities
May 28, 1992

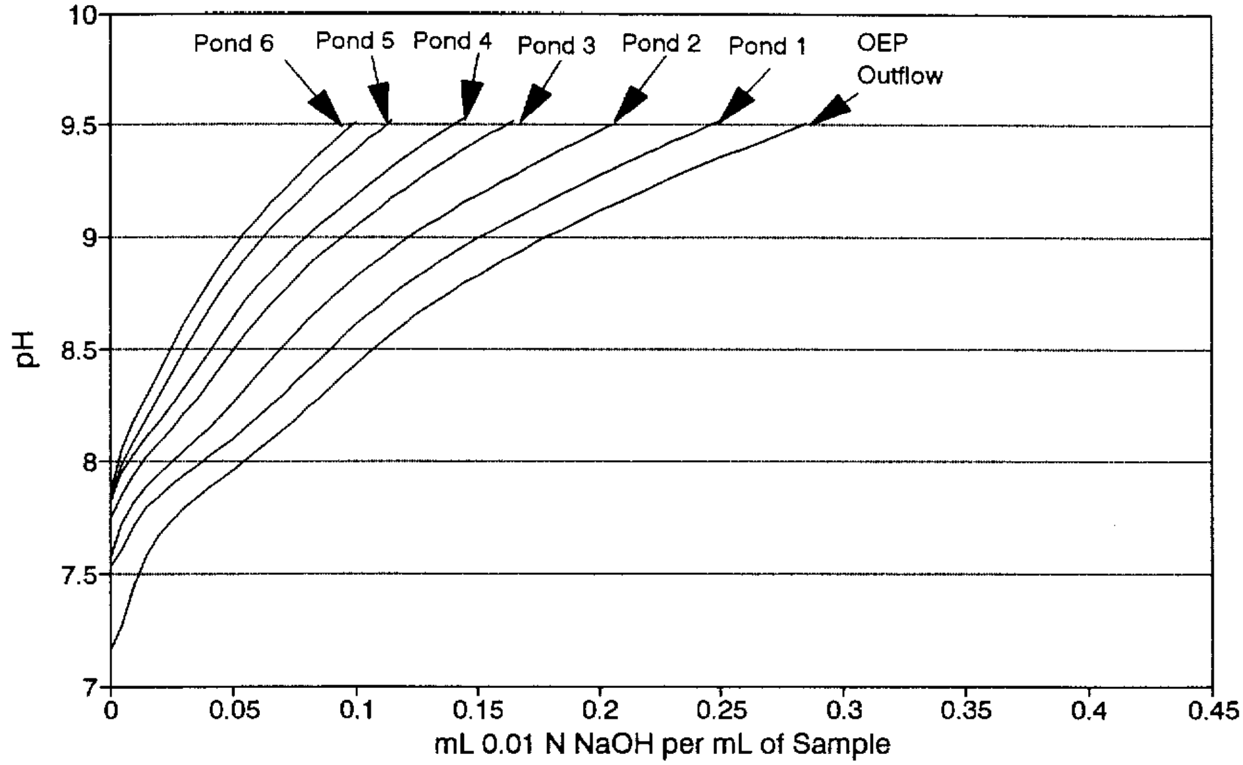


Fig. 3b: Polishing Ponds Acidities
August 29, 1993

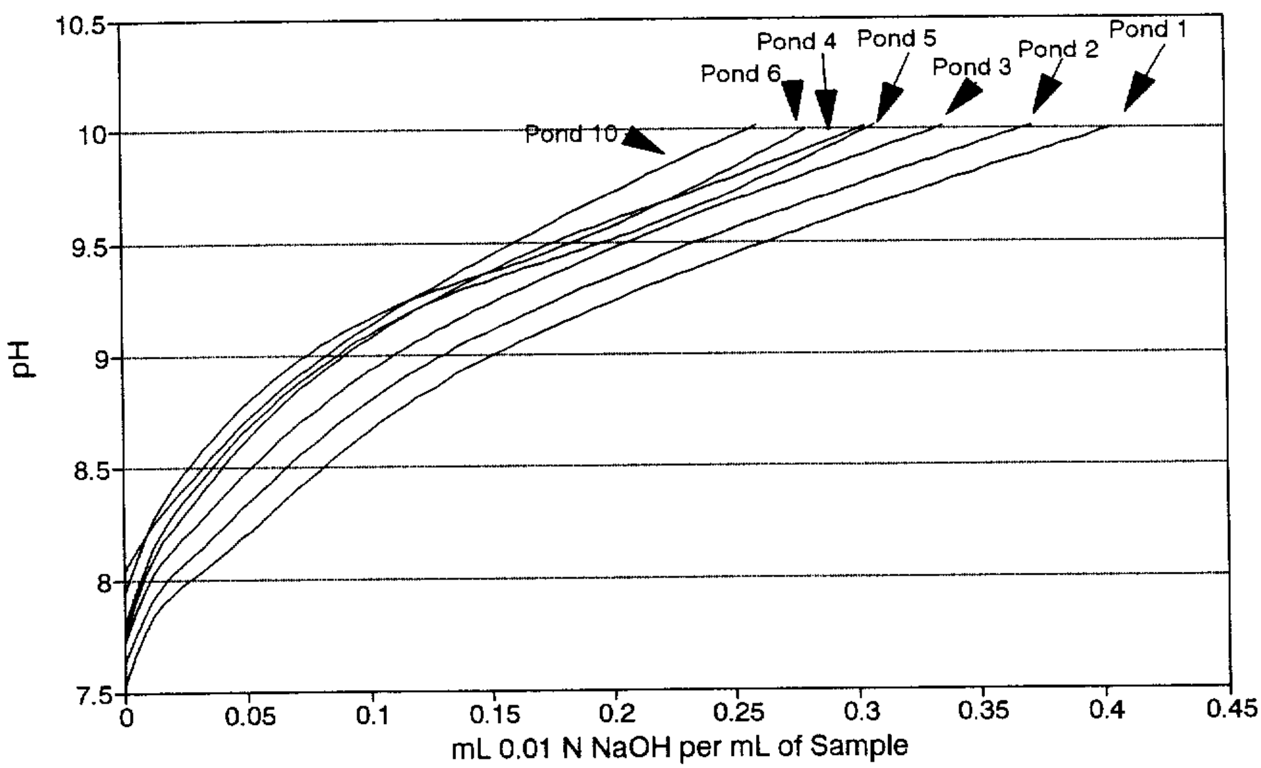


Fig. 3c: Polishing Ponds Alkalinities
May 28, 1992

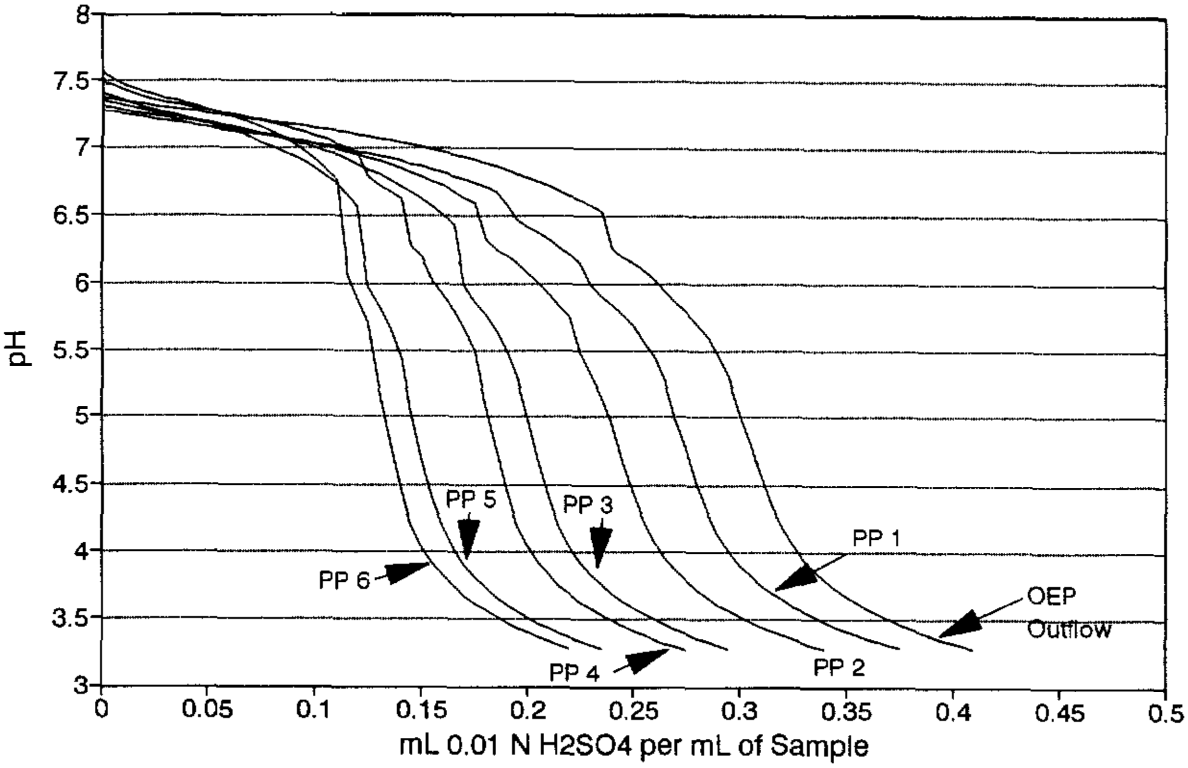
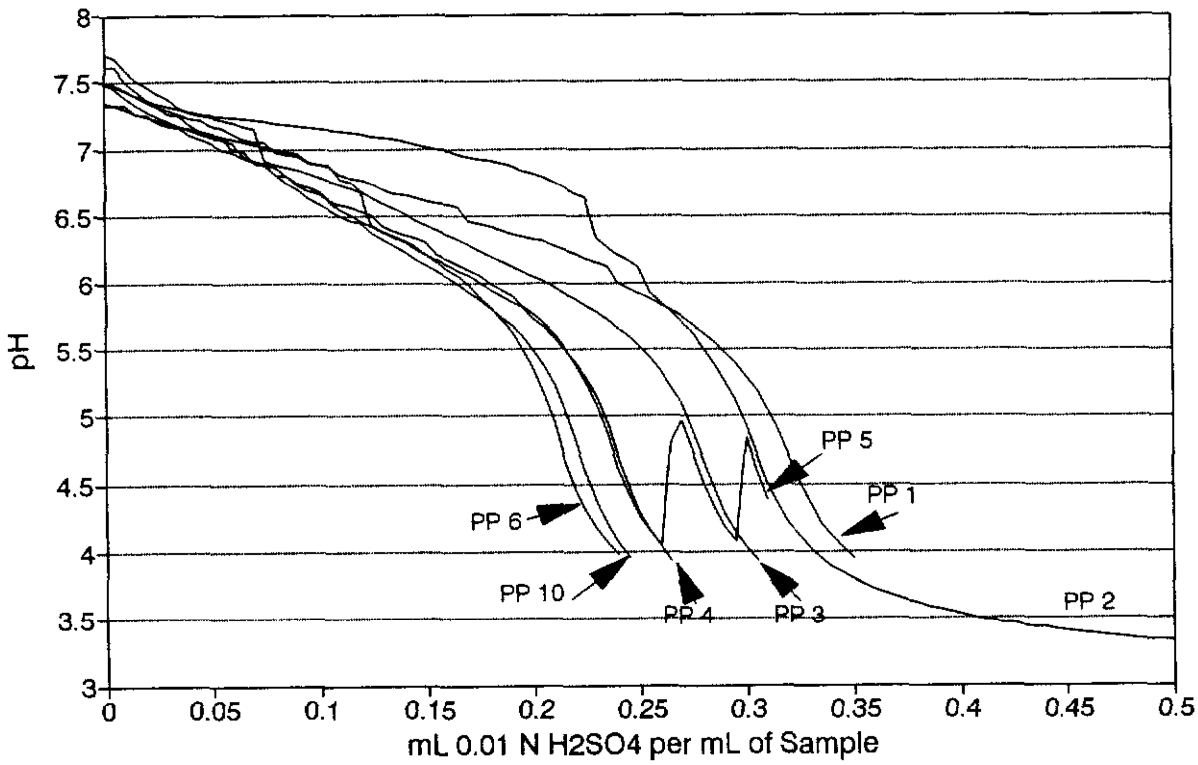


Fig. 3d: Polishing Ponds Alkalinities
August 29, 1993



Two approaches have been selected in order to arrive at the key operating parameters. The first approach examined the overall performance of PP1 to PP6, in terms of zinc removal, according to flow rates and subsequent retention times. Assuming that the same physical, chemical and biological processes will operate in a scaled-up Biological Polishing system, the dimensions of the ponds and the flow will determine the retention times and the expected performance can be projected.

The second approach to arrive at process performance uses algal growth rates and biomass zinc concentrations. These values can be used to estimate removal rates by the algal population for comparison with zinc loadings.

The two approaches assume that performance of the process is either purely a function of retention time (First Approach), or only biological in nature (Second Approach), neither of which being exclusively the case.

Thus, it is not surprising to find that, when percent zinc removal is calculated for the newly constructed scaled-up ponds, some zinc removal is taking place despite an extremely low retention time of 1 to 2 days and low algal biomass grown to date (Table 1). The calculations based on PP1 to PP6 data indicated a minimum retention time of 14 days for 68 % zinc removal. The new scaled-up polishing ponds (PP11, PP12, and PP13) show as much as 27 % zinc decrease with a retention time of less than 3 days.

Construction of Polishing Ponds 11, 12 and 13 was completed only in late fall, 1993. Alder brush, provided as a substrate for algal growth, was then placed on top of the ice cover in November, 1993. Since all of the flooded pit discharge had been passing through PP10 to PP13 (9.5 to 14.5 $l.s^{-1}$), retention times were very low in each pond, ranging from 0.91 to 3.29 days (Table 1). Adsorption of zinc onto any organics in the ponds is certainly an additional process which assists in zinc removal, independent of the biological polishing.

Table 1: Polishing Ponds 11 to 13, 1993 start-up.

Date	Polishing Pond	Flow USGPM	Flow L/s	Inflow [Zn]	[Zn], mg/L In outflow	[Zn], mg/L decrease	% [Zn] Decrease	Volume (m3)	Retention Time, days
23-Oct-93	11	180	11.36	19.15	17.3	1.85	9.7%	1138	1.16
	12	180	11.36	17.3	15.45	1.85	10.7%	1848	1.88
	13	180	11.36	15.45	11.25	4.2	27.2%	2693	2.74
30-Oct-93	11	220	13.88	22.85	18.855	3.995	17.5%	1138	0.95
	12	220	13.88	18.86	17.25	1.605	8.5%	1848	1.54
	13	220	13.88	17.25	12.6	4.65	27.0%	2693	2.25
08-Nov-93	11	230	14.51	19.5	18.95	0.55	2.8%	1138	0.91
	12	230	14.51	18.95	17	1.95	10.3%	1848	1.47
	13	230	14.51	17	15.45	1.55	9.1%	2693	2.15
14-Nov-93	11	200	12.62	19.65	18.8	0.85	4.3%	1138	1.04
	12	200	12.62	18.8	18.05	0.75	4.0%	1848	1.70
	13	200	12.62	18.05	16.95	1.1	6.1%	2693	2.47
21-Nov-93	11	225	14.20	18.45	16.355	2.095	11.4%	1138	0.93
	12	225	14.20	16.36	17.3	-0.945	-5.8%	1848	1.51
	13	225	14.20	17.32	17.65	-0.33	-1.9%	2693	2.20
28-Nov-93	11	150	9.46	20.25	19.8	0.45	2.2%	1138	1.39
	12	150	9.46	19.8	20.15	-0.35	-1.8%	1848	2.26
	13	150	9.46	20.15	19.25	0.9	4.5%	2693	3.29

Using the two regression lines calculated in the section above, the projected performance of Polishing Ponds 10 through 13 can be estimated according to the first approach. Based on 2.2% zinc removal with each day of retention time (winter), 99 % zinc removal is estimated for the scaled-up PP10 to PP13, if the inflow is set at 1.55 $l.s^{-1}$, providing a retention time of 45 days (Table 2a).

Based on 5.2 % zinc removal per day (summer), 98% zinc removal is estimated at an inflow of 3.7 $l.s^{-1}$ (19 day retention time; Table 2b). The overall relationship between percent zinc removal, flow and retention time, estimated by the two regression lines, is shown in Figure 4a.

Table 2: Projected performance of Polishing Ponds 10, 11, 12 and 13.

2A: PROJECTED PERFORMANCE ACCORDING TO PP 1 TO 6 DATA	All Performance Data	Performance of Top 8 Dates	Units
Inflow set at	1.55	3.7	L/s
Total Pond System Volume	5998	5998	m^3
Residence time in system	45	19	days
Percent Zn removal, accordng to PP1-PP6 data	99	98	Percent

2B: PROJECTED PERFORMANCE: PP10 ALGAL GROWTH AND ZN CONTENT	1992 Projection	1993 Projection	Units
Growth rate (Avg 1993 Netting,Branch data)		0.745	g/m^2/day (100 d growing season)
	0.5 - 1.0	0.204	g/m^2/day over 1 year (no growth in winter)
Zinc content in PP10 algae ((1993 data)	62	115	g/kg dry wt
Alder surface area in ponds (2.8 trees/m^3)	900	17130	m^2 of trees
Zinc removed per day in polishing pond	0.007 (PP10,320 m3)	0.40 (PP10-13,5998 m3)	kg/day
1993 Avg [Zn] in OEP discharge	20	20	mg/L

Fig. 4a: Projected Zn Removal
Performance Data to Date

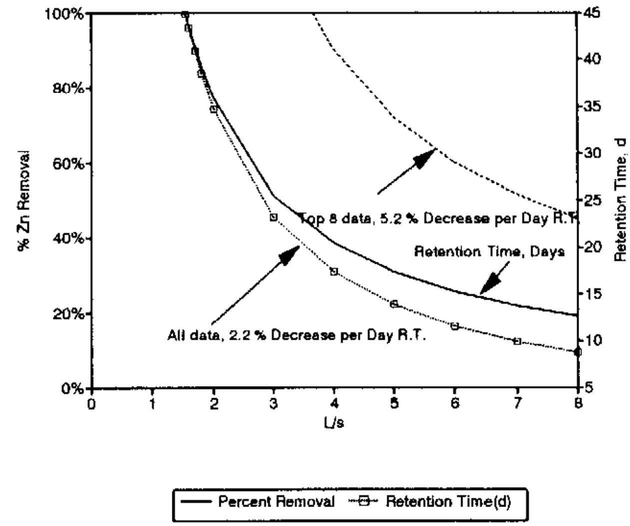
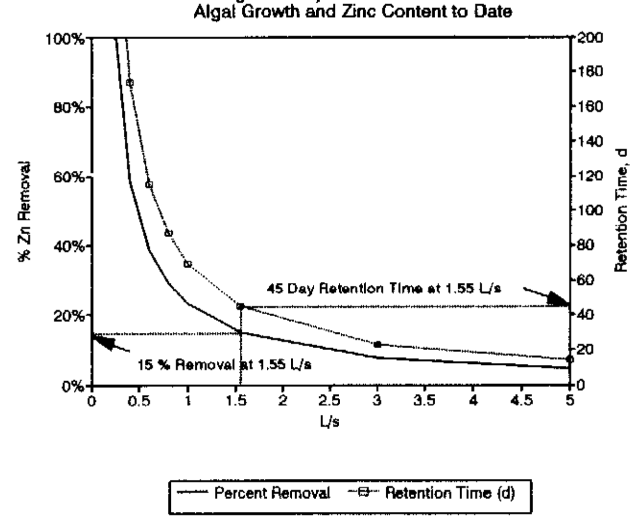


Fig. 4b: Projected Zinc Removal
Algal Growth and Zinc Content to Date



The second approach to projecting performance of the scaled-up Polishing Ponds is based strictly on algal growth rates and algal zinc content, which collectively determine the amount of new algal biomass, and subsequently the amount of zinc which can be removed, in a polishing system of a given volume per day.

Using 1992 algal growth rate data and zinc concentrations in algal biomass, it was projected in the 1992 report that algal biomass growing on alder trees could remove 115 g Zn per tree per year, or in alternative units, 121 g Zn per m^2 of tree per year (1 tree = 0.95 m^2). Using the growth data accumulated on alder branches placed in PP10, the average 1993 growth rate is estimated at 0.745 g per m^2 of substrate (tree or netting) per day (Table 2b). Assuming a growing season of 100 days, this average growth rate for the year is 0.204 g per m^2 of substrate per day (0.745 $g.m^2.d^{-1}$ * [100 d ÷ 365 d]).

These growth rates fall within the range of growth rates determined in the period October 1991 through July 1992 for the experimental ponds, PP1 to PP6. Growth rates ranged from 0.1 to 3.1 g per m^2 of substrate per day. In 1993, fertilizer (Plant Prod 10-52-10) was regularly added to Polishing Pond 10 between June 25 and July 12, 1993. Higher growth rates were anticipated as was noted in PP1 to PP6 where fertilizer was added to the peritraps. Growth rates had increased by September, 1992, to 1.5 to 4.7 $g.m^2.d^{-1}$.

In Table 3, the elemental composition of the algae is summarized. Generally, healthy plants contain on a dry weight basis 0.1 to 0.8 % phosphorus. The phosphorus content of the PP algae, 0.6 to 2.5 %, is well within this healthy range. Comparing the elemental compositions of the algae grown on netting supplemented with slow release fertilizer packets (PP6, PP10) and that growing the branches in the pond supplemented with liquid fertilizer (PP6), no consistent differences can be noted. Overall, brush cuttings and plastic netting support algal populations of similar elemental composition.

Table 3: Elemental concentrations in 1993 Polishing Pond algae.

% Dry wt.	PP 6 Algae on Perinet netting	PP 6 Algae on branches	PP 10 Algae on Perinet netting
Al	0.28	0.78	1.65
Ca	19.3	7.65	4.26
Fe	2.07	9.52	3.51
Mn	1.34	3.52	1.7
P	0.63	2.49	1.51
Zn	2.73	4.76	11.5
% L.O.I.	34	31	31

In Table 2b, the adjusted algal growth rate (0.204 $g.m^2.d^{-1}$) is used in combination with the 1993 zinc content in Polishing Pond 10 algae (115 kg.kg dry wt of $algae^{-1}$), and the number of trees in Polishing Ponds 10 through 13 required to achieve an average density of 2.8 trees per m^3 of pond (17,130 trees), to estimate zinc removal in the system per day. Using these values, 0.40 kg of zinc would be captured by the algal biomass growing each day in the scaled-up Polishing Pond system.

Using 20 $mg.L^{-1}$ zinc as the average zinc concentration in flooded pit discharge, it can be seen in Figure 4b that this Polishing Pond system could remove only 15 % of the zinc if the inflow was kept at 1.55 $L.s^{-1}$, or effectively, a retention time of 45 days. From these considerations, the use of the growth rate of, and the zinc content in, the algal biomass (Second Approach) to project percent zinc removal performance gives a very low estimate, compared to the Second Approach, where zinc concentrations changes (due to the operation of all zinc removal processes) are related to flow rates and the retention time (Table 2a and Figure 4a).

In Table 3, the elemental composition of the algae in PP10 is summarized. Generally, healthy plants contain on a dry weight basis 0.1 to 0.8 % phosphorus. The phosphorus content of the PP10 algae, 0.6 to 2.5 %, is well within this healthy range. Comparing the elemental compositions of the algae grown on netting supplemented with slow release fertilizer packets (PP6, PP10) and that growing the branches in the pond supplemented with liquid fertilizer (PP6), no consistent differences can be noted. Overall, brush cuttings and plastic netting support algal populations, and result in similar elemental composition. The remarkably high zinc concentration in the biomass, 11 %, is noteworthy.

2.3 Substrate Standardization

In 1993, a more easily standardized method of quantifying algal growth was applied, compared to the original unit, algal growth per surface area of tree branch. Units of plastic netting (Dupont tubular webbing) of known surface areas, termed perinets, were suspended in neutral pH Buchans polishing ponds and in the Boomerang Lake, South Bay (pH 3.2), and algal biomass was quantified after a given number of days. Each perinet unit contained a packet of slow release fertilizer. Details of the data collected are given in Appendix 1 and 2.

The Buchans polishing ponds perinets produced 0.806 $g.m^{-2}$ $netting.d^{-1}$ on average, with a minimum of 0.269 $g.m^{-2}.d^{-1}$ and a maximum of 1.781 $g.m^{-2}.d^{-1}$ (Table 4a). These growth rates are comparable to the average 1993 growth rates derived from the biomass collected from the branches in the Buchans polishing ponds (1.248 $g.m^{-2}.d^{-1}$ on average; Table 4a). Therefore, the nutrients supplied by the packets of slow release fertilizer did not appreciably increase the algal growth rate on the perinets, compared to growth on the branches. With addition of nutrients (July, 1993), the neutral pH polishing ponds contained adequate nutrients for good algal growth.

In contrast, the slow release fertilizer stimulated growth of periphytic algae on the perinets in Boomerang Lake (0.296 $g.m^{-2}.d^{-1}$), compared to biomass growing on brush cuttings branches (0.017 $g.m^{-2}.d^{-1}$; Table 4b). This lake is relatively nutrient poor.

Table 4a: Summary of 1993 Periphyton Growth Rates - Buchans Polishing Ponds

SUBSTRATE	n	Min.	Max.	Avg.	Std. Dev.
Perinets, g/m2/day	12	0.269	1.781	0.806	0.451
LOI, %	9	21	35	30	5
Branches, g/m2/day	3	0.769	1.949	1.248	0.507
LOI, %	3	18	31	25	5

Table 4b: Summary of 1993 Periphyton Growth Rates - Boomerang Lake

SUBSTRATE	n	Min.	Max.	Avg.	Std. Dev.
Perinets, g/m2/day	18	0.134	0.675	0.296	0.138
LOI, %	11	31	43	38	3
Branches, g/m2/day	15	0.006	0.039	0.017	0.009
LOI, %	15	18	46	33	7

Overall, it appears that brush cuttings are not preferred by the algal population over nylon netting as a growth substrate, and that netting could serve well as a substitute for brush cuttings, where required.

2.4 Model Improvements and Verification

The purpose of the earlier model reported in I993 was to account for the observed decrease in metal concentrations in lakes and ponds in which periphytic algae have established. The model is based on empirical studies of periphytic growth and metal bioaccumulation, and is intended for use in polishing pond design. This section summarizes the previous biological polishing models developed for two sites, one at South Bay, Ontario, and one at Buchans, Newfoundland.

Two approaches have been selected to identify the key operating parameters of the process which were discussed in the previous sections for the Buchans effluent. They are here described in the form of the model, which is aimed to provide, ultimately, a tool to evaluate the process.

It should be emphasized that the final aim of modelling is to construct a biological polishing model which interrelates the various hydrological, biological, and geochemical cycles within the reactor system. As will be discussed in the following sections of this report, sediment chemistry is extremely important, especially iron cycling and, thus, for understanding the mass balance within a reactor system. Drawing on results obtained from the quantification of sedimentation rates and the composition of the collected precipitate, a lake/pond model is presented which can explain better the recent data from the field sites.

2.4.1 Summary of Biological Polishing Models

The application models for South Bay and Buchans are best described as algorithms for estimating the amount of metal contaminant sequestered by algae. Two main modelling approaches have been taken:

Overall Performance Model: In this approach, the metal removal for a reactor system is plotted against residence time. The amount of metal sequestered is assumed to depend only on residence time, determined by the volume of, and flow rate through, the system.

Algae Growth Model: In this model, the metal removal is quantified by assessing algal growth rates and biomass metal concentration. Model variables are measured both in the field and laboratory, and are logically related in a sequence of steps. The amount of metal removed by the periphyton is calculated by the following procedure:

1. Measure the density of the periphyton-precipitate complex (PPC) on trees and branches serving as substrate.
2. Estimate the growth rate of periphyton by using growth rate data from the field and laboratory.
3. Measure the density of metal within the PPCs.
4. Calculate the amount of metal sequestered by the algae by multiplying the growth rate by the metal concentrations in PPCs.

The metal removal rates within the reactor systems can also be measured directly by the following procedure:

(i) Measure the input metal loadings.

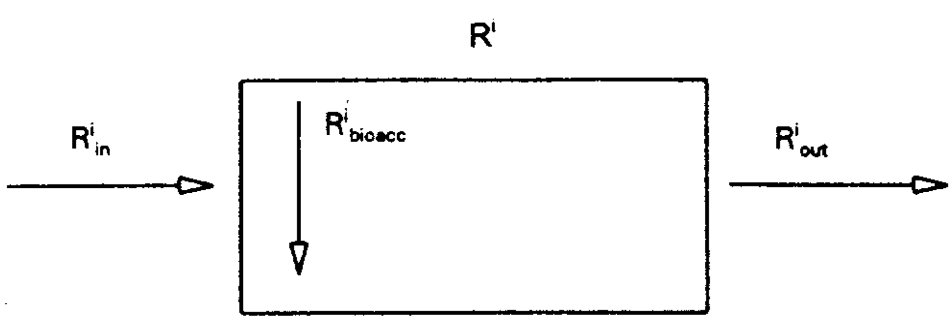
(ii) Measure the output loadings (i.e. the amount of metal leaving the lake/pond).

(iii) Calculate the net loading, i.e., the difference between (i) and (ii).

If algal bioaccumulation is the only metal sink in the reactor, then the amount of metal sequestered by the periphyton calculated in '4' above ought to equal the amount of metal actually deposited to the system as determined in (iii). This is, therefore, an important verification of the model. Before summarizing the results from South Bay and Buchans in terms of the algal growth model, the model is cast into algebraic form - in a so-called "box model".

In the simplest case, spatial variation is ignored and, instead, the system is idealized as a single box. Here, the first version of the 1993 polishing model is summarized; later, the additions which will be made to this model will be introduced. Schematic 1 shows the inflow rate, and outflow rate of species "i" to the box, and the removal rate of a species "i" within the box:

Schematic 1: 1993 Biological Polishing Box Model (simplest case).



R^i_{in}	= inflow rate of species i, Mass per unit Time ($M.T^{-1}$)	(1)
R^i_{out}	= outflow rate of species i ($M.T^{-1}$)	
R^i_{bioacc}	= rate at which algae bioaccumulate species i ($M.T^{-1}$)	
R^i	= rate of change of species i in lake/pond water ($M.T^{-1}$)	

Applying conservation of mass to the box gives the rate balance condition:

$$R^i = R^i_{in} - R^i_{out} - R^i_{bioacc} \qquad (2)$$

This equation simply states that the rate at which a species accumulates in the lake/pond water must equal the rate at which it flows in, minus the rate at which it flows out, minus the rate at which it is sequestered by the algae. The term accounting for bioaccumulation, R^i_{bioacc}, is calculated according to the procedure outlined above. Notice, at this stage, no account is made of metal cycling to and from the sediments.

2.4.2 Field Measurements

The above algae bioaccumulation model is now compared to the 1993 rate data for Boomerang Lake and the Buchans polishing ponds.

Boomerang Lake: The metal concentrations in Boomerang Lake have not increased markedly for a number of years. Table 5 summarizes the results for Boomerang Lake on the basis of the model presented. It is clear that the model does not account particularly well for Fe dynamics in Boomerang Lake, although it does not do badly for Zn and Al.

Table 5: Boomerang Lake, South Bay, Ontario (1993).

Metal i	R^i_{in}-R^i_{out} ($t.yr^{-1}$)	R^i_{bioacc} ($t.yr^{-1}$)	R^i ($t.yr^{-1}$)
Fe	2.0	80	- 78
Zn	1.2	0.15	+1.05
~~Al~~ SO_4	57.3 0.075 126.8 - 75.5 (t.yr^{-1})	0.4 na	-0.325 51.3 $t yr^{-1}$

* see Table 7

On the basis of Table 5, the [Fe] would be decreasing, [Zn] would be increasing, and [Al] would be decreasing in Boomerang Lake. Given the difficulty of estimating loadings and bioaccumulation, only the mass balance for Fe indicates trouble for the model.

The discrepancy between the model R^i and field observations suggests that some additional source of Fe must exist in Boomerang Lake. In this report it is proposed that Fe cycling from the sediments is vitally important in accounting for the Fe dynamics in Boomerang Lake. It is posited that Fe is re-cycled within lake, so that both a new source (diffusion from the sediments) and sink (sedimentation) should be added to the model.

Buchans: For the Buchans polishing ponds, the model gives slightly better results for Zn. Given the error in estimating loadings, growth rates, and algal metal concentration, the results are encouraging.

Table 6: Polishing Ponds, Buchans, Newfoundland (1993).

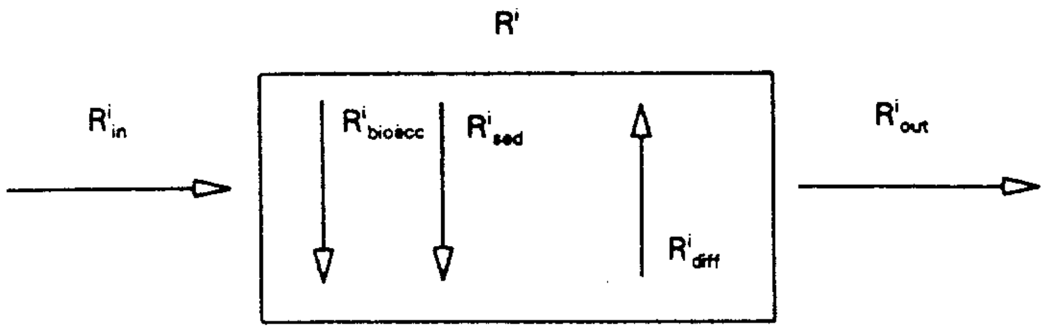
Metal i	R^i_{in}-R^i_{out} ($kg.yr^{-1}$)	R^i_{bioacc} ($kg.yr^{-1}$)	R^i ($kg.yr^{-1}$)
Zn	78	50	+28
Fe	32	88	-56
Al	< 1	10.6	-10.6

As in Boomerang Lake, in the Buchans polishing ponds some additional sources and sinks of Zn must be present since the algae alone cannot remove all of the Zn deposited in the ponds each year.

2.5 Iron Cycling: Additional Field Data for the System Model

In this section, some additions are made to the biological polishing models developed for Boomerang Lake at South Bay, Ontario, and for the polishing ponds constructed at Buchans, Newfoundland. The contaminant dynamics are framed in terms of rates, and the key equation is conservation of mass in a reactor system. The conceptual model is best summarized in Schematic 2 below:

Schematic 2: Biological Polishing Model with metal cycling.



$$R^i = R^i_{in} - R^i_{out} - R^i_{bioacc} - R^i_{sed} + R^i_{diff} \qquad (3)$$

Here

R^i_{in}	= rate of inflow of aqueous species i, Mass per unit Time ($M.T^{-1}$)
R^i_{out}	= rate of outflow of aqueous species i ($M.T^{-1}$)
R^i_{bioacc}	= rate of bioaccumulation of species i ($M.T^{-1}$)
R^i_{sed}	= rate at which species settles to sediment i ($M.T^{-1}$)
R^i_{diff}	= rate at which species in sediment is re-suspended into water column i ($M.T^{-1}$)
R^i	= rate of change of species in the lake/pond water i ($M.T^{-1}$)

Notice that cycling is now included in the model through the terms R^i_{sed} and R^i_{diff}. As discussed in the preceding sections, cycling - especially Fe cycling - has an important influence on the dynamics of all contaminants in the system. The same basic model applies to both Boomerang Lake and to Buchans' polishing ponds; however, the actual values for the various rates will be different.

2.5.1 Field Measurements

Boomerang Lake: Average annual rates for the various terms going into the overall mass balance of species i were calculated based on the field and literature data. These are summarized in Table 7.

Table 7: Mass Balance for Boomerang Lake (1993-1994).

Species i	R^i_{in} ($t.yr^{-1}$)	R^i_{out} ($t.yr^{-1}$)	R^i_{bioacc} ($t.yr^{-1}$	R^i_{sed} ($t.yr^{-1}$)	R^i_{diff} ($t.yr^{-1}$)	R^i ($t.yr^{-1}$)
Fe	5.0	0.61	80	29	58	-44
Zn	18.7	2.5	0.144	1.3	-10	-4.7
SO_4^-	126.8	75.5	na	15	937	973

The data presented suggest that the biological polishing model, based on algal sequestration, is encouraging but needs further development. For example, according to the model, in Boomerang Lake the Fe concentration should be decreasing by 44 $mg.l^{-1}.yr^{-1}$, and the Zn concentration by 4.7 $mg.l^{-1}.yr^{-1}$ (the volume of Boomerang Lake is approximately $1O^6 m^3$). Under the assumption that R^{SO4}_{bioacc} is negligible, the SO_4^- concentration should be increasing by 973 $mg.l^{-1}.yr^{-1}$.

These numbers require some explanation. To begin with, R^i_{in} and R^i_{out} are estimated from hydrological assessments of the site. Typically, loadings to a lake from a drainage basin are diffuse and cannot be precisely quantified. The values presented are representative of best estimates. Since R^i_{sed} is relatively straightforward to measure using sedimentation traps, the values presented are sound. On the other hand, R^{i}_{bioacc} is difficult to estimate. The bioaccumulation rate is calculated by measuring metal concentrations in the periphyton, estimating the periphyton growth rate, and by estimating the total number of trees in the lake. Estimating the number of trees (hence total surface area on which algae grow) is difficult as the branches were delivered as truck loads of cut brush. It may well be that R^{Fe}_{bioacc} and R^{Zn}_{bioacc} are overestimated in our calculations.

Finally R^{i}_{diff} is calculated from pore water peeper data collected in 1993 and considerations of diffusion based on Fick's Law. These parameters are probably close to their actual value. Because the diffusion fluxes are maximum values, our model suggests another mechanism for transferring species from the sediment to the water column operates. Although the rates presented may differ somewhat from actual values, it is more likely that additional mechanisms within the Boomerang Lake system are responsible for the weak fit between model and data. In brief, the model needs additional sources and sinks. One possible candidate is physical re-suspension of iron hydroxide as a result of perturbation of sediment back into the water column by the action of currents in the lake.

Buchans: The sources and sinks of Zn for the Buchans polishing ponds are summarized in Table 8.

Table 8: Mass Balance for Buchans Polishing Ponds.

Species i	R^{i}_{in} ($kg.yr^{-1}$)	R^{i}_{out} ($kg.yr^{-1}$)	R^{i}_{bioacc} ($kg.yr^{-1}$)	R^{i}_{sed} ($kg.yr^{-1}$)	R^{i}_{diff} ($kg.yr^{-1}$)	R^{i} ($kg.yr^{-1}$)
Zn	166.7	88.8	50.3	na	-0.032	28
Fe	32.4	2.06	88	na	0.62	-57
Al	0.29	0.29	10.6	na	0.067	-10.5

On the basis of the model, $R^{Zn} = 28$ kg.yr^{-1}, predicting an increase in zinc concentration in the ponds over the last year of 116 mg.l^{-1} (volume of ponds is taken as 240 m^3). Clearly, some explanation is required. R^{Zn}_{diff} is calculated using Fick's Law in the same way sediment fluxes were calculated in Boomerang Lake, and represents the maximum diffusion flux from the sediments. R^{Zn}_{bioacc} is calculated indirectly by measuring density of Zn in periphyton, estimating the growth rate of the algae, and by estimating the number of alder branches in the ponds. The estimation of number of branches (hence growing surface) is subject to error. Finally, no account has been made of either R^{Zn}_{sed} or of re-cycling from the sediments to date. These terms are important for overall mass balance, and will be determined in future work.

2.6 Continuous Time Reactor Models

The values given in Table 7 and Table 8 are average rates over a year and do not consider differences which take place in the different seasons, when the lakes or the ponds are covered with ice. In reality, the dynamics of contaminants in a lake operate continuously, and should be described in terms of differential equations.

Applying conservation of mass to species i at each instant t gives a mass balance condition valid at all times t:

$$R^i(t) = R^i_{in}(t) - R^i_{out}(t) - R^i_{bioacc}(t) - R^i_{sed}(t) + R^i_{diff}(t) + R^i_{resusp}(t) \quad (4)$$

Here

$R^i(t)$ = rate of change of species i in the lake/pond water (M.T^{-1})

The other terms are interpreted similarly.

Notice that cycling is now included in the model through the terms $R^i_{sed}(t)$ and $R^i_{diff}(t)$. As discussed in the preceding sections, cycling - especially Fe cycling - has an important influence on the dynamics of all contaminants in the systems. The same basic model will apply to both Boomerang Lake and to Buchans polishing ponds. However, the actual values for the various rates will be different.

The total mass of species i in the lake/pond water at time t is represented as:

$$M^i(t) = VC^i(t) \tag{4}$$

where

V = volume of the lake/pond (L^3).

$C^i(t)$ = concentration of species i in the lake/pond water ($M.L^{-3}$)

The instantaneous rate of change of species i, $R^i(t)$, is the derivative of $M^i(t)$:

$$R^i(t) = \frac{dM^i(t)}{dt} = V\frac{dC^i(t)}{dt} \tag{5}$$

Depending on how the various terms in Equation 4 are represented mathematically, different rate equations result. Here a tentative model is presented for the dynamics of species i in a reactor system:

$$\frac{dC^i(t)}{dt} = k_{ex}(t)C^i_{in}(t)-k_{ex(t)}C^i_{out}(t)-\frac{C^i(t)\ n\ A_{tree}}{C^i(t)+K_m}\frac{da(t)}{dt}-v_{set}A_{l.b.}C^i(t)+A_{l.b.}J_{diff}(t) \tag{6}$$

$$\frac{da(t)}{dt} = (G_p-D_p)a(t) \tag{7}$$

Here

$C^i(t)$ = concentration of species i in lake/pond water ($M.L^{-3}$)

$a(t)$ = density of periphyton on branches ($M.L^{-2}$)

kex(t) = Q(t)/V where Q(t) is inflow rate of water ($L^3.T^{-1}$)

K_m = Half-saturation constant ($M.L^{-3}$)

n = number of trees in the system

A_{tree} = surface area of a standard tree (L_2)

$A_{l.b.}$ = Area of lake/pond bottom (L^2)

v_{set} = Settling velocity of precipitated species in water column ($L.T^{-1}$)

$C^i_{prec(t)}$ = Concentration of precipitated species in water column ($M.L^{-3}$)

$J_{diff}(t)$ = Fick diffusion ($M.L^{-2}.T^{-1}$)

The dynamics of all the species in the system is then represented by a coupled set of differential equations, one balanced equation for each species.

In building lake/pond models, it is important to carefully measure all variables appearing in the model in order to calibrate and ultimately verify the model. The concentrations of various contaminants should be measured throughout the year at regular intervals, as should the various kinetic coefficients, and system parameters such as $k_{ex}(t)$, $A_{l.b.}$, and v_{set}. Once all these are measured, the time variation predicted by the model can be compared to the data.

In summary, continuous time models are a refinement on models based on yearly or seasonal averages. The main challenge remains to arrive at measured loading rates, growth rates, sedimentation rates, and re-cycling rates, and to test model predictions against these.

3.0 SEDIMENT CHEMISTRY: IRON CYCLING

3.1 Iron Chemistry and Cycling in the Aquatic Environment

Iron is an abundant element. Sedimentary rocks, overall, comprise 5 to 6 % iron (Stumm and Sulzberger, 1992). Chemically, iron is very reactive and, through redox reactions, probably had a major role in establishing the oxygen content of the atmosphere on earth. This element is required by all organisms in trace quantities and is used by some microorganisms in energy-releasing electron transfers. Iron can exist in the oxidation states Fe^0, Fe^{2+} and Fe^{3+}. Fe^0 rarely occurs in nature since it is readily oxidised to Fe^{2+} in most environments.

The oxidation of Fe^{2+}, the reduction of Fe^{3+} and subsequent chemical reactions are very important in determining iron concentration and mobility between environmental compartments. Iron oxidation is important in the formation of minerals including soil components. This process is also important in acid generation which takes place in mining wastes, and is also very relevant in metal recovery processes by leaching.

This literature review emphasizes the microbial aspects of the iron cycle between sediments and water, as this is relevant to processes which could ameliorate or enhance acidic conditions.

The surface chemistry of the solid phases of iron compounds enables them to act as semiconductors, which can participate in photoredox reactions. The reactivity of the surfaces and the large surface area of iron solid phases (such as oxyhydroxides or geothite which predominate in most ecosystems), play a major role in adsorption of a wide diversity of solutes. Hence the iron cycle is interdependent with that of many elements, organics and oxyanions such as phosphate.

Many of the reactions involving iron are mediated by, or catalysed directly or indirectly by, microorganisms (Ehrlich, 1990; Ghiorse, 1988; Lovley, 1991, 1993). Microbial ecology and physiology are therefore essential components in controlling iron cycling in ecosystems.

Iron reduction will increase the dissolved iron concentration in the sediments, but this process may assist in ameliorating AMD. This process results in a net consumption of protons (Stumm and Morgan, 1981; Mills et al., 1989) and an increase in pH, which will result in the precipitation of metals as hydroxides (aluminum) or sulphides (zinc, nickel, iron, copper). A similar phenomenon is associated with sulphate reduction, which is fuelled by sulphate, another ion abundant in AMD.

Sulphate reduction is inhibited by Fe^{3+} reduction (Chapelle and Lovley, 1992) but is likely to occur deeper in sediments where the Fe^{3+} does not penetrate. The significance of abiotic reduction of Fe^{3+} is not clear, but it is worth noting that photo-reduction of iron can substantially increase the dissolved Fe^{2+} concentration in streams

(McKnight et al., 1988) or wetlands (Wieder, 1992) receiving AMD.

The enhancement of reducing conditions may provide a means of ameliorating AMD. Wetlands have been designed to enhance bacterial sulphate reduction (EPA, 1993) and the importance of iron reduction in constructed wetlands for AMD is now being realised (Wieder, 1992).

Pond systems have been designed to promote reducing conditions for AMD treatment (Kalin, 1993). Such systems incorporate oxidation and reduction cells, both of which help ameliorate AMD. The oxidation cells are designed to remove iron by oxidation, hydrolysis and precipitation, and other metals by co-precipitation. In the reducing cells, additions of readily decomposable organic materials rapidly produce reducing conditions (through fermentation reactions), which support iron and sulphate reduction processes.

Recently, progress has been made in modelling the overall iron cycling in lake ecosystems (Stumm and Sulzberger, 1992; Barry et al., 1994; Deng and Stumm, 1994). In general, the stratum of water above the thermocline is oxic and well mixed, providing favourable conditions for abiotic oxidation, hydrolysis and precipitation as Fe^{3+} oxyhydroxide colloids of any iron entering the system.

In lake sediments, or below lake thermoclines, oxygen concentrations decline rapidly with depth and reducing conditions predominate, favouring the reductive dissolution of

Fe^{3+} oxyhydroxides.

Iron Oxidation: In most water bodies and soils, oxidising conditions predominate. If the pH exceeds 5, any Fe^{2+} present is readily oxidised abiotically to Fe^{3+}. At pH < 5, chemically-mediated oxidation rates are slow. However, it is now well established that at low pH (< 3), bacteria mediate the oxidation of Fe^{2+} as a source of energy, where Fe^{2+} is the electron donor for respiration. The bacterially-mediated oxidation is a very important process in acid generation in mining wastes and also in bioleach processes for the recovery of metals. The oxidation of pyrite ores in particular has been extensively studied, owing to this process's economic importance. However, the microbial ecology of iron oxidation, the mechanism of this process and its role in natural ecosystems is still poorly understood.

Fe^{3+} is readily hydrolysed and precipitated as Fe^{3+} oxyhydroxides when the pH exceeds 5. Fe^{3+} may also be removed from solution by adsorption, ion exchange and complexation processes. The role of bacteria in Fe^{2+} oxidation at pH > 5 is uncertain because of the ease of abiotic oxidation in such conditions. *Gallionella spp.* can carry out this reaction at near neutral pH but requires a low redox potential. It is reported to be active at the boundary of oxidising and reducing conditions in sediments. Since bacteria are undoubtedly associated with surfaces where most oxidation occurs, it is likely that, even if not directly involved in the oxidation process, they will have a significant effect on the processing and transport of products of oxidation. For example, Fe^{3+} oxyhydroxides have been shown to accumulate on the surfaces of bacteria in near neutral lakes (Ferris et al., 1989a, b).

Fe^{2+} oxidation by O_2 is influenced by many factors (Stumm and Sulzberger, 1992; Barry et al., 1994). Oxidation is favoured by the hydrolysis of Fe^{2+} compounds. The OH^- ligands present in such moieties increase reducing power substantially (Luther, 1990). Above pH 5, oxidation shows a second order dependence on OH^- concentration (Stumm and Lee, 1961), whereas at pH 3 to 5, the dependence is first order, and at pH < 3, zero order. In other words, the reaction is much slower in acidic conditions (Wehrli, 1990). At low pH (< 3), oxidation of pyrite is mediated by Fe^{3+} and catalysed by bacteria, such as *Thiobacillus ferrooxidans*.

The oxidation of Fe^{2+} in relation to the overall functioning of the aquatic environment is still poorly understood, but is likely a very important process in those sediments enriched with iron such as water bodies receiving AMD. The rate of Fe^{2+} oxidation may be increased by the presence of amorphous Fe^{3+} precipitates, organic ligands and reactive chemical species which may be photochemically or biotically generated, for instance H_2O_2 and O_3 (Stumm and Sulzberger, 1992).

<u>Iron Reduction:</u> When reducing conditions prevail in sediments, Fe^{3+} is reduced to Fe^{2+}. Where H_2S is present as a product of bacterial sulphate reduction (a process requiring reducing conditions and sufficient sulphate and hydrogen concentrations), Fe^{2+} is precipitated as iron sulphide. Iron reduction is also directly mediated by bacteria, either as a minor side reaction or with iron as the electron acceptor for respiration

(Lovley 1991, 1993). This process utilises Fe^{3+} hydroxides. The reduced Fe^{2+} is soluble in the sediment where the pH is generally higher than 5. Therefore, the net effect of this process is the dissolution of solid Fe^{3+} oxyhydroxides. The importance of this bacterially-mediated iron reduction has only recently been realised (Jones et al., 1983; Lovley 1991, 1993). It has been substantiated by the isolation and characterisation of bacteria able to couple oxidation of organic substrates to Fe^{3+} reduction as a source of energy (Lovley and Phillips, 1988; Semple and Westlake, 1987).

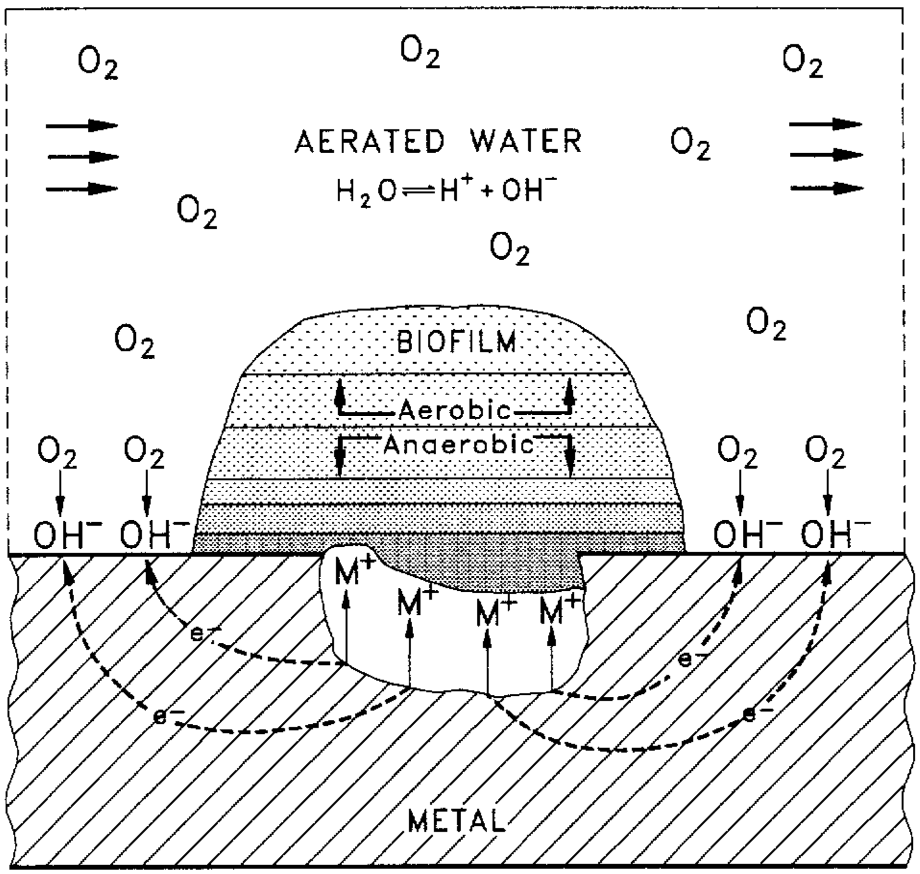
Microbial Fe^{3+} reduction provides a very important mechanism for the oxidation of natural or contaminant organic compounds in aquatic environments. Lignocellulose and carbohydrates are not used directly by Fe^{3+} reducing bacteria. Rather, they utilize products of microbially-mediated fermentations of organic matter which occur when oxygen has been used up. These products include short-chain fatty acids, alcohols, simple phenolics and hydrogen. Acetic acid, phenolics and hydrogen are oxidised completely to CO_2 by *Geobacter metalloreductans* (utilises short-chain fatty acids or aromatics) or *Shewanella putrefaciens* (utilizes H_2 or formate; Lovley, 1991). There are undoubtedly many other bacteria which can carry out oxidation of organics coupled to Fe^{3+} reduction in sediments, but few have been isolated and characterized to date.

It has been shown that iron reduction may not take place unless bacteria are present, a low redox potential prevails and suitable electron donors and acceptors are available. A further requirement is direct contact between the electron acceptor and the reducing organism (Lovley et al., 1991). In addition to bacterial mediation, Fe^{3+} reduction may be carried out through the *abiotic reductive dissolution* of Fe^{3+} oxyhydroxides, with or without photocatalysis (Stumm and Sulzberger. 1992; Deng and Stumm, 1994).

Biofilms: Conditions pertaining in the sediment as a whole are reflected on a smaller scale in biofilms. In sediments and soils, most surfaces are covered with organic matter. Often, this layer is comprised of carbohydrates derived from bacteria and other microorganisms. The properties of these 'biogels' are dominated by the presence of gradients. The bacteria are located at the bottom of the biofilm, attached to the substrate but furthest away from the aqueous medium. Therefore, the bacteria may be exposed to very different conditions from the external milieu, whether that be considered the open water or a single pore in the soil or sediment.

The structure and functioning of biofilms in relation to iron and sulphur cycling have been studied by Kuhl and Jorgensen (1992) and others, using microelectrodes to measure the concentrations of, for example, sulphate and oxygen. These studies indicate that there are sharp gradients within the biofilm, and that conditions within the biofilm change in response to changes within the medium outside the biofilm.

It is clear that the measurement of conditions in the bulk medium will not give an indication of reactions occurring on surfaces within biofilms. Another important consideration with respect to biofilms is that changes occurring within the biofilm may not result in changes in the medium. Recycling of iron may occur within the biofilm as given in Schematic 3, modified after Characklis et al. (1990). The location and functioning of biofilms will change continuously, due to the accumulation of precipitates and depletion of substrates. The functioning of biofilms in ecosystems is not clearly elucidated but is, in all likelihood, of great importance in determining overall concentrations of many ions in the pore water of sediments.



SCHEMATIC 3: CROSS-SECTION OF BIOFILM
(after Little et al., 1990)

Iron Adsorption: In addition to the direct effects of redox conditions and pH on the form of iron and its abundance in the sediment, iron concentrations are appreciably affected by 'sorption' processes such as ion exchange and complexation.

Most surfaces of sediments and suspended particulates, and all surface of algae (phytoplankton and periphyton) are coated with organic materials. These surfaces possess ion exchange sites. For instance, peat is reported to act as a cation exchange surface for protons (Wieder, 1990).

The cation exchange surface will equilibrate relatively rapidly, but changes in conditions, such as pH, redox potential and concentrations of other ions, will influence the cation exchange capacity. Therefore, the amount of iron or other cations bound in this manner will vary in different parts of the sediment. Adsorption processes are probably of importance in iron removal in the early stages of constructed wetland development for treatment of AMD (Wieder, 1992). Incorporation within, or on, surfaces (co-precipitation) may be an important means of removing heavy metals from AMD (Singh and Subramanian, 1984).

Adsorption of ions to surfaces of living organisms (biosorption) is also important in iron cycling. Iron hydroxides and sulphides are among a variety of compounds, identified by electron microscopy coupled to EDX, and X-ray diffraction, which accumulate on bacterial surfaces in aquatic environments. Such surfaces may be important nucleation sites for authigenic mineral formation (Ferris et al., 1987, 1989a).

<u>Redox Boundaries:</u> The importance of redox boundaries as barriers to, or active sites of, processes is well established (Davison, 1985). Because of the mixing and rapid diffusion of oxygen in the water column, oxygen is generally present throughout

and oxidising conditions predominate. In contrast, oxygen diffusion is slow in sediments, anoxic conditions develop rapidly with depth and reducing conditions predominate. As a result, a sharp redox boundary forms just beneath the sediment surface.

Iron-rich colloids near the redox boundary, in one case, have been shown to have a diameter range of 0.04 to 0.4 μm (Buffle et al., 1989). It is important to note that such colloids may pass through most filters prior to chemical analysis of waters and, therefore, dissolved iron concentration determinations may be overestimates. The colloids formed in the natural environment are very difficult to study because of handling difficulties. The properties of colloids formed in laboratory conditions, such as their rate of formation and dissolution, vary considerably according to the chemical and physical environment in which they are formed (Deng and Stumm, 1994). The presence of clay minerals, aluminum oxides, living bacteria or light may enhance the rate of formation. Clays may also enhance the dissolution of the colloids.

The redox boundary is a very active zone for cycling of iron, other elements and organics. When reducing conditions prevail, reductive dissolution of colloids of Fe^{3+} hydroxide will take place, with the consequent release of co-precipitated cations, oxyanions and organic moieties (Stumm and Stukberger, 1992). As colloids dissociate, Fe^{2+} may diffuse upwards in the sediment were it will rapidly re-oxidise when passing the redox boundary, or it may diffuse downwards where changes in the chemical environment (ion concentration gradients) will result in precipitation of, for example, FeS and $Fe_3(PO_4)_2 \cdot 8H_2O$. The same reactions can occur at the sharp redox gradients found in biofilms and individual sediment pores.

The kinetics of colloid formation and dissolution can have a profound effect on concentrations of nutrients and heavy metals in the water column as, for example, phosphate ion incorporation into colloids (Deng and Stumm, 1994).

Over time, conditions at any location in the sediment may change, becoming more reducing or oxidising. Changes may be diurnal, seasonal or occur over even longer periods, or may be a function of changes in weather or hydrology. Diurnal changes will occur as a result of chemical photooxidation/ reduction processes, and either directly or indirectly as a result of the activity of photosynthetic organisms.

Iron Cycling in Sediments: Sediments are not merely depositories for materials removed from the water column above. They can also provide a significant source of elements to the water column. The flux to and from the sediments is very important in determining the overall composition of lake water. Iron reduction affects the composition of sediment pore waters and thereby plays a role in controlling the flux to the water column.

In sediments, transport of dissolved materials depends on the process of diffusion, the movement of molecules along concentration gradients from regions of higher concentrations to lower concentrations (Davison, 1985). Dissolved molecules must negotiate between the particles. This increases the length of the diffusion pathway to such an extent that the rate of molecular oxygen diffusion is 100 to 1000 fold slower in sediment than in open water. It is reported that organic matter in the water column sinks to the sediment surface more rapidly than molecular oxygen can diffuse through the sediment-water interface. Oxygen demand during decomposition of organic particles usually exceeds the oxygen supplied by diffusion into the sediment, and molecular oxygen is maintained at a very low concentration just below the sediment-water interface.

Reducing conditions therefore predominate here. In some circumstances, such as in periods following establishment of ice covers (Ellis-Evans and Lemon, 1989), thermoclines (Hamilton-Taylor and Morris, 1985; Stauffer and Armstrong, 1986) or eutrophic conditions (Buffle et al., 1989), reducing conditions may extend into the water column. This also takes place when chemoclines are established, which is frequently the case in man-made lakes.

In sediments containing decomposable organic matter, redox reactions will occur in a predictable sequence following molecular oxygen depletion (Stumm and Morgan, 1981). Most of the reactions are mediated by microorganisms which utilise organic substrates as sources of respiratory energy. This sequence is determined by the electron activity of the redox reaction and occur with decreasing electron activity.

Oxygen is consumed first. Denitrification (reduction of NO_3 to N_2O and N_2) will then proceed until NO_3 is consumed. Iron reduction will occur after denitrification but before sulphate reduction and methanogenesis. Because of the slow diffusion of substrates into and within the sediment, this sequence of reactions can be demonstrated through the concentrations of electron donors and acceptors. The flux of materials within, to and from sediments may be modified by upward flow of pore water caused by hydrostatic pressure of ground water and also by mixing processes (bioturbation and water turbulence) at the sediment surface.

Some authors have emphasised the importance of hydrogen concentration rather than redox potential in determining which reaction will take place (Lovley, 1991). The sequence is the same but, for example, sulphate reduction requires a higher hydrogen concentration than iron reduction. Therefore, bacterially-mediated iron reduction will out-compete sulphate reduction (Chapelle and Lovley, 1992).

Dissolved Fe^{2+}, resulting from Fe^{3+} reduction, may slowly diffuse into more reducing or more oxidising conditions. In the former, the Fe^{2+} may enter the sulphate reduction zone, where it will react with the product of sulphate reduction, S^{-}, to form sulphide precipitates. If sulphate is absent, Fe^{2+} may accumulate with depth. Fe^{2+} will also diffuse upwards and eventually encounter oxidising conditions, where it will be re-oxidised to Fe^{3+} and most likely precipitate as a hydroxide.

Over time, iron hydroxides will be buried and exposed to more reducing conditions. At any given location near the water-sediment interface, active cycling of iron is likely to occur. Above the 'redox' boundary, where oxidising conditions are maintained, Fe^{3+} will remain in the water as a dissolved or particulate compound. Below the boundary, Fe^{2+} will remain in solution (concentration dependant on diffusion processes) or be fixed as a sulphide precipitate.

3.2 Elemental Concentrations in Sediment Pore Waters

During formation of Fe^{3+} hydroxides, a significant quantity of contaminants, for example zinc, is being co-precipitated. Fe^{3+} hydroxides captured by algal biomass is relegated to the sediment upon sedimentation of the algal biomass. Therefore, the sediments in the Buchans polishing pools and in Boomerang Lake, used as a polishing pond, will contain very high iron concentrations. Iron cycling between the overlying water and the sediment is undoubtedly a key factor in the performance of biological polishing.

As the concentration of dissolved iron in sediment pore water will, in part, determine the rate of iron flux from the sediments to the overlying water, the pore water composition in these sediments is of overall importance to the water chemistry and the biological polishing process. Sediment interstitial solution samplers, or "pore water peepers", modified after Carignan (1984), were installed in the sediments of Boomerang Lake (Map 2) and in the polishing pools 1 to 6 in Buchans (Map 1).

The goal of these measurements using the pore water peepers is to determine the concentrations of specific compounds in the interstitial water which are mobile, or free to diffuse along concentration gradients within the sediment.


3 t Code 31
(1992)
B12
B11
B2
B1
14,000N
FDN
DAM
MILL POND
W/L 1384.25 ±
LEGEND
Water sampling location
Pore Water Peeper Locations
Source of contaminated runoff
1992 phosphate rock distribution (Code 31)
1993 phosphate rock distribution (Code 30/132)
1994 phosphate rock distribution (Code 132)
Log boom