

# THE APPLICATION OF ECOLOGICAL ENGINEERING TO SELMINCO SUMMIT

FINAL REPORT

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July 1993

#### SUMMARY

All relevant experiments have been carried out to derive the design parameters for the implementation of the Ecological Engineering system to treat, with low maintenance requirements, the AMD seepage from the Selminco coal dump.

The iron precipitation ponds were originally designed for the oxidation of ferrous iron in the seepage and for collection of precipitates. The precipitation mechanism was to be facilitated by mixing fresh water with seepage water, a process observed at the old culvert. Unfortunately, the hydrological conditions of the drainage basin and the ponds produced too much water and additional AMD. It was determined that chemical additions to the ponds were required to precipitate iron.

In 1992, experiments were carried out to utilize natural phosphate rock to enhance precipitation. Two berms, composed of Long Harbour sand, an unwashed phosphate rock material, were constructed in the Selminco precipitation cells. Upon passage of AMD through the phosphate berms, the acidity of the water decreased considerably. Initially, acidity decreased by 500 mg L<sup>-1</sup> but, later, the decrease stabilized at 100 mg L<sup>-1</sup>. While the retention time in the berms was sufficient to considerable decrease acidity, pH did not rise. The phosphate rock reacted only with the iron, while aluminum concentrations were unaffected. However, in the laboratory experiment, where a more granular material produced by Texasgulf was used, the acidity was removed, the pH was raised, and iron and aluminum concentrations were drastically reduced. Implementation of the precipitation process using phosphate should, therefore, utilize the Texasgulf material.

Structurally, the original system of ponds could not handle the high spring and fall runoff volumes. Snow melt and rain storm run-off had to be diverted away from the precipitation ponds. A five-fold difference in flow between summer and winter was noted, and a total annual flow contribution of approximately 85,000 m<sup>3</sup> a<sup>-1</sup> was

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estimated. With the diversion of run-off, completed in the summer of 1992, it is expected that total annual flow should decrease to below 35,000 m<sup>3</sup> a<sup>-1</sup>.

In addition to the precipitation ponds, two ARUM (Acid Reduction Using Microbiology) cells were constructed, which were designed to maintain a 0.4 m deep ponds for treatment. Unfortunately, in the years before 1992, the weirs experienced problems and hence, very little water was being retained in the ponds. In order to provide a carbon source for the alkalinity generating process, hay bales were placed in the first cell in 1990. However, due to the problems encountered with the precipitation cells, the material was coated with iron precipitate.

ARUM is a sediment-based microbial process, which reduces sulphate while precipitating metals and generating alkalinity. These processes require reducing conditions. Therefore, floating cattail mats are required over the microbially-active sediments, to assist in reducing water turbulence, to deoxygenate the water, and to provide carbon and nutrients to the sediments in the long term. Cattails rafts were first installed at the Selminco site in 1991. The floating cattails successfully overwintered 1991-1992, and flourished in 1992, reaching heights of over two meters.

In 1992, ARUM experiments conducted in the lab demonstrated that potato waste and alfalfa pellets were excellent carbon sources for the initiation of ARUM in jars. Jars with potato waste and organic sediments developed active ARUM populations. Potato waste and inorganic sediments also produced ARUM populations, but the resulting ARUM activity was slower, relative to those treatments where organic sediments were included. ARUM activity was indicated by elevated pH, lowered acidity and lowered redox potential in the water overlying the sediment.

To extrapolate the laboratory results of ARUM to the field, and to demonstrate the use of cattail covers, a 40 m<sup>3</sup> enclosure was constructed at the outflow of the precipitation

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ponds. Hay bales containing ARUM inoculum, potato waste and alfalfa pellets were added to enclosure, and the surface covered with cattail rafts.

This pilot-scale implementation of the ARUM system immediately began to generate alkalinity, decrease acidity, and increase pH. Within weeks, the pH had increased to pH 6, although later, pHs dropped and stabilized above 3.0. Acidities were also considerably reduced for 2 months. The pH decrease, after the initial rise, may be partially attributable to flow of ground water seeps from beneath the enclosure, which would have added AMD directly to sediment and disrupted the ARUM process. Due to lack of sampling data in 1993, conclusions concerning long-term performance cannot be made.

Biological polishing using periphyton was studied intensively during 1991 and 1992 (Kalin and Wheeler 1992). Studies in 1992 confirmed that growth of periphyton could take place in Selminco seepage water, once the oxidation of iron was complete and the pH was above 4. Laboratory experiments used two different growth conditions to determine growth rates, which could be used to implement biological polishing if needed.

The first set of growth conditions tested lower seepage periphyton in high density cultures, such as are found in the seep areas. Rates of growth varied between -1 and  $1.7 \,\% d^{-1}$ , depending on light and nutrient conditions. The best growth was seen in treatments with the highest light intensity and where both phosphate and nitrate were added. Laboratory experiments, using a much lower stocking density, produced much higher growth rates. In these tests, rates as high as 6.9 and 7.4 % d<sup>-1</sup> were measured. This corresponds to a doubling time of 9 and 10 days, respectively.

In summary, the results of the 1992 work facilitate the implementation of the passive treatment system. It is estimated that three berms of Texasgulf phosphate rock, representing a total of 100 tonnes, placed in the precipitation ponds would induce a pH

increase, and reduce iron and aluminium concentrations in the seepage water. Arum treatment would follow, requiring a minimum of about 600 m<sup>3</sup> covered with floating cattails. Given that the existing cell contains about 1500 m<sup>3</sup> at a depth of 0.4 m, it is recommended that the entire ARUM cell should be equipped with a cattail cover. This would buffer the treatment capacity of the system, as flow fluctuations can always be expected.

Predictions have been made, assuming a annual flow of 35,000 m<sup>3</sup> of seepage to be treated by the system. The discharge from the system is expected to be essentially free of aluminium and iron, and pH is expected to be increased to around 6.

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## **1.0 INTRODUCTION**

Experiments have been carried out over the last 4 years to develop a low maintenance AMD treatment system for a seepage from the abandoned Selminco coal dump (Map 1,2). In the first year, the chemical characteristics of the seepage were determined and seasonal fluctuations in elemental concentrations in Boojum and Kilkenny Brooks were characterized. From this, the performance requirements were calculated. Based on this work, a system was designed to oxidize the iron in a precipitation pond (S1 to S5, Map 3), and then reduce acidity and remove metals with ARUM (Acid Reduction Using Microbiology) and biological polishing (S6-S8, Map 3).

#### 1.1 Background

The Selminco project is a demonstration project for the application of an Ecological Engineering approach to treat acid mine seepages from inactive coal piles. The system is composed of two parts: iron precipitation ponds; and biological treatment ponds.

In 1990 and 1991, problems were encountered with high flows and short water turnover times in the precipitation and ARUM cells. Spring and fall flows exceeded the capacity of the system, washing out weirs and biological experiments. The drainage basin had to be reduced, and the run-off diverted. The details of the required changes were translated into a work order to be carried out by CBDC as soon as conditions on site allowed.

Problems were also encountered with the iron precipitation ponds. Iron did not precipitate when fresh water or run-off was mixed with the AMD. The reasons were two fold: a) the correct ratio (AMD seepage and fresh water) which produced the precipitation (observed previously at the culvert where the seepage mixed with the fresh water creek on the other side of the railway tracks) could not be achieved in the

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Map 1: Northwest Brook Drainage Area with Selminco Summit



Map 2: New Waterford Summit area map



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Selminco Summit 1992 Annual Report Cape Breton Development Corporation precipitation ponds; and b) the pond construction resulted in interception of more AMD, as ground water entered the cells from a discontinuous till layer. This resulted in additional un-oxidized seepages emerging into the precipitation pond.

Due to the large amount of iron hydroxide precipitate covering all biological experiments described in the CANMET report (Kalin and Wheeler 1992), an alternative to fresh water mixing had to be found. Some preliminary work suggested that phosphate mining waste products could provide the solution. This alternative was discussed with the regulators and test work was approved, beginning in 1992. At the same time, work on reducing the catchment area was initiated, and a run-off bypass was constructed.

## 1.2 Task Definition For 1992

<u>Task 1</u>: The AMD seepage characteristics at CBDC were reviewed, with respect to the applicability of phosphate rock. The objective of this task was to carry out all the necessary bench-scale work with phosphate rock from Texasgulf. Emphasis was placed on the Selminco seepage, where the field trials were carried out.

<u>Task 2:</u> Phosphate rock was placed in the Selminco test cells. At the time of placement, Boojum staff was present and took measurements (mainly phosphate concentration and acidity) to monitor the performance of the rock. At the completion of the task, a monitoring program was designed to further track the performance of the phosphate rock.

<u>Task 3:</u> The floating cattails and the ARUM test cell were evaluated and steps taken to promote ARUM and cattail development. The result of this task was the definition of those measures which were necessary for the working of the ARUM cells. Cattails survived the winter and grew well in 1992. Floats remained intact and were moved to the new ARUM enclosure.

Further tasks were addressed under the same purchase order. Those tasks have been completed under separate cover, and are not related to the Selminco work.

#### 2.0 METHODS AND MATERIALS

#### 2.1 Field and Laboratory Methods

Standard methods were used for field chemistry methods. Portable meters: pH and  $E_h$  Corning Model 103 with Fisher  $E_h$  electrodes, Conductivity with YSI Model 33 or Orion (WTW) 140 were used. The pH meter was calibrated with buffers after every 5 to 10 measurements.

 $E_m$ , the measured electrode potential 'Eh meter' is converted to an  $E_n$  value standardised to 25 °C from the following formula:

 $E_h (mV) = E_m (mV) + (241 - 0.66(T - 25))$ 

where T is the measured temperature (°C). Redox potential is also affected by pH.  $E_h$  is corrected for pH by the following formula (Wetzel 1983):

 $E_7 (mV) = E_h (mV) + 58(pH - 7)$ 

Field water samples were collected in polyethylene bottles, filled to the brim, with no air spaces, and kept chilled until filtered. Water was filtered through 0.45  $\mu$ m cellulose acetate filters. Acidity and alkalinity were determined by manual titrations in the field. The filtered, acidified sample was accompanied by a duplicate sample which was kept cool for determination of changes which might take place after collection. In the laboratory, for the last two years, acidimetric and alkalimetric titrations were carried out with a Beckmann Titrino auto-titrator, and E<sub>7</sub>, pH and conductivity were remeasured, with the same instruments as used in the field.

Elemental concentrations of both water and solid samples were carried out by ICP (Inductively Coupled Plasma Spectrophotometry), U.S. EPA Method No.200.7 at certified laboratories. To assure the validity of the results, blanks and standards were sent together with field samples. These samples were packaged and marked as per the field samples. Standards with different concentrations of metals were sent (0.1, 1,

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10, 100, 1000 mg L<sup>-1</sup> of metals) every few months. U.S. National Bureau of Standards 1645 (River Sediment) and 1571 (Orchard Leaves) samples were sent as solid standards.

In 1991 12 standards were sent to Chauncey laboratories and 24 to X-Ral. In 1992, 4 Boojum standards were sent to X-Ral and 18 standards were sent to EPL. The standard analyses were not consistently accurate for any of the three laboratories. The quality control data for the blank analysis is available on request.

These analytical results obtained from the various laboratories were subjected to cation and anion balances to determined major errors in the results. Samples with obvious inaccuracies or anomalies were submitted for reanalysis to the respective laboratory to obtain the actual result.

#### 2.2 Phosphate Experiments

Laboratory experiments with phosphate rock were conducted at Boojum and CBDC. To compare phosphate rock reaction efficiencies and to better control the field treatment, three sets of experimental data were compared.

<u>Boojum Experiments:</u> A11 and S1 water samples were collected in May 1992. Both samples were tested with waste Texasgulf phosphate gravel (Natural Phosphate Rock - NPR). A volume of 200 mL of S1 and A11 water was mixed with 200g and 100g of phosphate gravel, separately. Water and phosphate rock were sampled after different intervals, and acidimetric titrations performed using the Beckman Titrino auto-titrator.

<u>CBDC Experiment:</u> To complement the on-site field test program, and to examine the chemical reactions taking place between NPR and AMD in Selminco water in detail, a bench-scale experiment was carried out at CBDC.

The laboratory experimental system design is shown in Schematic 1. A total of 4.1 kg (3 litres) of NPR (granule diameter, 3-5 mm) was packed as three layers into the inner column (H; Schematic 1). The inner column had a diameter of 15 cm and a height of 42 cm. In order to prevent NPR from forming hardened, concreted layers with accumulating precipitate, each of the one litre layers of NPR was separated with a one litre layer of styrofoam packing chunks (diameter, 2.2-2.5 cm). Precipitates could settle into the large void spaces in the styrofoam. Overall, then, the column had six layers, each 6 cm thick. The column was suspended in an acrylic Plexiglas outer sleeve. Water level was controlled by the overflow port in the outer sleeve. The water level was just above the upper NPR layer in the column.

Water was pumped from Feed Tank A into the column. The pump, set at 4.6 L d<sup>-1</sup>, is run for 16 hours d<sup>-1</sup>, giving a final flow rate of 3 L d<sup>-1</sup>. From December 21 to January 4, the pump was set at 1.125 L d<sup>-1</sup>. From January 5 until the experiment was shut down on January 22, 1993, the pump was set at 2.25 L d<sup>-1</sup>.

Water passing through the NPR-styrofoam layers in the inner column had a turnover time of 0.8 days. Water drained from the inner column into the outer sleeve through a bottom sieve. The combined turnover time of water in the inner column and outer sleeve was 6.8 days. Water overflowed from the outer sleeve through the overflow port (J) into a series of settling containers, as shown in Schematic 1 (K).

Most of the iron precipitates formed following NPR treatment settled in the NPR and styrofoam layers (i - iii), or at the bottom of the outer sleeve (iv). Some suspended precipitates, or precipitates formed later in the settling container (K) settled out in the settling containers. Precipitates floating on the surface of the settling containers (top, vi) were collected separately from the bottom (v) precipitates. Acidimetric titrations were performed manually, twice weekly until December 10, and then on December 17, January 4, and January 20, 1993.



Schematic 1: CBDC laboratory phosphate rock column, experimental setup.

<u>Selminco Field Trial:</u> In late July, 1992, two permeable berms, built from railway ballast rock, were constructed across a section of Cell 2 and Cell 3 of the Selminco Test Cell System (Map 3). At construction, each berm was approximately 16 m long, rising from the bottom of the cell (1.3 m deep) and emerging above the water level, then sloping back to the cell bottom on the downstream side. In this way, all water flowing through the cell must pass through the upstream face of the berm, over an approximate area of 143 m<sup>2</sup>.

During placement of the ballast, sampling tubes mounted on posts were integrated into the berm. These tubes were installed so that water could be sampled from within the berm at the centre and edges of the highest point in each berm at 1 m, 50 cm and 5 cm below water level. Therefore, 9 water samples could be recovered from each berm, at 3 locations x 3 depths.

Long Harbour phosphate sand (LHPS), an aggregate with a high phosphate content, was spread over the upstream face of each berm. Each berm received 16 tonnes of LHPS which, following spreading, formed a layer approximately 8 cm thick over the ballast on the upstream side. The 8 cm thickness was chosen, based on the results of a simple permeability test. If the permeability were too low, water would not enter the berms, but flow over the top.

In the weeks following construction, wave action at the water line of each berm eroded LHPS and exposed the ballast. Flow through the berms was then probably not in contact with much LHPS. On August 31, 1992, discarded conveyor belt strips were placed horizontally along the upstream side of each berm, extending from 15 cm below the water level to above the water line. LHPS was redistributed onto the submerged edge of the belt, to reduce the amount of water passing through the berm, and potentially increase the area of LHPS contacting water passing through the berm.

In October, 1992, the berms were further modified. LHPS was scraped from the base of the upstream berm to the surface. Ballast was then removed from the upstream base, and LHPS redistributed over the reduced surface area. This was done to form a thicker layer of LHPS over the upstream face of the berm, thus reducing the probability of water short-circuiting through gaps in the LHPS layer.

#### 2.3 ARUM Experiments

To provide a readily-usable source of carbon, Boojum initiated a number of experiments in the laboratory to test a variety of organic materials for their ability to establish ARUM communities in acidic water. Two products which showed promise at other sites were dried, powdered potato waste from McCain Foods, and dried, ground alfalfa in pellets (used as animal feed). The following experiments detail the work with potato waste and Selminco S1 water.

Laboratory Experiments: Jars (2 L) were set up in the Boojum lab with 1 L of S1 water, 40 g sediment from the ARUM systems (as an ARUM seed), and various amounts of potato waste. The black sediment was collected from the alfalfa pellet patch between Cell 3 and the hay dam. This patch had established reducing conditions (negative Eh) and evidence of ARUM activity was found in 1991. The red sediment was from outside the alfalfa patch. The red colour was due to the presence of ferric hydroxide precipitate, and thus, oxidizing conditions. Acidity titrations were carried out using a Metrohm Titrino 702 titrator. Conductivity, pH, and Eh were monitored over time.

In 1990, isolated pockets of ARUM activity (elevated pH, low Eh, and blackening) were present within hay bales spread over the large ARUM cell. However, high flow rates, combined with iron precipitation, have since provided unsuitable conditions for widespread ARUM activity. Presently, it is envisaged that construction of a series of enclosures over the ARUM cell should provide appropriate conditions for ARUM activity sufficient to reduce iron and sulphate and generate alkalinity.

<u>Field Experiment:</u> An enclosure 13.2 m x 7.6 m in area, averaging 0.4 m deep was built between the C and D culverts at the head of the large ARUM cell (see Map 3). Posts were placed every 10 feet around three sides of the rectangle, the berm was used as a fourth side. A waterproof Fabrene curtain was placed around the three sides, and held in position with horizontal beams. Scrap chain from the Lingan site was placed along the base of the curtain, in order to hold the curtain in the sediment, thereby completely enclosing 40 m<sup>3</sup> of water.

Approximately 15 bales of hay, originally from the hay dam, were distributed in the enclosure. The lower halves of the hay bales harboured an ARUM microbial community, as indicated by a strong hydrogen sulphide smell and blackening (most likely iron sulphide precipitates). Therefore, the microbial communities required for ARUM were present in the enclosure.

Two bags of saturated alfalfa pellets, originally placed around the hay dam in 1991 as "Alfamators" were relocated. The contents, originally weighing 22 kg (dry) per bag, were spread in the enclosure. In addition, 150 kg of dry potato waste were spread in the enclosure.

The twelve floating cattail rafts were towed from the centre of the large ARUM cell into the enclosure, and positioned into a 3 x 4 configuration using rope. These rafts likely reduced oxygenation of the underlying water, promoting the onset of ARUM.

The enclosure was constructed as a batch system. It was designed such that, once ARUM had treated the water within the enclosure, the water could be replaced. The enclosure could be converted into a flow-through system. However, there was some indication that the enclosure is located over a seepage, and new AMD may be continuously entering and leaving the enclosure, making it already a low-volume flowthrough system.

## 2.4 Periphyton Experiments

Samples of periphyton from the A11 ditch and the lower seepage ditch were collected during the summer of 1992. Reference samples, preserved in Lugols fixative, were kept for species identification. The biomass was cleaned of debris, dried, powdered, and sent for elemental analysis to a certified laboratory. There, subsamples were oxidized with a mixture of nitric and perchloric acids, and analyzed by Inductively Coupled Plasma Spectroscopy (ICP).

Fresh weight was determined by blotting the cleaned biomass dry between paper towels. To determine the ratio of fresh biomass to dry biomass weight, samples were oven-dried at 60° C for 24 h. Another subsample was dried to a constant weight at 110° C, and ashed in a muffle furnace at 500° C for 30 minutes. The difference between the oven dried (60 °C) weight and ashed weights gave the Loss On Ignition (LOI). LOI reflects the percentage of organic material in the biomass.

Seepage or AMD water from the nearby study sites was also collected and used as a solution in which the growth experiments were carried out. The pH, Em, conductivity and temperature were determined in the field, and tightly capped samples brought back to the lab. The samples were filtered through 0.45  $\mu$ m cellulose acetate filters, acidified with nitric acid to a pH of 1, and analyzed by ICP.

In the laboratory, plant material was manually cleaned of debris and 2 g (fresh weight; gfw) were placed in 500 mL of field-collected water. Growth rates of *Ulothrix* and *Temnogametum*, filamentous green algae from the A11 seep, were measured in modified Station S1 water, in the laboratory. Light was provided by daylight fluorescent

bulbs, over a 12 h : 12 h, light : dark cycle. Temperature was maintained at 25 ° C. In some treatments, water was amended with nitrate and phosphate.

Periphyton were maintained under these conditions for 5-10 days. This was considered the adaptation phase and the periphyton under these conditions were further separated from sediments, debris, and dead material which could not be washed off manually.

After the adaptation phase, the periphyton were filtered through paper coffee filters in a Büchner funnel. Material was collected from the filters, blotted dry, and weighed. New jars were set up (1 L jars with 500 mL of field-collected water), with the following conditions.

3	Full Light	270 µE m <sup>-2</sup> s <sup>-1</sup>
3	1 Nitex screen	126 $\mu$ E m <sup>-2</sup> s <sup>-1</sup>
3	2 Nitex screens	60 µE m <sup>-2</sup> s <sup>-1</sup>
3	3 Nitex screens	27 $\mu$ E m <sup>-2</sup> s <sup>-1</sup>

Irradiance was measured with a Biospherical Instruments QSL-100 quantum meter. All Irradiance jars contained 0.2 g  $KNO_3$  slow-release fertilizer and 0.2 g waste natural phosphate rock.

- 2 Full Light with only KNO<sub>3</sub>
- 2 Full Light with only phosphate rock
- 2 Full Light controls with no added nutrients.

Jars were continuously bubbled, ensuring that periphyton were agitated. The pH and water temperature were recorded before and after the experiment. Experiments were run for 15 days, at which time the plant material was filtered through coffee filters in a Büchner funnel, blotted dry, and weighed.

Periphyton culture densities of 0.1 gfw in 500 mL water were achieved when 1.0 gfw of newly-collected periphyton material was blended for 1 minute at high speed in a

Waring blender in a solution of 100 mL of tap water. A 10 mL aliquot of homogenized periphyton slurry was pipetted into each treatment jar containing 500 mL of mine waste water. Three 10 mL aliquots were filtered through glass-fibre filters and dried. These were used to determine the initial weight of each aliquot.

Growth jars were continuously aerated and lighting was provided by high intensity coolwhite fluorescent lamps on a 12h:12h light:dark cycle. Experiments were run for approximately 7 days.

At the end of the experiment, periphytic biomass was washed from the culture jars through a glass-fibre filter and dried. The dry weights of the periphyton before and after the experiment were used to determine the relative growth rate (RGR;  $ln(W_2,W_1^{-1}).t^{-1})$ ).

In some cases, the filter papers were further analyzed for elemental composition by Inductively Coupled Plasma Spectroscopy after wet oxidation with a mixture of nitric and perchloric acids.

#### 3.0 HYDROLOGY

#### 3.1 Flow Rates and Turnover Times

Table 1 describes data collected by Boojum on flows, volumes and turnover times of the Selminco system at several points during the summers of 1991 and 1992. System volumes were estimated from on site depth measurements and map dimensions. The A11 seepage ditch has an estimated volume of 120 cubic meters. The iron precipitation cells are larger, with a total volume of about 4000 cubic meters. The two biological treatment areas (large and small ARUM cells) were estimated to have volumes of 4000 and 1500 cubic meters, respectively. The turnover time (volume divided by flow) of water in the entire system during summer months, including the A11 ditch, averaged about 66 days or 2 months. However, these average summer flows and turnover times were not applicable year round. Variations in flow, based on all available data for station S1 are evident (Figure 1). The seepage flow increases late in the year, peaking in January. Flows then decrease to a low in August-September. Flows in the summer are thus the lowest of the year. This means that turnover times for the system are correspondingly shorter in the winter. The difference between summer and winter flows is dramatic. An average of measured flows in the months of November, December, January, and February was 233 cubic meters per day. The corresponding summer average (June, July, August, September) was 94 cubic meters per day. If flows are plotted by sampling date, the peaks in December and January (520 m<sup>3</sup> d<sup>-1</sup>) and the troughs in late summer (19 m<sup>3</sup> d<sup>-1</sup>) are obvious (Figures 1.2). The total flow including high winter runoff has been estimated at between 58,000 m<sup>3</sup> a<sup>-1</sup> and 85,000 m<sup>3</sup> a<sup>-1</sup>. Total flows without including winter runoff average around 34,300 m<sup>3</sup> a<sup>-1</sup> (94 m<sup>3</sup> d<sup>-1</sup>). The differences in flows between winter and summer have considerable effects on contaminant loadings.

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Table 1: Flows, volumes and turnover times for E.E. system sections

	Date	Area	Depth	Volume	Weir	Flow	Flow	Turnover
			-					Time
		(m2)	(m)	(m3)		(m3/min)	(m3/day)	(days)
A11 Collection	17-Aug-91	120	0.1	12	W 5	0.059	85	0.14
Ditch	15-May-92	120	0.1	12	W 5	0.164	237	0.05
	27-May-92	120	0.1	12	W 5	0.011	16	0.75
	04-Jun-92	120	0.1	12	W 5	0.092	133	0.09
	26-Jun-92	120	0.1	12	W 5	0.050	73	0.17
	22-Jul-92	120	0.1	12	W 5	0.050	73	0.17
	11-Aug-92	120	0.1	12	W 5	0.035	50	0.24
	31-Aug-92	120	0.1	12	W 5	0.027	39	0.31
Cell 1	17-Aug-91	1730	0.66	1142	Avg bef/aft	0.044	63	18.23
	15-May-92	1730	0.66	1142	Avg bef/aft	0.162	234	4.89
	04-Jun-92	1730	0.66	1142	Avg bef/aft	0.071	102	11.20
	31-Aug-92	1730	0.66	1142	Avg bef/aft	0.035	50	22.75
Cell 2	17-Aug-91	1344	0.8	1075	A+B	0.028	41	26.48
	15-May-92	1344	0.8	1075	A+B	0.160	231	4.66
	04-Jun-92	1344	0.8	1075	A+B	0.049	71	15.18
	31-Aug-92	1344	0.8	1075	A+B	0.043	61	17.57
Cell 3	17-Aug-91	866	0.8	693	C+D	0.034	49	14.07
	15-May-92	866	0.8	693	C+D	0.430	619	1.12
	04-Jun-92	866	0.8	693	C+D	0.096	138	5.01
	31-Aug-92	866	0.8	693	C+D	0.038	55	12.66
Enclosure	31-Aug-92	100	0.40	40		0.000	0	infinite
Large ARUM Cell	17-Aug-91	3968	0.40	1587	W 6	0.034	49	32.23
	16-Jan-92	3968	0.40	1587	W 6	0.306	441	3.60
	15-May-92	3968	0.40	1587	W 6	1.904	2742	0.58
	27-May-92	3968	0.40	1587	W 6	0.110	159	9.98
	04-Jun-92	3968	0.40	1587	W 6	0.145	208	7.62
	26-Jun-92	3968	0.40	1587	W 6	0.095	137	11.55
	22-Jul-92	3968	0.40	1587	W 6	0.088	127	12.50
	11-Aug-92	3968	0.40	1587	W 6	0.024	35	45.93
	31-Aug-92	3968	0.40	1587	W 6	0.016	23	67.62
Small ARUM Cell	17-Aug-91	1586	0.40	634	W 7	0.033	48	13.35
	16-Jan-92	1586	0.40	634	W 7	0.306	441	1.44
	15-May-92	1586	0.40	634	W 7	0.853	1228	0.52
	27-May-92	1586	0.40	634	W 7	0.067	96	6.61
	04-Jun-92	1586	0.40	634	W 7	0.073	105	6.02
	26-Jun-92	1586	0.40	634	W 7	0.067	96	6.61
	22-Jul-92	1586	0.40	634	W7	0.024	35	18.36
(leakage before weir)	31-Aug-92	1586	0.05	79	W 7	0.000	0	0.00



#### 3.2 Water Chemistry

Selminco seep water contains iron, sulphate, and aluminum, and emerges from the waste pile at pHs between 3.6 and 4.5. When seepage water flows into the system, the process of iron oxidation (from ferrous to ferric) begins, and iron precipitates as ferric hydroxide. This changes water colour to orange and reduces the pH.

$$4Fe^{+2} + 10H_2O + O_2 = 4Fe(OH)_3 + 8H^+$$

With longer water turnover times, more iron is oxidized and precipitated. Using the system volumes in Table 1, it was possible to calculate the length of time seepage water would spend in each section of the system, at a given flow rate. This is shown in Figures 3 and 4, where five elemental concentrations are plotted as a function of turnover time on May 13, and August 31, 1992. The flow, measured at station S1, was high in May, 237 m<sup>3</sup> d<sup>-1</sup>. In May, all elements decreased in concentration as water passed through the system. Since sodium is generally non-reactive, it can be used a tracer. Thus, there is an indication that clean water entered the system during the time that contaminants were resident. The drop in sodium concentrations indicates that the original seep water was diluted about 3.6 times. The confluence of fresh and contaminant water enhanced the precipitation of iron, and it decreased at a rate of about 10.4 g m<sup>-3</sup> d<sup>-1</sup>. If dilution was accounted for, then iron decreased at a rate of 2.8 g Fe m<sup>-3</sup> d<sup>-1</sup>.

In August, the flow, measured at S1, was 39 m<sup>3</sup> d<sup>-1</sup>. At this low flow, the turnover time of seep water in the system was much longer than in May. Sodium concentrations remained relatively constant as water passed through the system, suggesting that there was little or no dilution of the seepage water at this time (Figure 4). Iron decreased at a rate of 1.5 g Fe m<sup>-3</sup> d<sup>-1</sup>.





In July, CBDC installed a run-off diversion ditch at the Selminco site. This should have shunted most of the surface run-off away from the system. It is likely, then, that the flow rates at S1 in August were seepage flow only, and that little or no dilution from fresh water run-off was occurring at that time. The peak flows measured in the previous spring and fall were roughly five times this base flow. Seepage flow in the summer of 1992 was between 40 and 50 m<sup>3</sup> d<sup>-1</sup>, and previous "average" summer rates were near 80 m<sup>3</sup> d<sup>-1</sup> (Figure 1). Peak flows were between 200 and 250 m<sup>3</sup> d<sup>-1</sup>, with the exception of 1990 flows, which were much higher. This relationship between "peak" and "base" flow is a roughly the same as the ratio of fresh to contaminated water calculated using "tracer" data during the May 1992 sampling. The fact that there appeared to be no dilution, and a "base" flow in August 1992, is further evidence that spring and fall flows have a considerable fresh water component.

Iron concentrations at the system inflow (S1) and the differences in iron concentration between S1 and S8 are shown in Figure 5 (1989 to 1991; CBDC data). Iron concentrations at S1 were relatively high in summer, and low in winter. If the rate of iron dissolution in the waste dump was relatively constant year round, then concentrations would be higher if dissolved in a smaller volume of water. Low iron concentrations in the winter months would be due to the larger volume of water moving through the waste dump. The difference in iron concentrations between S1 and S8 reflects the turnover time of water in the system. At long turnover times in summer, decreases are greater. Higher summer water temperatures would also tend to enhance oxidation rates. In winter, when turnover times are shorter, differences between S1 and S8 are smaller. This relationship can be abrogated if large amounts of fresh water enter the system at spring run-off as was seen in May. In this case, turnover time is short, but iron precipitates more readily in the presence of fresh water.

Aluminum concentrations in water are affected by several factors. At pHs below 3.5, aluminum can only decrease if it is co-precipitated with iron. At pH ranges between 3.5 and 4.5, aluminum will precipitate naturally as a hydroxide.



Aluminum concentrations at S1 have varied considerably since the system was built. Mid-summer concentrations as high as 100 mg L<sup>-1</sup> were recorded in 1990 (Figure 6). Winter concentrations, during significant run-off periods, were as low as 3 mg L<sup>-1</sup>. If aluminum were diluted by run-off, rather than by ground water, then aluminum concentrations at the A11 seep would be relatively constant. On the other hand, if the seep contained large amounts of uncontaminated (or differently contaminated) ground water, then the concentrations would change. Figure 7 shows the concentration of aluminum in the A11 seep plotted by sampling date. Concentrations range from 15 mg L<sup>-1</sup> to 94 mg L<sup>-1</sup>. This variation suggests that there is a strong seasonal component to aluminum concentrations in the seep.



Given these variations in flow, the drainage basin needed to be modified to reduce the range of variation. The drainage basin needed to be reduced by shunting surface runoff away from the treatment system. A diversion ditch was completed in July of 1992. Flows thereafter, through October, showed reductions, although at least one year of monitoring will be required before the actual extent of the reductions in flow are noted.

#### 4.0 PHOSPHATE ROCK

When phosphate rock is added to Selminco seep water, phosphate ions precipitate with iron and aluminum, and react with hydrogen ions to raise water pH.

 $PO_4^{-3} + Fe^{+3} = FePO_4$   $PO_4^{-3} + AI^{+3} = AIPO_4$   $PO_4^{-3} + H^+ = H_2PO_4^{-2}$   $HPO_4^{-2} + H^+ = H_2PO_4^{-1}$  $H_2PO_4^{-1} + H^+ = H_3PO_4$ 

The chemical reactions outlined above proceed based on equilibria which follow generally in a sequence. The first reaction is the formation ferric phosphate which is followed by formation of aluminium phosphate. Once this reaction has taken place, and most of the iron and aluminium is precipitated or has reacted, the pH will rise, due to the formation of phosphoric acid. This phosphate is then consumed by the biological processes, either ARUM and or the algae.

Given this expected sequence of reactions, a combination of laboratory and field experiments were carried out to arrive at design criteria for applications of the material. Each experimental set will yield information about different reactions.

## 4.1 Laboratory Experiments

Experiments with phosphate rock were performed with S1 and A11 water in the laboratory at Boojum. Acidimetric titrations of S1 and A11 water in contact with phosphate rock for different length of time are shown in Figures 8 and 9. The flat "steps" in the titration curves represent the formation of metal precipitate which are present at concentrations greater than 1 mg L<sup>-1</sup>. From the shape of the curves (Figures 8 and 9) two primary steps are evident. The first step is between pH 4 and 5. This



represents aluminum. The second step, between pH 5.5 and 7, represents ferrous iron. As time elapses, both iron oxidation proceeds and the reactions with phosphate sand proceed. The overall result is decreases of acidity with exposure to phosphate rock. The acidity decrease was due to the disappearance of: first, aluminum, and, then, ferrous iron primarily through oxidation and subsequent reaction as ferric phosphate.

Due to budgetary constrains, the chemical analysis of waters from the experiments was kept to a minimum. However from the titration curves, iron concentration decreases can be estimated. The estimates are presented together with the phosphate rock contact time in Table 2. The data indicate that the iron reductions in the water correlate well with the contact time between water and phosphate rock.

No.	Hours	Fe	reacted Fe	water	PR
		(mg/L)	(mg/L)	(mL)	(g)
1	0	231	0	200	100
	3	182	49		
	6	16 <b>8</b>	63		
	22	84	147		
	46	18	213		
2	0	225	0	200	200
	3	168	57		
	6	151	74		
	22	84	141		
	46	28	197		
3	0	101	0	1.48E+10	3.3E+07
	11	27	74		
4	0	121	0	2.01E+05	4.1E+03
	24	0	121		

Table 2: Phosphate rock reaction rates

No.1 Boojum experiment by A11 water.

No.2 Boojum experiment by S1 water.

No.3 Time by field flow measurement on Aug.17, 1992. Fe concentrations are from S2 and S7 ICP data. Total treated water volume to January 4, 1993 is calculated by average flow rates measured in the field in August and September.

No.4 Cape Breton experiment. Water volume is calculated to January 4,1993. Fe concentration estimated by titration curves.
A CBDC laboratory column experiment was performed using S1 water. Acidity and pH of the inlet and the outlet from the column were measured twice weekly for 3 months (Figures 10 and 11). The experiment ran from early October 1992 through the 20th of January 1993. Throughout this time, the acidity of outlet water remained below inlet water. The pH of inlet water for the first and last samples was below 3. The outlet pH climbed after the start of the experiment to a stable value of 8. Unfortunately the experiment was terminated for lack of source water (i.e. Selminco was frozen).

At termination 209 L of S1 water had passed through the column, containing about 4 kg of phosphate rock. The average contact time of each litre going through the column was about 24 hours. The configuration of the column may be considered as sequences of berms, in which a retention time of 8 h in each phosphate layer,

facilitates the stepwise reactions to take place and the pH of the effluent is significantly improved (Figure 10).







# 4.2 Field Phosphate Trials

In late July 1992, two berms were built across the flow path of water in the system at positions shown in Map 3. The phosphate rock berms were built between S1 and S3, and S5 and S6. Both berms were constructed with thirty-two tonnes of Long-Harbour phosphate rock. As water passed through the berms, the orange colour of the water disappeared, indicating that ferric iron no longer precipitated. To assess the effect of the phosphate berms on water quality, iron concentration changes (as % iron change between stations) between S1 and S3, and between S5 and S6 were compared from 1989 to 1992 (Table 3; decrease(1)).

Decrease(1) = { $[Fe]_{(S3)}$  -  $[Fe]_{(S1)}$ } [Fe]\_{(S1)}^{-1} Decrease(1) = { $[Fe]_{(S6)}$  -  $[Fe]_{(S5)}$ } [Fe]\_{(S5)}^{-1}

S1 to S3 S5 to S6				
Date	Decrease(1)	Decrease(2)	Decrease(1)	Decrease(2)
17-Oct-89	-24.0%	9.3%	-23.7%	-8.5%
06-Nov-89	-10.0%	-14,1%	25.0%	22.7%
07-Dec-89	90.2%	29.4%	-19.2%	-11.1%
26-Jan-90	221.9%	155.2%	16.7%	-125.6%
23-Mar-90	-85.8%	-21.6%	156.4%	151.3%
12-Apr-90	-58.1%	-9.5%	-31.3%	-31.3%
18-May-90	-51.5%	-18.8%	-45.5%	-22.7%
22-Jun-90	-37.4%	-18.7%	-8.8%	-8.2%
19-Jul-90	-26.7%	-8.5%	-14.2%	-17.2%
12-Oct-90	-46.3%	-29.0%	-6.7%	-0.9%
23-Nov-90	-40.8%	-30.8%	-1.0%	-7.3%
14-Dec-90	-9.3%	-11.2%	4.9%	-1.3%
18-Jan-91			-24.0%	4.7%
27-Feb-91			-6.9%	5.1%
26-Apr-91	-30.2%	-11.4%	-7.6%	-5.9%
22-May-91	-26.0%	-14.6%	-8.5%	-6.7%
16-Jan-92	-69.4%	3.5%		
27-May-92	-28.2%	-19.2%	-54.6%	-6.2%
26-Jun-92			-81.3%	-71.3%
22-Jul-92	-62.0%	-35.8%	-25.0%	-22.7%
11-Aug-92	-55.2%	-51.1%	-32.0%	-25.7%
22-Sep-92	-67.7%	-67.7%	-20.0%	-44.2%
22-Oct-92	0.0%	59.9%	173.6%	171.4%

Table 3: Percentage iron decrease, S3-S1, and S6-S5

Sulphate ions were used as a conservative tracer to estimate dilution, as sodium concentrations were not available. The possibility that sulphate ions would precipitate between S1 to S3 and S5 to S6 is remote. Furthermore, sulphate and sodium behaved very similarly (Figure 3, 4). If there were no chemical reactions taking place, the expected iron concentrations at S3 and S6 were estimated according to the change in sulphate concentration ratio. Decrease(2) is the estimated percent decrease in iron concentration.

Decrease(2) = { $[Fe]_{(S3)}$  - expect  $[Fe]_{(S3)}$ }  $[Fe]_{(S1)}^{-1}$ , or Decrease(2) = { $[Fe]_{(S6)}$  - expect  $[Fe]_{(S6)}$ }  $[Fe]_{(S5)}^{-1}$ , where

Expected  $[Fe]_{(S3)} [Fe]_{(S1)}^{-1} = [SO4]_{(S3)} [SO4]_{(S1)}^{-1}$  or Expected  $[Fe]_{(S6)} [Fe]_{(S5)}^{-1} = [SO4]_{(S6)} [SO4]_{(S5)}^{-1}$ 

If sulphate concentrations remained constant between stations, then there was no dilution by run-off or ground water. If concentrations of sulphate increased, then contaminated ground water was entering the system between the two stations. Finally, if sulphate concentrations decreased, fresh water run-off or precipitation entered between the two stations. Thus, if the iron concentrations dropped between two stations, the fractional decrease (decrease2) would be negative, indicating that iron was precipitated. A positive value represented the possible contribution of contaminated ground water.

Figures 12 and 13 show the trends in decrease(2) from 1989 through 1992. The major (+) peaks in the curves represent major rain events, which added contaminated ground water to the system. Without these major rain events included, the average decrease between stations S1 and S3 before the phosphate berm was installed was -15.7 %. This represents the average rate of iron oxidation by aeration. After the berms were installed, the decrease rose to -51.5 %, indicating that phosphate significantly enhanced iron removal as it was intended. The same calculations for the second berm provide a pre-berm average decrease of 12.6 % and a post-berm decrease of 27.4 %. Thus, the chemical removal of iron rose between S1-S3 and S5-S6 after July 1992, as during the summer months iron oxidation. This indicates that the LHPS reacted with ferric iron as it was expected.

Passage through the phosphate berms, reduced the acidity of the water considerably as it removed iron. Figure 14 displays water acidity at S1, and the decrease in acidity between S1 and S6 (CBDC data). Initially, the acidity decrease was greater (500 mg  $L^{-1}$ ), but it reduced with time to a stable 100 mg  $L^{-1}$ . Since December 17, however, the berms must have been plugged or frozen as no further decreases are noted.





After the water passes through the berms, although iron concentration are reduced, it still contains 20-30 mg L<sup>-1</sup> Fe and has a pH of around 3. It indicates in contrast to the laboratory column experiment, the in the field system, the phosphate rock has only reacted with ferric ion. The remainder of the iron is present in the ferrous form, which has a relatively high solubility at low pH. The chemical analyses also indicated that the aluminum concentrations were unaffected throughout the system. Acidity titration curves demonstrate that aluminum precipitates in the pH range 3.5-4.5. To decrease aluminum concentrations, then, the pH must rise.

To achieve a functional configuration for the placement of phosphate rock reaction efficiency were determined, based on the existing set of experiments. The first reaction of phosphate is the formation of iron phosphate. The decrease in iron concentration is therefore a function of contact time, which can be defined as the phosphate rock reaction efficiency. Thus, efficiencies can be calculated for laboratory column experiments, and the field system.

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In the field system the flow rates inside the berms were estimated from flow before and after the berm. Thirty-two tonnes of phosphate rock have a volume of 23.8 m<sup>3</sup> (density: 1.37 g cm<sup>-3</sup>). The contact time of the water in the berm was estimated as phosphate volume divided by the flow rate. Based on calculated contact time, the phosphate rock reaction efficiency was calculated.

Phosphate reaction efficiencies can also be calculated for the lab experiments. From the laboratory experiments carried out at Boojum iron reductions were determined based an water sample analysis. In the CBDC experiment, iron reductions were estimated from the acidity curves. The volume of water treated in the CBDC column was estimated based on flows from the beginning of the experiment to January 4, 1993 (Table 3). The rates of iron decrease with contacting time are shown in Figure 15, expressed as the slope of the lines. The slopes of the lines can be calculated. Thus, when all data from the experiments carried out in the laboratory of Boojum were used in the linear regression equations, 5.1 mg Fe L<sup>-1</sup> h<sup>-1</sup> and 4.8 mg Fe L<sup>-1</sup> h<sup>-1</sup> were calculated for A11 and S1 waters, respectively. The CBDC experimental column removed 5.0 mg Fe L<sup>-1</sup> h<sup>-1</sup>, and the field berms removed 7.0 mg Fe L<sup>-1</sup> h<sup>-1</sup>. These suggest that the rates of iron removal from all experiments were similar. These rates include natural iron oxidation rates.



The precipitation cells were originally intended to provide sufficient retention time to oxidize ferrous to ferric iron and precipitate the ferric iron. However, at no time was ferrous iron completely oxidized in the field system. Typical acidity curves such as those from S1 and S6 in May and June 1992 clearly show the flat step between 5.5 and 7 which is characteristic of ferrous iron (Figure 16a,b). Ferrous iron was also present in water which passed through the phosphate berm (CBDC acidity curves; Figure 16c). When this water finally oxidizes further downstream, ferric hydroxide will be formed, precipitating and further depressing the pH.

For the above reasons, two strategies must be adopted to raise water pH further. The first strategy is to increase water retention time in the pond system to maximize ferrous oxidation which in turn would facilitate reaction with phosphate rock berms. This has been implemented by construction of the bypass ditch, to reduce the total volume of water entering the system.

The second strategy is to increase water and phosphate sand contact time by improving the retention time in the phosphate berm, through development of different placement techniques.



# 5.0 ARUM EXPERIMENTS

ARUM (Acid Reduction Using Microbiology) utilizes the ability of microbial processes to generate alkalinity in acid mine drainage. Under reducing conditions (i.e. low Eh), some bacteria are capable of using sources other than oxygen as electron acceptors in respiration. These include sulphate (used by sulphate-reducing bacteria), ferric iron (used by iron-reducing bacteria) and nitrate (used by denitrifying bacteria). In AMD, generated by oxidation of coal wastes, sulphate is abundant. Therefore, sulphate reduction is a potential energy source for microbially-mediated alkalinity-generation. The sulphate reduction process may be summarized as follows:

 $SO_4^{2-}$  +  $CH_3CHOHCOO^- \rightarrow H_2S$  +  $CH_3COO^- + 2OH^$ sulphate lactate sulphide acetate hydroxide

Sulphate reduction also:

- 1) Removes sulphate from solution
- 2) Generates hydroxide ions (alkalinity)
- 3) Increases pH (net consumption of H+)
- 4) Generates  $H_2S$  which, in turn, precipitates metals as sulphides.

Sulphate-reducing bacteria can also use other carbon sources (sugars, organic acids, alcohols). With lactate (a decomposition product of organic matter) as carbon source, two hydroxide ions are generated for every sulphate ion reduced. To use this process for AMD treatment, it is necessary to produce reducing conditions (i.e. low Eh), and provide available sources of carbon and other nutrients for the ARUM microbes.

ARUM can be initiated by providing organic matter which, first, feeds oxygenconsuming microbial processes, and second, provides carbon sources (organic acids, sugars) for sulphate-reducing bacteria. Organic matter can be provided by adding

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organic wastes, or in the long-term, by decomposition of dead material from vegetation covers.

Oxidation of iron, prior to establishment of ARUM processes, coats surfaces of ARUM substrates with ferric hydroxide precipitates. This coat inhibits the normal decomposition process, lowering the availability of smaller-chain carbon molecules, necessary for the nutrition of sulphate-reducing bacteria. Removal of most of the iron prior to ARUM treatment, therefore, is necessary. The Selminco system was designed to remove excess iron prior to biological treatment.

# 5.1 The Selminco ARUM System

Biological treatment of Selminco seep water was designed to take place in the bog areas below the precipitation ponds. Organic material (hay) was added to the upper bog in 1989 to act as a food source for ARUM microbes. The hay soon became coated with iron hydroxide and did not appreciably decompose. Without the organic carbon source, ARUM microbes did not develop properly. Water level control was essentially not achieved until 1992, as the weirs of the ARUM cells were destroyed during high flows in spring and fall.

The implementation of ARUM can of course not take place, if there is no water retention in the cell. By 1992 however, the floating cattail rafts had been overwintered the second winter, and growth was for the first rows well on the way. It was therefore proposed, to build a smaller enclosure, over which the cattail rafts were placed. Such and enclosure would demonstrate under field conditions that indeed alkalinity can be generated. In addition, given the high iron concentrations in the sediments of the ARUM cell and on the haybales, laboratory tests were carried out to determine if the sediments would interfere with the development of ARUM at implementation.

In this section, the results from both field and laboratory work is reported.

#### 5.2 Laboratory Experiments

To test whether or not ARUM microbes could treat Selminco water with the proper organic carbon additions, experiments were carried out at Boojum in static, batch jars (reactors). From the Selminco system, two types of sediments were collected. A black sediment contained an active organic microbial ecosystem and a red sediment composed of iron precipitates, was mostly inorganic. To some of these sediments, organic amendment in the form of potato waste was added. The development of the ARUM community (as exemplified by metabolic products) was followed in the experiment.

<u>Red (oxidized) sediment</u>: Figure 17 shows the Em (Eh without correction) in the presence of red sediment and various amounts of potato waste. Jars with 2 g L<sup>-1</sup> and 10 g L<sup>-1</sup> of potato waste produced reducing conditions (Em <-200 mV) within 7 and 14 days, respectively. This was accompanied by a rise in pH (Figure 18). Em values subsequently rose, and pH continued to rise. With 2 g potato waste L<sup>-1</sup>, pH reached 6.35 after 44 days incubation (Figure 18). Sulphate determinations after 7 days incubation (Table 4) showed that a substantial drop in sulphate concentrations occurred within 7 days, possibly due to sulphate reduction. This conclusion is also suggested by the reduction of acidity after 51 days as shown by the titration curves (Figure 19). Potato waste at 0.5 g L<sup>-1</sup> failed to generate reducing conditions (negative Em) and produced only a slight rise in pH. Without potato waste, Em and pH remained stable through the course of the experiment (data not shown).

<u>Black (reduced) sediment:</u> If black sediments were used in the jars, reducing conditions (negative Em) were generated with all additions of potato waste within 7 days (Figure 20). Em values subsequently rose slowly. Without potato waste there was no dramatic drop in Em. A rise in pH was also evident by seven days (Figure 21). The pH continued to rise throughout the experiment with the highest values in the



Fig. 17: Selminco Potato Waste Jars Red sediment, Em

Fig. 18: Selminco Potato Waste Jars Red sediment, pH





Table 4:	Potato waste jar experiment
S	ulphate content after 7 days

Oupride content and i daye				
Sediment	Potato waste	Sulphate		
	g/L	mg/L		
Red	0	1800		
	0.5	1400		
	2	1400		
	10	960		
Black	0	1560		
	0.5	999		
	2	1200		
	10	1041		
None	0	2800		
	0.5	1000		
	2	800		
	10	1129		



# Fig. 20: Selminco Potato Waste Jars Black sediment, Em





presence of 0.5 g L<sup>-1</sup> potato waste. Titrations for the 0.5 g L<sup>-1</sup> potato waste jar (Figure 22) show that a reduction in acidity had occurred within 7 days. Acidity continued to decline throughout the course of the experiment.



The flat part of the acidity curve at pH 2.5-3 in control jars was due to the precipitation of ferric iron. In the presence of potato waste, this plateau disappeared and was replaced by another plateau at pH 6.5, which was attributable to ferrous iron. After 31 days, this part of the acidity has also disappeared, suggesting that most of the iron in the jar has been precipitated. The reduction in acidity and rise in pH were accompanied by a reduction in sulphate concentration (Table 4), suggesting that sulphate reduction was occurring and may have accounted for the observed improvements in water quality.

<u>No sediment:</u> In the absence of a sediment layer, additions of potato waste generated reducing conditions (Figure 23), but only the largest additions (10 g  $L^{-1}$ ) resulted in elevation of pH (Figure 24). There were reductions in sulphate (Table 4) in these conditions suggesting that ARUM was not dependent on the presence of a sediment.





These results indicate that potato waste is a very effective ARUM stimulant. Microorganisms and sulphate are present in the water column and the potato waste provides the carbon and nutrient source to fuel the process. The presence of a sediment increased the rate and effectiveness of potato waste at initiating ARUM. A reduced (low Em) sediment (black) was more effective than an oxidised sediment (red).



# Fig. 24: Selminco Potato Waste Jars No sediment, pH

#### 5.3 ARUM Enclosure

Field experiments in 1991 with dried, ground alfalfa pellets in the ARUM areas of the Selminco system established that reducing conditions could be enhanced and the pH elevated in sediments. Alfalfa generated and maintained reducing conditions. Laboratory experiments established that potato wastes were very effective in reducing acidity of Selminco seepage water. The cattail rafts planted in 1991 demonstrated that cattails could thrive in the ARUM bog at Selminco. Cattails reached heights in excess of 2 m by the beginning of September 1992.

Cattail rafts were moved to the ARUM enclosure in July 1992 to provide a cover to inhibit wind-driven water mixing, thereby assisting in the generation of reducing conditions throughout the water column. In the long-term, litter from the cattails will provide a continuous carbon source for the ARUM microorganisms.

<u>Performance of the ARUM enclosure</u>: A pH survey was conducted within the enclosure on September 2, 1992. Readings were taken at the surface and bottom at twelve points between the cattail rafts. Surface readings were in the range 5.83 to 5.99 and bottom readings from 5.29 to 6.30. Readings outside the enclosure were pH 2.84 at the surface and pH 5.74 on top of the hay bales (bottom). These elevated pHs suggest that the conditions within the enclosure had enhanced the conditions for ARUM communities.

CBDC acidity monitoring data from the ARUM enclosure before and after the phosphate rock berms were installed are shown in Figure 25. During the period of heavy precipitation in October, the acidity of the enclosure water was similar to that of the other sites. However, from November 10 to early December, the acidity of enclosure water was consistently about 500 mg L<sup>-1</sup> (CaCO<sub>3</sub> equiv.) less than that found outside. Values for pH were higher in the enclosure for most of the study period (Figure 26).







These observations indicate that ARUM microbes were established and working in the enclosure.

On November 16, 1992, water from the ARUM enclosure and station S6 were analyzed. Chloride was 30% lower in the enclosure, indicating that, at that time, there may have been some dilution of the enclosure water. Sulphate, nickel and cadmium were all 39-40% lower in the ARUM cell, suggesting that some reduction and/or adsorption was taking place. Acidity dropped by 69 %, further suggesting that ARUM activity was still present. Nitrate and ammonium increased by 90 and 190%, respectively. Aluminum decreased slightly, at 56%, and pH increased slightly, the hydrogen ion concentration decreased by 50%. The same pattern was shown on December 16 and January 6, but less pronounced (Table 5a and 5b).

Starting in December, the acidity in the cell dropped to very nearly the outside level. Either the ARUM communities slowed in winter, or the cell was breached, allowing outside water in. Further monitoring will determine the proper scenario.

Based on the rates of iron and acidity reduction, scale-up parameters for the ARUM process at Selminco have been calculated. These are presented in Section 7.

	ARUM encl	S6	% diff
	mg/L	mg/L	100*(S6-AE)/S6
Alkalinity	0.4	0.4	0.0
Acidity	136	441	69.2
Sulphate	491	856	42.6
Chloride	20.4	29.2	30.1
Nitrate/nitrite	0.73	0.39	-87.2
Ammonium	1.26	0.43	-193.0
Total Phosphorus	0.05	0,05	0.0
Aluminum	11.8	26.9	56.1
Cobalt	0.14	0.23	39.1
Nickel	0.32	0.56	42.9
рН	3.3	3	-49.9

Table 5a: Element Comparison: ARUM enclosure vs. S6 November 16, 1992

Table 5b: Element Comparison: ARUM enclosure vs. S7 December 16, 1992

	ARUM encl	S7	% diff
	mg/L	mg/L	100*(S7-AE)/S7
Alkalinity	0.4	0.4	0.0
Acidity	242	504	52.0
Sulphate	920	1212.6	24.1
Chloride	35.4	40.3	12.2
Total Phosphorus	0.11	0.07	-57.1
Iron	4.27	30.2	85.9
Aluminum	12.7	23.5	46.0
Cobalt	0.14	0.23	39.1
Nickel	0.3	0.48	37.5
pН	3	2.8	-36.9

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# 6.0 PERIPHYTON GROWTH

Periphyton are an integral part of the decommissioning scenario for Selminco. Periphyton are surface-bound algae and moss that provide a living, growing surface for the adsorption of dissolved metals. Periphyton metabolism also provides extracellular polysaccharides which trap precipitates. Finally, periphyton photosynthesis oxygenates water, enhancing the precipitation of metals.

In 1991, Boojum Research, with the aid of CBDC and CANMET, studied the conditions necessary to initiate the growth of periphyton in the Selminco E.E. system (Kalin and Wheeler 1992). The primary criteria for the establishment of periphyton populations were: 1) an elevation of pH above 3.5, and 2) a reduction in iron content of the water. Attempts to grow periphyton in areas where pHs were lower than 3.3, where nutrients were limiting, or where oxidation rates were high, resulted in death of transplants. The result of the work suggested that if the conditions at Selminco Summit could be ameliorated, that periphyton could grow, and provide a significant metal reducing capacity. The high iron content and oxidizing conditions in the ditches and system provided the conditions necessary for rapid changes in the redox state of the water. The rapid oxidation of the iron precipitated any available phosphorus, and dropped pH below the tolerance limit.

Once water has been treated with a combination of phosphate rock and ARUM microbes, periphyton will probably grow well in Selminco water. Tests described above suggest that iron concentrations can be reduced and pH increased significantly with either process alone or together. The application of phosphate also acts as a nutrient for periphyton growth.

#### 6.1 Laboratory Experiments

Since most of the criteria for the establishment and growth of periphyton are provided by the application of phosphate rock, further tests on the suitability of periphyton as a biological polishing agent were carried out. Selminco S1 was modified by stirring the water (initial pH 2.9) with natural phosphate rock (Texasgulf) until the pH had risen above pH 4. Maximum growth rates occurred under the highest lab irradiance, 270  $\mu$ E m<sup>-2</sup> s<sup>-1</sup>, which is about 18 % of full sunlight, together with added phosphate and nitrate (Figure 27).



Fig. 27: Selminco Growth Rates Ulothrix, Microspora

Selminco periphyton were sensitive to changes in light intensity. At the lowest light intensity, the Selminco population lost weight. They responded to nutrient additions, where, under high light, growth was significantly greater than the controls. High light conditions in these experiments (270  $\mu$ E m<sup>-2</sup> s<sup>-1</sup>) were approximately 1/6 full sunlight. Thus, it can be expected that in the field, where periphyton are generally found in high density, growth rates would be at least as high.

In these laboratory experiments, biomass density was high (1.5 gfw L<sup>-1</sup>), with no water turnover. As periphyton are normally found in slow-flowing streams, water turnover occurs continuously. It is reasonable to assume that in the high density experiments, the nutrient supply might have been limiting, thus slowing growth rates. However, these high densities were more representative of densities found in field populations, and may therefore have better represented the growth rates occurring in the waste waters.

In the low density cultures, growth rates of Selminco algae were much higher. Relative growth rates are shown in Table 6, along with culture pH and weights. The highest growth rate recorded under these conditions was 7.4 % d<sup>-1</sup>. The experiment was conducted twice, and a similar growth rate of 6.9 % d<sup>-1</sup> was recorded in the second experiment. These rates correspond to doubling times of 9 and 10 days, respectively.

Table 0. Euboratory direttint there are a series in the						
Taxa	Water	PH	FP #	W1	W2	RGR
•				(gdw)	(gdw)	(%/d)
Ulothrix	Selminco S1	4.32	29	0.0209	0.0338	6.9
Ulothrix	Selminco S1	4.16	30	0.0209	0.0350	7.4

Table 6: Laboratory Growth Rates of Selminco Periphyton

Average growth rates achieved with the different methods (high and low density, nutrients, and irradiance) are similar to those found in the field at other sites. The experiments suggest that biological polishing rates can be increased through fertilizer additions.

Periphyton, if they can be grown below phosphate and/or ARUM treatment areas, will adsorb aluminum and sieve iron. Current periphyton growing in both the A11 ditch and the lower seepage already sequester high concentrations of iron and aluminum (Figure 28). This can be seen from looking at the elemental scans of representative 1992

periphyton samples and the water from which they were collected (Figure 28). The lower curves represent the water, where open boxes represents the A11 seepage water, and closed boxes represent the lower seepage water. Between the upper two curves, the crosses represent periphyton growing in the A11 seepage ditch, and pluses represent those periphyton growing in the lower seepage. Those elements in the highest concentration in the periphyton were iron and sulphur, in concentrations above 10,000  $\mu$ g gdw<sup>-1</sup>. Those elements above 1000  $\mu$ g gdw<sup>-1</sup> were calcium, magnesium, sodium, potassium, aluminum, and phosphorus. Both periphyton populations had nearly identical elemental compositions. Those periphyton growing in the A11 seepage had 10 x more silicon, 20 times more iron, and 6 times more phosphorus. These concentrations can be used to calculate the quantity of contaminant metals which could be removed if biological polishing were scaled up.

Scale-up parameters for biological polishing at Selminco are discussed below.





#### 7.0 IMPLEMENTATION OF THE SYSTEM

Ecological Engineering processes can be implemented at the Selminco Summit after four years of experimentation. The four years were in part used to understand the processes and at the same time it was demonstrated that they are applicable to improve the AMD seepage from the dump significantly. Originally the aim was to arrive at maintenance free system for the seepage, but this had to be abandoned when the iron precipitation ponds did not perform as per design. Unfortunately during construction of the ponds the underlying clay layer, which was expected to seal the bottom of the ponds was disturbed and fresh, unoxidized seepage entered the precipitation ponds. Thus a low maintenance solution was thought through addition of a sedimentary phosphate rock, which facilitates iron removal, prior to the microbial alkalinity generation.

The objective of the system is to meet downstream regulatory requirements at station 7 (Map 2, page 3) protecting Kilkenny brook.

With the completion of the series of experimentation the appropriate sequence of processes, given the results from the experiments is as follows:

Iron oxidation and precipitation with phosphate in the existing precipitation ponds Cell
to Cell 3.

2) ARUM, a alkalinity generating sediment over the old precipitates and haybales in ARUM bog 1 and 2.

3) Biological polishing with algae in the downstream area around of the outflow of ARUM bog 2.

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The experimental data are used in the sections below, to determine the expected water quality and the quantities of material needed to implement the system, within the given areas.

# 7.1 Phosphate Rock.

Calculations to determine the amount of phosphate rock required are presented in Table 7. The quantity of phosphate rock is based on the present configuration in the berms and the use of the unwashed Long Harbour Sand, in contrast to the Texasgulf waste material which was used in the CBDC column experiment.

Water characteristics were used collected on August 17th 1992, one of the few times when both, flows within the precipitation ponds and the concentrations were determined.

The characteristics of the seepage at S2 is described in Lines 1-5 of Table 7. The discharge water quality at station S7 is shown in Lines 6-10. Calculations also used the characteristics of long Harbour Sand (Line 11), the quantity of phosphate rock in the system (Line 12), and the volume of rock (based on a density of 1.37; Line 13). The flow rates of water moving through the berms were calculated based on flow rates measured before and after the berms (Lines 15 and 17) from Table 1. Using these parameters, a contact time can be calculated for water passing through berms 1 and 2. These contact times in hours are presented in Lines 16 and 18. The total contact time for both berms was 13.4 hours. This is lower than used in the CBDC column experiment where the water remained in each layer for 8 h resulting in a total contact time of 24 h.

The reaction rates of iron with phosphate rock presented in Section 4 (Figure 15; Line 19), are used along with similarly calculated reaction times for aluminum (Line 20), hydrogen ion (Line 21), and acidity (Line 22).

1   Water inflow(L/min.)     2   Fe(mg/L)   10     3   Al(mg/L)   45.     4   pH   2.     5   Acidity(mg/L)   82     WATER DISCHARGE QUALITY   6     6   Water outflow(L/min.)     7   Fe(mg/L)   26.     8   Al(mg/L)   48	1 3 7 7
2   Fe(mg/L)   10     3   Al(mg/L)   45.     4   pH   2.     5   Acidity(mg/L)   82     WATER DISCHARGE QUALITY     6   Water outflow(L/min.)     7   Fe(mg/L)   26.     8   Al(mg/L)   48	1 3 7 7
2   Fe(mg/L)   45.     3   Al(mg/L)   45.     4   pH   2.     5   Acidity(mg/L)   82     WATER DISCHARGE QUALITY   6     6   Water outflow(L/min.)     7   Fe(mg/L)   26.     8   Al(mg/L)   48	3 7 7
4 pH 2. 5 Acidity(mg/L) 82 WATER DISCHARGE QUALITY 6 Water outflow(L/min.) 7 Fe(mg/L) 26. 8 Al(mg/L) 48	7 7 7
5Acidity(mg/L)82WATER DISCHARGE QUALITY66Water outflow(L/min.)7Fe(mg/L)8Al(mg/L)48	7
WATER DISCHARGE QUALITY 6 Water outflow(L/min.) 7 Fe(mg/L) 26. 8 Al(mg/L) 48	
6 Water outflow(L/min.) 7 Fe(mg/L) 26. 8 Al(mg/L) 48	
7 Fe(mg/L) 26.	
$8 \operatorname{Al}(\operatorname{mg}/l) \qquad 48$	9
	0
9 pH 2	7
10 Acidity(mg/L) 68	0
TREATMENT PARAMETERS	
11 Phosphate type L.H	١.
12 Phosphate weight(ton) 3	3
13 Phosphate volumn(M3) 2	24
14 Water retention time(hour)	
15 Berm 1 Water flow(L/sec.) 0.	5
16 Phosphate contacting time(hour) 7.	0
17 Berm 2 Water flow(L/sec.) 0.	5
18 Phosphate contacting time(hour) 6.	4
REACTION RATES	
19 Fe(mg/L/hour) 5	5
20 Al(mg/L/hour) -0.	2
21 H+(mg/L/hour) -1E-0	5
22 Acidity(mg/L/hour) 11.	0
EXPECTED WATER QUALITY	~
23 Fe(mg/L) 0.	0
24 Al(mg/L) 0.	0.
25 pH 4	.0
26 Acidity(mg/L) 30	C
27 Bhosenhate contacting time/bourt)	2
27 Phosphate contacting time(hour) 47	.0
29 Water flow(L/sec.) 03	86
30 Water flow(L/sec.)	4
	•
31 Phosphate volume(M3) 65	.2
32 Phosphate weight(ton) 89	.3
33 Phosphate volume(M3) 17	0
34 Phosphate weight(ton) 23	33

Table 7: Phosphate rock extrapolations

The quantity of phosphate rock needed at Selminco depends on the end result desired leaving cell 3. In Table 7 estimates for ideal conditions the NPR requirements with Long Harbour sand as follows:

a) complete removal of iron, and

b) complete removal of iron, aluminum, and an increase in pH to 4.0 (Lines 23 to 25).

Based on the original concentrations of these ions in the water, the final acidity leaving the cell will be no more than 305 mg  $L^{-1}$  (CaCO<sub>3</sub> equiv.; Line 26). This acidity would then be removed by the ARUM cell.

To meet the requirements of extrapolation a) (no iron), first the phosphate rock contact time is calculated. This is done by dividing the amount of iron to be removed (Line 2 minus Line 23) by the current iron reaction rate (Line 19), 18.3 hours (Line 27) are required. To remove all iron, aluminum and bring pH to 4, requires even greater contact time. By dividing the concentration difference (Line 5 minus Line 26) by the acidity reaction rate (Line 22), a contact time of 48 hours (Line 28) is calculated.

To achieve these contact times, the flow rate of AMD from the A11 seep and ground water can be calculated. On August 31, flow was about 0.5 L s<sup>-1</sup> (43.2 m<sup>3</sup> d<sup>-1</sup>). From Section 3 (Figure 1), it can be seen that this flow is near the minimum flows of the year. However, flows needed to remove iron are lower. By dividing the phosphate rock volume (Line 13) by the phosphate rock contact time (Line 27), it can be seen that flow rates must decrease to 0.36 L s<sup>-1</sup>, or be decreased by 28 %.

To completely remove iron and aluminum and bring the pH to 4 would require (Line 13 divided by Line 28) about 0.14 L s<sup>-1</sup>. It is clear that even with the current bypass ditch, the current amount of phosphate rock is not enough to remove all the iron.

To calculate the quantity of phosphate rock necessary, given current flow rates, the flow rate (Line 15 + Line 17) is multiplied by the contact time (Line 27). This results in a volume of phosphate rock equal to about 65 cubic meters (Line 31). To convert this to mass, the volume is multiplied by the rock density. The end result is that about 90 tonnes of NPR (Line 32) should provide the contact time necessary to remove 101 mg Fe L<sup>-1</sup> at a flow rate of 0.5 L s<sup>-1</sup>. If the removal of all of the iron, aluminum, and some hydrogen ions are required, the quantity of rock rises to 233 tonnes (Line 34).

Estimating the phosphate rock requirements based on the performance of the berms in the cells alone is unrealistic, since the column experiment, using Texasgulf NPR and a contact time of 8 hours in each NPR layer, the results were significantly more effective. The same calculations made with Long Harbour sand, but using the results from the column experiment with Texasgulf NPR, result in a requirement of 80 ton of phosphate rock to treat the A 11 seepage. The final water quality can be expected to reach a pH higher then 7 and the acidity will be reduced to 62 mg/L CaCO3 equivalent.

Although we do not have the length of time for which the reaction will continue as neither the column experiment or the berms have been run to exhaustion, it can be reasonably assumed, that one railcar (100 tonnes) of Texasgulf material will provide sufficient material for one year treatment of the seep.

#### 7.2 ARUM

ARUM scale-up calculations were based on the rate of acidity reduction which occurred in the ARUM enclosure between initial set up and November 16, 1992 (Table 8). Over this period of 55 days, 560 mg L<sup>-1</sup> CaCO<sub>3</sub> equiv. of acidity were removed from the enclosure water (Line 1). Since the volume of the enclosure is about 40 m<sup>3</sup> (Line 2), this translates into a total of 22.4 kg of acidity removed. When this is divided by the

length of time over which the ARUM enclosure was in operation, the reduction rate becomes 283 mg min<sup>-1</sup> (Line 3). If the acidity reduction rate (Line 3) is divided into the enclosure volume (Line 2), then the actual ARUM reduction rate as a function of water volume can be calculated. This rate is the number of cubic meters of water treated per mg of acidity reduced per minute (Line 4).

# Table 8: Selminco Summit - Requirements for ARUM

~~~~		
1	Acidity removed	560 mg/L
2	Volume of AE	40 m3
3	Acidity removed from AE	283 mg/min
4	Acidity removed - volume to remove unit weight per unit time	0.14 m3/mg/min
5	Base flow (S1) - summer conditions	94 m3/day
6	Acidity after removal of metals with phosphate rock	62 mg/L equiv. CaCO3
7	Annual acidity loading	2,127 kg/year
	, <u> </u>	or 4.05 g/min
8	Volume required to remove acidity @ 450 mg/L	571 m3
9	Area required at 40 cm depth	0.14 ha
10	Area required at 1 m depth	0.06 ha
11	Turnover time	109 days
12	Area of existing ARUM cells	0.39 ha

Based on data for AE of November 16, 1992 and at S6 at time of AE set up (September 22, 1991)

# Organic Carbon Requirements for Treatment of S6 Water by ARUM

13	Acidity after removal of metals by phosphate rock	62 mg/L or 0.62 mmol/L
14	Annual acidity loading with base flow of 94 m3/day assuming	or 21,270 moles/year
	1 mol energy source required for 1 mol acidity consumption	
	by sulphate reducers	
15	Energy source required (acetic acid)	21,270 mol/year or 1.32 tonne/year
16	Potato waste contains 60 % starch, all degradable to acetic acid	
17	Potato waste required	2.20 tonnes

Based on data for AE of November 16, 1992 and at S6 at time of AE set up (September 22, 1992)

A seepage base flow of 94 m<sup>3</sup> d<sup>-1</sup> (34,310 cubic meters per annum) was used to scale up the process (Line 5). If the flows are higher than the base flow (dilution), then final areas and required amendments can be scaled up accordingly. In the phosphate rock calculations above, the acidity was calculated which would remove iron, aluminum and bring the pH to 4.0, for both using Long Harbour sand and up to 7 using Texasgulf NPR material.

If we assume that the remainder of acidity would have to be removed by ARUM, the sediments must remove 62 mg L<sup>-1</sup> CaCO<sub>3</sub> equiv. (Line 6). Using the estimates derived from Texasgulf material is realistic, since the Long Harbour sand does not provide a long term supply. If this concentration is divided into the annual seepage flow (Line 5), then it can be seen that the ARUM process must remove about 2 tonnes of acidity per year (Line 7) or 4 g of acidity per minute. Using the removal rate in Line 4, this would require an active ARUM volume of 570 m<sup>3</sup> (Line 8). In the existing ARUM cell with a depth of 0.4 m of water a volume of about 1600 m3 are available. If the average depth of the ARUM bogs is 0.4 m, then 0.14 ha are required to treat the water (Line 9). On the other hand, if the system can be made a little deeper, (1 m), then only 0.06 ha are required to treat the seepage flow (Line 10).

If the ARUM process is to remove 2 tonnes of acidity per year (Line 14), then there must be additional food added for the ARUM microbes, until the floating cattails provide sufficient organic matter to sustain the microbial activity.

To calculate the needed carbon supply on a theoretical basis, it has been assumed that 1 mol of acidity consumed by ARUM bacteria will require 1 mol of an energy source. Thus, about 21 kmol of energy are required per year (Line 15). In 1992, Boojum Research experimented with potato waste as an energy source for ARUM. These experiments are detailed above. Since the potato waste is 60% starch, and starch is directly degradable to acetic acid (the preferred food for ARUM bacteria), the amount of potato waste required is simply the energy required divided by 0.6. This results in a requirement of 2.2 t of potato waste.

Using the acidity removal rates observed in the enclosure and using the previously discussed nutrient supply requirements it can be estimated, that for this system on an annual bases about 2 tonnes of potato waste are needed annually to maintain the ARUM removal rates.

#### 7.3 Biological Polishing

Biological polishing using periphyton could provide a buffer below the first ARUM cell in the second enclosure or further downstream. To extrapolate the quantities of periphyton required to remove contaminants from the Selminco effluent the same concentrations of aluminium and iron at station S7 weir 6 were used as in the estimation for the phosphate rock requirements.

In Table 9 the predictions are made what the expected performance would be, given the data collected on the biological polishing process discussed in detail in the CANMET report.

In lines 1 to 5 the parameters are listed with respect to the loading expected, if the precipitation ponds with the phosphate rock and the ARUM cells would not exist.

Biological parameters to estimate the expected performance of the algae are described in Lines 6-14, giving the assumptions used to arrive at a growth surface area for a unit tree. Details on these parameters along with the data used have been given in the CANMET report.

	WEIR 6 (S7)		
1	Aluminium concentration	48	mg/L
2	Iron concentration	26.9	mg/L
		04.000	
3	Seepage flow	34,300	m3/a
4	Aluminum loading	1,646	kg/a
5	Iron Loading	923	kg/a
6	Area per unit branch	0.0089	m2/gdw
7	Mass per spruce branch	200	g
8	Spruce branches per tree	200	
9	Usable mass/spruce tree	40,000	g
10	Growth area per tree	356	m2
	GROWTH RATES - PPC		
11	Peritraps - summers only	1.43	gdw/m2(sub)/d
12	Density in A11 ditch	199	g/m2
13	Lab low density	14.7	gdw/m2(sub)/d
14	Lab high density	3.0	gdw/m2(sub)/d
	METAL REMOVAL		
15	AI	5,450	ug/gdw
16	Fe	129,500	ug/gdw
17	Al	7.8	mg Al/m2 (sub)/d
18	Fe	185	mg Fe/m2 (sub)/d
19	AI	1.4	g Al/m2 (sub)/a
20	Fe	33.3	g Fe/m2 (sub)/a
			Tree Based
21	AI	0.5	kg Al/tree/a
22	Fe	11.9	kg Fe/tree/a
23	AI	3,297	# of trees
24	Fe	78	# of trees

Table 9: Selminco Biological Polishing of Aluminum and Iron

Using spruce trees in the polishing pond, then the surface area per spruce branch and the number of spruce branches per tree are as outlined in Lines 6 -10. Since field growth rates of periphyton were not measured at Selminco, field growth measurements from other sites were used. There, peritraps produced summer PPC growth rates of 1.4 gdw m<sup>-2</sup> (sub) d<sup>-1</sup>. Laboratory growth measurements suggest that growth rates of Selminco periphyton as high as 7.4 % d<sup>-1</sup> are possible under the proper conditions (Table 6).From high density cultures in the lab, growth rates of 1.5 % d<sup>-1</sup> are possible (Figure 27).

In Table 10, measurements of algal densities in the A 11 ditch are given. Using the maximum growth rate and multiplying it by the density of periphyton found in the A11 ditch, then a maximum growth rate of 14.7 gdw  $m^{-2} d^{-1}$  is estimated and a minium growth rate of 3.0 gdw  $m^{-2} d^{-1}$ . Thus a growth rate per square meter is derived by utilizing either high or low density growth rates obtained in the laboratory combined with actual biomass collected per square meter in the A11 ditch (Line 13 and 14).

SEEPAGE	DENSITY
m from A11	g/m^2
0	95.6
4.2	216.0
9.2	178.6
12.4	199.0
14.4	199.0
18.5	306.0
AVG	199.0

Table 10: Periphyton density in A11 ditch, October 1992

From field and laboratory experiments ranges of growth rates were determined for different density cultures. The growth rates for high and low density situations in a polishing pond are significantly different, since in the same volume for a high density population the same amount of nutrients are available then for a low density population.
To design the system with the most conservative growth rate per square meter, the growth rate 1.4 gdw  $m^{-2} d^{-1}$  obtained in the peritraps (Line 11) was used to estimate the removal capacity. Since it is difficult to predict which growth rates can actually be achieved, the densities from the A11 ditch give confidence, that higher removal capacity can be expected.

The concentrations of metals in periphyton from the A11 ditch indicate that both aluminum and iron are accumulated above water concentrations. The concentrations in the algae were derived from the samples presented in Figure 28, representing the upper and lower ditch with algal growth at Selminco. Thus, periphyton from the Selminco A11 ditch accumulated 5.4 mg Al gdw<sup>-1</sup> and 129.5 mg Fe gdw<sup>-1</sup> (Lines 15,16).

If the metal in the periphyton is multiplied by the growth rate (1.4 gdw m<sup>-2</sup> d<sup>-1</sup>; Line 11), the aluminum removal rate can be calculated, 7.8 mg Al m<sup>-2</sup> (sub) d<sup>-1</sup> and 185 mg Fe m-2 (sub) d-1 (Line 17 and 18). For a 180 day growing season is imposed on biological polishing, the annual removal rate becomes 1.4 g Al m<sup>-2</sup> (sub) d<sup>-1</sup> and 33.3 g Fe m<sup>-2</sup> (sub) d<sup>-1</sup> (Lines 19,20).

Using the conversions from substrate area to trees are used (Lines 6-10), biological polishing can be expected to remove 0.5 kg Al tree<sup>-1</sup> a<sup>-1</sup> and 11.9 kg Fe tree<sup>-1</sup> a<sup>-1</sup> (Lines 21,22).

In order to remove the annual loadings estimated at 1.6 tonnes of aluminium and 0.9 tonnes of iron per year the number of trees required is 3 297 (Lines 23 and 24) if all the aluminium loading should be removed by biological polishing alone. This would result in a tree density of about 5 trees per m3, which is too high. However by reducing the annual load through the implementation of both Arum and precipitation with phosphate, biological polishing would be a buffer to assist in the variations which can be expected from the other processes and the flows.

## 8.0 CONCLUSIONS AND RECOMMENDATIONS

The field and laboratory work carried out at Selminco during 1992 leads to the conclusion that further small scale tests and or experimentation are not required. The conditions of the existing system are relatively well described, and a treatment sequence has been determined.

If it is assumed that the effect of the diversion of surface run-off has produced an average annual flow of 35,000 m<sup>3</sup>, and a 0.4 m water level is maintained in the ARUM cells, seepage treatment should be implemented as follows.

1) Placement of 100 tonnes (one rail car) of Texasgulf phosphate rock in the precipitation ponds should be completed in such a manner that the seepage experiences a total contact time with the rock of 24 h.

2) The existing sediment in the ARUM bog should be supplemented with 2 tonnes of potato waste, based on an annual loading to the cell of 2 tonnes of acidity remaining after phosphate rock contact.

Although the sediment in the ARUM bog is not ideal, laboratory experiments indicate that they are not inhibitory to microbial activity. Therefore, they can remain in their present location.

3) Floating cattails rafts should be installed to cover as much of the open water as possible in the ARUM pond. They can be added row by row, starting with the presently tested raft design, followed by equally effective, reduced cost alternatives as they are designed. Meanwhile, the methods for establishing the cattail populations have been developed, as described in earlier reports.

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4) As a final polishing step, and as a back-up to the treatment system, the second ARUM pond could be modified to serve as a biological polishing system. The existing brush in the cell could be cut during the winter, and distributed as substrate for algae. Growth in the first year could be used to obtain on-site scale-up parameters, if polishing is needed further downstream.

## 9.0 REFERENCES

Kalin M. and W.N. Wheeler. 1992. A study of algal establishment and growth in acid mine drainage (AMD) seeps and precipitation ponds. Final Report to CANMET, Canada Centre for Mining and Energy Technology, Energy, Mines and Resources Canada. DSS File # 034SQ.23440-1-9010. 37 p. + appendices.

Wetzel, R.G. 1983. Limnology. 2nd Edition. Saunders College Publishing, New York, NY. 767 p. + appendices.