THE APPLICATION OF ECOLOGICAL ENGINEERING TO ACID COAL SEEPAGES IN EASTERN CANADA[1]

Margarete Kalin[2], Martin P. Smith[2] and Greg Landry[3]

Abstract: Seepages from a coal waste dump in Cape Breton, NS contain a considerable amount of iron (up to 300 mg/L) and acidity (200 to 1250 mg/L equiv. $CaCO_3$). Upon exposure to air, ferrous iron oxidizes, hydrolyzes, and precipitates, reducing the pH to 2.7. An experimental passive treatment system was developed to remove iron and acidity from the seepage water. A trench system, providing sufficient retention time for iron removal through precipitation of ferric hydroxides, was constructed. Laboratory experiments established that a phosphate-rich rock could effectively enhance iron removal from the seepage water. Consequently, two berms of phosphate rock were constructed to intercept the seepage water. Early results show some reduction in acidity and iron concentration. Water leaving the trench system enters a chemical reducing zone where, through microbial activity, alkalinity is generated and the pH is increased. Laboratory experiments established that potato waste (0.5 g/L) with sediment from the proposed reducing zone could effectively remove acidity from the seepage water. An experimental enclosure, amended with potato waste and covered with floating cattails, was set up. The results were encouraging, until retention time in the enclosure decreased below that required for the reduction process. Overall, the results show that an oxidation/reduction passive system has promise for treatment of coal-waste AMD, provided that sufficient retention time is achieved both for the iron oxidation process and its precipitation and for the alkalinity-generating process, which requires the maintenance of reducing conditions.

Additional Key Words: acid mine drainage, sulfate reducing bacteria, passive treatment.

Introduction

The Selminco Summit is a 50 ha abandoned coal waste dump near Sydney, N.S. which received waste rock from several coal mining operations from 1911 to 1973. From 1981 to 1987, a coal recovery project was undertaken on the site. Following this project, the site was graded (contoured), amended with peat and hydroseeded with a mixture of grasses. As with many mineral waste dumps, acid drainage has occurred at the Selminco Summit. The Selminco Summit has been the test site for development of a passive treatment system for acid mine drainage (AMD). The existing technology to deal with acid discharges involves chemical treatment to neutralize the water, precipitation of the metals, and discharge of an acceptable effluent to the environment. Treatment is required in perpetuity; hence passive systems are of interest, as they would offer a low-cost, low-maintenance method of AMD treatment.

Site Description

The elevation of Selminco Summit is lowest at the southeast section of the site, an area bounded by a rail line and a ditch, along which acidic seeps occur. The drainage from the site was characterized by elevated metals (particularly Fe and Al), high acidity, and low pH.

The development of a passive system started with construction of a drainage collection system (fig. 1), a series of three precipitation cells, and two cells for establishment of chemical reducing conditions for acid reduction (Mills et al. 1989, Cairns et al. 1991, Kalin and Smith 1991, Kalin 1993). The precipitation cells have a mean depth of 1.3 m, a total volume of 2,910 m^3 and a retention time of 10.7 to 53 days, depending on flow rate. The two reduction cells have areas of 4,000 and 1,600 m^2, depths of 0.3 to 1.0 m, and estimated retention times of 0.6 to 6.8 and 0.5 to 18.4 days, respectively, depending on flow rate.

Problems were encountered due to highly variable runoff flows. For example, rain and snow melt caused excessive flows, which caused damage to berms. A freshwater runoff diversion system was installed to reduce peak flow rates. However, seepage was still entering the precipitation cells from the bottom, and natural precipitation rates were insufficient to remove most of the iron. In 1992, phosphate rock was added to the second and third precipitation cells to help precipitate iron and aluminum. A batch reducing enclosure was constructed to demonstrate the feasibility of scaling up the microbial alkalinity process to the entire reducing cell area. Potato waste was added to the enclosure to enhance the bacterial activity, and floating cattail mats were installed as a cover. The configuration of the system is shown in fig. 1.
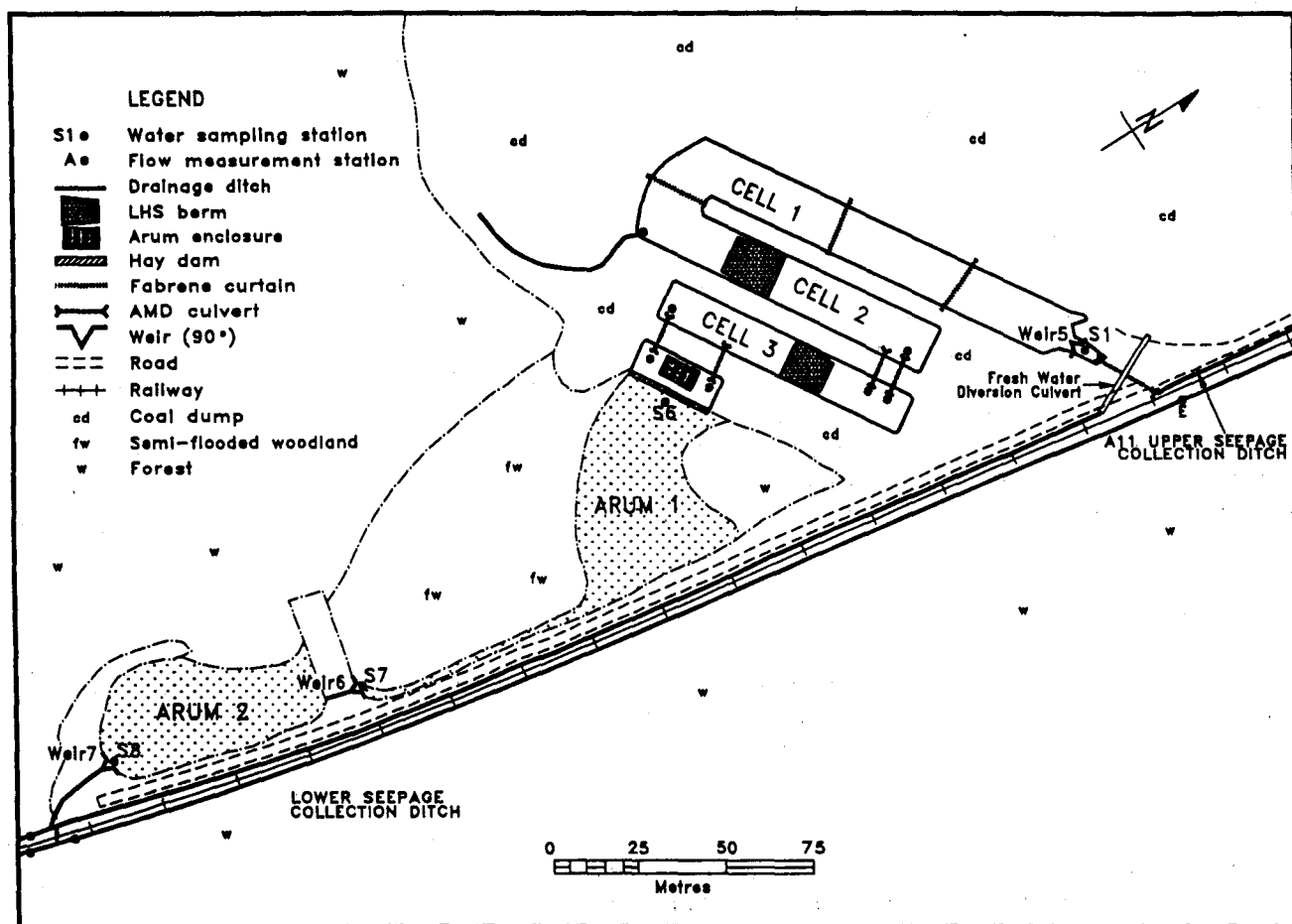

Figure 1.   Layout of the Selminco Summit test cell system. Station S-1 is the inlet to the system. Cells 1, 2 and 3 are the precipitation cells. Station S-6 is the inlet to the reducing cells. Station S-8 is at the discharge from the system.

Methods and Materials

Field and Laboratory Methods

Standard methods were used for determination of redox potential (reported as E_m) and pH. Acidity and alkalinity were determined by manual titration with NaOH and H_2SO_4 or with a Metrohm 702 SM Titrino autotitrator to end points of 8.3 and 4.5 respectively. Iron was determined by inductively coupled plasma spectrophotometry (ICP), U.S. EPA method 200.7 at certified laboratories. The presence of sulfate reducing bacteria was determined in the field using an immunological assay (Rapidchek II, Conoco Ltd) that determines the presence of adenosine phosphosulfate reductase, an enzyme specific to this group of bacteria.

Laboratory Phosphate Rock Experiment

A laboratory experiment was carried out to study the chemical reactions between phosphate rock and the seepage water to help determine whether phosphate rock could be usefully applied in the field. The results of the laboratory experiment assisted the development of design parameters for construction of berms in the test cells. A phosphate-rich gravel (natural phosphate rock, Texasgulf) with a diameter of 3 to 5 mm was employed for the experiment. Three litres of natural phosphate rock (NPR) were packed into an acrylic column (i.d. 15 cm, height 42 cm). To prevent concretion, 1 L aliquots of NPR were separated by 1 L of polystyrene chips. Precipitates could settle into the void spaces of the polystyrene layer. The column was comprised of six 6-cm-thick layers. The column was suspended in an acrylic outer sleeve. Water level was controlled by an overflow port in the outer sleeve. The water level was maintained just above the top of the upper NPR layer. Water was pumped from a feed tank at a rate of 3 L/day. The inner column had a turnover time of 0.8 days. Water drained from the inner to the outer sleeve. The inner + outer sleeve had a total turnover time of 6.8 days. Water overflowed from the outer sleeve into a series of settling tanks.

Field Experiment

In late July 1992, two permeable berms were constructed, using railway ballast rock, across cell 2 and cell 3 of the precipitation system (fig. 1). Each berm was approximately 16 m long, rising from the bottom of the cell (1.3 m deep) to just above water level. All the water that passed through the cells had to pass through the berms. Sampling tubes were inserted into the berms at the time of construction to enable water samples to be taken from within the structures.

Unprocessed NPR was used because it was available from a nearer location than the processed Texasgulf material used in the laboratory column experiment. This material was spread over the upstream face of the berms to a depth of 8 cm. A total of 16 mt was applied to each berm.

Flow Rates

Flow rates were measured at various points through the system. There was a large seasonal variation in flows due to the contribution of runoff. Measured flows at station S-1 (inlet to system) ranged from 16 to 366 m^3/day with lower rates (< 50 m^3/day) in winter and much higher (and variable) rates (>200 m^3/day) in early winter and in spring. A runoff diversion was installed in July 1992, but there are no data at this point indicating whether the diversion system has, in fact, decreased the flow variation. Visually, the flow through the system appears to have stabilized.

Results and Discussion

Water Chemistry

Seepage water at the Selminco Summit contains iron, sulfate and aluminum, and it emerges from the waste pile at pH's between 3.6 and 4.5, with high acidity. When the seepage water flows into the system, the process of iron oxidation (from ferrous to ferric) begins, iron precipitates as ferric hydroxide, and the pH is further decreased.

$$4Fe^{+2} + 10\ H_2O + O_2 \rightarrow 4\ Fe(OH)_3 + 8H^+ \tag{1}$$
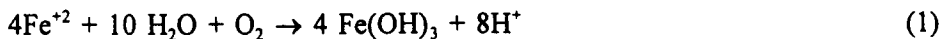
Chemical analysis has been done on water samples collected at various points in the system. Table 1 shows the yearly average for several parameters since the construction of the system in 1989. The data indicate aluminum and iron are precipitating, and that pH decreases to about 2.9 at station S8.

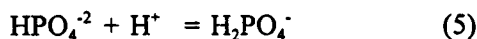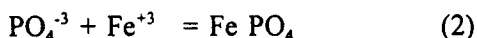Table 1. Selminco Summit water chemistry, 1989-93.

Year	Acidity, mg/L			Fe, mg/L			Al, mg/L			SO4, mg/L			pH		
	S-1	S-6	S-8	S-1	S-6	S-8	S-1	S-6	S-8	S-1	S-6	S-8	S-1	S-6	S-8
1989	610	403	342	52	38	39	40	27	30	1,150	993	913	3.19	3.14	3.02
1990	637	490	404	141	83	63	61	51	42	1,725	1,398	1,113	3.68	3.42	3.27
1991	798	635	531	197	87	49	56	44	37	2,091	1,557	1,400	3.61	3.23	3.20
1992[1]	705	266	247	114	35	25	40	14	12	1,927	785	751	4.12	3.60	3.17
1992[2]	754	499	384	93	35	20	35	29	25	1,690	1,395	1,114	3.30	2.76	2.72
1993	815	555	484	169	64	38	29	21	19	1,737	1,660	1,344	3.56	3.17	2.95
Average	720	475	399	128	57	38	44	31	28	1,720	1,296	1,106	3.58	3.22	3.06

[1] Before placement of phosphate berms.
[2] After placement of phosphate berms.

Phosphate Rock Tests

Phosphate rock was tested as a means of precipitating iron and aluminum and raising pH. This is achieved through the following reactions:

$$PO_4^{-3} + Fe^{+3} = Fe\ PO_4 \tag{2}$$

$$PO_4^{-3} + Al^{+3} = AlPO_4 \tag{3}$$

$$PO_4^{+3} + H^+ = HPO_4^{-2} \tag{4}$$

$$HPO_4^{-2} + H^+ = H_2PO_4^- \tag{5}$$

$$H_2PO_4^- + H^+ = H_3PO_4 \tag{6}$$

Reactions 2 to 6 proceed in sequence. Once the iron and aluminum precipitation reactions have taken place, the pH will rise owing to the formation of phosphoric acid. This phosphate is then consumed by biological processes. The results of the column experiment are presented in fig. 2 and fig. 3. The bench-scale system was very effective and demonstrated that phosphate rock has the potential to treat Selminco seepage water.
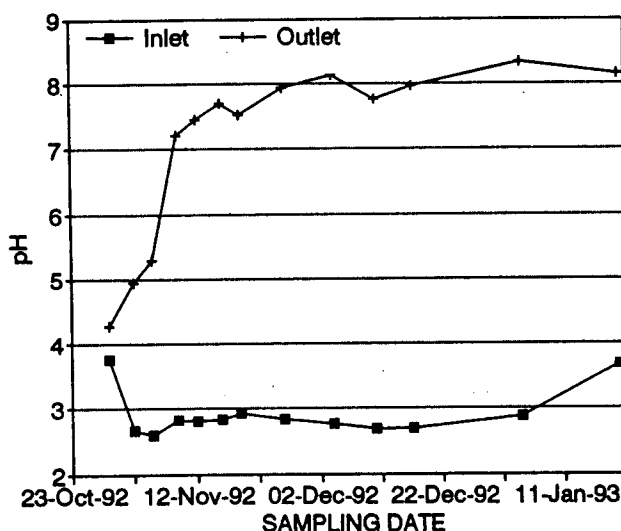
Figure 2.   Solution pH at inlet and outlet of phosphate rock laboratory column experiment.

The field berms were installed in July 1992. An initial short-term impact was noted, but the effect was short-lived, as is evident in fig. 4. The reasons for the poor initial performance may have been low contact time between the rock and water and/or low permeability of the material. Since the installation of the berms, a high percentage of the iron is being removed within the system, but this removal cannot be solely attributed to the phosphate rock, owing to other changes in the flow regime, including the installation of a fresh water diversion system.

The Reducing Cells

Laboratory jar experiments demonstrated that when 0.5 g/L potato waste was added to sediment from the reducing cells, the pH increased from 2.7 to nearly 5 (fig. 5). When 10 g/L potato waste was added, pH increased to 7. Addition of potato waste also caused the E_m to drop dramatically (fig. 6) and reduced the water's acidity (fig. 7). This sediment from the reducing cell had received, in previous years, an organic amendment (hay bales) to cover the accumulated iron precipitate. The decomposition of potato waste led to a drop in E_m and provided energy sources for bacteria whose activity mediated the pH increase and removal of acidity.

The results of these tests led to the construction of an enclosure in the first reducing cell in September 1992. This enclosure contained a water volume of 40 m^3. Potato waste was added (3.75 g/L) and the water surface was covered with 12 floating cattail rafts which had been established in 1991. After about 6 weeks, the acidity within the enclosure was substantially lower than the acidity outside (fig. 8). This pattern continued until mid-December, when the differences in water quality between the inside and outside of the enclosure were no longer apparent. It is not clear why the enclosure failed, as other enclosures have remained active for 1,200 days (Kalin 1992).
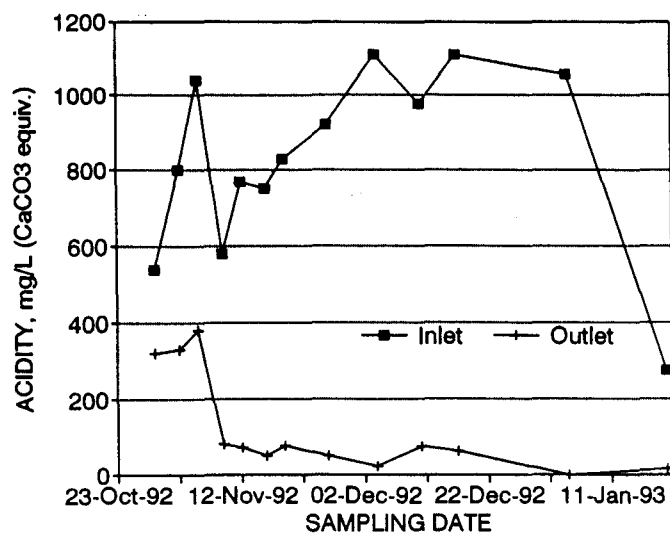

Figure 3.   Solution acidity at inlet and outlet of phosphate rock laboratory column experiment.
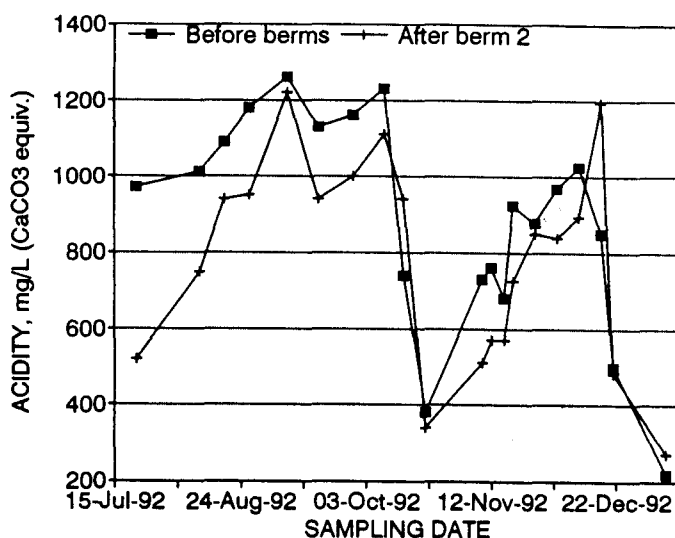

Figure 4.   Acidity of water before berms and after berm 2 in Selminco Summit test cell system.

Conclusions

Through the development of a passive treatment option for the coal seepage over the 4 yr period, it became evident that flow control is essential in order to design the iron oxidation-precipitation ponds with adequate retention time. Although natural phosphate rock might be effective in assisting in removal of iron and aluminum, this field test indicates that placement methods and grain size must be more rigorously controlled for a successful application.

After iron and aluminum precipitation, alkalinity can be generated microbially, as demonstrated by the laboratory experiments and the field enclosures. From the test work carried out on-site and in the laboratory, it is anticipated that design parameters can be derived for the implementation of a passive treatment system.
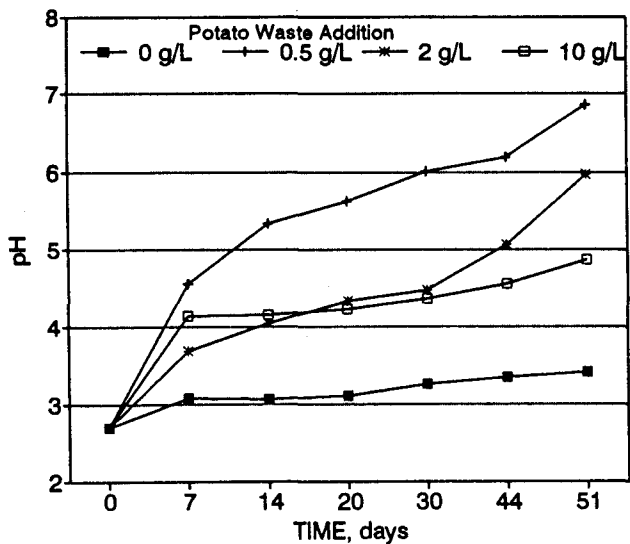

Figure 5.   Solution pH in laboratory jar experiment where potato waste was added to Selminco Summit water overlying reducing cell sediment.
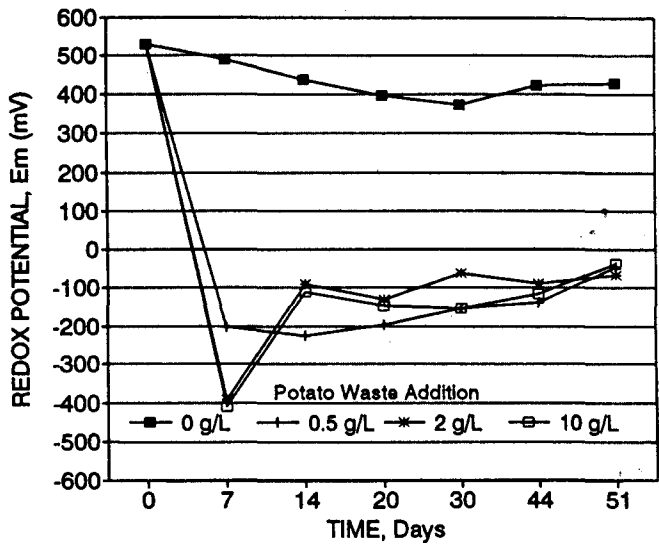

Figure 6.   Solution redox in laboratory jar experiment where potato waste was added to Selminco Summit water overlying reducing cell sediment.
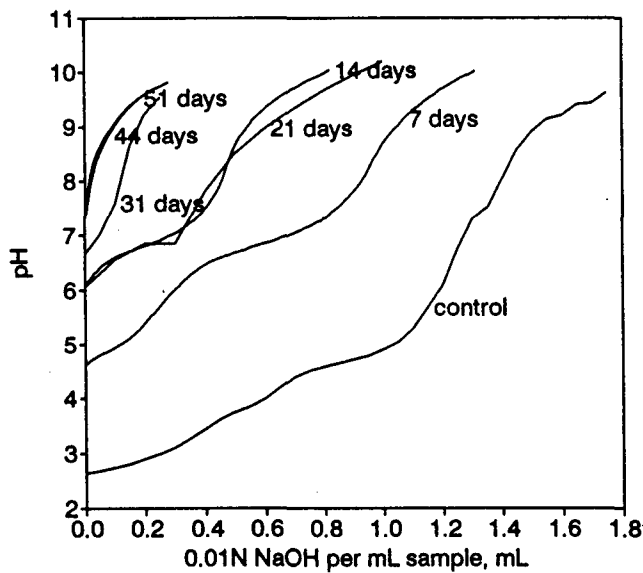

Figure 7.   Acidity titration curves for solutions sampled from the laboratory jar experiment where potato waste was added to Selminco Summit water overlying reducing cell sediment.
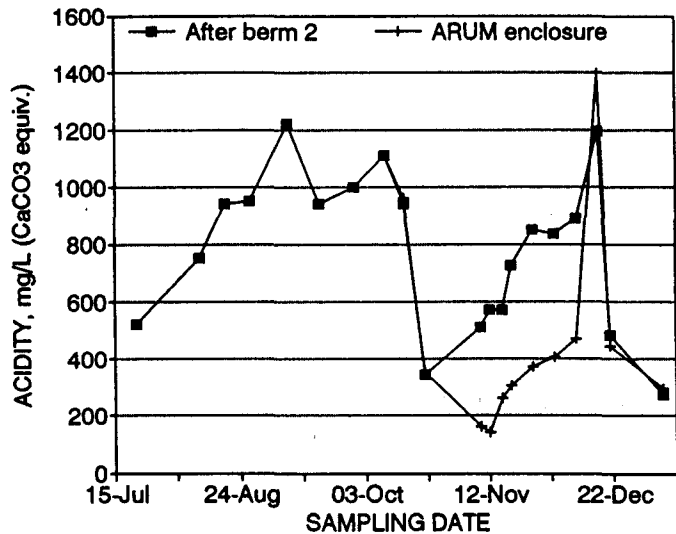

Figure 8.   Solution acidity in enclosure constructed in the Selminco Summit test cell system.

301

Acknowledgment

References

Cairns, J. E., R.G.I. McCready and M. Kalin. 1991. Integrated field and laboratory experiments in ecological engineering methods for acid mine drainage treatment. p 409-425. In Proceedings of the Second International Conference on the Abatement of Acidic Mine Drainage (Montreal, September 16-18, 1991) v.2.

Kalin, M. 1992. Decommissioning open pits with ecological engineering. Paper 27. In Proceedings of the Canadian Mineral Processors (Ottawa, Ontario, Jan 21-23, 1992).

Kalin, M. 1993. Treatment of acidic seepages using wetland ecology and microbiology: Overall program assessment. Final Report for Canada Centre for Mineral and Energy Technology, EMR Project 23440-2-9217/01-SQ, Ottawa. 57 pg.

Kalin, M. and M.P. Smith. 1991. Biological amelioration of acidic seepage streams. p 355-368. In Proceedings of the Second International Conference on the Abatement of Acidic Mine Drainage (Montreal, September 16-18, 1991) v.1.

Mills, A. L., P.E. Bell and A.T. Herlihy. 1989. Microbes, sediments and acidified water: The importance of biological buffering. p 1-19. In Acid stress and aquatic microbial interactions. S.S. Rao (ed.) CRC Press, Boca Raton, FL.