

POSSIBLE OPTIONS FOR *IN SITU* TREATMENT OF ACID MINE DRAINAGE SEEPAGES¹

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Abstract: Noranda Technology Centre conducted bench-scale evaluations of various passive techniques developed by other institutions and potential processes for *in situ* treatment of base metal acid mine drainage (AMD) seepages. The passive methods assessed included: anoxic lime drains (ALD), where limestone is kept under anoxic conditions; a limestone-organic mixture (LOM), in which the function of the process is based on the activity of sulphate reducing bacteria; a biosorbent (BIOS) approach where metals are taken up by wood wastes; and a biotrench (BT), which differs from LOM in that different nutrient types are used. Prior work suggested that the best process could be obtained by using combinations of the first three methods and that the performance of the microbiological processes was substantially affected by low temperatures. With further laboratory tests, the best combination(s) and operation parameters were determined to provide a basis for the design of field tests. The results obtained from the test of combined systems indicated that a LOM connected to a smaller size ALD bed in series would be the best combination for treating AMD. With this system, the pH can be raised from 2.5 to 7.2 and concentrations of Al, As, Cd, Cu and Fe are lowered to less than 1 mg/L. Zn and Mn concentrations are reduced from 482 and 49 mg/L to 8 and 14.7 in the final effluent. TSS, BOD and COD levels in the final effluent are 9, 1.5 and 40 mg/L, respectively. In addition, it was found that a BIOS/ALD combination can selectively remove Cu and Cd to < 0.01 mg/L and increase pH to 6.5 and its performance is not affected by low temperature. Pilot tests for the LOM/ALD system were recommended to demonstrate the efficiency of the method for removing metals and increasing pH under field conditions.

Additional Key Words: metals, removal, passive treatment, anoxic limestone, sulphate reducing bacteria, biosorbent, biosorption, biological treatment, woodwastes

Introduction

Passive methods (e.g. wetlands, use of sulphate reducing bacteria (SRB) and anoxic lime drains) have been proposed as alternatives to conventional chemical treatment (Hammer 1989; Machemer *et al.* 1990; Kuyucak *et al.* 1991; Brodie *et al.* 1992). Particularly, these processes would be useful for low flow streams or seepages of acid mine drainage, of which collection and routing to a treatment plant is unaffordable. Current passive processes being developed by other institutions include: anoxic limestone drains (ALD), lime-organic mixture (LOM), biotrenches (BT) and biosorption (BIOS). An ALD system, first developed by the Tennessee Division of Water Pollution Control (TDWPC) and the Tennessee Valley Authority (TVA) (Brodie *et al.* 1990), consists of an excavated seepage interception trench backfilled with crushed limestone and covered with plastic and clay to keep air out. The main function of such a system is to pretreat AMD by increasing alkalinity prior to a wetland.

In the LOM method, investigated by the Colorado School of Mines (Wildeman 1992; Machemer *et al.* 1990), a bed which is made up of a mixture of limestone and manure (with some soil to increase permeability) is used to remove metals and increase alkalinity. The process is mainly based on the activity of SRB and is enhanced by the presence of limestone and organic material. The BT process has been investigated by CANMET, Canada (Bécharde *et al.* 1990). A pilot-scale test has been conducted for treating pyritic slates at the Halifax Airport. In this process, removal of metals and generation of alkalinity from AMD

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is also based on SRB activity, using slow-release carbon-based nutrients such as straw, sawdust or wood shavings.

The BIOS process involves use of biological materials such as sphagnum moss, or algae as adsorbents (or biosorbents), and has been investigated by several institutions and Noranda Technology Centre (NTC) for removing metal ions from mine effluents (Jeffers et al. 1993; Kuyucak *et al.* 1989). In another NTC study, woodwastes (e.g. sawdust, wood chips) were found to be potential biosorbents. Therefore, woodwastes as biosorbents were further examined as a passive treatment option. A bed of biosorbents can be used as a passive treatment process by placing it where the seepage occurs. When the bed is saturated by metals, the proponents suggest it can either be disposed of (with tailings or recycled to a smelter), or washed with an appropriate eluant for recovery of metals and/or reuse of the bed.

Experience has demonstrated that the influent flow rate, contaminant concentrations, pH, alkalinity (or acidity), the capacity of the treatment system to resist changes in pH and other variables are all extremely important to system performance. In addition, most investigations to date have been limited to drainage from coal mines and pyritic slates, which are quite different from the AMD associated with sulphide metal mines. Therefore, NTC and New Brunswick Mineral Development Agreement decided to assess the capabilities of several passive processes, with the objective of developing effective methods for treating small volumes of AMD.

Phase I work showed that better treatment efficiency could be achieved with the use of combined systems (Kuyucak and St-Germain 1993a). Phase II work was designed to confirm operational parameters for the combined systems and to provide a basis for the design of the field evaluation. In addition to design and operating requirements, economical feasibility was assessed.

Materials & Methods

The Combinations Evaluated

Each combination consisted of a main reactor connected in series to one or two other small reactors. Based on materials used, three types of reactors were employed: LOM, BIOS and ALD. The combinations tested were: LOM/BIOS/ALD, BIOS/ALD and LOM/ALD. In two combinations, LOM was used as the main reactor and, in one combination, the biosorbent bed was the main reactor (Figure 1).

The efficiency of each combination in treating moderate strength AMD at 10°C and with a retention time of 14 days, which was the optimum retention time obtained at 20°C for LOM alone, was assessed. The flow rate was set to maintain 14 days of retention time based on the void volume of the main reactor in each combination. The flow rate, therefore, varied for each combination.

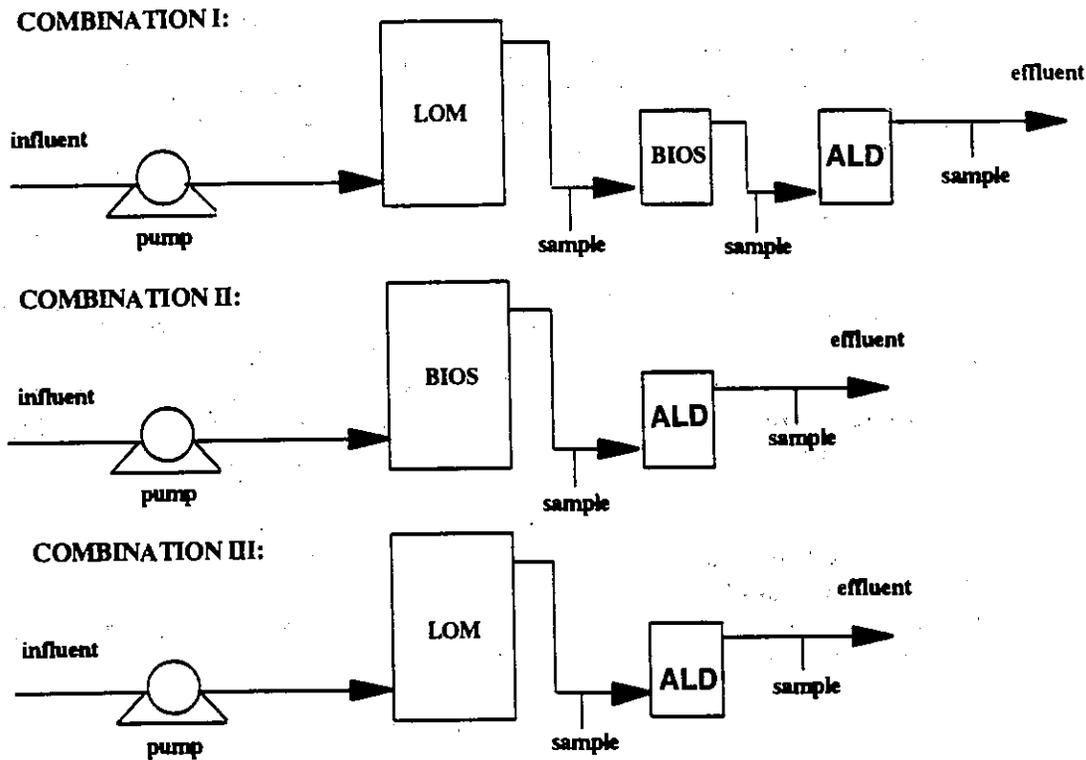


Figure 1. Reactor Configurations.

Reactor Specifications

All reactors were made of plexiglass cylinders. The main reactors, with 28.8 cm I.D. X 100 cm height, had a total working volume of either 20 or 30 L, depending on the combination. Small reactors were 10 cm I.D. x 30 cm high columns with a working volume of 4 L. Influent and effluent ports (1.25 cm dia. for main reactors and 0.63 cm for the small reactors) were located on opposite sides of the reactor. The influent port was 5 cm above the base of each reactor. The effluent level in the reactors was controlled by the height of the effluent port. A drain was provided at the bottom of the reactors over which two layers of geofabric material were placed to prevent clogging of the drain. All reactors were operated in upflow mode where the influent AMD was added to the main reactor via a peristaltic pump and the overflow passively flowed through the other small reactors. Effluent out of the last reactor was collected and analyzed.

Materials Used in Each Reactor

Materials and procedures used to conduct tests with each reactor have been described elsewhere (Kuyucak and St-Germain 1993a). Specifications are also given in Table 1.

Table 1: Reactor specifications for phase II studies.

Combination	Main Reactor			Small Reactor		
	Materials Used	Working Vol.(L)	Void Vol.(L)	Materials Used	Working Vol.(L)	Void Vol(L)
LOM/BIOS/ALD	Cow manure, soil, limestone	30	14	BIOS: ¹ sawdust, bark, paper sludge	4	2.5
				ALD: limestone (>93% CaCO ₃)	4	2.1
BIOS/ALD	Bark, Woodpulp, Wood chips	30	7	limestone (>93% CaCO ₃)	4	2.1
LOM/ALD ²	Cow ³ manure, soil, limestone	20	4.5	limestone (>93% CaCO ₃)	4	2

¹ Soaked with acidified tap water (pH 3) for 7 days to remove excess buffering and absorbing capacity.

² Constructed for the Phase II studies.

³ 0.63 cm grade limestone used instead of 2.5 cm grade as was used in the first LOM reactor (i.e. in LOM/BIOS/ALD combination).

Composition of AMD

Moderate strength mine water (e.g. F-Group AMD from Mattabi Mines) was used throughout the experiments; its composition is given in Table 2.

Table 2: Composition of F-group mine water used in the tests.

Parameter	pH	Al	Cu	Fe	Zn	SO ₄
Average Conc. (mg/L)	2.5	220	60	325	460	6300

Sampling Strategy and Analytical Procedures

Samples of the final effluent from each combination were collected every week. After approximately one month of operation, effluent samples (1 L volume) were collected weekly from each stage. The pH, redox and DO were measured using appropriate electrodes. SO₄ and metal concentrations were analyzed with an inductively coupled plasma (ICP) after samples were filtered and acidified with 3% HCl. Once a month, the same samples were also analyzed for volatile suspended solids (indicating amount of bacteria; VSS), total suspended solids (TSS), total organic carbon (TOC), biological oxygen demand (BOD), chemical oxygen demand (COD), total Kjeldhal nitrogen (TKN) and total phosphorous (TP). Except for total organic carbon (TOC), which was preserved by acidification to pH 2, VSS, TSS, BOD, COD analyses were

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performed on unfiltered 500 mL samples, preserved at 4°C. They were analyzed as respectively described in methods 5310B, 2540E, 2540D, 5210B and 5220C (Standard Methods 1989).

Results and Discussion

LOM/BIOS/ALD

Effluent Quality. The pH in the final effluent averaged 6.3. As, Cd and Cu concentrations were below the detectable limits of 0.25 mg/L while Al was at 0.7 mg/L. Fe and Zn concentrations were lowered from 305 and 449 to 21 and 181 mg/L, respectively. SO₄ was reduced by approximately 50%, the final concentration being 2887 mg/L. Mn was not removed. BOD and COD concentrations were low after each stage of the treatment. Total organic nitrogen (TKN) and total phosphorous (TP) concentrations were 5.1 and 0.05 mg/L, respectively. The ALD reactor contributed to increase the pH to 6.3 and reduce Al and Fe concentrations to those observed after the LOM stage as well as reestablishing post-LOM treatment levels offset by the BIOS stage.

SO₄ and Metal Removal Rate. The overall SO₄ removal rate, for the LOM/BIOS/ALD combination, was 0.968 mol/m³/d, most of which occurred in the LOM reactor. The corresponding metal removal rate was 0.481 mol/m³/d and the volumetric flow rate was 27 L/m³/d. In spite of the fact that the total moles of SO₄ removed was greater than those of metals removed, all metals were not completely extracted from the water. The SO₄ removal rate obtained from the LOM alone at 10°C was much higher than what was expected according to the literature (i.e. 0.15 mol/m³/d, Kuyucak and St-Germain 1993b; Kuyucak and St-Germain 1994), implying a significant contribution from the limestone present in the LOM system.

BIOS/ALD

Effluent Quality. In the BIOS/ALD process, the pH was increased from 2.4 to 6.3. The Al concentration decreased from 218 mg/L to below 0.7 mg/L and As, Cd, and Cu concentrations were lowered from 1.5, 1.8 and 61 mg/L, respectively, to below detectable limits. Fe and Zn concentrations were 3.8 and 276 mg/L in the effluent. As BIOS removed Cu and Cd, the ALD increased pH and reduced concentrations of Al, As and Fe in the final effluent. BOD and COD concentrations were negligible. The BIOS/ALD performance was also not affected by the low temperature when compared to the other systems.

SO₄ and Metal Removal Rate. For a volumetric flow rate of 14.7 L/d/m³ at 10°C, 0.27 mol/m³/d of metals and 0.509 mol/m³/d of SO₄ would be removed by the BIOS/ALD system, essentially due to the ALD reactor. In the BIOS alone, the SO₄ removal rate was lower than that of the metal removal rate, indicating that the metal removal (e.g. Cd and Cu) was probably due mainly to adsorption onto the wood waste, since there was no limestone in the system.

LOM/ALD

Effluent Quality. The overall treatment results are shown in Table 3. The pH increased from 2.4 to 7.2 and the concentrations of Al, As, Cd, Cu and Fe decreased to less than 0.7 mg/L. As, Cd and Cu concentrations were under detectable limits while the Zn concentration was lowered from 482 to 8 mg/L and Mn was reduced from 48 to 15 mg/L, which was not observed before with the other tests.

The LOM reactor increased the pH to 6.0 and removed Al, As, Cd, Cu and Fe to less than 0.8 mg/L. In LOM alone, Zn and Mn concentrations decreased to 100 mg/L (i.e. 79% of total Zn) and 24.4 mg/L, respectively. The ALS system subsequently reduced the remaining Zn to 8 mg/L and Mn to 14.7 mg/L. BOD and COD levels were both negligible. The ALD reactor seemed to act as a filter by lowering VSS, TSS

and TOC levels coming from LOM. TP was low in the effluent, indicating a deficiency of phosphorous in the system. In process optimization, the use of phosphorous supplements (e.g. phosphate rocks, fertilizer) might improve the process efficiency.

Table 3: Final effluent quality achieved by the LOM/ALD combination.

STREAM	pH	Concentration (mg/L)									
		BOD	TSS	TKN	NO ₃	Al	As	Cd	Cu	Fe	Zn
INFLUENT	2.45	n/av	n/av	n/av	1.30	222	0.87	0.98	56	307	472
EFFLUENT	7.17	2	9	9.2	0.96	0.69	0.13	0.01	0.01	0.10	7.68

SO₄ and Metal Removal Rate. Table 4 shows that at 10°C, for a volumetric flow rate of 14.6 L/d/m³, 0.58 mol/m³/d of SO₄ and 0.334 mol/m³/d of metals were removed in the LOM/ALD system. The majority of the treatment was performed by the LOM reactor while the ALD reactor only served as a polishing treatment. In spite of high SO₄ removal, metals removal (e.g. Zn) was not complete. This may imply that the limestone present in the system is making a major contribution, similar to what was observed in the LOM/BIOS/ALD system. When the data were compared to those obtained in Phase I at 20°C, better performance (particularly in Zn removal) could be expected with a longer residence time (e.g. >20 days).

Table 4: SO₄ and metal¹ removal rates in the LOM/ALD combination.

Reactor type	Flow rate (L/d)	Vol. ² flow rate (L/m ³ /d)	Bed volume (m ³)	Net SO ₄ removal (mmol/L)	SO ₄ removal rate (mol/m ³ /d)	Net metal removal (mmol/L)	Metal conc. in influent (mmol/L)	Metal removal rate (mol/m ³ /d)
LOM	0.321	18.9	0.017	38.4	0.726	21.5	23.0	0.405
ALD	0.321	64.2	0.005	1.56	0.100	1.43	1.57	0.0916
L/A	0.321	14.6	0.022	40.0	0.584	22.9	23.0	0.334

¹ Includes Al, Cd, Cu, Fe and Zn

² Volumetric

Conclusions and Recommendations for Field Design

The LOM/ALD system would be a suitable option for treating low to moderate strength AMD; however, its capability for treating AMD should be demonstrated under field conditions where the effect of low temperature and fluctuating flow rates would be evaluated. In addition, the biosorbent bed at 10°C and 14-day retention time can efficiently remove Cd and Cu. The BIOS/ALD combination can be considered for selectively removing Cu and/or Cd and increasing pH. The field system for the LOM/ALD process should be designed for a longer retention time (e.g. 30 to 40 days) to ensure a good performance of the system. Addition of Ca₃(PO₄)₂ or slow-release fertilizers into the LOM cell may eliminate nutrient deficiency (i.e. P) and improve the bacterial activity. The inclusion of an ALD reactor is beneficial for maintaining the pH above 6.0 in all cases. It also acts as a filter; however its long-term performance should be monitored. Under

steady-state conditions, K, Mg and Na were unchanged from influent concentrations; only the release of Ca from the limestone was observed.

The design should also provide good flow distribution, as well as conditions to prevent the system from freezing and to keep the beds (particularly LOM) flooded at all times. Introduction of AMD to the system as down flow rather than upflow, and covering the system (e.g. with a plastic membrane and/or some bails of hay) may help to maintain anaerobic conditions and reduce heat loss. The effluent exiting the LOM/ALD system should be aerated for further polishing (particularly for removal of excess Fe, Mn, BOD and TSS).

The systems studied are more effective against low strength AMD. Seeps with SO_4 levels below 2200 mg/L and low concentrations of Fe and Al could effectively be treated with such a system for a long period of time since no armouring of limestone would occur. The cost of such a system (LOM/ALD) for treating 12 L/min of AMD is estimated to be in the range of \$80 thousands (Canadian). Although life expectancy of such a system, when calculated based on theoretical requirements and available C moles in the organic materials, might be as long as 40 years (Kuyucak and St-Germain, 1993b), the life span under actual conditions should be expected to be much shorter due to physical, biological and chemical effects. Therefore, the longevity of the system should be determined for actual conditions. The form of metal precipitates in the substrate and possible options for disposal of metal-laden substrate, once it is used up, should also be investigated.

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