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January 20, 1997
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Edited by L. Lortie, P. Bédard & W.D. Gould

BIOTECHNOLOGIE ET ENVIRONNEMENTS MINIERS

COMPTE RENDU DE LA TREIZIÈME RÉUNION GÉNÉRALE ANNUELLE DU BIOMINET

Le 20 janvier 1997
Ottawa, Ontario

Révisé par L. Lortie, P. Bédard & W.D. Gould

BIOMINET

BIOMINET NETWORK

The BIOMINET Network was established in 1983 and the scope of the network can be described as follows: "BIOMINET is a network of companies, research organizations and associated agencies interested in the applications of biological systems in all aspects of the recovery and environmental protection associated with the processing of minerals and fossil fuel resources."

OBJECTIVES

BIOMINET's objectives are to promote interaction among the academic, business and government communities and to promote the adoption of biotechnology based processes in the mining and fossil fuel sectors in Canada.

ACTIVITIES

The activities of the network include publishing three newsletters annually, organizing an annual meeting and publishing the proceedings from the annual meeting. The BIOMINET Secretariat also serves as a source of information concerning the applications of biotechnology in the mining and fossil fuel sectors.

CANMET is also responsible for contracting out National Biotechnology Strategy (NBS) funding to encourage the application of biotechnology in the fossil fuel and mining sectors by funding research for the development of biotechnology based processes.

MEMBERSHIP

The network has presently 450 members in industry, academia and government. Membership in BIOMINET is free and open to anyone interested in the network's objectives.

MANAGEMENT OF BIOMINET

The network is funded by NBS and administered by CANMET. It is run by a chairman and a secretary who are provided by CANMET and a steering committee which consists of members from the mining and fossil fuel industries, government and academia. One of the industry members chairs the steering committee.

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LE RÉSEAU BIOMINET

Le réseau BIOMINET a été établi en 1983 et l'envergure de ses activités peut être décrite de la façon suivante: "BIOMINET comprend un réseau d'entreprises, d'organismes de recherche et d'organismes associés intéressés à l'application de systèmes biologiques couvrant tous les aspects de la récupération et de la protection environnementale associés au traitement des ressources minérales et des combustibles fossiles."

OBJECTIFS

Les objectifs du BIOMINET sont de promouvoir l'interaction entre les milieux universitaire, des affaires et gouvernementaux ainsi que l'adoption de procédés basés sur la biotechnologie dans les secteurs de l'exploitation minière et des combustibles fossiles, au Canada.

ACTIVITÉS

Les activités du réseau comprennent la publication annuelle de trois bulletins d'information, l'organisation d'une réunion annuelle ainsi que la publication du compte rendu de cette réunion. Le Secrétariat du BIOMINET sert aussi de source d'information sur les applications de la biotechnologie dans les secteurs de l'exploitation minière et des combustibles fossiles. CANMET est également responsable de l'octroi de marchés à contrat relativement à la stratégie nationale en matière de financement de la biotechnologie. L'objectif poursuivi est d'encourager l'application de la biotechnologie dans les secteurs de l'exploitation minière et des combustibles fossiles par le financement de la recherche portant sur le développement de procédés basés sur la biotechnologie.

NOMBRE D'ADHÉRENTS

Actuellement, 450 membres provenant des milieux industriel, universitaire et gouvernemental sont affiliés au réseau. L'adhérence au BIOMINET est gratuite et toute personne intéressée aux objectifs du réseau peut obtenir le statut de membre.

GESTION DU BIOMINET

Le réseau est financé par le fond de la stratégie nationale en matière de biotechnologie et administré par CANMET. La direction comprend un président et un secrétaire dont les services sont assurés par CANMET ainsi qu'un comité de direction composé de membres provenant des industries de l'exploitation minière et des combustibles fossiles, du gouvernement et des universités. La présidence du comité de direction est assurée par un membre de l'industrie.

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ORGANIC COVER MATERIAL FOR ORGANIC TAILINGS: DO THEY MEET THE REQUIREMENTS OF AN EFFECTIVE LONG TERM COVER?

L.C.M. ELLIOT, L. LIU and S.W. STOGRAN

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ABSTRACT

Three different organic materials (peat, lime stabilized sewage sludge (LSSS) and municipal solid waste (MSW) compost) were evaluated in a combination of bench and pilot scale laboratory test programs. A fourth non-organic material, desulphurized tailings, was also tested to provide comparative data. The organic cover materials tested demonstrate that there are significant differences in the ability of each material to provide a beneficial tailings cover. The results to date from the test program show that, of all the materials tested, the LSSS performed best at meeting the objectives of a good tailings cover. The desulphurized tailings (DST) cover also showed promise with some modification to the single layer approach. The following paper summarizes the results of bench scale tests and a one year pilot scale test program designed to evaluate the effectiveness of organic cover materials at reducing acid generation.

LES COUVERTURES DE MATIÈRES ORGANIQUES POUR RÉSIDUS ORGANIQUES : SONT-ELLES EFFICACES À LONG TERME?

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RÉSUMÉ

Trois différents types de matières organiques (la tourbe, les boues résiduaires stabilisées à la chaux et le compost de résidus urbains solides) ont été évalué par une série d'essais en atelier et à l'échelle pilote dans le cadre de programmes de véfification en laboratoire. Une quatrième matière non organique, soit des résidus désulfurés, a également été soumise à des essais en vue d'obtenir des données comparatives. Les matières organiques qui ont été vérifiées ont révélé que la capacité de contenir les résidus varie grandement selon le genre de couverture utilisée. Les résultats obtenus à ce jour par le biais du programme d'essai révèlent que de toutes les matières qui ont fait l'objet d'essais, les boues résiduaires stabilisées à la chaux constituent la meilleure couverture pour résidus. La couverture de résidus désulfurés s'avère prometteuse; il ne s'agirait que de modifier l'approche « couche simple ». Le présent document résume les résultats des essais menés en atelier et d'un programme d'essai à l'échelle pilote d'une durée d'un an qui a été conçu pour évaluer la capacité des couvertures de matières organiques à réduire la production d'acide.

INTRODUCTION

Large quantities of organic material are now stockpiled, or may be available in the near future, from urban and industrial sources. The cities in Ontario, alone, are capable of producing approximately 680,000 tonnes of municipal solid waste (MSW) compost annually and create comparable amounts of sewage sludge, which is currently landfilled [1]. Peat from bogs in the Canadian Shield region, although not a waste material, represents a vast renewable source of organic matter. Peat bogs are often found near base metal and precious metal mines.

These materials may provide effective and affordable solutions to the reclamation of acidic mine tailings. A literature review of the physical and chemical characteristics of MSW compost and other organic materials [1] revealed that an organic layer on sulphide tailings could be beneficial in the suppression of tailings oxidation and acidic mine drainage, in the following five ways: (1) *Physical oxygen barrier* - The organic cover layer may be saturated with water over at least part of its depth. This saturation would provide the limiting factor for the rate of oxygen diffusion into the tailings and this rate would be approximately the same as the low diffusivity of oxygen in water; (2) *Oxygen-consuming barrier* - The continued decomposition of organic material may create a large biological oxygen demand which would act as a sink for atmospheric oxygen and dissolved oxygen in infiltrating water; (3) *Chemical inhibition* - Compounds and decomposition products in the organic material that leach into the tailings may inhibit the growth and metabolism of sulphate-producing (acidifying) bacteria; (4) *Chemical amelioration* - Organic compounds in the organic material may cause the reductive dissolution of iron oxides (either directly or indirectly by providing metabolic substrates for bacteria), the reduction of sulphate, and the prevention of indirect ferrous sulphide oxidation and acid generation; and (5) *Reduced water infiltration* - The decomposition and resultant compaction of an organic cover layer may result in the decrease of the hydraulic conductivity of the cover. This would result in a subsequent decrease in infiltration, thus decreasing tailings ground water flow.

Sulphate and iron reduction rates may be limited in a tailings system by a lack of organic substrates for bacterial metabolism. Consequently, an organic cover layer on the tailings may provide an important source of carbon compounds for bacteria as decomposition and leaching proceeds. The biological oxygen demand of an aerobic, actively-decomposing organic layer also constitutes a strong sink for atmospheric oxygen, preventing it from moving down the oxygen concentration gradient toward the AMD oxidation processes in the tailings.

If fresh organic material is not added, the continued oxidation of an organic cover layer material will eventually decline as the remaining material becomes more humified and more resistant to further decomposition [1]. Therefore, the biological oxygen demand of the organic cover layer will eventually reach a lower level based on a lower input rate of natural carbon compounds and other nutrients into the cover layer. The resistance that the cover layer will still be able to offer to the downward diffusion of atmospheric oxygen will then be determined by its physical properties, especially its depth and gas-filled porosity. Gas-filled porosity, in turn, will be mainly determined by the structural composition of the material and the degree that the pore spaces are filled with water (i.e. water content).

MATERIALS AND METHODS

The purpose of this program was to investigate the effectiveness of various organic materials on eliminating or reducing acid generation and the movement of acidity and heavy metals from tailings ponds. The program involved a study of four different cover materials. The materials studied included: peat, MSW compost, lime-stabilized sewage sludge (LSSS), and desulphurized tailings (DST). The organic materials investigated were selected for their physical and chemical characteristics that would decrease the rates of acid generation processes in sulphide tailings or reverse the acid generation processes. These would result in the precipitation of sulphides. It was believed that these materials could also decrease the movement of water through the tailings pond [1, 2]. The organic materials studied were also potentially available in large quantities at low cost. DST were used as a contrasting, non-organic cover layer that may prove to be cost-effective. A control cell was used to evaluate the differences between the tailings with and without a cover.

Background information from previous studies illustrated that it was important to evaluate the process of organic leachate interaction with tailings. This interaction was assessed by examining the processes *in situ* during the pilot experiments.

The research project had the following objectives: (1) To experimentally compare the effectiveness of organic and inorganic cover layers in reducing acid generation and the mobilization of trace metals from partially oxidized acid generating tailings; (2) To evaluate the extent and rates of upward salt migration in a range of cover materials under worst case conditions, and assess the need and effectiveness of a capillary barrier; (3) To monitor the organic and inorganic chemistry of three organic and one inorganic tailings cover systems in an effort to understand and quantify the aerobic and anaerobic organic degradation rates and processes and their interaction with acid generating tailings; (4) To evaluate the physical characteristics of three organic and one inorganic cover in an effort to determine their ability to remain saturated enough to minimize oxygen transport.

Program Design

The covers evaluation test program included three main components of study: (1) Characterization of Tailings and Cover Materials; (2) Salt Migration Column Bench Scale

Test; and (3) Pilot Scale Cover Test Program. This paper will focus on the results of the Pilot Scale Cover Test Program.

Pilot Scale Cover Test Design

Pilot scale models were designed to simulate a section taken out of a tailings pond. The section is shown in Figure 1, and contains several interactive components of the tailings cover system. Atmospheric/weather effects, tailings cover interaction and water flows through the system are some of the system components which are replicated in the models. The pilot model is, in effect, a microsystem of a tailings pond area. Due to the ability to control some of the external factors (such as rainfall), to measure and correlate others to the field (such as evaporation and temperature) and to monitor the water balance of the system, the complex field system is somewhat simplified allowing for more direct interpretations of cause-effect relationships.

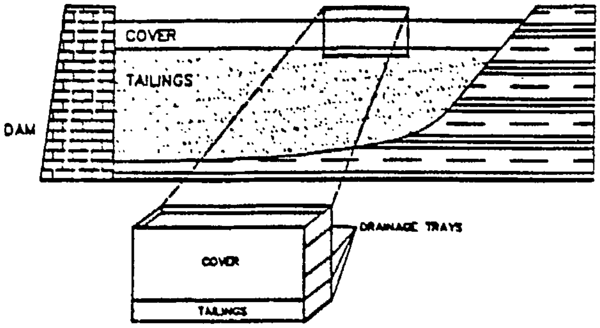

Figure 1: Pilot Scale Model of a Tailings-Cover System

Pilot Cell Design

The pilot scale models (pilot cells) were constructed of 0.0125 m thick sheets of polyethylene chloride (PVC) plastic welded together and supported within a frame of angle iron. The pilot cells are 2.5 m long, 1.5 m high and 0.6 m wide (Figure 2). One sheet of clear Plexiglas™ forms one long side of the cells, (2.5 m by 1.5 m) to permit visual observations of the layered systems. The back, sides and bottom are constructed of opaque PVC. One end of each pilot cell was covered with a filter fabric to allow the cover and tailings layers to drain freely. This was welded into place using PVC strips and a PVC welder. Seven sets of sampling and monitoring sensor ports were installed vertically in the Plexiglas™ side of the cells, to allow for the collection of profiles of pore water and sensor data from the cover and tailings. Two sets of sampling and monitoring ports were installed in the tailings layer and five sets of ports were installed in the cover layer(s). The ports were installed at 0.15 m vertical intervals up the Plexiglas™. The ports were installed 1.75 m from the cell end covered with the filter fabric to reduce boundary effects on the data collected.

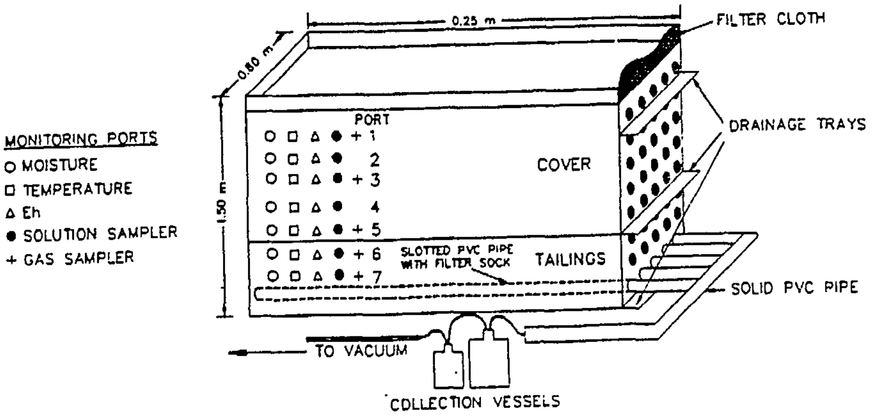

Figure 2: Pilot Cell Configuration

A dual probe time domain reflectometry (TDR) Moisture Probe system was installed in the cells along with temperature probes, electrical potential as hydrogen electrode (Eh) probes, and solution samplers. PVC collection trays were installed at the drainage end of the cells to collect runoff water from the surface, at the cover-tailings interface and from the base of the tailings layer.

Monitoring Program

Sampling and monitoring of the pilot cells was conducted immediately after loading, one week after cell saturation, and then 2 weeks, 1 month, 3 months, 9 months and 12 months after cell saturation. Samples were analyzed for: pH, sulphate, total sulphur, total iron, ferric iron, ferrous iron, total phosphorus, nitrates, nickel, copper, and lead. Additional analyses were conducted for phenols, PAH's and pathogens. Full 24 element metal scans were conducted on the pore water every 6 months and similar scans were conducted on the tailings discharge, or leachate, collected from the base of the cells.

Simulated rainwater was added to the cells at a pH of 4.2. The simulated rainwater pH was adjusted using a 60/40 mixture of sulphuric (H_2SO_4): nitric (HNO_3) acid. This rainwater was used for the initial saturation and rainfall application on the cells. The rainwater was applied once weekly at a rate calculated to approximate the average annual precipitation rate at Sudbury, Ontario. The laboratory pan evaporation rate and the field pan evaporation rate for the Sudbury Airport were used to calculate a ratio of lab:field conditions and this was used to generate the weekly rainfall rate.

In-situ monitoring was conducted for Eh and temperature one week after cell saturation, and then 2 weeks, 1 month, 3 months, 6 months, 9 months and 12 months after cell saturation. The moisture content using TDR was monitored before and after the weekly rainfall events. This TDR method was unable to accurately measure moisture contents greater than 40% by volume in the tailings or cover materials being tested. Fortunately, the design of the cells permitted destructive testing without compromising the integrity of the test. Destructive coring and moisture content determinations were, therefore, conducted at several stages during the program.

To provide information useful to water balance determinations, the rainfall application, pan evaporation, free drainage from the cells and the vacuum drain water volumes were monitored. Laboratory relative humidity and temperature were also recorded to supplement the laboratory climatic information.

In-situ pore gas sampling was added to the program after 6 months of operation. The gas samples were extracted using a syringe, through a stainless steel tube fitted with a septum, and oxygen (O_2) concentration analysis was conducted.

RESULTS

The oxidized tailings received at Lakefield exhibited the typical trends of acid rock drainage (ARD), i.e. a low pH and high dissolved metals content. The following results summarize the physical and chemical differences exhibited by the tailings under the different cover materials. The data plotted in Figures 3 to 10 are the results of analyses conducted on the pore water extracted from approximately 0.25 m below the tailings-cover interface.

Moisture Content and Degree of Saturation

The volumetric moisture content data from the destructive coring conducted on the cells is plotted in Figure 3. The equivalent degree of saturation for each material is plotted in Figure 4. The data plotted in both Figures 3 and 4 are from a single sampling event conducted near the end of the one year monitoring program. The results from previous samplings were very similar to those plotted. Figure 3 shows that fairly large fluctuations in moisture contents occurred with depth in the peat, while fairly consistent moisture contents over depth were noted in the control, DST, the LSSS and the compost. The degree of saturation plotted in Figure 4, however, shows that only the LSSS and the DST were able to maintain >90% saturation throughout their depth.

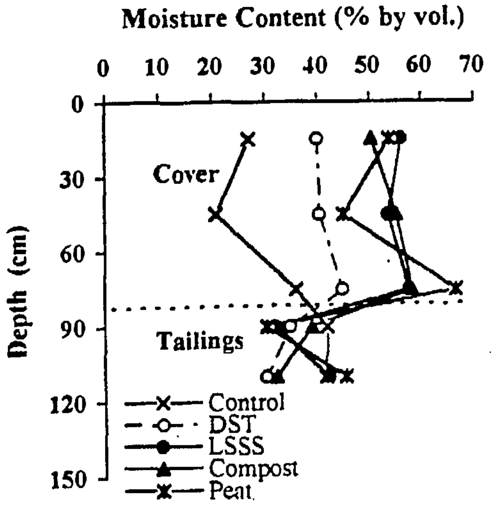

Figure 3: Volumetric Moisture Content Versus Depth in the Covers and Tailings

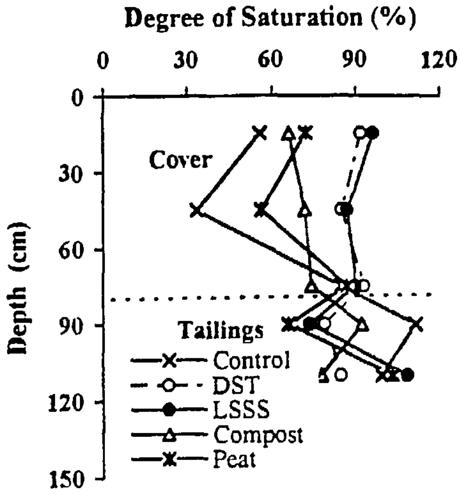

Figure 4: Degree of Saturation Versus Depth in the Covers and Tailings

Pore Water pH

The migration of metals as relatively stable, soluble, organo-metal complexes will largely be controlled by the solution pH. Under conditions where the pH of the solution is imposed by factors other than the presence of the organic acids, metal dissolution through complexation will be greater at pH above 5 than at pH below 4. However, metal dissolution due to low pH will generally increase progressively with decreasing pH (the classic ARD mechanism). Consequently, the combined effects of ARD and organic acids on metal dissolution and migration are likely to be very complex.

Figure 5 illustrates the changes which occurred over the one year test program to the pH in the oxidized tailings pore water under the various cover materials. The results show that the pH in the tailings pore water under all but one of the covers remained essentially constant around 3.5 to 4. The pH in tailings beneath the lime stabilized sewage sludge (LSSS) showed a marked increase from 3.5 to 6.1 after a period of twelve months.

Pore Water Sulphate Concentrations

In typical ARD, sulphide minerals oxidize and release both soluble metals and sulphate to the receiving environment. Sulphate concentrations in the oxidized tailings under the various cover materials are plotted in Figure 6. The data show that the sulphate concentrations under the LSSS cover decreased both quickly and substantially from initial concentration levels. The compost cover appears to have had no effect on sulphate production, while the desulphurized tailings cover resulted in the generation of much higher sulphate production than the control cell.

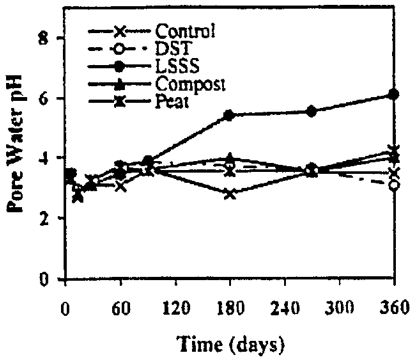

Figure 5: Pore Water pH in the Oxidized Tailings Under Various Cover Materials

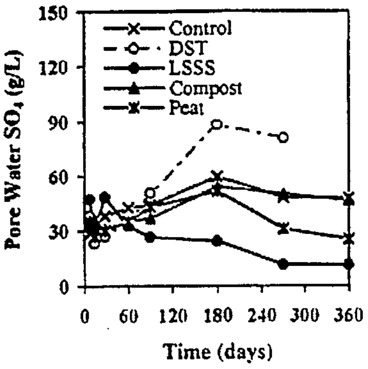

Figure 6: Total SO_4 in the Oxidized Tailings Under Various Cover Materials

Dissolved Organic Carbon

A potential problem associated with the use of organic materials as covers is the effect of decomposition products, particularly organic acids, on the solubility of tailings minerals and on the mobility of dissolved metals [1]. In a short term experiment using MSW compost as a cover layer on oxidized tailings, an increase in the concentrations of trace metals in pore water was observed in some bench scale models tested. This trace metal increase observed may have been due to dissolution or chelation by organics in methods similar to the acid generation process in sulphides; or, the dissolution of previously oxidized and precipitated metals as they are reduced to a sulphide form through soluble phases during the reduction process (reductive dissolution). An example of reductive dissolution would be the transformation of ferric iron through ferrous iron to iron sulphide. To evaluate the effect of the interaction of organic leachates with the oxidized tailings, the dissolved organic carbon (DOC) content of the pore waters was measured. The change in DOC over time is plotted in Figure 7.

It was noted that the DOC content in the underlying tailings porewater remained effectively unchanged under both the compost and peat, while a steady increase in DOC concentrations was noted under the LSSS cover. This indicates that organic rich leachates are migrating downwards from the LSSS into the underlying tailings porewater.

Dissolved Iron Concentrations

Although analyses for several metals were conducted during the program, in general the concentration versus time trends were similar. Therefore, only the dissolved iron concentrations are plotted in Figure 8. By comparing the data shown in Figure 8 with the DOC concentrations plotted in Figure 7 it is apparent that metals concentrations did not increase with the increase in organic leachate interaction with oxidized tailings under the LSSS. In fact the results show that the increase in DOC is mirrored by an approximately equally large decrease in dissolved iron concentrations in the underlying tailings pore water. Results for the remaining cells are similar to those shown by the sulphate concentrations, with substantial increases occurring under the DST cover, a minor change under the compost, and a slight decrease, after an initial increase in concentrations noted under the peat cover.

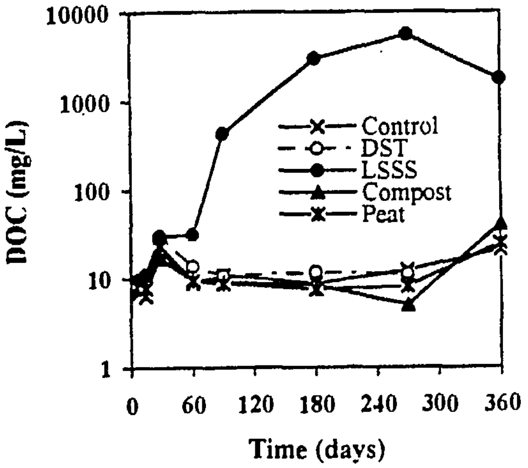

Figure 7: Pore Water DOC in the Oxidized Tailings Various Cover Materials

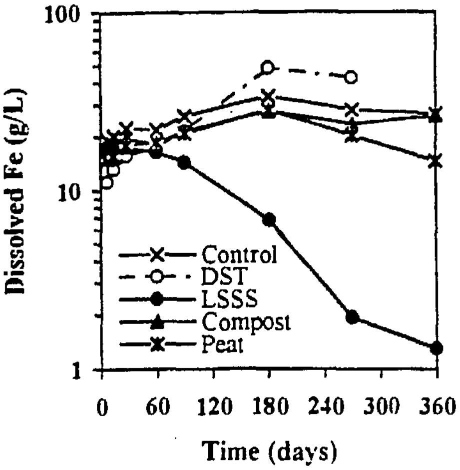

Figure 8: [Fe] in the Oxidized Under Tailings Under Various Cover Materials

Visible evidence of this interaction between the leachates from the LSSS and the underlying oxidized tailings was noted in the pilot cell. After a period of approximately 6 months a thin black band started to form at the interface. This band grew to approximately 0.6 metres thickness by the end of one year. The band has been interpreted to be evidence of the reduction of sulphides and precipitation of metals.

Oxygen Gas Concentrations

Direct measurements of oxygen gas concentrations versus depth in the cover tailings system are plotted in Figure 9. The plot shows the marked decrease in O_2 concentrations in the control cell, which was to be expected by the consumption of oxygen in the oxidation of sulphides. Similarly strong decreases in O_2 concentrations were evident in the compost and LSSS cover materials. The desulphurized tailings and peat contained relatively high oxygen concentrations throughout their entire depth.

Cell Loading Calculations

Measurements of the volumes of runoff, interface discharge and basal leachate and their respective water quality analyses were used to calculate the total cell loading for sulphate, nickel and iron. These are shown relative to the control which is represented by 100% loading in Figure 10. Figure 10 indicates that the DST and LSSS covers resulted in a lower release of Fe and Ni metals and sulphate to the environment than the other covers.

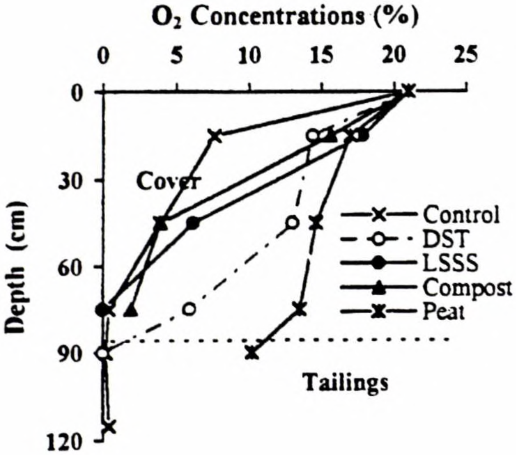

Figure 9: Oxygen Gas Concentrations with Depth

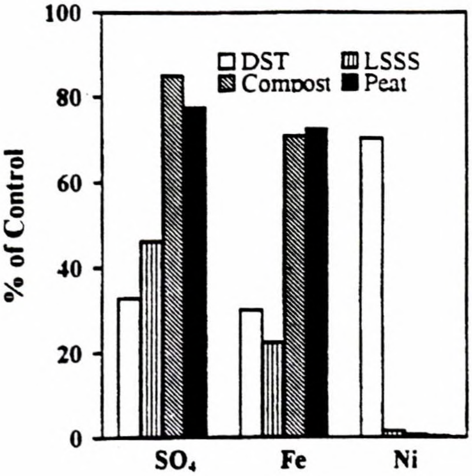

Figure 10: SO_4, Fe and Ni Loading Relative to the Control Cell

DISCUSSION

Fairly large fluctuations in moisture content occurred with depth in the peat and control cells. The compost, although able to maintain a constant moisture content, only maintained a 60-70% degree of saturation. High degrees of saturation (>90%) and consistent moisture contents over depth were noted in both the DST and the LSSS. This ability to maintain consistent moisture content levels during cyclic rain and dry events and maintain >90% saturation levels will provide a benefit to the underlying tailings by limiting the rate of oxygen infiltration to approximately the rate of diffusion through water. This reduction in O_2 infiltration will serve to decrease the rate of tailings oxidation and increase the life of the cover.

The pH in tailings beneath the lime stabilized sewage sludge (LSSS) showed a marked increase (from 3.5 to 6.1) after a period of twelve months. This may be largely due to the leaching of alkalinity from the LSSS downwards into the underlying tailings as the LSSS had an initial pH of 12. The positive effects of the interaction of the leachates from the LSSS with the underlying tailings is also evident in the decreases in the sulphate and iron concentrations noted. In addition, visible evidence of sulphide reduction at the interface has been noted.

The increasing immobilization of metals by complexation to organic compounds and the formation of metal sulphide precipitates are mediated primarily by the soluble humic acids and by the sulphate-reducing bacteria (SRB) that are found in anoxic environments. These anaerobic microbes require organic compounds, particularly simple organic acids, for their metabolism and thereby consume acidity. This consumption of organic acids results in an increase in pH which would further enhance the SRB activity. SRB and other bacteria also cause an increase in pH through an acid consuming process, which result in the formation of methane or hydrogen gas. Increasing pH and certain organic compounds also suppress the acid-generating process by inhibiting the growth and activity of the autotrophic iron bacteria *Thiobacillus ferrooxidans* that thrive at the low pH range of 1.5 to 3.5 [1]. Through this interactive system a reversal of the ARD process is seen to be occurring beneath the LSSS cover.

The observed decreases in oxygen concentrations over depth in the LSSS and compost materials are believed to be due to the combination of the high moisture contents in these covers and the active consumption of oxygen in the ongoing biological decomposition of the organic cover. The minor decrease in O_2 concentration seen in the peat, which has a lower degree of saturation and is an older largely decomposed (aged) material, supports this conclusion.

The DST, however, which has >90% saturation and contains sufficient sulphides to actively consume incoming oxygen, is not acting as effectively as might have been assumed.

The desulphurized tailings cover allowed the generation of much higher sulphate and dissolved iron production in the underlying tailings than the control cell. This may be due to the continuous formation of cracks at the surface which extend to considerable depths in the DST cover. These cracks create direct pathways for oxygen migration into the cover and underlying tailings from numerous directions.

Further work is on-going. Destructive sampling of the interfacial area and at several depths through the covers and tailings has been conducted and mineralogical examinations, hydraulic conductivity tests and chemical analyses are being conducted to identify and quantify the changes which have occurred both to the covers and the underlying tailings. Tests are also planned to examine methods of reducing cracking of the DST tailings, and the effects of mixing the LSSS with DST. Incubation tests are being conducted to evaluate the active oxygen consuming life of the LSSS.

CONCLUSIONS

Of the covers tested, the DST and LSSS appear to offer the greatest potential for reducing metal loading in water migrating from oxidized tailings to the environment. The reasons for this effect are different for each cover. The LSSS is actively changing the underlying tailings environment by reversing the ARD processes with an increase in pH, decrease in dissolved metals concentrations and formation of a reducing environment at the tailings - cover interface. The DST has a low hydraulic conductivity that results in the slow release of high concentration pore waters to the environment, however, the oxidation process is continuing in the underlying tailings. The effects of reducing cracking and of mixtures of the two materials is under investigation.

ACKNOWLEDGMENTS

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URANIUM MINING OPERATIONS DECOMMISSIONING: ^{226}RA FLUX REDUCTIONS FROM SEDIMENTS BY AQUATIC VEGETATION COVERS

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ABSTRACT

Decommissioning of mining operations generally requires management of drainage basins where waste materials are located or to which effluents from such materials are discharging. To reduce the discharge of the contaminant load from affected drainage basins, submerged or emergent aquatic vegetation covers are evaluated.

Mine slimes, generated during development of an open pit of a uranium mine in northern Saskatchewan, were discharged to 22 ha lake, creating a delta in the lake. ^{226}Ra is being mobilized from these slimes and represents the largest annual ^{226}Ra load in the drainage basin. ^{226}Ra concentrations in pore water in the mine slimes, in lake sediments and under a wetland vegetation cover were measured between 1989 and 1994. Estimates of ^{226}Ra fluxes from the sediment to the overlying water indicate that most of the ^{226}Ra flux from sediments is originating from only a small (1.9 ha) shallow area (0.2 to 0.6 m deep) of the mine slime delta. The portion of the delta covered with emergent wetland vegetation (water depth less than 0.2 m) displays ^{226}Ra pore water concentrations four times lower than in sediment without vegetation. Wetland vegetation covers are found to effectively reduce ^{226}Ra flux from sediments.

DÉCLASSEMENT DES MINES D'URANIUM: RÉDUCTION DES FLUX DE ^{226}RA CONTENU DANS LES SÉDIMENTS PAR DES COUVERTURES DE VÉGÉTATION AQUATIQUE

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RÉSUMÉ

Pour déclasser des établissements miniers, il faut en général gérer les bassins versants dans lesquels les déchets sont accumulés ou dans lesquels les effluents de ces déchets sont déchargés. Pour réduire la charge de contaminants pouvant émaner des bassins en cause, nous avons évalué le mérite des couvertures de végétation immergées ou émergentes.

Les boues produites pendant l'exploitation d'une mine d'uranium à ciel ouvert dans le nord de la Saskatchewan ont été rejetées dans un lac de 22 ha, créant un delta dans le lac. Le ^{226}Ra mobilisé dans les boues constitue la plus forte charge annuelle de^{226} Ra dans le bassin versant. Entre 1988 et 1994, nous avons mesuré les concentrations de ^{226}Ra dans l'eau interstitielle des boues de mine, dans les sédiments lacustres et sous une couverture de végétation. Les estimations des flux de ^{226}Ra relâchés par les sédiments dans l'eau sus-jacente indiquent que la plus grande partie du ^{226}Ra des sédiments provient d'une petite zone de 0,2 à 0,6 m à peine de profondeur dans le delta de boues de mine. La partie du delta recouverte de végétation de marais émergente dans une profondeur d'eau de $< 0,2$ m titre cinq fois moins de ^{226}Ra dans l'eau interstitielle des sédiments que dans les sédiments non recouverts de végétation. Les couvertures de végétation de marais réduisent effectivement les flux de ^{226}Ra provenant des sédiments.

INTRODUCTION

During extraction of ore from mineral deposits, waste materials are generated which are located either as surface or subaqueous deposits within a drainage basin surrounding the mining operation. These waste materials (waste rock or tailings) weather and release, depending on their mineralogy, metals and radionuclides to surface or ground water. This results in contaminated lakes and rivers in the drainage basin immediately associated with the mining wastes. Lakes, however, have a natural capacity to decontaminate the water by altering the contaminant form through biological and chemical reactions. These changes result in variations in contaminant transport within the drainage basin and can be utilized in waste management [1].

Weathering and release of metals and radionuclides from waste materials are expected to continue at some sites for decades. Active waste water treatment processes employ chemical additions to the water, which precipitate and collect the contaminants in sludges, resulting in a further disposal problem [2]. Contaminant removal through promotion of natural decontamination processes is an alternative to chemical water treatment particularly well suited for decommissioning [3].

Reductions of dissolved ^{226}Ra concentrations in the lower half of a drainage basin surrounding a uranium mine in northern Saskatchewan by natural decontamination processes have been demonstrated [4]. These reductions were due to an aquatic plant population which had been growing in the drainage basin prior to mining. In the upper half of this drainage basin, elevated ^{226}Ra concentrations are present in a 22 ha lake due to run-off from waste rock piles. Additional ^{226}Ra is released from mine slimes forming a delta covered by a shallow portion of the lake. A species of the Characeae, a group of macrophytic algae both endemic to the region and known for exceptional metal and radionuclide uptake [5, 6, 7], was introduced to this lake.

In order to quantify ^{226}Ra releases from the mine slimes and their contribution to the total annual load of ^{226}Ra leaving the drainage basin, sediment pore water samples were collected. The ^{226}Ra concentrations were used to estimate sediment flux from lake sediments, from the mine slimes forming the subaqueous delta and from the vegetated area of the mine slimes.

Site Description and Project History

The Rabbit Lake ore body, located in northern Saskatchewan on the Harrison Peninsula of Wollaston Lake (58° 11' N, 103° 41' W), was discovered in 1968 by Gulf Minerals Canada. By 1975, the ore body, located beneath Rabbit Lake, had been developed into a pit and milling had commenced [8]. The open pit, formerly Rabbit Lake, is the first in a chain of three small shallow lakes, each approximately 20 ha, in series which drain a 10

km^2 drainage basin to Pow Bay, a portion of Wollaston Lake (Figure 1). During pit development, the water and the sediments from Rabbit Lake were displaced downstream to Upper Link Lake, the second in the chain of lakes. Due to the resulting high turbidity, this lake was furbished with a sedimentation dam. From 1975 to 1977, open pit run-off containing mine slimes was also directed to Upper Link Lake, resulting in the development of both a subaerial and subaqueous delta at the inflow of Upper Link Lake. The solids which were displaced into Upper Link Lake destroyed the original submerged aquatic plant populations. New plant populations had not invaded Upper Link Lake after 11 years, when planning of decommissioning approaches commenced for the drainage basin. Lower Link Lake, downstream from the sedimentation dam (Figure 1), had extensive submerged aquatic vegetation, dominated by Characean species, which reduced the ^{226}Ra load in water draining to Pow Bay.

Waste rock run-off with elevated ^{226}Ra concentrations reports to Upper Link Lake. Further increases in the ^{226}Ra load are evident between the inflow and outflow of Upper Link Lake. The origin of this increase is attributed to diffusion of ^{226}Ra from mine slimes which had accumulated in the delta in Upper Link Lake. High concentrations of ^{226}Ra were determined in the upper 10 cm of sediment cores collected in 1987 in the delta.

As part of a decommissioning approach, the feasibility of introducing *Nitella flexilis* (Characeae), a species of aquatic vegetation with high ^{226}Ra affinity which populates Lower Link Lake, was assessed. In 1989, 12 tonnes of *Nitella* were transplanted in four zones in Upper Link Lake where water depths exceeded 0.5 m, in order to stabilize sediments and reduce ^{226}Ra concentrations. As ice scouring destroys the algal underwater meadow in areas less than 0.5 m deep, the subaqueous delta remains a significant source of ^{226}Ra. The subaerial portion of the mine slime delta is completely colonized by *Calamagrostis canadensis* and the sedge, *Carex aquatilis*. It was suggested that, due to the reduction in water circulation over the vegetated mine slimes, a vegetation cover might reduce diffusive ^{226}Ra flux. The results of a field study designed to estimate the sediment flux of ^{226}Ra in three regions of Upper Link Lake (deep, shallow and subaerial) are presented.

MATERIALS and METHODS

Surface water quality in the drainage basin is monitored monthly as part of regulatory requirements. Water is analyzed by the Saskatchewan Research Council Analytical Services for determination of anions, cations, metals and radionuclides. Pore water and solid samples were submitted to the same laboratory for chemical analysis.

Sediment interstitial solution samplers, or pore water peepers, were designed after Hesslein [9] and Carignan [10]. The samplers were constructed from acrylic plastic, and consist of 50 cm long chambers 1.7 cm^2. A series of 0.25 cm diameter holes cover the length of one side of each pore water peeper. This series of holes is covered with a strip of 0.45 μm polysulfone membrane sealed with silicone. The membrane separates sediment solids from the chamber solution, allowing only mobile or dissolved elements in the sediment pore water to diffuse into the chamber's solution. The 0.14 L chambers of the pore water peepers were filled with distilled water and deoxygenated by purging with nitrogen gas for 20 minutes. The pore water peepers were stored in nitrogen purged, heat-sealed plastic bags until insertion into the sediment. Pore water peepers were inserted at a 45° angle until the top of the pore water peeper was 0.05 m below the sediment-water interface, exposing the membrane to a 0.3 m sediment profile. Pore water peepers were installed at a total of 43 locations, in the years 1989, 1992 and 1994 (Figure 2) and were left to incubate for at up to 320 days, and for at least 14 days, a period determined sufficient for equilibration.

RESULTS and DISCUSSION

Upper Link Lake is a circumneutral freshwater lake with relatively low dissolved solids concentrations (conductivity 35 to 206 μS.cm^{-1}; see Table 1). The surface water contained, in 1989, 1992 and 1994, 0.33, 0.27 and 0.24 Bq.L^{-1} ^{226}Ra on average, respectively (Table 1). The surface water quality objective requires a concentration of 0.11 Bq.L^{-1} ^{226}Ra.

Concentrations of ^{226}Ra and uranium in the whole sediment samples of the delta were determined from sediment cores collected in 1987. These samples delineated areas of the delta with high concentrations of ^{226}Ra and uranium, including both the subaerial (vegetated) and subaqueous sections of the mine slime delta in Upper Link Lake. The concentrations of ^{226}Ra decreased in the cores with depth, being highest in the first 0.1 m (95 Bq.g), decreasing rapidly to a concentration less than 2 Bq.g^{-1} at a depth of 0.3 m. From these results, it was evident that the imported mine slimes comprising the delta were a potential source of ^{226}Ra to the water. The ^{226}Ra flux is determined by diffusion, driven by the ^{226}Ra concentrations in the pore water relative to the concentration in overlying lake water. However, the flux of ^{226}Ra which is released to the water may not be directly related to the total concentrations of ^{226}Ra in the sediment, as the correct environmental conditions must be present in the sediment for ^{226}Ra dissolution.

In Table 1, pH, Eh and electrical conductivity of lake water and of pore water are summarized. The pH of pore water is circumneutral, similar to lake water. The electrical conductivity is, as expected, higher than lake water, due to dissolution of substances in the sediment. Although the Eh values are lower in the pore water than in the lake, they are higher than typically measured in organic-rich sediments. The ^{226}Ra concentrations in the pore water widely vary, ranging from 0.25 to 26 Bq.L^{-1} (Table 1). The pore water ^{226}Ra concentrations are grouped by sampling location for the entire sampling period between 1989 and 1994. In Figure 2, the areas are designated as Area A, the subaerial vegetated delta with 6 sampling locations; Area B, the subaqueous delta with 26 sampling locations; and Area C, sampled at 24 stations throughout the lake in natural sediment. A line separating Area B and C can be drawn using stations with pore water ^{226}Ra concentrations greater than 2 Bq.L^{-1} (Area B) and stations where ^{226}Ra concentrations were 2 Bq.L^{-1} or less (Area C). The average pore water ^{226}Ra concentration in Area B, the mine slimes submerged beneath a shallow water layer, was 9.8 Bq.L^{-1}, substantially higher than in Area A, the vegetated delta, where the average pore water ^{226}Ra concentration was 2.5 Bq.L^{-1}. The lowest concentration of ^{226}Ra were reported for the lake sediments in Area C (Table 1).

Diffusion of solutes between sediment and the water column is described by Fick's equation as the amount of solute, such as ^{226}Ra, crossing a certain area per unit time, the flux *J*, in this case as Bq ^{226}Ra.m^{-2}.day^{-1}. The force driving diffusion is the concentration gradient (ΔC_{226Ra}) over a distance (*x*). Flux of ^{226}Ra is proportional to this concentration gradient, and is influenced by the specific diffusion coefficient (*D*) of ^{226}Ra. In its simplest form, Fick's first equation for ^{226}Ra can be written as:

$$J_{226Ra} = D_{226Ra} \cdot \frac{\Delta C_{226Ra}}{\Delta X}$$

Imboden and Lerman [11] modified Fick's equation, in order to examine diffusion of ionic species across the sediment-water interface, and incorporated components representing the unique conditions below and at the sediment-water interface.

Diffusion coefficients for solutes diffusing through sediment pore spaces (10^{-8} m^2.s^{-1}), are an order of magnitude lower than the diffusion coefficients through water (10^{-7} m^2.s^{-1}). The sediment porosity ($0 < \Phi_s < 1$) is factored in, as decreasing porosity increases the path length of solutes and thereby slows diffusion. Downward advection for both pore water and sediment are also taken into account by Imboden and Lerman [11] to arrive at modifications of Fick's equation. In the flux estimates derived in this paper, downward advection of pore water and sediments was not taken into account, as the lake is shallow with a low water retention time.

Fluxes of ^{226}Ra are estimated for the different areas of Upper Link Lake using the following parameters:

$$^{226}\text{Ra Flux} = \frac{(C_{pw} - C_{lw}) \cdot D_{pw} \cdot \Phi_s}{X_d}$$

Where

C_{pw} = [^{226}Ra] in pore water (Bq.m^{-3}); 1989-94 PWP data used.

C_{lw} = [^{226}Ra] in lake water (Bq.m^{-3}); [^{226}Ra] for year examined used.

D_{pw} = Diffusion Coefficient of ^{226}Ra through sediment (m^2.s^{-1}); 1×10^{-8}m^2.s^{-1} used (Imboden & Lerman, 1978).

Φ_s = Porosity of Sediment ($0 < \Phi_s < 1$); 48 to 89% water in cores.

x_d = Thickness of diffusion boundary (m) at the sediment-water interface. The sediment thickness between sediment surface and the top of the pore water peepers, 0.05 m, was used.

The flux of ^{226}Ra in Bq.m^{-2}.d^{-1} was calculated for each pore water peeper location and flux estimates were averaged if multiple pore water peepers were incubated within the same m^{2} (Table 1). The ^{226}Ra flux from subaqueous delta sediments (Area B; Figure 2) is estimated at an average of 134 Bq.m^{-2}.d^{-1}, which is equivalent to 929 MegaBequerels (MBq) of ^{226}Ra diffusing from the 1.9 ha of subaqueous delta each year. The flux from the lake sediments (Area C; Figure 2) is estimated at 8.7 Bq.m^{-2}.d^{-1}, equivalent to 704 MBq.y^{-1} for the 22.2 ha lake area. For the vegetated subareal delta (Area A, 1.6 ha), an average of 29 Bq.m^{-2}.d^{-1} is estimated, resulting in an annual load of 169 MBq.y^{-1} from this area.

Comparing the annual ^{226}Ra loads based on flux estimates to the differences noted in surface water between the inflow and the outflow of Upper Link Lake (363, 321 and 88 MBq.y^{-1} for 1989, 1992 and 1994, respectively) attributed to the mine slimes, the flux estimates suggest higher release from the sediments. The introduced *Nitella* population, expanding over Area C sediments since 1989, is expected to capture a fraction of the ^{226}Ra released from the sediment. The lower annual ^{226}Ra loads measured at the lake outflow suggest that this process is at work. The biomass of the *Nitella* population presently covering 15 ha of Upper Link Lake sediments is estimated at 30 t (200 g.m^{-2} dry weight) and contains 21 Bq ^{226}Ra.g^{-1}, equivalent to 630 MBq of ^{226}Ra captured by this biomass. The *Nitella* standing biomass is replaced by new growth twice a year, capturing 1,200 MBq ^{226}Ra.y^{-1}, approximately 67 % of the estimated annual ^{226}Ra flux from Areas A, B and C sediments (1,800 MBq.y^{-1}).

Direct comparison of ^{226}Ra flux estimates for Area B with Area C is realistic since the conditions in both areas consist of a submerged sediment surface in contact with a circulating water column. In the lake, movement of water over the sediment maintains the concentration gradient between the sediment pore water and the lake and, subsequently, the steady depletion of ^{226}Ra from the sediment pore water. The measured pore water ^{226}Ra concentrations are the result of the equilibrium between the ^{226}Ra release from the mine slimes into the pore water and the flux of ^{226}Ra in pore water to overlying water. The high pore water ^{226}Ra concentrations in the subaqueous delta (Area B) suggest the more ^{226}Ra is dissolving into the pore water of the mine slimes with a high total ^{226}Ra content, compared to the lake sediment with a lower ^{226}Ra content (Area C).

The flux estimates derived for the subaerial vegetated delta (Area A) may not be comparable to the water-covered areas (Areas B and C), since very heterogenous conditions prevail in the dense emergent vegetation cover, including shallow, discontinuous water cover and partly stagnant wetland conditions. Water movement through Area A is mainly driven by atmospheric precipitation. The diffusion of ^{226}Ra from wetland pore water into overlying stagnant water is likely slower than into freely circulating water, as accumulation of ^{226}Ra in stagnant water would reduce the concentration gradient. Assuming that the dissolution of ^{226}Ra from the mine slimes to the pore water is the same in Area A as in Area B;^{226} Ra concentrations in Area A pore waters were expected to be similar to or, considering reduced water movements in the wetland area, potentially higher than in the Area B mine slimes exposed to freely circulating water. However, much lower ^{226}Ra concentrations were observed in Area A pore waters. The lower ^{226}Ra pore water concentrations in Area A suggests that either the vegetation cover has affected the dissolution of ^{226}Ra from the mine slimes, or the presence of organic material restricts mobility of ^{226}Ra. If ^{226}Ra dissolution and mobility are affected by redox conditions, then microbial activity in a decomposing vegetation layer may be responsible for the lower pore water concentration and the resulting lower estimated flux. Alternately, the organic layer maintained by the subaerial delta vegetation may adsorb a significant fraction of upwardly diffusing dissolved ^{226}Ra, thereby maintaining lower interstitial concentrations.

While the specific factors responsible for lower ^{226}Ra pore water concentrations in an organic layer covering mine slimes have not been yet been identified, the emergent vegetation cover over the mine slimes is, in effect, reducing ^{226}Ra flux from the underlying contaminated sediments in Area A.

Considering the effects of both underwater algal populations and those of the wetland vegetation covering the mine slimes, the utility of natural decontamination processes for the trace element ^{226}Ra is evident. Through establishing conditions which would facilitate more extensive coverage of the mine slimes with wetland vegetation, a reduction of the discharge of ^{226}Ra load could be achieved and maintained. The decommissioning approach suggested for this drainage basin, based on the data collected, consists of creating wetland habitat over the mine slimes, and maintaining water levels in the lake which allow continued growth of the aquatic vegetation cover, dominated by the *Nitella* population.

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Table 1: Lake Water Quality; Sediment pore water quality, summarized according to area sampled (subaerial delta, subaqueous delta, lake sediment).

	pH	Conductivity (uS/cm)	Eh (mV)	Surface Water [Ra226] (Bq/L)
Upper Link Lake Water Quality				
1989	6.6	96		0.33
1992	6.5	123	384	0.27
1994	6.9	132	370	0.24

	pH	Conductivity (uS/cm)	Eh (mV)	Pore Water [Ra226] (Bq/L)	Ra226 Flux (Bq/m2/d)
Area A: Subaerial Delta (collected in 1994, n=6)					
Average	6.3	263	186	2.5	29
Maximu	6.1	520	222	4.5	55
Minimu	6.6	52	148	0.25	0.1
Area B: Subaqueous Delta, [Ra226] > 2 Bq/L (collected in 1989, 1992, 1994)					
Average	6.6	403	136	9.7	134
Maximu	6.0	833	192	26	331
Minimu	7.1	140	89	0.65 *	10
N	25	24	19	26	21
Area C: Lake Sediment, [Ra226] 2 Bq/L or less (collected in 1989 and 1992)					
Average	6.7	211	162	1.0	9
Maximu	6.6	325	191	2.0	24
Minimu	7.2	138	121	0.25	2
N	24	24	12	24	16

* lowest value of 3 replicates; average of 3 replicates > 2 Bq/L.

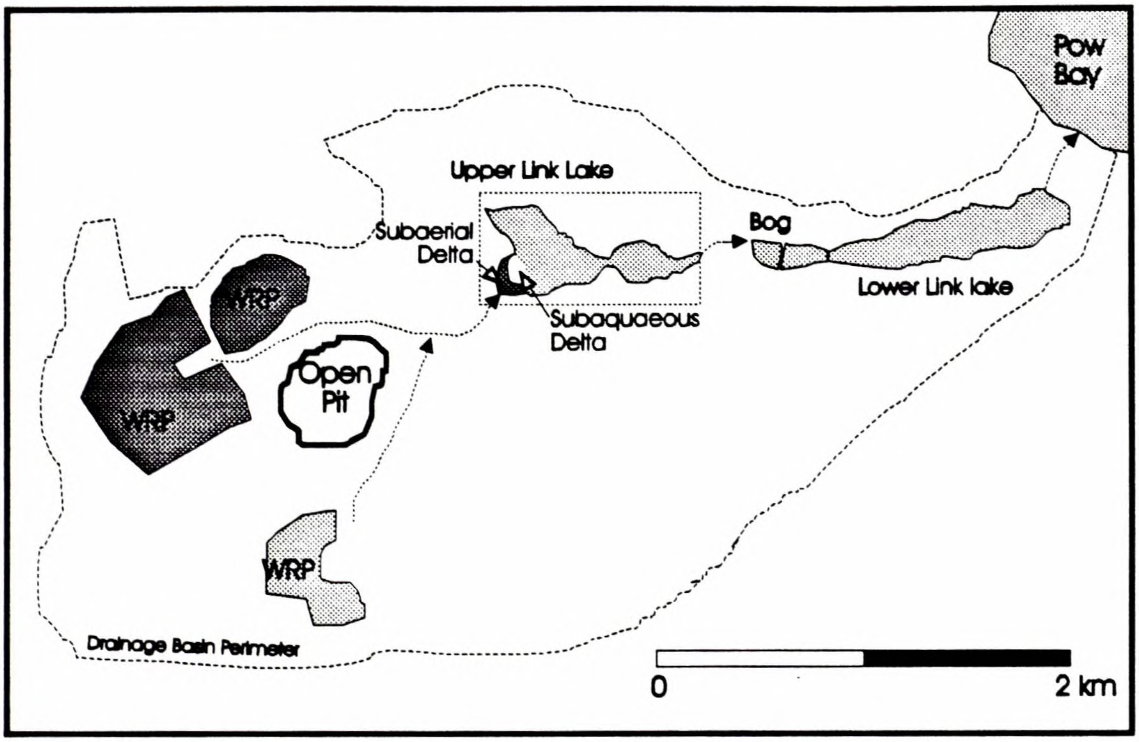

Figure 1: Rabbit Lake drainage basin. Detail of boxed area of drainage basin shown in Figure 2.

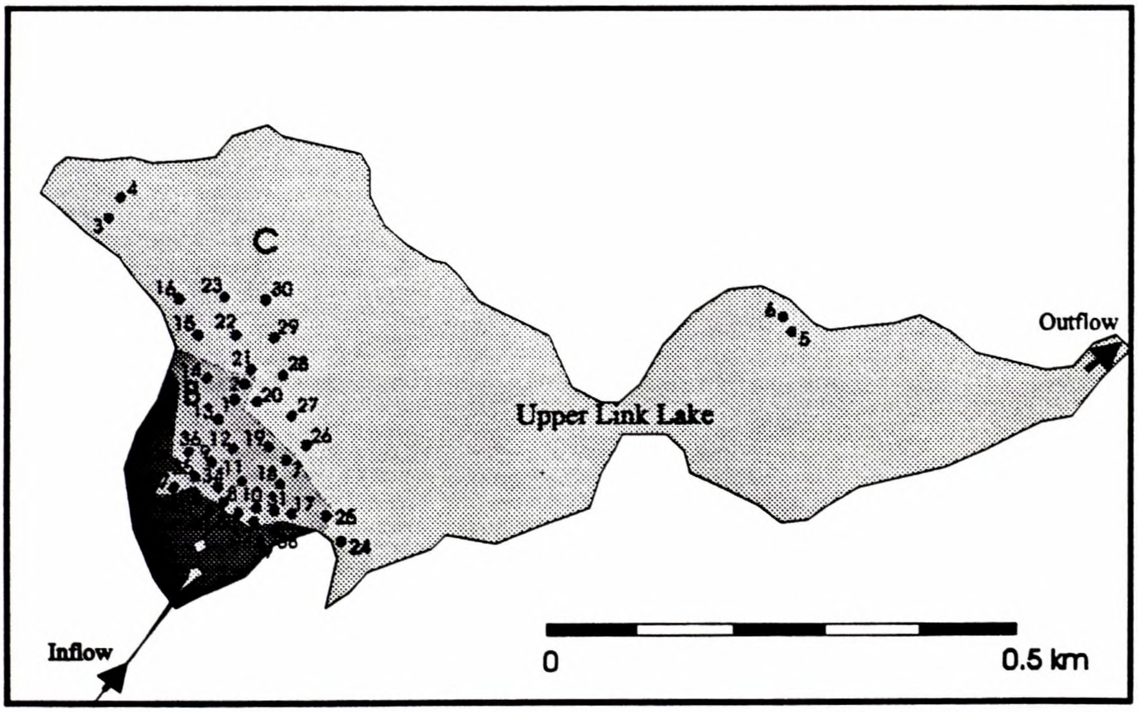

Figure 2: Locations of sediment interstitial sampling stations, 1989, 1992 and 1994. Area A is subaerial vegetated wetland, area B is subaqueous delta and area C is lake sediment area.

TREATMENT OF ACIDIC DRAINAGE FROM THE BRITANNIA MINE WITH THE BIOSULPHIDE PROCESS - RESULTS OF A 10 M^3 ON-SITE PILOT PROJECT

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ABSTRACT

A 10 m^3 pilot plant was constructed and operated at the former Britannia Mine near Vancouver, B.C. to demonstrate the effectiveness of the Biosulphide Process (patents pending) for the treatment of acid mine drainage (AMD). The Britannia Mine provides an excellent site for the demonstration due to the lack of other viable options for treatment resulting from the combination of high flow (up to 38,000 m^3/day), relatively low solution strength (pH 3 to 4, [Cu] and [Zn]=12 to 28 mg/L, [Cd]=0.1 mg/L), and lack of disposal space for waste sludges. The Biosulphide Process uses Sulphate Reducing Bacteria (SRB) in a bioreactor stage to generate sulphide for the precipitation of metals in a separate chemical treatment stage. By utilizing a high-efficiency bioreactor design using inexpensive nutrients, and by minimizing the flow to the bioreactors, a highly cost-effective treatment was demonstrated. In addition, potentially saleable concentrates of copper and zinc are recovered during the treatment, avoiding the production of waste sludge. The results of the Phase II Britannia pilot project show the effectiveness of the Biosulphide process at treating the AMD to below the target values of 0.01 mg/L Cu, 0.001 mg/L Cd, and 0.05 mg/L Zn, with the concurrent production of metal concentrates to off-set or eliminate operating costs.

TRAITEMENT DU DRAINAGE ACIDE DE LA MINE BRITANNIA À L'AIDE DU PROCÉDÉ AU BIOSULFURE - RÉSULTATS D'UN PROJET *IN SITU* DE 10 M^3

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RÉSUMÉ

Une usine pilote de 10 m^3 a été construite et exploitée sur le site de l'ancienne mine Britannia près de Vancouver, C.-B., pour faire la démonstration de l'efficacité du procédé au biosulfure pour le traitement du drainage minier acide (DMA). La mine Britannia constitue un excellent site pour faire cette démonstration en raison de l'absence de toute autre option de traitement viable du fait d'une combinaison d'éléments particuliers : débit élevé (jusqu'à 38 000 m^3 par jour), concentration relativement faible de la solution (pH = 3 à 4; [Cu] et [Zn] = 16 à 28 mg/L, [Cd] = 0,1 mg/L) et absence d'endroit où déposer les boues excédentaires contaminées. Le procédé au biosulfure fait appel à des bactéries sulfato-réductrices pour produire du sulfure pour la précipitation des métaux dans une étape de traitement chimique antérieure. On peut obtenir un traitement hautement rentable si on utilise un concept de bioréacteur à haute efficacité, des éléments nutritifs peu coûteux et si l'on n'achemine dans les bioréacteurs qu'un mince filet d'eau de procédé. De plus, on obtient au cours du traitement des concentrés du sulfure de Cu et de Zn que l'on pourrait vendre. De cette manière, aucun déchet n'est produit. Les résultats du projet pilote, phase II de la mine Britannia, démontrent que le procédé au biosulfure est efficace pour le traitement des DMA jusqu'à une valeur inférieure aux concentrations cibles de 0,01 mg/L pour le Cu, de 0,001 mg/L pour le Cd et de 0,05 mg/L pour le Zn, tout en produisant en même temps des concentrés de métaux qui pourraient être vendus pour réduire ou éliminer complètement les frais d'exploitation.

INTRODUCTION

The former Britannia Mine, located about 50 km north of Vancouver, operated from 1905 to 1974 and was once the largest copper producer in the British Empire. The mine has continued to be a source of minerals, however, as ground and surface water combine and pass through hundreds of miles of underground workings, leaching toxic metals such as copper, zinc, and cadmium. The largest drainage stream exits the mine through a concrete bulkhead in the main haulage adit (the 4100 adit) and is piped into the receiving waters of Howe Sound without treatment. Serious drainage also exits the mine from upper adits, rendering streams toxic to aquatic life.

The main flow of drainage at Britannia is highly seasonal, ranging from approximately 5,000 m^3 per day to 40,000 m^3 per day, with a year-round average of about 12,000 m^3 per day. Copper and zinc levels range from 12 to 28 mg/L, with cadmium levels of about 0.1 mg/L. The pH of the drainage is typically 3 to 4, with a redox of +300 to +550 mV. The high flow and relatively low solution strength of the Britannia drainage make the site an ideal locale for the Biosulphide pilot work, as the costs associated with constructing and operating a lime plant that could remove copper, zinc and cadmium effectively at these levels and flows is considered prohibitive. SRK estimated the annual operating costs to be over $900,000 per annum in 1991 [1]. In addition, there is no realistic option for large scale sludge disposal at or near the site. The prospect of paying "in perpetuity" for water treatment has prevented the development of the 942 acre site by private real estate interests, leaving the property as possibly the worst untreated mine drainage site in North America.

In July of 1995, NTBC Research was awarded a grant from BC21 Power Smart Special Projects to demonstrate the Biosulphide process using the Britannia drainage, based on the potential energy savings and environmental benefits when compared to the lime treatment option. The most important aspect of the Biosulphide process in its application at Britannia, however, is the recovery of metals from the drainage, simultaneously eliminating the production of waste sludges and generating revenue through the sale of metal sulphide concentrates. Preliminary cost projections indicate that a full-scale Biosulphide plant would actually operate at a net profit of about $100,000 per annum.

The application of sulphate reducing bacteria (SRB) to sulphate-containing wastes has been studied in considerable detail [2 to 9]. Sulphate reduction processes generally utilize a bioreactor where SRB grow on some form of solid support or in a sludge bed. Sulphate is metabolized according to equation 1, below. Hydrogen sulphide generated by the SRB contacts metal cations, forming insoluble metal sulphides which precipitate in the bioreactor, according to equation 2.

$$SO_4^{=} + \text{Nutrients} + H_2O \rightarrow H_2S + HCO_3^{-} \qquad \text{(Eqn. 1)}$$

$$M^{++} + S^{=} \rightarrow MS_{(s)} \qquad \text{(Eqn. 2)}$$

In this manner, these processes treat the entire stream in a bioreactor, which limits the range of applications and the effectiveness of treatment. The sensitivity of the bacterial population to low pH and high metal loading necessitates prohibitively long retention times for the treatment of highly contaminated streams. In addition, because the entire AMD stream enters biological treatment, the bioreactor is subjected to widely varying conditions of flow and feed stream strength with seasonal fluctuations, making it difficult to maintain the chemostat conditions necessary for optimum bioreactor performance. The sludge produced by these processes could also present problems. The sludge contains a mix of metals, with valuable, toxic and other waste metals combined, all requiring relatively expensive disposal. The sludge also contains biomass from the bioreactor, further increasing the volume of sludge for disposal. Sulphate reduction processes are, however, well suited to certain applications, particularly those concerning the treatment of streams with low metals concentrations, or sites where complete removal of sulphate is required [10].

Adaptation of sulphate reduction for the treatment of wide range of AMD streams has resulted in the development of the Biosulphide Process over the past 8 years, culminating in the 10 m^3 Britannia pilot project. Earlier work (1992 to 1994) with a 100 L laboratory pilot system has been previously described [11, 12]. The Biosulphide process differs from sulphate reduction by the combination of the following features: 1) the biological component of the process is separated from the chemical precipitation/neutralization stage; 2) only a fraction of the stream volume, as determined by sulphide and/or alkalinity requirements, enters the bioreactors; 3) AMD treatment is carried out to whatever level is optimal, using bacterially-generated reagents, and; 4) metal concentrates, metal sludge, and biomass can be removed selectively for sale or disposal.

The Biosulphide process completely separates the chemical precipitation of sulphides from the biological conversion of sulphate to hydrogen sulphide. Raw AMD enters the chemical circuit and is contacted with hydrogen sulphide generated in the biological circuit. Some fraction of the treated AMD enters the biological circuit as the sulphate source. By operating a multi-stage chemical precipitation circuit the Biosulphide process permits metals to be removed and isolated selectively. Selective separation is achieved by pH control in each stage, as specific metal sulphides begin to precipitate at different pH values. Alkalinity requirements for the stepwise pH adjustments can be supplied by the biological circuit. Alkalinity is produced simultaneously with the biological reduction of sulphate to sulphide in the form of carbonate (see equation 1).

The precipitation of metals as sulphides has several advantages over hydroxide precipitation. Sulphides form more rapidly, create a denser sludge, and are less soluble than hydroxides [13, 14]. Also, in some cases isolating the most toxic metals as a selectively precipitated sulphide sludge, separate from the bulk of the waste sludge and from the metals deemed valuable, could greatly reduce the volume of waste requiring more expensive disposal techniques such as concrete stabilization. In addition, the cost of treatment can be offset or eliminated in streams with significant recoverable metals through the sale of metal sulphide concentrates to smelters. Most heavy metals are readily removed as sulphides. Aluminum does not form a sulphide, but can be precipitated as an hydroxide at a pH of 4 to 4.5.

This paper summarizes the methods and results of the Phase II Britannia pilot project from July 1995 to October 1996. The results focus on specific pilot runs intended to address and test specific aspects of the process.

METHODS AND MATERIALS

Description of the Britannia Pilot Plant

Overview The configuration of the Britannia pilot is shown in figure 1.

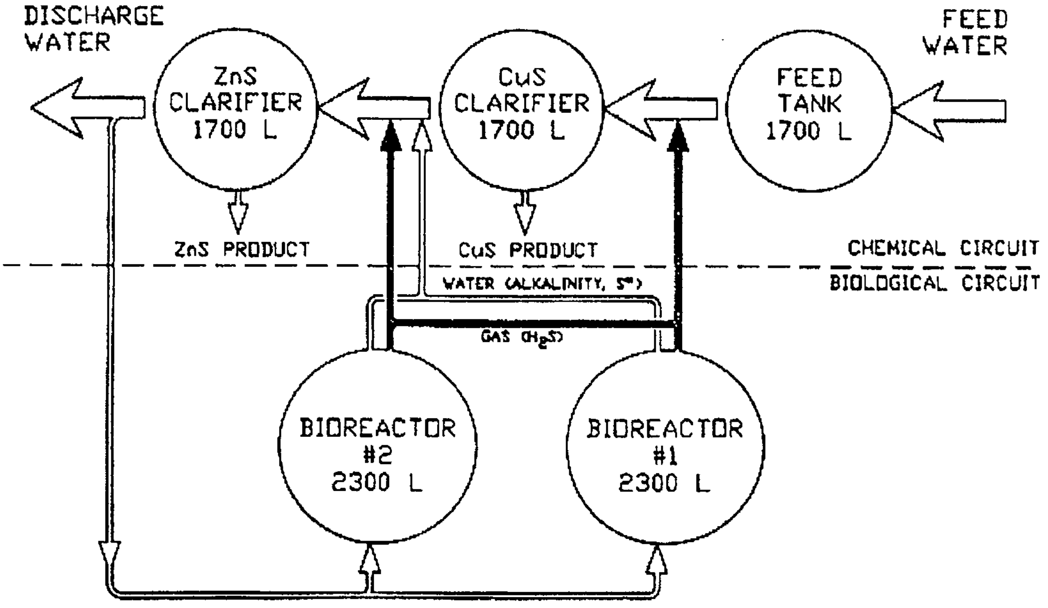

Figure 1. Britannia Biosulphide configuration.

Chemical Stage:

As shown in Figure 1, above, the chemical precipitation circuit consists primarily of a feed holding tank of 1700 L, and two conical-based clarifiers of 1700 L each. A centrifugal pump submerged in the drainage flow pumps raw water into the feed holding tank from outside the building. Centrifugal pumps transfer the raw and processed water between the vessels at a rate of 32 to 48 L/min. Treated water exits the plant from the chemical circuit through a 60 L stripping vessel (not shown in Fig. 1). A 2800 L biofeed holding tank receives treated water to provide a reserve of bioreactor feed water, permitting continuous bioreactor operation when the chemical stage is not operating.

Biological Stage:

The biological stage consists of two 2300 L polyethylene anaerobic bioreactors of a design developed specifically for the Biosulphide process during bioreactor comparison tests in 1990 and 1992. During Phase II the bioreactors were continuously fed chemical stage discharge water from the biofeed tank by peristaltic pumps at a rate of typically 0.8 L/min to each bioreactor. Bioreactor solution was recycled continuously from an overflow by an additional peristaltic pump at a rate of 8 L/min. Nutrient salt solution consisting of 17.5 g/L $(NH_4)_2SO_4$), and 5 g/L K_2HPO_4, was added to the recycle water by peristaltic pumps at a rate of 5 to 8 mL/min to each bioreactor. Bacterial carbon and energy requirements were met through the addition of carbon dioxide and hydrogen gases to the recycle water to accurately simulate full-scale operation. Nitrogen gas was also used to move gases within the circuit. Bioreactors were maintained at 32 °C with 2000W heaters located in the bioreactors.

The mixed cultures of SRB used throughout Biosulphide process development and piloting are derived from samples originally obtained from bog water in 1988. These cultures have been utilized continuously in Biosulphide development research for over eight years, and have been adapted to a variety of specific operating conditions.

Analyses:

Dissolved sulphate was determined by turbidimetric analysis with a spectrophotometer at an absorption wavelength of 420 nm, following barium sulphate precipitation at low pH. Bioreactor off-gas analyses were performed using an SRI 8610 Gas Chromatograph equipped with a 25 foot long, 1/8" O.D. teflon column packed with 100/120 mesh Hayesep D material, a Thermal Conductivity Detector (TCD), and a Photoionization Detector (PID). Solid and solution samples were analyzed by ICP and Atomic Absorption Spectrophotometry at MinEn laboratories.

RESULTS

In this section, results from specific pilot plant runs are presented to demonstrate the effectiveness of the Biosulphide process in treating the Britannia drainage under a variety of circumstances. These runs were designed to address and test specific areas of the

Biosulphide process, based on conversations with government, mining industry, and financing representatives.

Metal Removal

Because of the extreme insolubility of metal sulphides, very low levels of dissolved metals were easily achieved in the plant discharge. Pilot operations to date have routinely achieved and maintained discharge levels of <0.01 mg/L copper, <0.001 mg/L cadmium, and <0.05 mg/L zinc. Levels as low as <0.001 mg/L copper and <0.001 mg/L zinc have been attained, further demonstrating the potential of the process to provide a very high degree of metal removal.

Metals are removed in a multi-stage chemical precipitation circuit. Typically, a Biosulphide treatment plant will include one stage for each metal that is to be recovered, with the possible inclusion of a final stage for the the production of a waste sludge at some sites. At Britannia, a two-stage sequential precipatation circuit is used to remove copper, zinc, and cadmium. Cadmium is present at low levels and apperars as a minor contaminant in the zinc product. Figure 2 uses Britannia pilot results to illustrate the degree of separation that is achieved in the system.

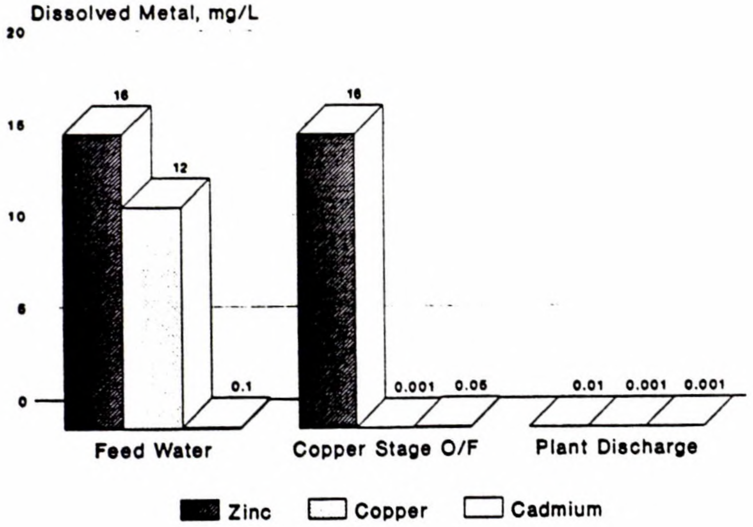

Figure 2. Selective Metal Removal

Product Precipitate Quality

The production of saleable zinc and copper sulphide products is essential to the feasibility of the Biosulphide process at Britannia. At a minimum, the products must be of sufficient value to be given to potential users as a method of disposal. By maintaining the highly selective recovery of copper and zinc shown above, essentially pure CuS and ZnS can be isolated from the drainage and sold to smelters for recovery of metal values.

Product concentrate assays are presented in Table 1.

Table 1 - Product

Pilot Plant Products	Cu %	Zn %	Fe %	As ppm	Cd ppm	Ag ppm	Al %	S, total %	S, SO4 %
CuS Concentrate	**41.2**	0.36	7.71	2800	230	21	0.9	26.2	1.14
ZnS Concentrate	22.6	**26.1**	3.11	6	1340	2.1	0.81	27.9	13.0

Due to the relatively low levels of metals in the Britannia drainage, product concentrates are accumulated over a multitude of runs and circumstance. As a result, the zinc product detailed above has some degree of copper contamination resulting from the incomplete copper removal of earlier runs and does not reflect the optimum grade of zinc obtainable.

Sustainable Treatment

Although the bioreactors operated continuously throughout Phase II piloting, the chemical circuit has been operated only in the presence of NTBC engineering staff due to a lack of process automation. As a result, most runs were of 12 hours duration or less. In July of 1996, a period of 5 day (106 hour) continuous operation was completed to demonstrate that the supply of alkalinity and sulphide from the bioreactors is sufficient on a long-term basis to provide a continuous treatment. Table 2 presents the results of the 5 day run.

Table 2 - Results of 106 Hour Continuous Pilot Run

Hours	Rate	Feed, mg/L			Cu Stage O/F, mg/L			Plant Discharge, mg/L			% Removal		
	(L/min)	Cu	Cd	Zn	Cu	Cd	Zn	Cu	Cd	Zn	Cu	Cd	Zn
0 to 12	34.0	11.6	0.093	16.0	0.10	0.020	14.9	<0.01	<0.01	0.11	>99.9	>89.2	99.3
12 to 24	34.0	11.9		16.1	0.02	0.049	15.7	0.01	<0.001	0.02	99.9	>98.9	99.9
24 to 36	34.0	11.9		16.2	0.02	0.026	14.8	0.01	<0.01	0.18	99.9	>89.2	98.9
36 to 48	34.0	11.9		16.3	0.02	0.061	15.9	<0.01	0.002	0.01	>99.9	97.8	99.9
48 to 60	34.0	12.0		16.1	0.01	0.039	14.7	<0.01	<0.01	0.25	>99.9	>89.2	98.4
60 to 72	34.0	12.0		16.4	0.02	0.048	16.3	0.01	0.001	0.02	99.9	98.9	99.9
72 to 84	34.0	11.9		16.8	0.01	0.012	14.8	<0.01	<0.01	0.37	>99.9	>89.2	97.8
84 to 96	37.8	11.7		16.1	0.01	0.069	15.8	0.01	0.001	0.29	99.9	98.9	98.2
96 to 106	37.8	12.1	0.085	16.2	0.01	0.054	16.1	<0.01	<0.01	0.17	>99.9	>89.2	99.0

Samples were composited every 2 hours for each 12 hour period. **Drainage Treated: 221,256 L**

During the continuous run, experiments were conducted to evaluate and confirm the process control mechanisms, particularly concerning the selective removal of zinc. The highly controllable nature of metal removal in the Biosulphide system is shown by the "Plant

Discharge" zinc levels in Table 2, above, where the operators were able to control the removal of zinc between 0.01 mg/L and 0.37 mg/L.

Seasonal Flow Changes

The drainage at Britannia has a high degree of seasonal variation; the 4100 adit drainage ranges between 5,000 and 40,000 m^3/day. The effectiveness of many biological systems suffers with such wide and sudden changes due to the inability of the bacteria to adapt quickly to their changing environment. The Biosulphide Process, however, is not a biological process so much as a chemical treatment process using inexpensive biologically-generated reagents. The chemical stage is completely isolated from the biological stage, and thus, a complete and effective treatment can be achieved regardless of the state of the bioreactors, provided that a reserve of sulphide and alkalinity is available. NTBC has developed a method of storing bioreactor sulphide safely and economically during low-flow seasons for application during peak flows or operational upsets. In this manner the bioreactors can be operated at a constant optimum level of productivity year-round. As shown in figure 3, the bioreactors of a full-scale Biosulphide plant would be operated at a constant level of production that is above the anticipated full year requirement. During the seasons of low flow, sulphide would be stored as the concentrated sulphide reagent. Stored sulphide would be applied during periods of peak flow or operational upsets to replace some or all of the additional demand on the bioreactors, as required.

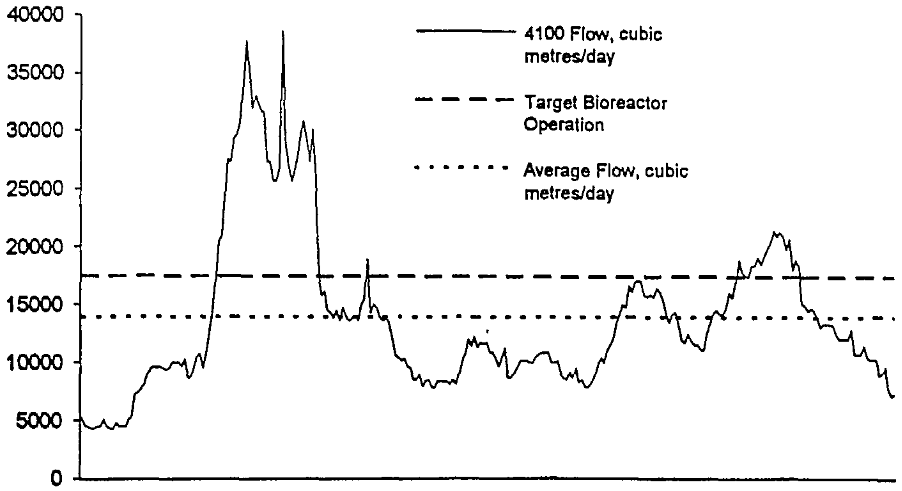

Figure 3. Drainage flow at the 4100 adit, Sept. 1995 to Aug. 1996

To demonstrate the effective nature of the sulphide storage system, and to demonstrate that complete treatment of the water would not be compromised during a substantial increase in flowrate through the circuit, a run was conducted in which the bioreactors were maintained at a normal and constant rate of operation while the extra sulphide required to match the increased flow came from sulphide produced and stored earlier (see Table 3). The higher flow tested (45.4 L/min) is the maximum flow through the pilot plant; full-scale application of the Biosulphide process will be designed to accommodate the near order of magnitude changes in flow at Britannia.

Table 3 - Results with a Simulated Seasonal Flow Change

Hours	Rate (L/min)	Stored Sulphide	Cu Stage O/F		Plant Discharge		% Removal	
			Cu	Zn	Cu	Zn	Cu	Zn
2	34.0	no	0.20	15.2	0.01	0.36	> 99.9	97.7
4	34.0	no	0.12	16.4	0.01	0.05	> 99.9	99.7
6	34.0	no	0.07	16.4	0.02	0.07	99.8	99.6
8	34.0	no	0.01	16.5	0.01	0.01	> 99.9	> 99.9
10	45.4	YES	0.01	16.1	0.01	0.01	> 99.9	> 99.9
12	45.4	YES	0.03	16.0	0.02	0.02	99.8	99.9

Results in mg/L (=ppm). Feed composite: 12.6 mg/L Cu, 15.85 mg/L Zn

Operational Upsets

To demonstrate the resiliency of the bacteria to operational upsets, the entire plant was turned off for nearly two days after months of normal operation. The shutdown included heat, feed, nutrients and mixing. After 47 hours mixing, nutrients, feed, and heat was restored to normal levels. The bioreactors immediately returned to normal operation, displaying no measurable loss of performance as a result of the shut-down.

In addition, the chemical circuit was operated during the shut-down to demonstrate the ability of the process to function in the absence of active bioreactors by using only the sulphide produced and stored earlier. The process functioned well throughout this test, providing complete drainage treatment.

DISCUSSION

Results/Operation

Continuous bioreactor operation began in September, 1995, and was maintained essentially uninterrupted until September 1996, when Phase II operations were reduced pending new financing and potential larger scale work. Bioreactor performance was poor during the first two months of operation due partly to air leaks in the recycle pumps. With this problem solved, bacterial activity increased quickly, demonstrating good resistance to oxygen toxicity. Their activity (as measured by the sulphate reduction rate), did not reach the projected level. The limitation was found to be due to poor hydrogen uptake (approximately 25%) resulting from inadequate dissolution of the gas in the bioreactor recycle line. The application of in-line mixers increased hydrogen uptake and resulted in improved sulphate reduction rates. Additional improvements to the bioreactor gas system are planned for future work to further improve hydrogen uptake. The bioreactors were operated in this configuration from January, 1996 through the remainder of the Phase II pilot project. Throughout this time they proved to be a reliable source of sulphide and alkalinity. The dependability of the biological stage is a result of both the bioreactor design and the configuration of the Biosulphide process. By placing the chemical stage prior to the biological stage, the bioreactors receive an almost metal-free solution, and sulphate loading can be controlled to maintain optimum bioreactor performance.

Like the biological stage, the chemical stage performed reliably throughout Phase II testing, although a lack of process automation made it impossible to operate continuously without supervision. For this reason, 24 hour operation was limited to the 5 day continuous run described above. The selective precipitation of copper and zinc was found to be essentially self-regulating, and required only "off-the-shelf" equipment to monitor and optimize. As observed in batch tests conducted since 1988 [11], metal sulphides are extremely rapid to form. At Britannia, copper sulphide is formed in-line with essentially no retention time. Zinc was found to require a retention of several minutes for complete removal.

The two product sludges isolated from the AMD - copper and zinc sulphide concentrates - are intended to be sold to smelters to offset treatment costs during commercial-scale operation. Based on the results above, resource industry personnel have stated that the copper product should be easily saleable as it would be higher grade than most copper concentrates. As mentioned above, the quality of the zinc product suffered due to previous runs with incomplete copper-stage copper removal, resulting in the presence of copper in the zinc stage feed water, and the subsequent precipitation of copper with the zinc product. As demonstrated by the selective metals removal shown in Figure 2, very high grade products should be relatively easy to obtain. Future assays of the zinc product are expected to better reflect the selective precipitation of the chemical circuit.

The on-going production and storage of a concentrated sulphide product from bioreactor off-gas has been found to be an effective method of accommodating periods where the chemical stage demand for sulphide (ie metal loading) exceeds the biological stage production of sulphide. The result is a simple and effective method of providing a complete drainage treatment during the sudden flow increases that occur at Britannia and similar sites. This method of sulphide storage also provides for drainage treatment in the absence of active bioreactors, such as routine maintenance, and equipment or mechanical failures.

Cost Estimates

Based on the pilot results, the capital costs of a full-scale treatment plant at Britannia are estimated at $2.5 million. For comparison, SRK estimated the capital cost of a lime plant to be $3.5 million in 1991 [1], and operating costs were estimated at over $900,000 per annum. The estimate for a Biosulphide plant is for a net operating profit of approximately $130,000 per annum, resulting from the sale of sulphide concentrates to smelters or mines. This estimate assumes a 65% net smelter return on the CuS product and 50% on the ZnS product (further processing on-site for the recovery of copper metal may improve revenues but this has not yet been investigated in detail). No waste sludge requiring disposal would be produced because the plant effluent would be discharged at depth in Howe Sound, allowing the seawater alkalinity to carry out the final neutralization and precipitation of the small quantities of iron and aluminum remaining in solution.

CONCLUSIONS

The results to date from the 10 m^3 on-site Britannia pilot project have demonstrated the Biosulphide process to be highly effective at removing zinc, copper, and cadmium to levels as low as <0.1, <0.01, and <0.001 mg/L, respectively, on an on-going, consistent, and predictable basis. The recovered precipitates fluctuated in quality while consistent plant operation was being established, but later steadily improved to the point where the copper product was of higher grade (Cu>41%) and quality than copper concentrates from most mines. The zinc product was not fully optimized, but also reached a grade which would allow metal recovery, demonstrating that the process could entirely avoid waste sludge production at Britannia. Favourable reaction kinetics, metal recovery and lack of waste sludge combined to demonstrate a very favourable comparison with lime treatment at this site. The project also demonstrated the reliability of the bioreactor operation, and an effective method was developed to store excess sulphide to ensure complete treatment through the large seasonal fluctuations which occur in drainage volume.

The pilot project also highlighted limitations in the existing bioreactor design, related mainly to solution/gas mixing and hydrogen utilization. Redesign of the gas introduction system promises to significantly improve process efficiency and hence process economics. Along with these changes, the next stage in the development of the process will be further scale-up and the introduction of sufficient process control to allow continuous automated operation with routine maintenance. While the ownership, development and liability issues at the Britannia site remain unresolved, this pilot study has shown that the costs of dealing with the drainage need not be as prohibitive as previously believed. It is hoped that this work will lead directly to an end to the on-going environmental damage being caused by this drainage, which remains an embarrassment to both the government and the mining industry.

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REMOVAL OF HEAVY METALS BY A NEW BIOSORBENT

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ABSTRACT

A family of new biosorbent materials is derived from the biomass of selected seaweeds. These materials are capable of binding more than 10% of their dry weight in heavy metals from solutions. The binding of heavy metals by *Sargassum* biosorbent was examined in equilibrium batches and in a flow-through sorption column. Cations including Cu^{2+}, and Fe^{2+} were sorbed by the biosorbent in a stoichiometric exchange for protons and Ca^{2+}. *Sargassum* seaweed biosorbent contains 2.3 meq of binding sites per gram of dry acid washed biomass. Experiments demonstrated a continuous selective removal of Cu^{2+} from equimolar aqueous solutions of $Cu^{2+}$and Fe^{2+}(2mM) in a biosorption column giving Cu free effluent. Metal-loaded biosorbent in the column was regenerated by first using acid to desorb the metals, followed by a wash with a Ca solution at pH>7. The desorption carried out with HCl permitted 100% Cu recovery while concentrating Cu substantially with respect to the Cu concentration in the original column feed. The combined H/Ca-cycle was recommended for continuous operation of a biosorption column selectively removing toxic heavy metals from wastewater charged with a high level of dissolved solids. The technical feasibility of the biosorption process was demonstrated. A mathematical model was fitted to the experimental biosorption data for several multimetal systems (Fe-Ca, Cu-Ca, Cu-Fe-Ca) in order to facilitate designing and optimizing the biosorption process.

ÉLIMINATION DES MÉTAUX LOURDS À L'AIDE D'UN NOUVEL AGENT DE BIOSORPTION

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RÉSUMÉ

Un nouveau groupe de matériaux biosorbants est fondé sur la biomasse d'algues selectionées. Ces matériaux sont capable de fixer plus de 10% de leur poids sec en métaux lourds. La fixation des métaux lourds par la biomasse de *Sargassum* a été examiné en système fermé (batch) et en colonne à lit fixe. Les cations de Cu et Fe ont été retenus par le biosorbant dans un processus d'échange stoichiométrique dans lequel des protons et des cations de Ca ont été relargué dans la solution. Après un lavage acidique la biomasse de *Sargassum* sèche contient 2.3 meq de sites de sorption de métaux lourds par gramme de poids sec. Les résultats ont démontrés que les cations de Cu étaient sélectivement enlevés de solutions aqueuses contenant les même concentrations de Cu^{2+} et Fe^{2+}. Le biosorbant dans la colonne a été régénéré par l'injection d'acide hydrochlorique suivi d'un rinçage à l'aide d'une solution de Ca^{2+}. L'injection d'acide a libéré les métaux retenus par la biomasse en permettant de récupérer 100% du Cu. La concentration de Cu de la solution résultante était nettement plus élevée que celle de la solution originale. Les expériences ont démontrés la faisabilité technique du cycle combiné H/Ca appliquée en colonne de biosorption. Afin de faciliter la conception et l'optimization du processus de biosorption, un modèle mathématique a été ajusté aux données obtenus pour plusieurs systèmes multimétalliques (Fe-Ca, Cu-Ca, Fe-Cu-Ca).

INTRODUCTION

Lime neutralization is currently a dominating active treatment system used by industry to clean mining wastewater. However, the costs associated with handling and safely disposing of the toxic sludges produced by the lime precipitation, together with the very stringent regulations imposed on heavy metal pollution, create an incentive for developing new technologies.

The biosorption of heavy metals onto inexpensive biological material such as fungi [1], algae [2], and peat moss [3], have been studied in the past decade. Biosorption not only offers the advantage of being efficient and low cost for heavy metal removal from very diluted streams, but it also offers a possibility of recovery of the heavy metals [4]. Although research in the past few years has progressed in that the principal metal binding mechanism has been determined [5, 6] and biosorption of heavy metals from industrial effluents has been tested [3, 7], the engineering aspects of the process related to the scale-up and modeling of the process have received only a limited attention.

Typically, industrial effluents and Acid Mine Drainage (AMD) polluted streams are charged not only with dissolved toxic heavy metals such as Cu, Zn, Ni, and Cd but also with relatively high concentration levels of Fe and light metals including Na, Ca, and Mg. The volumetric flow rates of contaminated streams vary widely from 250 gpm to less than 1 gpm [8].

Traditionally, biosorption has been viewed only as a potential polishing (tertiary) treatment of wastewater for the two following reasons. First, biosorbents are very effective at sequestering metals from very diluted solutions. Second, total metal loadings commonly encountered in industrial wastewater entering a secondary treatment unit have been considered too high to be managed by biosorbents with a limited number of metal binding sites. However, if biosorbents proved to be selective for toxic heavy metals, the metal loadings targeted for removal by a biosorption process would drop substantially. Consequently, a biosorption process could then be applied to effluents with higher heavy metal contents and/or higher volumetric flow rates and not just to aqueous discharges from secondary treatments.

MATERIALS AND METHODS

Biomass

Brown marine alga *Sargassum fluitans* was collected beach-dried on the Gulf Coast of Florida in August. In the laboratory, the seaweed biomass was washed first with 1M HCl and then with distilled water until the pH of the water after washing reached pH value 4.5.

Flow-through column experiments

Acid washed dry *Sargassum* biomass was packed in the chromatography column. The column parameters are listed in Table 1a. The characteristics of the water pumped through the column is summarized in Table 1b. Nitrogen gas was bubbled through the column feed tank and E_h of the feed was periodically checked. Samples of the column effluent were collected via a fraction collector (Gilson 2100) and the Cu, Fe, and Ca contents in the samples were determined by AAS (Perkin- Elmer 3100). Ca-biomass was prepared by washing the biomass with a solution of $CaCl_2$. The desorption of metals from the saturated column was carried out using 0.1M HCl. The acid was pumped into the column until the heavy metal concentration in the effluent dropped below 30 mg/L.

Equilibrium batch experiments

Approximately 200 mg of dry acid pretreated biomass was mixed with 50 mL of metal solution in a 125 mL Erlenmeyer flask and the mixture was let to equilibrate for 4 hours in a shaker at 25°C . A solution of 0.1M NaOH was used to adjust the pH. The metal uptakes were determined from the difference between initial and final metal concentrations.

Electrode Potential (EP)

E_h was measured using a combination ORP electrode (Cole-Parmer 2006-25) combining gold disk and Ag/AgCl electrodes, respectively. EP values mentioned throughout this manuscript are given with respect to the Standard Hydrogen Electrode (SHE).

RESULTS and DISCUSSION

Biosorption Equilibrium

Models describing biosorption equilibrium for multimetal systems have recently been developed [5, 9]. Reliable equilibrium models are essential for, quantitative evaluation of phenomena such as the competitive sorption and sorption inhibition encountered in the biosorption of metals from multicomponent mixtures, as well as for analyzing the performance of flow-through biosorption columns.

Schiewer [5] developed a model which is based on ion exchange and which takes into account the presence of several different binding sites in the biomass. The model introduces one constant per type of binding site and one binding constant per ionic species per type of binding site. The constants are usually determined by fitting the model to the experimental data for a given system. Figure 1 shows a fit of the model to the experimental equilibrium data for the sorption of Fe^{2+} onto Ca-biomass (a Fe-Ca system) at pH=3. Table 2 lists the values of binding constants for some of the metals that have been studied [10]. The constants listed in Table 2 are related to the metal binding by carboxyl groups which are prevalent in algal biosorbents. Since the values of the binding constants are related to the free energy of binding, the metals can be arranged in descending order of affinity towards the biomass as follows: $Cu^{2+}>Ca^{2+}>Fe^{2+}$.

Furthermore, the model helps to estimate the trend of inhibition of sorption of one metal due to the increasing presence of another metal in solution. Figures 2a and 2b summarize the effect of increasing concentrations of Fe^{2+} and Ca^{2+} on the sorption of Cu^{2+} from solutions containing 1, 3, and 6 mM of Cu. Figures 2a and 2b show that the reduction of the Cu uptake due to the presence of interfering species, i.e. Fe and Ca , is more pronounced at $C_f(Cu)$=1mM than at $C_f(Cu)$=6mM. Moreover, the hyperbolic shape of the curves in Figure 2a and 2b demonstrates that after an initial drop in Cu uptake, caused by increased concentrations of interfering species, only a relatively small further decrease in Cu uptake can be achieved by multifold increases of Fe and Ca concentrations.

Another important feature of the equilibrium model is its ability to provide ion exchange equilibrium isotherms for different concentration levels of the metals of interest [10]. The effect of the shape of the isotherm for a binary metal system on the performance of a fixed-bed sorption column is discussed below.

Optimizing Selective Removal of Cu in a Flow-through Column

Figures 4a and 4b show that regardless of the ionic form of the biomass, i.e., Ca-form and H-form, Fe broke through the column much faster than Cu, thereby rendering the Cu removal selective. The selectivity of Cu removal over Fe removal can be explained by the fact that the Cu binding constant K_{Cu} is approximately 10x greater than the similar constant for Fe, i.e. K_{Fe} as listed in Table 2.

The principal mechanism of biosorption by algae is ion exchange [5, 6]. One cycle of a conventional ion exchange process taking place in a flow-through sorption column consists of three stages including sorption (exhaustion), desorption, and rinsing. It follows that the ratio of the sorption (service) time and the time required to complete one full cycle, is a measure of the technical feasibility of the ion exchange process evaluated at a given hydraulic loading. The results presented in Figures 4, 5, and 6 demonstrate the performance of a biosorption column during the three stages of one biosorption cycle.

Figures 4a and 4b show that the column service time, based on the breakthrough of Cu, was approximately 3x longer with Ca-biomass than with H-biomass. The fact that Ca-biomass yielded longer service time than H-biomass is related to the shape of the respective

Cu equilibrium isotherms shown in Figure 3. The concave Cu isotherm on Ca-biomass brings about a 'self-sharpening' exchange zone in a column whereas the convex Cu isotherm on H-biomass results in the formation of a broadening zone. The sharper the zone in the column the higher the degree of column utilization during the sorption of heavy metals, hence the longer the service time of the column.

The desorption of metals from the exhausted column was performed with HCl and the corresponding elution curves for Cu and Fe are displayed in Figure 5. Figure 5 shows that the desorption was approximately 8x faster than the column exhaustion. Furthermore, the peak copper concentration C(Cu) of 3.4g/L demonstrates the ability of the *Sargassum* biosorbent to concentrate the heavy metal substantially with respect to the C(Cu) in the feed being purified in the column.

After the desorption, the biomass in the column was in H-form. In order to extend the service time of the column in a subsequent new exhaustion with heavy metals, the washing with a solution containing Ca^{2+} was necessary for converting the biomass from H-form to Ca-form. However, previous work revealed that rinsing the biomass with 1% $CaCl_2$ was inefficient in that the displacement of protons with Ca^{2+} was slow because it was thermodynamically unfavorable [10]. The current study focused on amending the dynamics of the Ca-rinse by using a mixture of chemicals that provided not only Ca^{2+} but also enough alkalinity to neutralize the protons released from the biomass. Chemicals commonly used to accelerate the rinsing of peat moss and fungal biomass such as $KHCO_3$ and Na_2CO_3 could not be used with algal biosorbents since these chemicals solubilize alginate and other polysaccharides present in the *Sargassum* seaweed. Therefore, our tests were restricted to the use of limestone and lime. Figure 6 shows the evolution of pH in the column effluent during the Ca-washes with a mixture of $CaCO_3 + CaCl_2$ and solutions of $Ca(OH)_2$. Since it is known from previous work that the Ca uptake by *Sargassum* at a pH of 4 approaches the maximum possible Ca uptake, the pH 4 in the column effluent signals the completion of Ca-wash. Figure 6 shows that $CaCO_3$, despite its buffering capacity, does not provide sufficient amount of alkalinity to balance out the protons in the column. The use of $Ca(OH)_2$, on the other hand, proved to be very effective at shortening the rinsing time.

The performance of the column during one Ca/H cycle is summarized in Table 3. The Ca/H cycle applied to the algal biomass in the column is highly advantageous. The principle advantage lies in the fact that both the heavy metal removal and the heavy metal desorption are made thermodynamically favorable yielding a long column service time and 100% metal recovery [10]. The slow Ca-wash of the H-biomass is made favorable and accelerated by using $Ca(OH)_2$. Furthermore, the scale-up of the biosorption process is facilitated by the fact that favorable ion exchange processes yield a "constant pattern behavior" in flow-through columns. Consequently, the data in Table 3 can be used for a scale-up of the laboratory column provided that the hydraulic loading of the full scale column is the same, i.e. 2 L min^{-1} m^{-2}.

CONCLUSIONS

Significant amounts of Fe^{2+} can be removed from wastewater by biosorption onto *Sargassum* Ca-biomass provided that the Cu^{2+} content is low. However, when Cu^{2+} is present in the water, Fe^{2+} uptake is dramatically reduced and Cu^{2+} is selectively removed from the water. Since only the toxic heavy metal is targeted by the *Sargassum* biomass, the total biomass requirement of the purification step is lowered. Therefore, it is possible to apply this type of biosorption process to streams containing Cu as well as high metal loadings of Fe and Ca.

Symbols:

C(M)	concentration of metal M in liquid [mg/L]
C_0(M)	concentration of metal M in the column feed [mg/L]
C_0	total normality of the metal laden solution [meq/L]
C_f(M)	final equilibrium concentration of metal M in liquid
K_M	binding constant of metal M [L/mol](see Table 2)
M	bivalent metal
q(M)	metal uptake [mg M/g dry biomass]

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TABLE 1

a) LABORATORY COLUMN PARAMETERS

PARAMETER	VALUE	UNITS
BED HEIGHT	40	cm
BED VOLUME	0.2	L
BIOMASS PACKING DENSITY	200	g L^{-1}
HYDRAULIC LOADING	2	L min^{-1} m^{-2}

b) CHARACTERISTICS OF COLUMN INFLUENT

pH [-]	Cu mg/L	Fe(II) mg/L	E_h mV	TDS mg/L
3.7	120	110	515	870

TABLE 2

EQUILIBRIUM MODEL PARAMETERS

BINDING CONSTANT	UNITS	FITTED VALUE
K_{Cu}	L/mol	32,250
K_{Ca}	L/mol	5,031
K_{Fe}	L/mol	3,510

Concentration of metal binding groups in *Sargassum* $C_{COOH} = 2.3$ meq/g

$M^{2+} + 2B <-> 2BM_{0.5}$ $$K_M = \frac{[BM_{0.5}]^2}{[M^{2+}][B]}$$

TABLE 3

LABORATORY COLUMN PERFORMANCE

STAGE OF OPERATION	TIME [hr]	TIME/ VOLUME [hr / L of biomass]	SOLUTION FED IN
SORPTION	15	75	polluted water
DESORPTION	2	10	0.1 M HCl
RINSING	3.5	17.5	1% $CaCl_2$ + $Ca(OH)_2$ pH 12.8
TOTAL	20.5	102.5	

SORPTION AS % OF TOTAL = 73 % FLOWRATE = 2 L min^{-1} m^{-2}

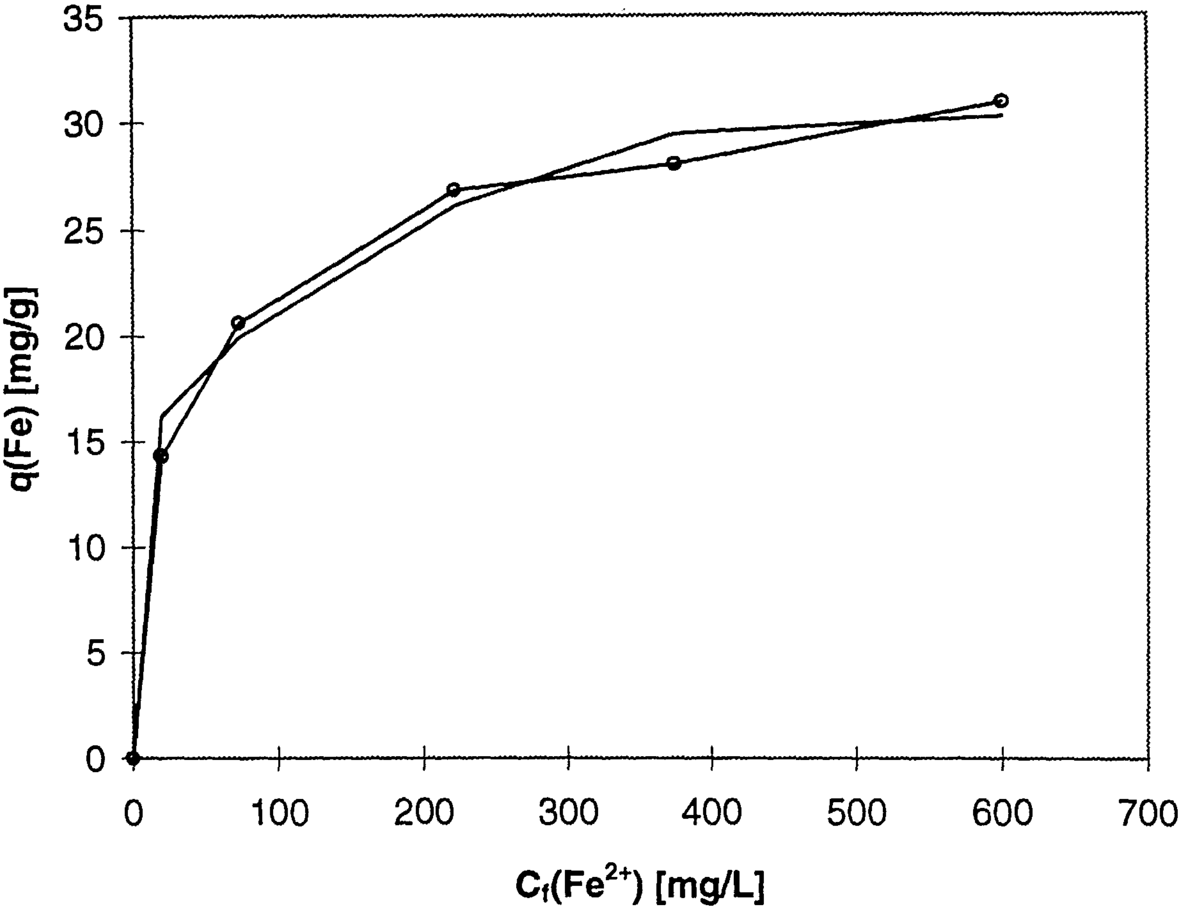

Figure 1: The fit of the equilibrium model to experimental data for the sorption of Fe^{2+} onto *Sargassum* Ca-biomass (Fe-Ca system)

(o) experimental data (-) model fit

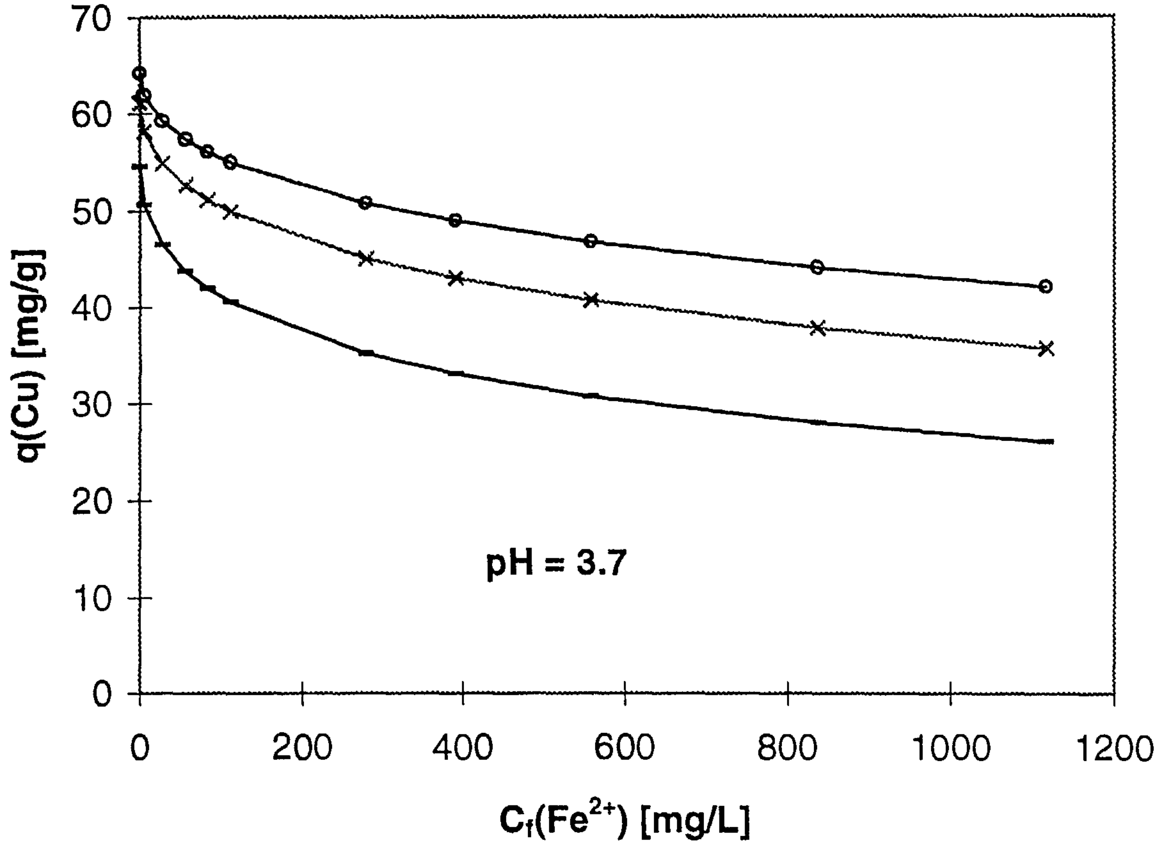

Figure 2a: The effect of Fe presence on the Cu uptake by *Sargassum* biomass at pH 3.7 and equilibrium concentration of Cu being

(o) C_f(Cu)=384 mg/L (x) C_f(Cu)=192 mg/L (-) C_f(Cu)=64 mg/L

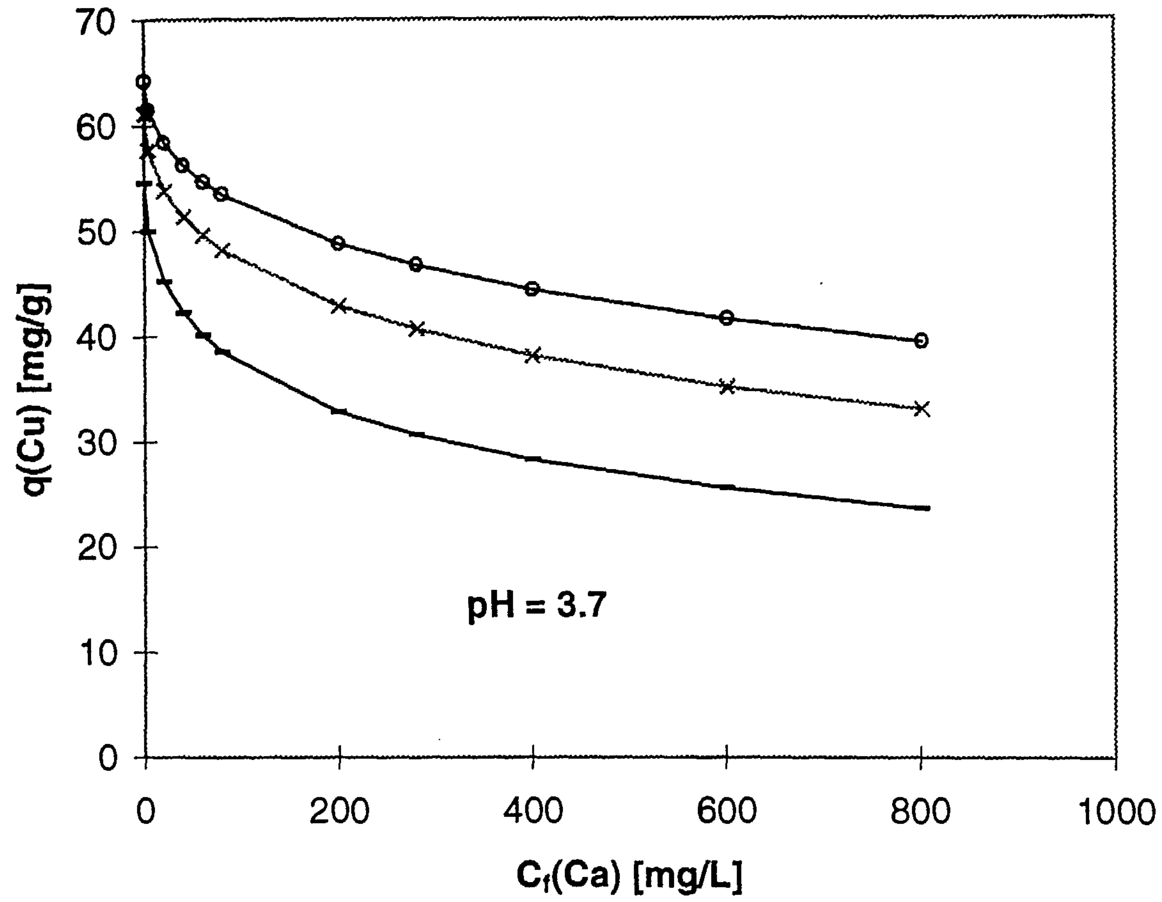

Figure 2b: The effect of Ca presence on the Cu uptake by *Sargassum* biomass at pH 3.7 and equilibrium concentration of Cu being

(o) C_f(Cu)=384 mg/L (x) C_f(Cu)=192 mg/L (-) C_f(Cu)=64 mg/L

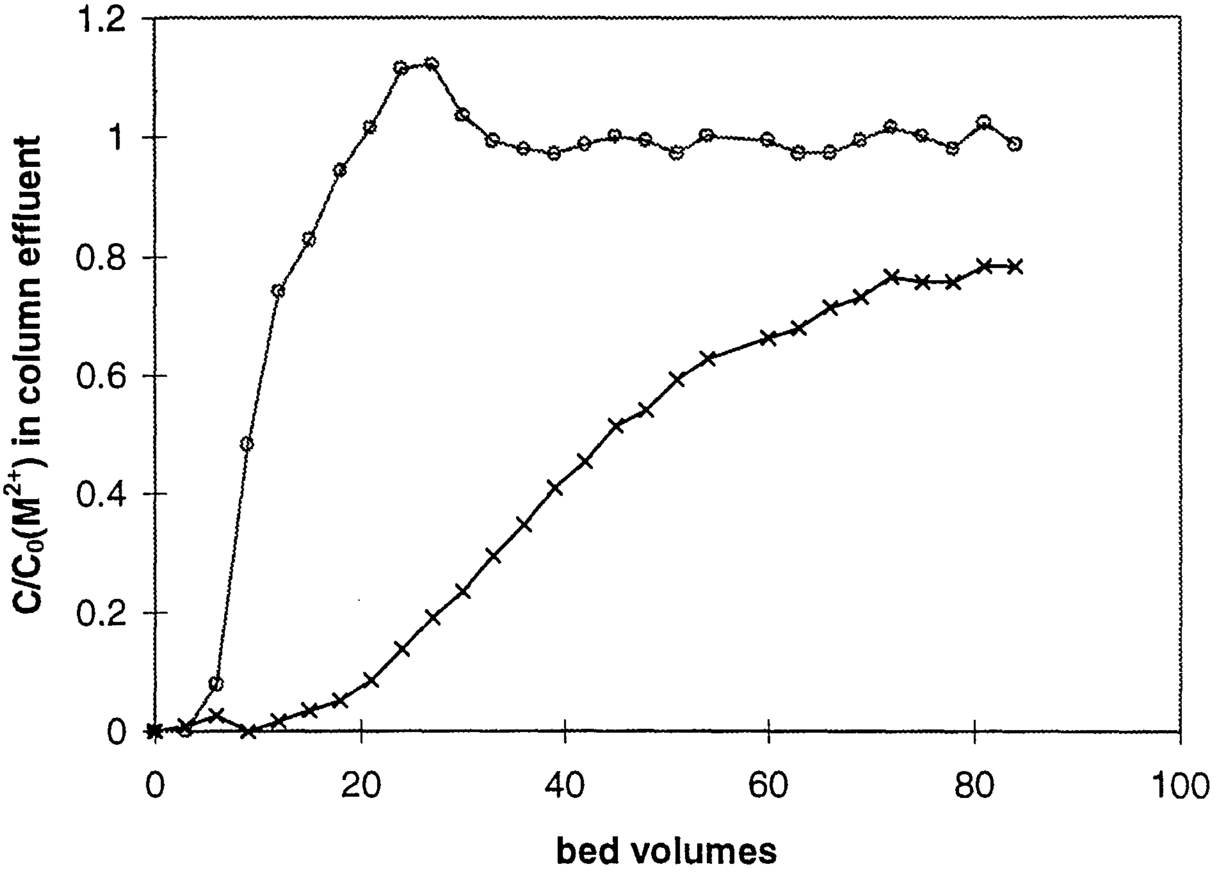

Figure 3a: Saturation of H-biomass in the flow-through column with a solution containing 2mM of Cu^{2+} and 2mM Fe^{2+} at pH 3.7. Breakthroughs of

(x) Cu (o) Fe

bed volume=200 mL; flowrate=2 L min^{-1} m^{-2}

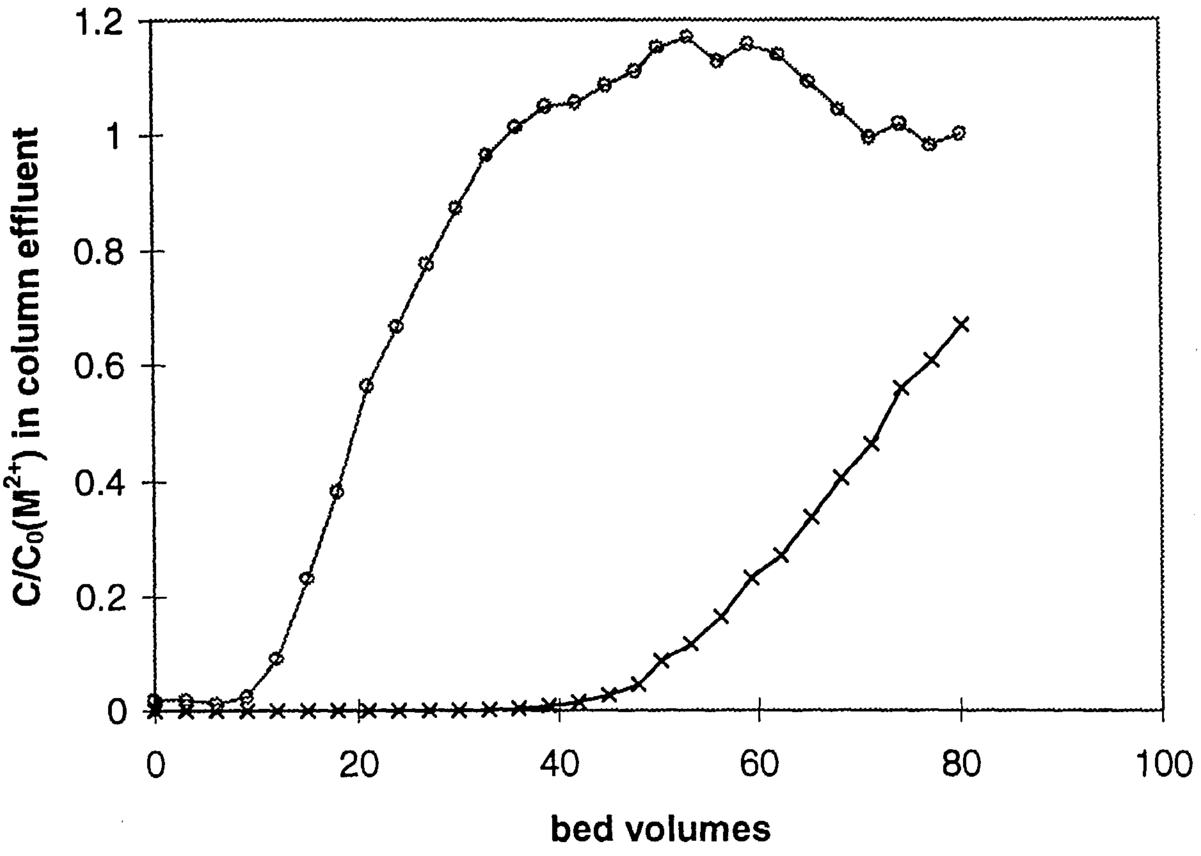

Figure 3b: Saturation of Ca-biomass in the flow-through column with a solution containing 2mM of Cu^{2+} and 2mM Fe^{2+} at pH 3.7. Breakthroughs of

(x) Cu (o) Fe

bed volume=200 mL; flowrate=2 L min^{-1} m^{-2}

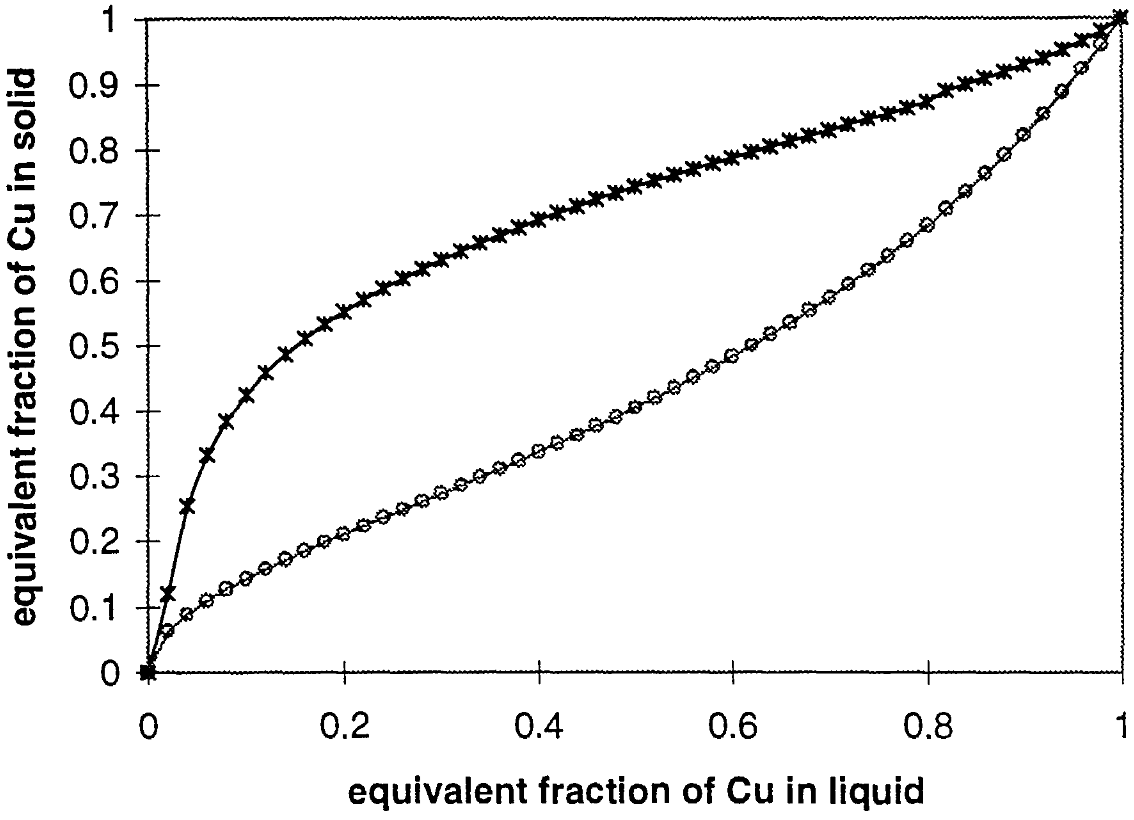

Figure 4: Equilibrium ion echange isotherm for Cu sorbing onto

(o) H-biomass (x) Ca-biomass

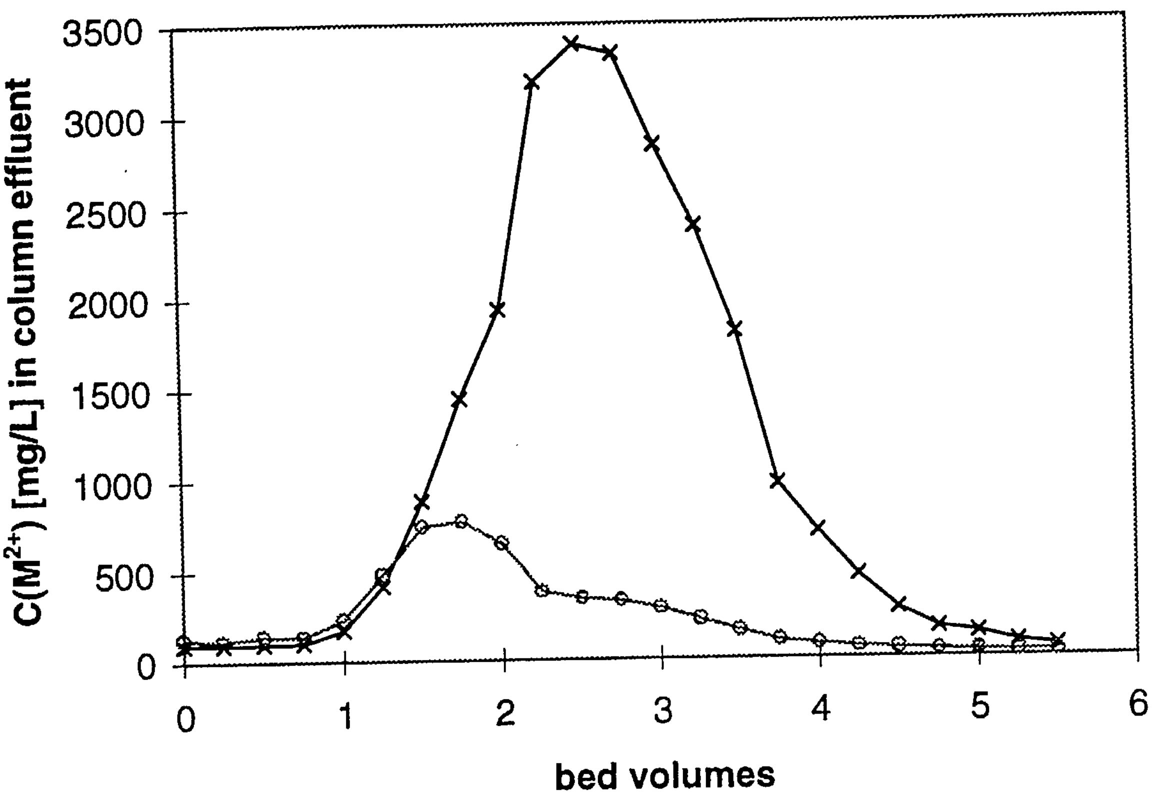

Figure 5: Elution of metals from the saturated column carried out with 0.1M HCl Concentration of metals in the column effluent

(x) Cu^{2+} (o) Fe^{2+}

bed volume=200 mL; flowrate=2 L min^{-1} m^{-2}

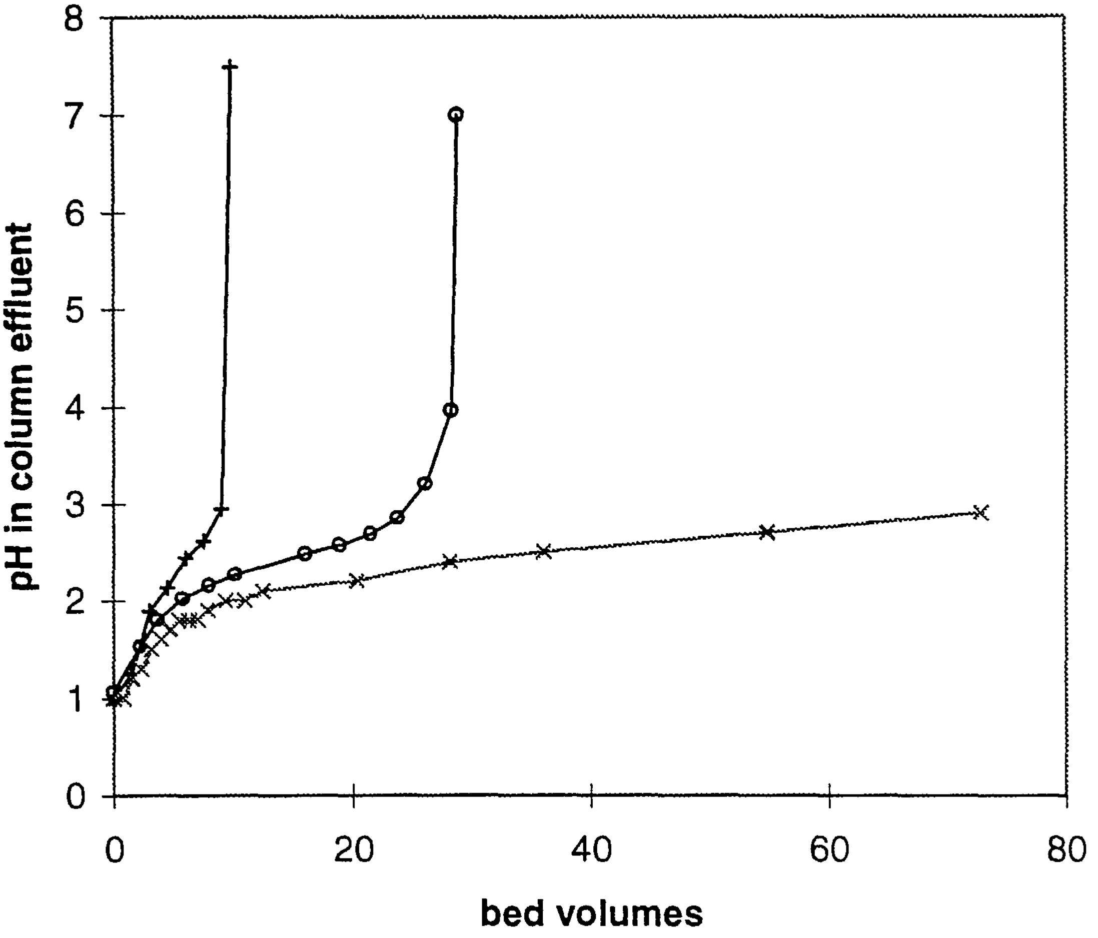

Figure 6: Evolution of pH in the column effluent during rinsing of H-biomass in the column with solutions containing Ca

(x) $CaCl_2$+$CaCO_3$ pH=9 (o) $Ca(OH)_2$ pH=11.6 (+) $Ca(OH)_2$ pH=12.6

bed volume=200 mL; flowrate=2 L min^{-1} m^{-2}

PREVENTION OF ACID MINE DRAINAGE USING A POROUS REACTIVE WALL: A FULL-SCALE FIELD TRIAL

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ABSTRACT

A porous reactive wall utilizing sulfate reduction was installed in August 1995 into an aquifer impacted by mine tailings drainage at the Nickel Rim mine site, near Sudbury, Ontario. The reactive mixture, composed of organic matter, was designed to maximize bacterially mediated sulfate reduction and subsequent metal sulfide precipitation. The installed structure is 15 meters long, 3.6 meters deep and the flow path length (wall width) is 4 meters. Results from sampling one month and nine months after installation, indicate that sulfate reduction is occurring. Comparing water entering the wall to treated water exiting the wall one month after installation; sulfate concentrations decrease from 2000-4600 mg/L to 0-200 mg/L, Fe concentrations decrease from 600-800 mg/L to < 1 mg/L, pH increases from 5.8 to 7.0 and alkalinity increases from 0-50 mg/L to 2000-4000 mg/L as $CaCO_3$. Populations of sulfate reducing bacteria are orders of magnitude higher within the wall compared with the adjacent aquifer. After passing through the reactive wall, the net acid generating potential of the aquifer water has been converted from acid producing to acid consuming.

MUR RÉACTIF POREUX POUR LA PRÉVENTION DU DRAINAGE MINIER ACIDE : ESSAI DUR LE TERRAIN PLEINE GRANDEUR

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RÉSUMÉ

Un mur réactif poreux sulfato-réducteur a été érigé en août dans une nappe aquifère exposée aux eaux de drainage des résidus de la mine Nickel Rim près de Sudbury en Ontario. Le mélange réactif, composé de matière organique, a été conçu pour maximaliser la réduction des sulfates par voie bactérienne et la précipitation ultérieure des sulfures métalliques. L'ouvrage a 15 mètres de long, 3,5 mètres de haut et 4 mètres de large (distance d'écoulement). Les résultats des échantillonnages effectués un mois et un an après l'installation du mur indiquent qu'il y a réduction des sulfates. La comparaison entre l'eau entrant dans le mur et l'eau traitée à la sortie un mois après l'installation révèle : une baisse de concentration des sulfates de 2 000-4 600 à 0-200 mg/L, une baisse de concentration du fer de 600-800 à <1 mg/L, une hausse du pH de 5,8 à 7,0 et une hausse de l'alcalinité de 0-50 à 2 000-4 000 mg/L sous forme de $CaCO_3$. Les populations de bactéries sulfato-réductrices sont de 4 à 6 ordres de grandeur supérieures dans le mur qu'elles ne le sont dans la nappe aquifère adjacente. L'eau de la nappe, acidifiante d'un côté du mur réactif, est devenue nettement avide d'acides après son passage de l'autre côté.

INTRODUCTION

Treatment of acidic metal-rich drainage from mines and mine wastes using bacterially mediated sulfate reduction and metal sulfide precipitation has received increased interest in recent years [1-6]. Sulfate reduction is an attractive solution because it results in the consumption of soluble metals and an increase in alkalinity, both lower acid generating potential of the impacted water. In addition, remedial strategies can be designed to operate passively, potentially reducing operating costs. Finally, sulfate reduction has been documented to occur naturally at mine sites [7]. We have combined bacterially mediated sulfate reduction with the passive, *in situ* technology of porous reactive walls to treat groundwater containing mine tailings-derived contamination. We describe the installation of the first, full-scale, permeable reactive wall for the prevention of acid mine drainage and present results of that installation.

Acid mine drainage

The oxidation of sulfide minerals in mine-wastes, and the subsequent oxidation of dissolved Fe(II), produces acidic drainage through the reactions [8,9]:

(1) $FeS_2(s) + 7/2O_2 + H_2O \text{ ----> } 2SO_4^{2-} + Fe^{2+} + 2H^+$,

(2) $Fe^{2+} + 1/4O_2 + 5/2H_2O \text{ ----> } Fe(OH)_3(s) + 2H^+$

This reaction sequence results in the production of H^+, Fe^{2+} and SO_4^{2-} to the water. Similar reactions, involving other sulfide minerals can release dissolved As, Cd, Cu, Ni, Pb, and Zn.

In mine tailings impoundments the oxidation of sulfide minerals and the oxidation of Fe^{2+} are often de-coupled [10,11]. Sulfide oxidation (Reaction #1) occurs in the unsaturated zone of the tailings and the reaction products (SO_4^{2-}, Fe^{2+}, H^+) are carried downward by infiltrating precipitation water into the underlying aquifer. At most sites, the H^+ released by sulfide oxidation is attenuated by reaction with minerals contained in the tailings, and underlying aquifer material. Dissolved Fe^{2+}, and SO_4^{2-}, however, remain in solution. When the groundwater plume, containing high concentrations of SO_4^{2-}, Fe^{2+} and other metals, discharges to oxygenated surface-water bodies, Fe^{2+} is oxidized releasing two moles of H^+ per mole of Fe^{2+} (Reaction #2). The resulting low pH conditions are harmful to biota, and increase the mobility of dissolved metals such as Cd, Cu, Ni, and Pb, greatly enhancing their bioavailability. In many cases the flux of low quality water from tailings impoundments will continue for many decades, even centuries [10].

Current methods for the prevention and treatment of acid mine drainage include preventing the infiltration of meteoric water, preventing the oxidation of sulfides, and treatment of the acidic water discharge [12]. Conventional treatment of discharge waters involves oxidation and precipitation of Fe-oxyhydroxides by addition of lime. This approach can be effective but often involves high operating costs and produces large volumes of metal-rich sludge.

Sulfate reduction as a treatment strategy

Bacterially mediated reduction of sulfate can be expressed as:

$$(3) \qquad SO_4^{2-} + 2CH_2O + 2H^+ \Rightarrow H_2S + 2CO_2 + H_2O,$$

where *CH_2O* represents organic carbon. In the presence of soluble metals, hydrogen sulfide can react to form metal sulfides;

$$(4) \qquad Fe^{2+} + H_2S \Rightarrow FeS_{(s)} + H^+$$

Elements such as As, Cd, Cu, Ni, Pb and Zn can also react with H_2S to form other sulfide minerals.

This reaction sequence results in decreased concentrations of dissolved SO_4^{2-}, Fe, and other metals, an increase in alkalinity and increase in pH. All of these changes are desirable. Recently, interest in sulfate reduction has focused on its utility during remediation of acid mine drainage using constructed wetlands or bioreactors. The primary method of exploiting sulfate reduction has been to direct acidic, metal and sulfate-rich surface water into the subsurface of the wetland or bioreactor by an induced hydraulic gradient [6]. A variety of laboratory and field-scale projects have demonstrated the potential effectiveness of this process [1-6].

The success of these projects has been mixed. In many cases sulfate reduction and metal sulfide-precipitation has resulted in improved water quality. However, two factors have hampered this approach. First, high acidity can quickly consume the buffering capacity of the reactive organic material, resulting in a decrease in pH. Because sulfate reduction is optimized at moderate pH [13], these acidic conditions limit treatment capacity. Second, where neutral pH conditions have been maintained, the residence times within the reactive mixture are often not sufficient to remove the mass of sulfate and metals entering the system [5].

Blowes [11] proposed *in-situ* treatment of water contaminated with mine-related wastes by sulfate reduction within the saturated zone of the tailings or within permeable reaction zones installed into the aquifer down-gradient of tailings impoundments. By treating the water prior to the oxidation of the Fe^{2+} (Reaction #2), the generation of additional acidity is prevented. Additionally, it is easier to maintain the reduced geochemical conditions necessary for sulfate reduction below the water table within the aquifer.

Reactive wall technology

We have attempted to exploit advantages of treatment within the aquifer using the emerging remediation technology of a permeable reactive wall. This method consists of installing an appropriate reactive material into the aquifer, so that contaminated water flows through the material. The reactive material induces chemical reactions that remove the contaminants from the water or otherwise cause a change that decreases the toxicity of the contaminated water [14-18]. For the treatment of groundwater affected by leachate derived from mine wastes, organic carbon is used in the reactive wall to enhance sulfate reduction and metal sulfide precipitation [19,20].

A two year laboratory study was undertaken to assess the viability of using sulfate reduction in a porous reactive wall to treat groundwater impacted by mine tailings [21,22]. Batch studies were conducted to select the optimal organic substrate for inducing sulfate reduction. A variety of organic materials were found to be effective at inducing sulfate reduction.

Column experiments were conducted using the results of the batch experiments to simulate the dynamic flow and geochemical conditions that exist within a contaminated aquifer [21,22]. The influent water contained high concentrations of SO_4, Fe, Zn, and Ni and was maintained under anoxic conditions. Sulfate, Fe and Ni concentrations were significantly decreased and alkalinity increased after passing through the columns, indicating that, under dynamic flow conditions, rates of sulfate reduction are sufficient to treat fluxes typically found in contaminated aquifers on a sustained basis.

In Autumn 1993 and 1994, pilot-scale test cells were installed into the aquifer at the Nickel Rim mine site near Sudbury, Ontario. Canada [20]. The permeable cells of reactive material were designed to evaluate the potential of inducing sulfate-reduction and metal-sulfide precipitation reaction in groundwater under field conditions. The test cells continue to induce sulfate reduction 12 and 24 months after installation, indicating that the reactive wall technology for the treatment of mine-contaminated waters was transferable to a field setting.

METHODS

In August of 1995 a full-scale porous reactive wall was installed into the aquifer at the Nickel Rim mine site (Benner *et al.*, in submittal). Selection of the organic source material was based on the previous laboratory and field studies. The material for the porous reactive wall must satisfy five criteria; it must be reactive, permeable, have sufficient longevity, and be readily available and inexpensive. The material must be sufficiently reactive to reduce sulfate concentrations found in the aquifer at Nickel Rim. The material must be permeable enough to accommodate the groundwater flux rates at the site. The material must sustain its permeability and reactivity over a time period of years. Finally, the material must be readily available and affordable with respect to site conditions.

The results of Waybrant [21] indicate that leaf compost is an effective material for promoting sulfate reduction, and that mixtures containing a variety of different carbon sources are most effective. It is our belief that sources of fresh organic carbon are superior to older sources because they are likely to contain a higher concentration of short-chain, single-carbon-bond aliphatics, that are more biodegradable. In addition to a carbon source, sulfate reducing bacteria also require nitrogen, phosphate and other trace elements for growth. Based on these considerations, a substrate composed of 40% municipal compost, 40% leaf compost, and 20% wood chips was selected. Municipal compost was selected because it is readily available, is composed of a variety of materials, is rich in nitrogen and phosphate, as well as other trace nutrients, and can be acquired at a point during the composting sequence when only partial decomposition has occurred. Leaf compost was selected because it is readily available and was effective in long-term column experiments. Wood chips were selected because they are readily available, are a source of fresh carbon and their larger size may provide additional longevity.

Organic material was mixed with 50% washed pea gravel to obtain a hydraulic conductivity capable of accommodating the flux rates in the Nickel Rim aquifer. To obtain a uniform mixture of gravel and organic material, a 40 meter inclined conveyer belt was used. The organic materials and the pea gravel were simultaneously added to the conveyor and allowed to cascade into a conical pile. The materials were mixed as the pile formed at the end of the conveyer. This process was repeated until a uniform mixture was obtained.

The reactive wall was installed by cut and fill excavation; as the aquifer material was removed to underlying bedrock, the trench was back-filled with the organic carbon and gravel mixture (Figure 1). Sand fill was added at the up and down-gradient sides of the wall to square off the organic mixture with the sloping sides of the trench. The installed wall is approximately 15 meters long, 3.6 meters deep, and 4 meters wide. Nested piezometers were installed and sampled along a line parallel to flow, providing a cross-sectional sampling profile. Sampling and analyses were conducted as described in Waybrant [21] and Bain [23].

Two cores of reactive mixture were collected from the wall for enumeration of sulfate-reducing bacteria. The cores were collected and sampled as described in Starr and Ingelton [24]. Enumeration was conducted in an anaerobic environment using a Postgate B medium and a Most-Probable Number method [25].

RESULTS and DISCUSSION

The aquifer down-gradient of the reactive wall receives surface water recharge. Therefore, the water flowing through the reactive wall occupies only the lower portion of the down-gradient aquifer while the upper portion of the aquifer contains untreated water. Sampling one month and nine months after installation indicates that the reactive wall is greatly improving groundwater quality. Comparing water entering the wall to treated water exiting the wall nine months after installation; sulfate concentrations decrease from 2400-4800 mg/L to 60-3600 mg/L, Fe concentrations decrease from 260-1300 mg/L to 1.0-40 mg/L, pH increases from 5.8 to 7.0 and alkalinity (as $CaCO_3$) increases from 0-60 mg/L to 700-3200 mg/L (Figure 2). The water entering the wall has an average net acid producing potential of 6-46 meq/L and the water exiting the wall has an average net acid consuming potential of 16-45 meq/L (Benner *et al.*, in submittal).

Isotopic ratios for sulfate show enrichment of ^{34}S in the groundwater within the reactive wall and down gradient aquifer which is consistent with removal of sulfate by bacterially mediated sulfate reduction. Higher populations of sulfate reducing bacteria within the wall when compared to the up-gradient aquifer also suggest that sulfate reduction is the dominant process removing sulfate from the system.

The initiation of sulfate reducing conditions and the establishment of an active population of sulfate reducing bacteria within the porous reactive wall occurred rapidly. After 30 days, sulfate reduction lowered SO_4 concentrations at many locations within the wall from 2000-4500 mg/L to < 100 mg/L.

Iron and SO_4 removal is occurring at a 1:1 molar ratio, consistent with the precipitation of a Fe mono-sulfide (FeS). This stoichiometric constraint on the removal of Fe and SO_4 by sulfide mineral precipitation appears to limit the removal of SO_4. Once all of the Fe is removed, approximately half of the SO_4 is remaining. Because Fe is the acid generating constituent, it is preferable to remove all the Fe than all the SO_4.

Calculations based on comparison with laboratory column experiments of Waybrant *et al.* [22] suggest that the reactive wall will be effective for a minimum of 15 years (Benner *et al.*, in submittal).

CONCLUSIONS

The potential use of permeable reaction walls for remediation and prevention of acid mine drainage has been evaluated through a full-scale field installation. The results of this installation indicate that sulfate-reduction and metal-sulfide-precipitation reactions can be initiated and sustained, at rates that are suitable for treatment of plumes of tailings-derived water, under field conditions.

These studies indicate that permeable reactive walls, using bacterially mediated sulfate reduction, are a potentially effective treatment strategy for remediation of groundwater plumes impacted by drainage from mining activities. The groundwater exiting from the full-scale wall will continue to be monitored for a minimum of three years. Research is ongoing to more fully describe the biogeochemical transformations within the reactive wall.

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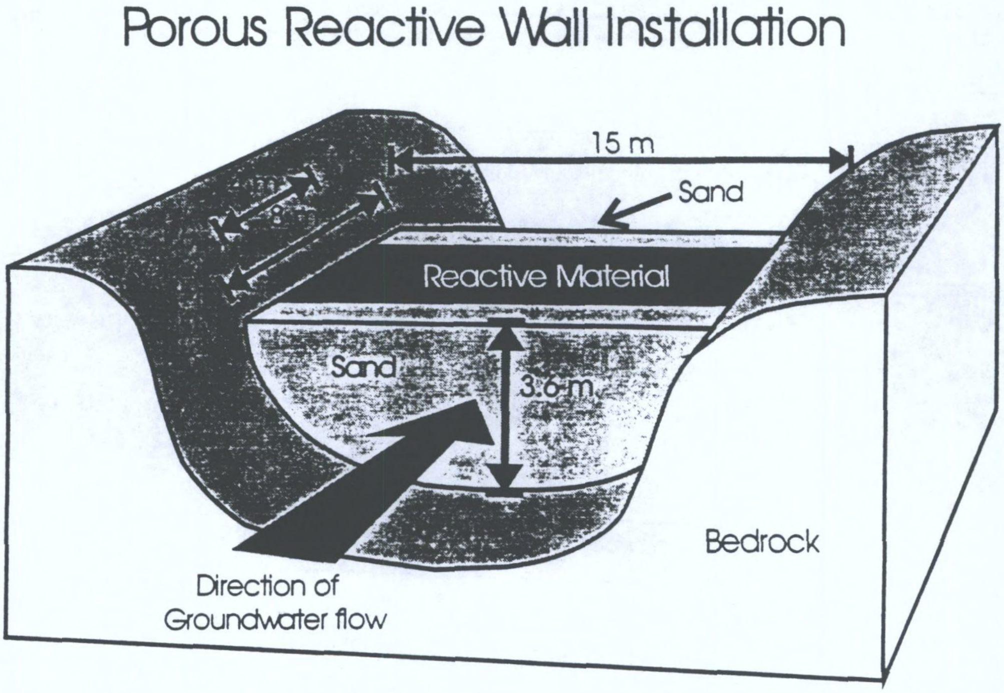

Figure 1. Schematic diagram of porous reactive wall installation

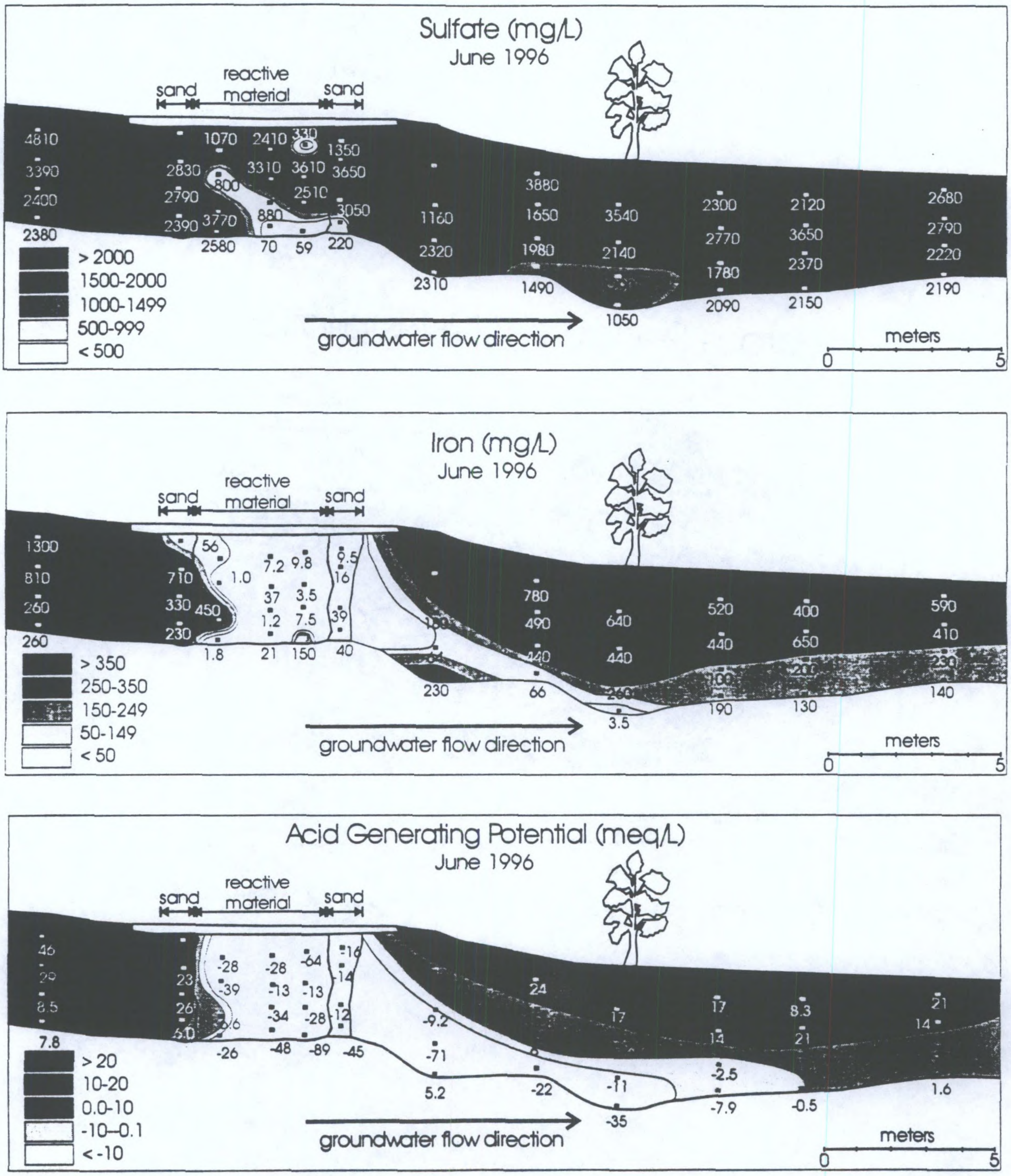

Figure 2. Cross-sectional view of reactive wall and adjoining aquifer. Small squares indicate sample locations. Profiles of sulfate, iron and "Acid Generating Potential" 9 months after installation are shown.

BACTERIAL ACTION ON BAUXITES IN COLUMNS FED WITH FULL-STRENGTH AND DILUTE SUCROSE-MINERAL SALTS MEDIUM

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ABSTRACT

The activity of bacteria associated with bauxite from Brazil and Jamaica in mobilizing Fe, Si, and Al from ore contained in columns fed at daily intervals with 2, 1, and 0.5% sucrose-mineral salts media was studied quantitatively. In all experiments, the bacteria generated anaerobic conditions in the columns within three days after initiating an experiment. Qualitatively similar Fe and Si mobilization was observed with both ores in concentrated and dilute media. Less Fe and Si were mobilized from each ore in dilute medium compared to concentrated medium. Al was mobilized from each ore in concencentrated medium after the pH of the effluent had fallen to about 4. In dilute medium, small amounts of Al were mobilized by the bacteria from Jamaican but not Brazilian ore. Also, in dilute medium, sulfate-reducing bacteria grew out from the flora associated with the Brazilian ore but not the Jamaican ore. They appeared to cause precipitation of some of the mobilized iron as iron sulfide in the column, which was manifested as large black patches in the upper two-thirds of the ore column.

ACTION BACTÉRIENNE SUR DES BAUXITES DANS DES COLONNES ALIMENTÉES AVEC UN MILIEU CONCENTRÉ ET UN MILIEU DILUÉ DE SACCHAROSE/SELS MINÉRAUX

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RÉSUMÉ

L'activité des bactéries associées à la bauxite du Brésil et à celle de la Jamaïque pour mobiliser Fe, Si et Al du minerai contenu dans des colonnes alimentées à des intervalles journaliers avec 2,1 et 0,5 % d'un milieu de saccharose/sels minéraux a fait l'objet d'une étude quantitative. Au cours de tous les essais, dans les colonnes, les bactéries ont produit des conditions anaérobiques dans les trois jours suivant le début d'un essai. Dans les deux minerais, une mobilisation qualitativement similaire du Fe et du Si a été observée dans un milieu concentré et dilué. Dans un milieu dilué, moins de Fe et de Si a été mobilisé dans chaque minerai comparativement à ce qui s'est produit dans un milieu concentré. Dans un milieu concentré, Al a été mobilisé dans chaque minerai après que le pH de l'effluent soit descendu à 4, approximativement. Dans un milieu dilué, de petites quantités de Al ont été mobilisées par les bactéries de la bauxite jamaïquaine mais non par celles de la bauxite brésilienne. Également, dans un milieu dilué, les bactéries réductrices de sulfate se sont développées à partir de la flore associée au minerai du Brésil mais non de la flore associée au minerai de la Jamaïque. Dans la colonne, les bactéries ont semblé provoquer la précipitation du fer mobilisé en tant que sulfures de fer ce qui s'est traduit par deux larges taches noires dans les deux tiers supérieurs de la colonne de minerai.

INTRODUCTION

A desirable composition of bauxite for aluminum production when using the low-temperature Bayer process is 45-50% Al_2O_3 as gibbsite, <4% as boehmite, ≤20 Fe_3O (hematite and/or goethite) and 2-4% combined SiO_2 (quartz, kaolinite). Previous work has shown that microbes are able to mobilize ferric oxide in the ore and thus exhibit a potential for lowering the iron content of bauxite. This mobilization may be achieved with metabolic products such as citric acid, produced by fungi under aerobic conditions [1]. In this case, bio-acid mobilizes the ferric iron in crushed ore by acidulation and/or complexation without change in oxidation state of the iron. Mobilization may also be mediated by bacteria through reduction of the ferric to ferrous iron in "as is" and crushed ore with a suitable reductant under anaerobic conditions [2]. In addition, Si in combined SiO_2 in bauxite can be mobilized by microbial solubilization [1, 2, 3 ,4, 5]. A common mechanism is acidolysis. The extent of Si removal reported in different investigations varied. Removals in excess of 30% (w/w) Si in some reports contrast with removals of only 2 to 3% in others. In at least one report, removal of combined SiO_2 by *Bacillus mucilaginosus* and *B. circulans* was due to adsorption of fines rich in combined silicates to exopolysaccharide and thus was not due to leaching, i.e. solubilization [1]. Some of the aluminum in bauxite may be mobilized by microbial activity, but the extent of its solubilization depends on the reaction conditions (see, for instance, 1, 2). The mechanism of Al mobilization involves acidulation, but may also include complexation.

In this report we compare microbial Fe, Si, and Al mobilization from a Brazilian and a Jamaican bauxite in 1 and 0.7 kg quantities, respectively, under anaerobic conditions in Lexan columns fed separately at daily intervals with either 2 or 1% sucrose-mineral salts medium or with 0.5% sucrose-mineral salts medium. We previously reported on anaerobic bacterial leaching of 47 g of a pisolitic bauxite with 2% sucrose-mineral salts medium in small glass columns [2].

MATERIALS and METHODS

Ore samples

Two bauxite samples were used, one from a Brazilian deposit and the other from a Jamaican deposit. The Brazilian sample contained 40% Al_2O_3, 11% Fe_2O_3 (mostly hematite), and 9% combined silica. The Jamaican sample contained 44%Al_2O_3, 20%Fe_2O_3 (mostly aluminian goethite), and 0.7% combined silica. Tests with both ores were carried out on "as is" bauxite ground to a particle size of <1.70 mm (-10 mesh).

Column design and setup

The column reactors consisted of Lexan tubing sealed at one end with a Lexan disc, 0.64 cm in thickness . The column design for all experiments in this report is illustrated in Fig. 1. All Lexan tubing diameters are indicated in ID values. The wall thickness of the large-diameter tubing was 0.32 cm , and that of the small-diameter tubing was 0.063 cm. Two pairs of autoclaved columns were loaded with 1 kg of unsterilized Brazilian ore each, and another two pairs with 700 g of unsterilized Jamaican ore each. Sterile culture medium was introduced into each column from a reservoir flask connected by sterilized rubber tubing to the top of the central 0.6 cm-diameter tube in each reactor. Medium was transferred from each reservoir flask to a column with the aid of a peristaltic pump. One column of each pair served as a control, being fed with appropriate culture medium to which 10% thymol solution in methanol to a final concentration of 0.05% had been added as growth inhibitor. The other column of each pair served as an experimental column, being fed corresponding culture medium without inhibitor. Extensive microbial growth developed in each experimental column in 3 to 4 days after initial flooding to the overflow sidearm with appropriate medium. Approximately 330 mL of appropriate fresh medium with and without thymol were then added over 25 min on successive days to the control and experimental columns, respectively. The columns were left undisturbed between feedings. Spent medium displaced each day via the overflow sidearm from each column as a result of feeding was collected in separate 600-mL beakers for analysis. All experiments were run at 37 °C.

Growth media

Full-strength culture medium was based on the original formulation of Belkanova *et al.* [6] and consisted of (in g L^{-1}) sucrose, 20; $(NH_4)_2SO_4$ 0.5; K_2HPO_4, 0.2; $MgSO_4.7H_2O$, 0.2; and NaCl, 0.1 (pH 6.5). Modified full-strength medium contained 10 g instead of 20 g sucrose per liter but otherwise featured the same salts concentrations as the full-strength medium. The dilute medium consisted of (in g L^{-1}) sucrose, 5; $(NH_4)_2SO_4$, 0.1; K_2HPO_4, 0.1; $MgSO_4.7H_2O$, 0.1; NaCl, 0.05 (pH 6.5). All media were prepared by aseptically mixing equal volumes of separate, autoclaved, double-strength solutions of sucrose and of combined mineral salts while still hot.

In the experiment using full-strength sucrose-mineral salts medium, columns containing the Brazilian ore were started and fed this medium throughout the run. By contrast, columns containing Jamaican ore were started with full-strength medium but only fed it on each of the first two days after growth had developed. Thereafter until the end of the experiment, these columns were fed daily with modified full-strength medium. In the experiment using dilute medium, both the Brazilian and Jamaican ore columns were started with and fed this medium throughout the respective runs.

Culture

The mixed cultures in each of the experimental columns developed from the microbial flora associated with each ore after initial flooding with appropriate medium. None of the columns were inoculated with special cultures.

Analytical methods

To enable estimation of total recoveries of Al, Si, and Fe, the total volume of each effluent collected each day was determined in a graduate cylinder. Measurements of Al, Si, and Fe were made on subsamples from 4-mL aliquots of effluents that had been centrifuged at 12,000 x g for 10 min to remove cells and/or other suspended matter and then fixed with 0.01 mL of concentrated HNO_3. Aluminum and silicon were determined by atomic absorption spectrophotometry with a Perkin-Elmer 1100B instrument using an acetylene/nitrous oxide flame. Ferrous and total iron were determined colorimetrically with *o*-phenanthroline reagent [7]. Sucrose concentrations were measured colorimetrically with anthrone reagent [8]. The pH of effluents was determined with Merck colorpHast indicator strips in some experiments and with a combination pH electrode attached to an Orion meter in others. Microscopic examination of effluent samples was in wet mounts using an American Optical phase-contrast microscope.

At the end of the experiment, an ore sample was taken from the experimental column containing the Brazilian ore after cutting across it at its middle. The moisture content (LOM) was determined on a subsample, and after appropriate preparation, other subsamples were examined by X-ray diffraction (XRD) for mineral identification, and by X-ray fluorescence (XRF) and inductively coupled plasma analysis (ICP) for elemental composition. Sulfur species associated with the ore were determined by ion chromatography on leachates obtained after treating subsamples by oxidative chemical leaching. The proportions of different minerals in the ore were estimated quantitatively from ICP and XRF results by use of an in-house program used by ALCAN called the HUNGALU method.

RESULTS

After flooding with sterile medium, heavy bacterial growth was usually noted within 3 to 4 days in the medium over the top of the ore in each experimental column. The depth of the medium over the ore was between 4 and 6 cm. In the case of the Brazilian ore fed with full-strength medium, daily feeding was not started until day 6 after flooding, whereas with the Jamaican ore it was started on day 3. Strong outgassing, presumably due to H_2 and CO_2 produced in bacterial attack of sucrose, was associated with this growth. The gas caused some expansion of the ore volume and resulted in some displacement of medium via the overflow sidearm into a receiving beaker between daily feedings. Microscopic examination of the spent medium from the experimental column showed the presence of many clostridia as well as vegetative rods of various lengths and diameters, some in chains. The effluent had a fruity odor, typical of butylic fermentation. These are indications that anaerobic conditions had developed in the experimental columns as bacterial growth occurred. The morphological appearance of the microbial flora in daily effluents changed gradually over time from a predominance of clostridia and large vegetative rods to thinner rods and long filaments and an absence of spores.

In Fig. 2, we compare cumulative recoveries of leached Fe, Si, and Al from Brazilian ore in an experimental column fed with full-strength medium with recoveries from a similar column fed with dilute medium. In the case of Fe solubilization, it is immediately evident that regardless of which medium was fed, the leached Fe in the daily effluents was mostly ferrous. It is also evident that over comparable time periods, approximately half as much Fe and Si were leached by the bacteria with the dilute medium than with full-strength medium. Significant amounts of Al were leached in the experimental column only with full-strength medium after about day 68, which corresponded to a pH drop in spent medium from an initial value of around 6.5 to around 4.0 (Fig. 3). Very minor, non-biologically mediated Al leaching occurred with dilute medium in both control and experimental columns. No Al leaching attributable to bacterial activity occurred in the experimental column. The lack of microbial mobilization of Al in the ore in the experimental column fed with dilute medium was probably due to insufficient acid production as reflected by a pH drop in the effluent to no lower than pH 4.5 compared to a drop to below 4.0 with full-strength medium. The average leaching rate of Fe ranged from ~1.3 to 0.7 $g.L^{-1}day^{-1}$ in full-strength medium and from 0.6 to 0.4 $g.L^{-1}$ day^{-1} in dilute medium. The average leaching rate of Si was 6 $mg.L^{-1}day^{-1}$ in full-strength medium and 4 $mg.L^{-1}day^{-1}$ in dilute medium. The average leaching rate of Al in full-strength medium, once leaching had begun, was 0.05 $g.L^{-1}day^{-1}$.

Black deposits became noticeable in the upper part of the experimental column of Brazilian ore fed with dilute medium. We suspect that these black deposits, which changed in appearance and position in the column were iron sulfide. Using the technique of Braun-Howland et al. [9], significant numbers of sulfate-reducing bacteria ($5.3x10^4$ out of a total of $7.1x10^6$ bacteria per mL) were detected in the only effluent sample tested. Two molecular probes specific for sulfate-reducers among the delta proteobacteria were employed. The source of sulfate for sulfate reduction in this experiment was mostly the sulfate salts in the feed solution.

In Fig. 4, we compare cumulative recoveries of leached Fe, Si, and Al from Jamaican ore in an experimental column fed full-strength medium on each of the first 2 days and modified full-strength medium daily thereafter with cumulative recoveries from a similar column fed daily with dilute medium. As with the Brazilian ore, it is clearly evident that most of the Fe recovered in the effluents, regardless of the strength of the medium, was ferrous and that about half as much Fe and three fourth as much Si were leached with dilute medium in comparable time periods than with full-strength/modified full-strength medium. In the case of Al, measurable leaching in full-strength medium started around day 65, coinciding with a pH drop in the medium to between 4.0 and 4.5. Unlike with the Brazilian ore, a small amount of Al was leached by the bacteria in the experimental column with dilute medium within 2-3 days after the start of feeding, but the leaching rate slowed significantly after about day 16. These findings can be correlated with pH measurements of 3.8 to 4.2 in the daily effluents during the first 15 days contrasted with a pH of around 4.4 from day 16 on for most of the rest of the experiment (Fig. 5). The average leaching rate of Fe in full-strength medium was 1.0 g.L^{-1}day^{-1} and in dilute medium 0.6 g:L day . The average leaching rate of Si in full-strength medium was 2 mg.L-1day-1 and in dilute medium 1 mg.L^{-1}day^{-1}. The average leaching rate of Al in full-strength medium was 0.1 g.L^{-1}day^{-1} and in dilute medium 0.0003g.L^{-1}day^{-1}. No evidence of sulfate reduction was noted, either as black deposit in the ore column or through the presence of sulfate-reducers in a test on a single column effluent, when the Jamaican ore was fed with dilute medium.

Table 1 summarizes cumulative recoveries of leached Fe, Al and Si from the Brazilian and Jamaican ores at the end of each of the experiments with dilute and concentrated medium.

We ran a few spot tests on bacterial sucrose consumption from the modified full-strength medium fed to the Jamaican ore and found that between 61 and 88% of the sugar was consumed between daily feedings during the most active phase of the run. During bacterial action in dilute medium, we found between 57 and 76% of the sucrose to be used daily in the experiment with Brazilian ore, and between 86 and 95% with the Jamaican ore.

The mixed flora in the experimental columns must have included facultative organisms which quickly scavenged any oxygen in the feed added each day. From the morphological and physiological similarity of the flora that developed from the two ores collected from the geographically widely separated deposits in this study and from ore from a different continent used in an earlier study [2], we infer that a similar group of bacteria played an integral role in the development and/or maturation of each of these bauxites. This aspect will be further examined in a future communication.

An ore sample collected from the middle of the column at the end of the experiment revealed the unexpected presence of siderite ($FeCO_3$) by XRD. Its concentration was estimated at 1.5%. Sulfide-sulfur was present at a concentration of ~0.6% whereas sulfate occured at a concentration of ~0.2%, when both values are expressed as sulfate. The presence of sulfide supports the interpretation that the black precipitate formed in the column during the course of the experiment was probably iron sulfide, but results to date from XRD do not allow specific mineralogical identification of the iron sulfide.

DISCUSSION

Our results indicate qualitatively similar bacterial action on Brazilian and Jamaican ore in full-strength and modified full-strength medium, namely extensive ferric iron reduction to soluble ferrous iron and limited Si and Al solubilization, the Al solubilization being especially pH sensitive. The rates of Fe solubilization were of the same order of magnitude for both ores despite the fact that the iron oxide in the Jamaican bauxite was mostly in the form of aluminian goethite and that in the Brazilian bauxite, hematite. The aluminum in the goethite thus did not exert a significant toxic effect on the bacterial action, perhaps because of its integration in the crystal lattice where it replaced some of the ferric iron.

Iron below the surface of ore particles could not have been directly accessible to the bacteria because they could not penetrate the ore particles for lack of suitable pores as first noted by study of an Australian bauxite [2]. Instead, the ferric iron below particle surfaces may have been chemically reduced to Fe^{2+} by bacterially generated ferrous iron, which as electron donor in this reaction would be transformed to bacterially accessible ferric iron. This ferric would then be quickly re-reduced to ferrous iron by bacteria to sustain the continued reduction of the hematite or aluminian goethite in the ore (Fig. 6). Rapid bacterial re-reduction of the ferric iron produced from interaction of ferrous iron with iron oxides below the surface of bauxite particles would be a thermodynamically essential step to sustain the mobilization of the iron from the iron oxide mineral, since the reaction of Fe^{2+} with iron oxide is by itself thermodynamically not favorable (Fig. 6). The great predominance of ferrous iron in all of the effluents from the experimental columns, regardless of the strength of the medium they were fed, is a reflection of the rapidity with which the bacteria reduce dissolved ferric to ferrous iron.

Bacterial action in dilute medium was also qualitatively similar with both ores, except that aluminum was not leached under influence of the bacteria from Brazilian bauxite but was leached to a very limited extent under their influence from the Jamaican bauxite. This bacterially leached aluminum from the Jamaican bauxite could have originated in the dissolution of aluminian goethite. The observed rates of bacterial leaching of those elements that were solubilized from both ores in dilute medium were slower than in full-strength and modified full-strength medium. In the case of the Brazilian ore, the amounts of iron measured in solution in each of the effluents from columns fed with dilute medium were probably underestimates of the total iron leached if some of the leached iron was reprecipitated with sulfide produced by the sulfate-reducing bacteria, detected in a column effluent. In the case of the Jamaican ore, the iron leach rate in dilute medium could have been sucrose-limited since most of the sucrose had been consumed after each day's feeding.

The finding of siderite in the experimental column of Brazilian ore fed with dilute medium at the end of the experiment suggests that conditions in the column permitted its formation from the bacterially formed ferrous iron and from carbonate in solution that resulted from CO_2 formed in the bacterial degradation of sucrose in the medium. The stability of the siderite in the column must have been supported by prevailing reducing conditions and by a local pH that was probably somewhat higher than that measured in the daily effluents as the experiment progressed. Its presence along with iron sulfide is somewhat surprising since the solubility product of siderite is significantly higher (10-10.8) than that of FeS (10-19). The answer probably lies in the fact that the Fe^{2+} concentration in solution in the column greatly exceeded the amount of sulfide formed at any time. Indeed, no readily detectable odor of H_2S was ever noted in the daily effluents after the black precipitate formed in the columns. We have not yet examined the experimental column containing Jamaican ore and fed with dilute medium nor the experimental columns of Brazilian and Jamaican fed with full-strength or modified full-strength medium to determine whether siderite was formed in them.

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Table 1: Cumulative recoveries of Fe, Si and Al in bacterial leaching of bauxite from Brazil and Jamaica in dilute and full-strength media

		Percent recovery	
Source of ore	**Metal leached**	**Dilute medium**	**Full-strength medium**
Brazil1	Fe as Fe_2O_3	16.8	48.0
	Al as Al_2O_3	0.002	0.4
	Si as SiO_2	0.25	0.9
Jamaica2	Fe as Fe_2O_3	13.4	34.7
	Al as Al_2O_3	0.007	1.27
	Si as SiO_2	1.8	3.4

1 The experiment in dilute medium ran for 73 days and in full-strength medium for 122 days.

2 The experiment in dilute medium ran for 75 days and in full-strength/ modified full-strenth medium for 107 days.

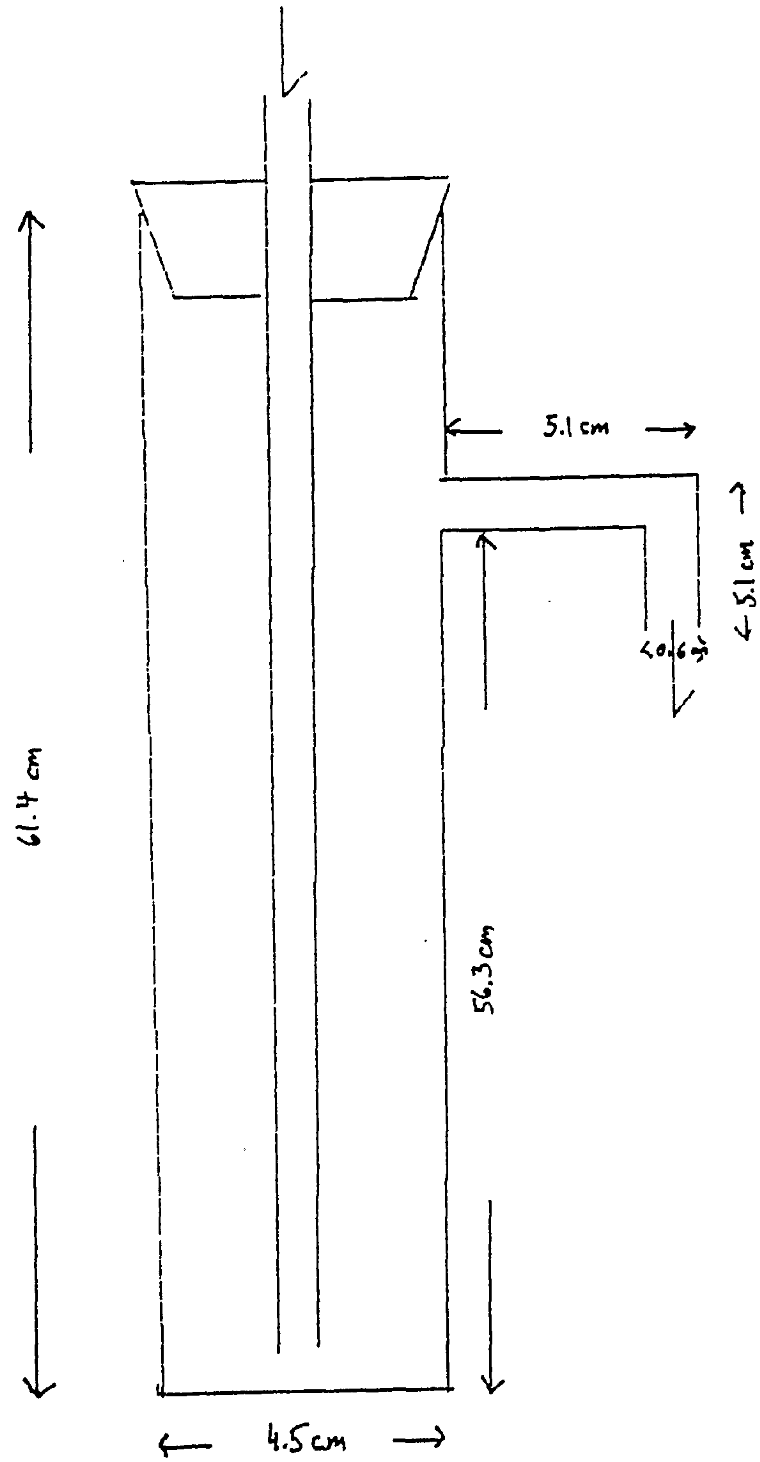


Figure 1. Schematic of column reactor constructed from Lexan tubing and rod.

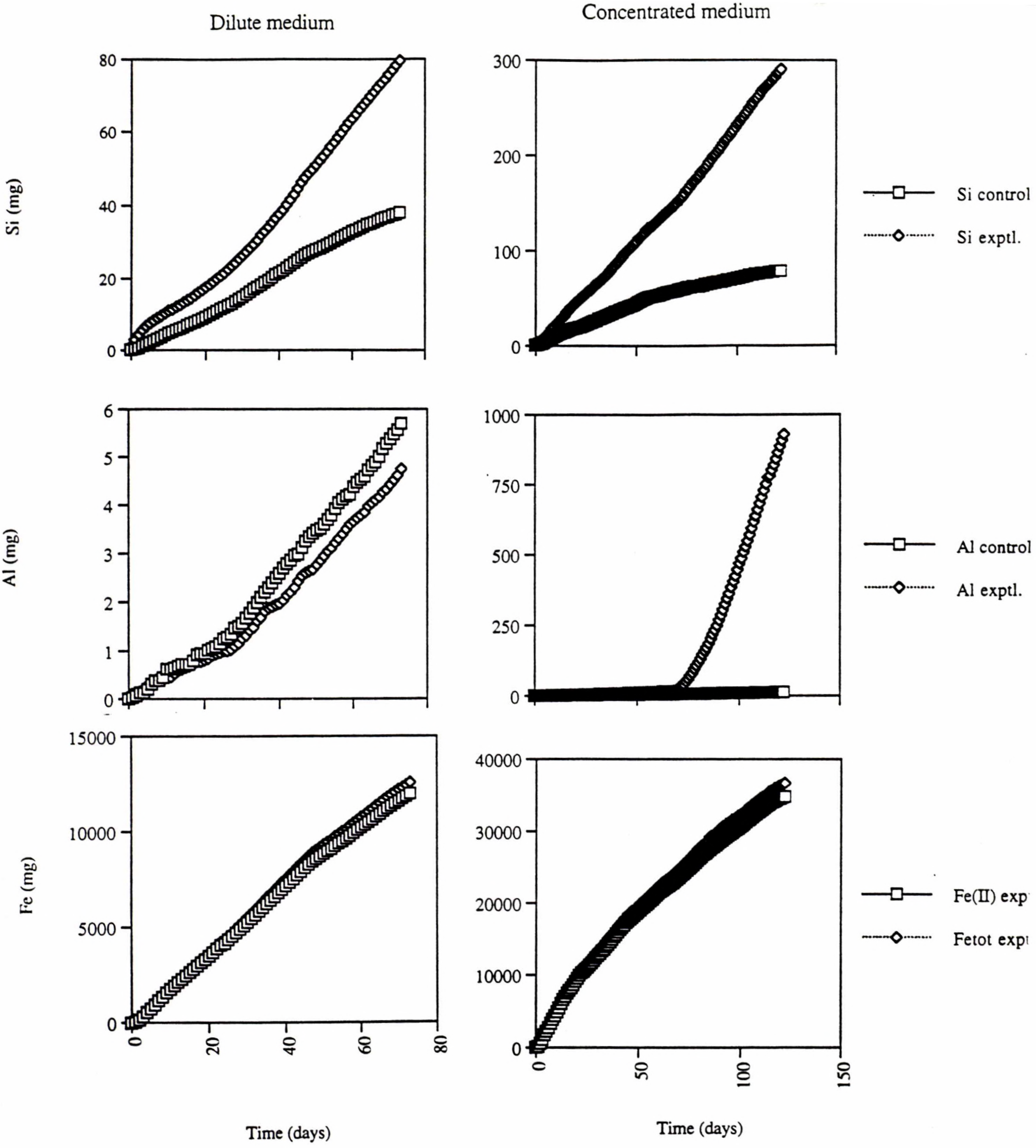
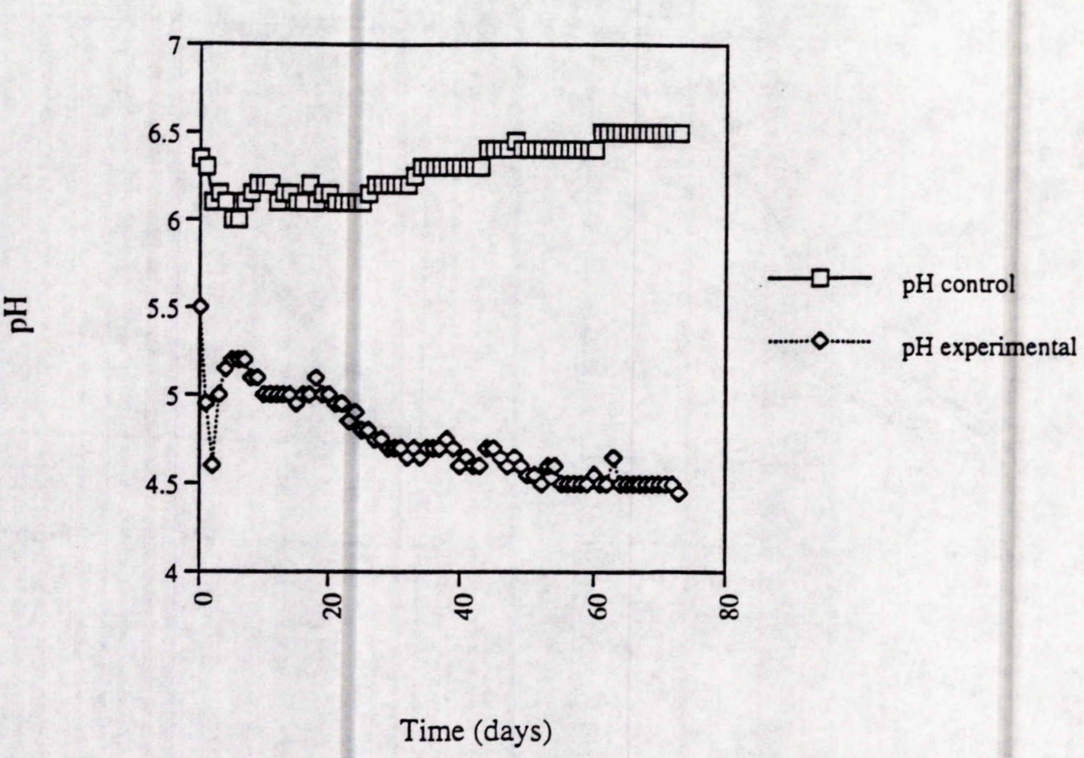


Figure 2. Cumulative recoveries of Si, Al, and Fe from Brazilian ore in columns fed with dilute and concentrated medium.

Dilute medium



Concentrated

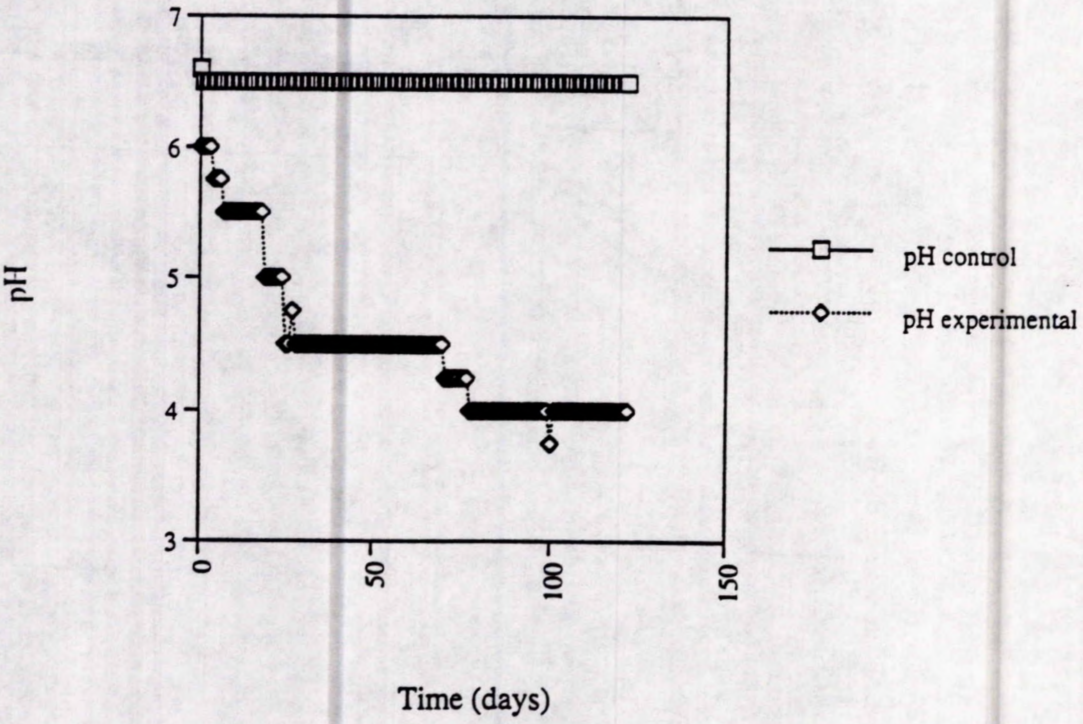


Figure 3. pH measured in daily effluent collections from Brazilian ore in columns fed with dilute and concentrated medium.

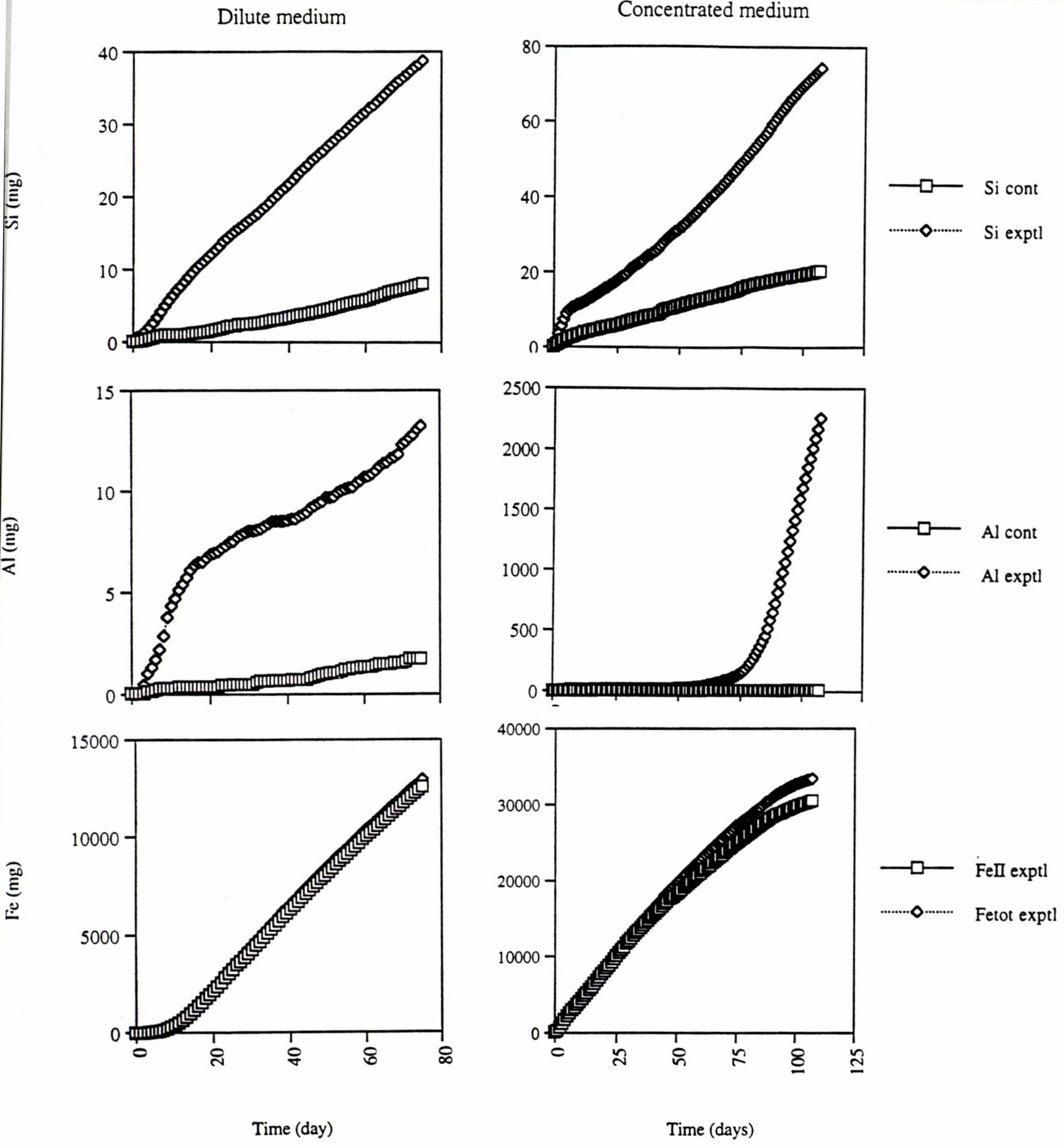
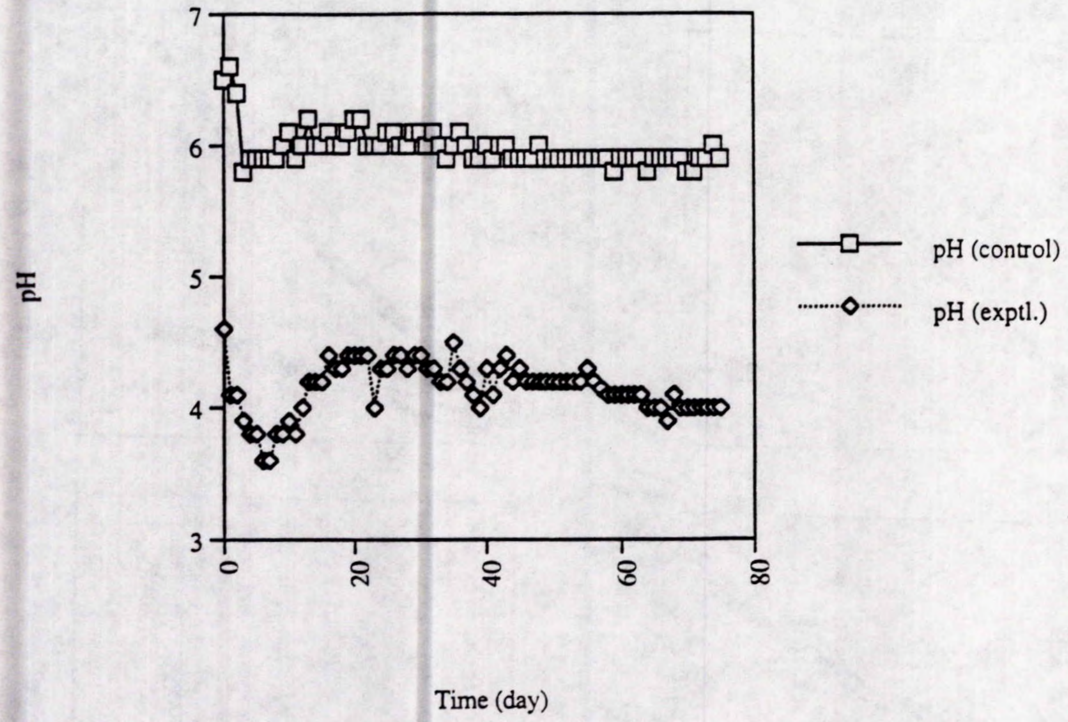


Figure 4. Cumulative recoveries of Si, Al, and Fe from Jamaican ore in columns fed with dilute and concentrated medium.

Dilute medium



Concentrated medium

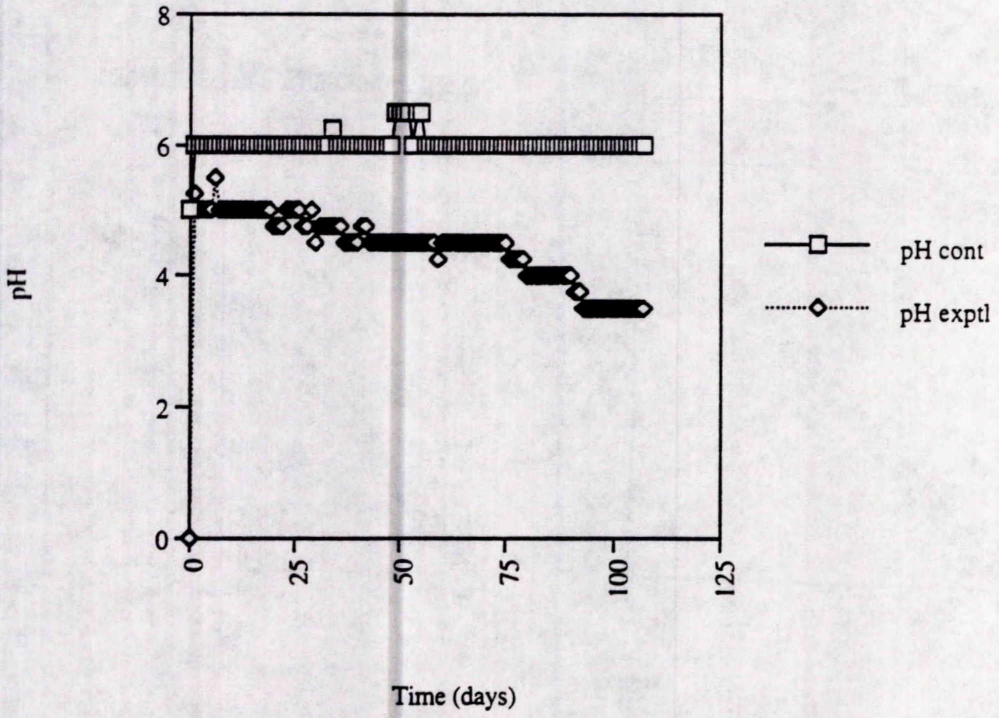
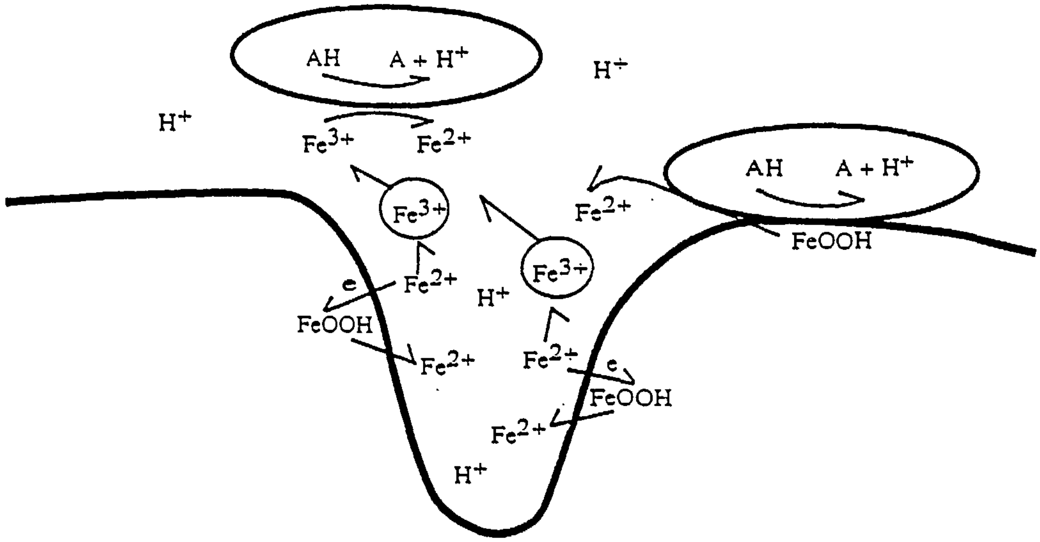


Figure 5. pH measured in daily effluent collections from Jamaican ore in columns fed with dilute and concentrated medium.



$$2Fe^{2+} + Fe_2O_3 + 6H^+ ===.> 2Fe^{2+} +2Fe^{3+} + 3H_2O \quad (\Delta' G_r^o = +1.36\ kcal)$$

$$2Fe^{3+} + H_2 ===> 2Fe^{2+} + 2H^+ \quad (\Delta G_r^o\ -35.56\ kcal)$$

Figure 6. Schematic representation of a model explaining how ferric iron in iron oxide minerals below the surface of bauxite particles is mobilized. The first equation on the bottom respresents the reduction of ferric oxide by ferrous iron, which is thermodynamically unfavorable. The second equation represents the bacterial reduction of Fe^{3+} formed in the reduction of ferric oxide, which is thermodynamically very favorable and provides the needed energy to make the first reaction proceed in the direction as written. H2 is a hypothetical reductant. In the columns, organic metabolites formed from sucrose may have been more likely reductants than H2, but their use would not change the thermodynamics in a major way.

FIELD STUDIES OF BIOLOGICALLY SUPPORTED WATER COVERS AT TWO NORANDA TAILINGS PONDS

P. ST-GERMAIN[1], H. LARRATT[2] and R. PRAIRIE[1]

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[2]H.M. Larratt Aquatic Consulting Ltd., Kelowna, B.-C.

ABSTRACT

Water covers for storage of pyritic mine residues are efficient at minimizing pyrite oxidation. The effectiveness of water covers can be improved by including a sediment layer which consumes oxygen through biological activity. In the resulting biologically supported water cover, maintenance of the sediment activity over time is ensured by a living plant cover. The feasibility of implementing a plant cover was assessed in the field at two Noranda sites.

The 80-ha Brenda Mine tailings pond is alkaline (pH 8.4) and water depths rangefrom 1 to 6 m. In September 1992, 850 submerged "sandwich" units with a plant mix of 75% *Elodea canadensis,* 15% *Potamogeton crispus* and 5% of other species, were distributed in 1 to 4 m of water. Rooting took place within two weeks and rapid plant growth produced weedbeds varying from 60 to 100% cover by 1995. Conditions in the sediment were reducing and up to 106 cells of sulphate-reducing bacteria/g of surface sediment were detected.

In the fall of 1995, a pilot scale demonstration test was initiated in the 90-ha Heath Steele tailings pond. The pond is very alkaline with a pH maintained between 9.5 and 10.5. Most of the sediment is settled lime sludge and water depths are generally less than 2 m. In total, 160 "sandwich" units covering an average area of 1300 m2 were put into the pond. Poor plant growth and low phytoplankton: zooplankton ratios (< 90%) suggested inhibition of photosynthesis. Maintenance of a pH lower than 9 is preferable for the establishment of a plant cover with submerged aquatic plants. As expected in a biologically inert pond, sediment conditions were not reducing and sediments were low in organic matter content.

ÉTUDE SUR PLACE DE COUVERTURES AQUEUSES AVEC APPORT BIOLOGIQUE DANS DEUX BASSINS DE DÉCANTATION ET DE STOCKAGE DES STÉRILES ET BOUES DE LA NORANDA

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RÉSUMÉ

Les couvertures aqueuses utilisées pour le stockage des résidus miniers pyriteux réduisent efficacement l'oxydation de la pyrite. Leur efficacité peut être améliorée par l'addition d'une couche de sédiments qui consomme de l'oxygène par suite de l'activité biologique. Dans la couverture d'eau avec apport biologique qui en résulte, l'activité des sédiments est assurée, à long terme, par l'installation d'une couverture végétale. La faisabilité de la mise en oeuvre d'une couverture végétale a été évaluée sur place dans deux sites de la Noranda.

Le bassin de résidus de la mine Brenda, qui couvre une superficie de 80 ha, est alcalin (pH = 8,4) et la profondeur d'eau varie de 1 à 6 m. En septembre 1992, 850 «sandwiches» composés d'un mélange d'espèces végétales comprenant 75 % d'*Elodea canadensis*, 15 % de *Potamogeton crispus* et 5 % d'autres espèces végétales ont été placés sous 1 à 4 m d'eau. L'enracinement s'est effectué en moins de deux semaines et une croissance végétale rapide a produit des lits de plantes aquatiques assurant une couverture variant de 60 à 100 %, en 1995. Les conditions dans le sédiments étaient réductrices et jusqu'à 106 cellules de bactéries/g réductrices de sulfate dans les sédiments de surface ont été détectées.

À l'automne 1995, une démonstration expérimentale à l'échelle-pilote a été effectuée dans le bassin de décantation et de stockage des stériles et boues, d'une superficie de 90 hectares, de la mine Heath Steele. Le bassin est très alcalin et son pH se maintient entre 9,5 et 10,5. La plus grande partie des sédiments est formée de boue décantée et la profondeur d'eau est généralement inférieure à 2 m. Au total, 160 «sandwiches» couvrant une superficie moyenne de 1 300 m^2 ont été placés dans le bassin. Il y a eu peu d'effort d'enracinement et peu de phytoplancton : les rapports zooplancton (<90 %) suggèrent une inhibition de la photosynthèse. Le maintien d'un pH inférieur à 9 est préférable pour établir une couverture végétale comprenant des plantes aquatiques submergées. Comme prévu dans le bassin biologiquement inerte, les conditions des sédiments n'étaient pas réductrices et les sédiments contenaient peu de matière organique.

THE USE OF PHYTOREMEDIATION FOR REDUCTION AND REMOVAL OF CONTAMINANTS FROM THE MINING OPERATIONS AND ENERGY PRODUCTION FACILITIES IN CANADA

T. MCINTYRE

Biotechnology Advancement Program, Environment Canada, Hull, Quebec

ABSTRACT

Plant-based remediation and stabilization techniques are demonstrating increasing promise for applications at Canadian mining and energy production sites soils. aquifers, and sediments are contaminated with a variety of organic and inorganic pollutants. The use of vegetative species to remediate and stabilize contaminated sites offers the advantage of a photosynthetic, solar driven. and cost effective process with a higher potential for public acceptance than a variety of existing technologies such as excavation and incineration. A variety of new research aproaches and tools throughout North America are rapidly expanding our understanding of plant physiology, molecular. and cellular biological techniques that can be utilized in phytoremediation. The capability of plants to absorb and accumulate many toxic heavy metals and metabolize- directly or indirectly- organic and inorganic compounds suggest their increased utilization in Canada as an emerging innovative environmental solution to process contaminants. In recognition of recent developments in phytoremediation and broader US government and industry support. the Biotechnology Advancement Program at Environment Canada is undertaking a feasibility study to explore its potential as a tool to address a variety of contaminant problems in Canada.

This presentation will provide an overview of recent developments in phytoremediation and its potential applicability to the mining and energy sector, introduce emerging genetically engineered techniques for site specific contaminants; and identify preliminary components of a feasibility study that will outline how Canadian government and industry can exploit the potential that this technology offers in addressing a variety of contaminants at selected mining and energy production facilities across Canada.

UTILISATION DE LA PHYTO-DÉCONTAMINATION POUR RÉDUIRE ET ÉLIMINER LES CONTAMINANTS DANS LES INSTALLATIONS MINIÈRES ET CENTRALES ÉLECTRIQUES, AU CANADA

T. MCINTYRE

Biotechnology Advancement Program, Environment Canada, Hull, Québec

RÉSUMÉ

Les techniques de décontamination et de stabilisation à base de plantes présentent beaucoup de possibilités d'application sur les sites mêmes des installations minières et centrales électriques, au Canada, dont le sol, le réservoir aquifère et les sédiments sont contaminés par divers polluants organiques et inorganiques. L'utilisation d'espèces végétales pour décontaminer et stabiliser les sites contaminés présente l'avantage d'un procédé photosynthétique rentable, actionné par le soleil, dont le potentiel d'acceptation par le public est plus élevé que celui de diverses autres technologies existantes, telles l'excavation et l'incinération. En Amérique du Nord, le recours à une vaste gamme de méthodes et d'outils de recherche divers améliore rapidement nos connaissances relativement à la physiologie des plantes et aux techniques biologiques moléculaires et cellulaires qui peuvent être utilisées en phyto-décontamination. La capacité que possèdent les plantes d'absorber et d'accumuler de nombreux métaux lourds toxiques et de métaboliser- directement ou indirectement- des composés organiques et inorganiques suggère leur utilisation accrue au Canada en tant que solution innovatrice émergente sur le plan environnemental pour traiter les contaminants. Pour reconnaître les développements récents dans le domaine de la phyto-décontamination et obtenir plus de soutien du gouvernement américain et de l'industrie, Environnement Canada a élaboré le Programme pour l'avancement de la technologie. Par l'intermédiaire de ce programme, une étude de faisabilité sera faite en vue d'explorer le potentiel de la phyto-décontamination en tant qu'outil pour résoudre divers problèmes causés par les contaminants, au Canada.

Cette présentation donne un aperçu des développements récents en phyto-décontamination et de son application possible dans les secteurs des mines et de l'énergie. Elle introduit les techniques émergentes issues du génie génétique qui sont utilisées pour éliminer des contaminants régiospécifiques. Elle détermine les composantes préliminaires d'une étude de faisabilité qui indiquera au gouvernement canadien et à l'industrie comment exploiter le potentiel que présente cette technologie pour résoudre les problèmes que posent divers contaminants sur les sites d'installations minières et de centrales électriques sélectionnés à l'échelle du Canada.

NEW SUBSTANCES NOTIFICATION REGULATIONS FOR PRODUCTS OF BIOTECHNOLOGY

J. LOUTER

New Substances Divison, Environment Canada, Hull, Quebec

ABSTRACT

A proposed regulatory amendment to the New Substances Notification Regulations under the Canadian Environmental Protection Act (CEPA) for products of biotechnology was published in *Canada Gazette* Part I on August 17, 1996 for a 60 day public comment period. When implemented, this amendment will extend the New Substances program to include biochemicals, biopolymers, micro-organisms and other organisms that are not regulated for a use under other federal Acts. The context of the amendment, how it will work and possible consequences for biotechnology in the energy and mining industry will be discussed.

RÈGLEMENTS SUR LES RENSEIGNEMENTS CONCERNANT LES SUBSTANCES NOUVELLES POUR LES PRODUITS ISSUS DES BIOTECHNOLOGIES

J. LOUTER

Division des substances nouvelles, Environnement Canada, Hull (QC)

RÉSUMÉ

Une modification proposée des dispositions de la *Loi canadienne sur la protection de l'environnement* concernant les produits issus de biotechnologies a été publiée dans la Gazette du Canada, Partie 1, le 17 août 1996. Le public disposait d'une période de 60 jours pour avis. Quand elle prendra effet, cette modification élargira le programme des substances nouvelles et incluera les produits biochimiques, les biopolymères, les micro-organismes et autres organismes dont l'utilisation n'est réglementée par aucune autre loi fédérale sur la protection de l'environnement et de la santé humaine. La discussion portera sur le contexte et l'application de la modification et sur les incidences possibles qu'elle aura sur la biotechnologie dans les domaines de l'énergie et de l'industrie minière.

INTRODUCTION

Federal Framework for Regulating Products of Biotechnology

Principles of the framework include:

1. maintain Canada's standards for protecting human health and the environment

2. there will be no new legislation or institutions; avoid duplication

   no "Gene Law"

   no "Department of Biotechnology"

   only one law will apply

3. clear guidelines in harmony with national priorities and international standards

   products will be evaluated in an open manner according to publicly available guidelines consistent with national and international partners

4. risk assessment of products will be science based

5. regulations will be developed with consultation and will be transparent

6. contributes to the prosperity and well-being of Canadians and leads to adoption of sustainable biotechnology products and processes

Canadian Environmental Protection Act

CEPA was first promulgated in 1988

New Substances Notification Regulations

July 1994 New Substances: Chemicals and Polymers

Unless it is on the Domestic Substances List (DSL), any new chemical or polymer to be imported into or manufactured in Canada must be notified.

DISCUSSION

Organisms: Canada Gazette Part 1, August 17, 1996

DSL, Exemptions, Schedules, Assessment Periods, Post-transitionals

Organisms regulated under another federal Act that provides for an assessment of toxic are excluded from CEPA including plants, pest control products, feeds, fertilizers and veterinary biologics.

The Domestic Substances List is a list of what is 'old' and therefore, not notifiable under the New Substances provisions.

Organisms in unrestricted use in Canada during the 1984 to 1986 period are eligible to be nominated for the DSL.

Exemptions: research and development organisms imported in quantities of less than 50g or 50mL to a contained facility or manufactured in volumes less than 1000L (risk group 1 micro-organisms) or 250L (risk groups 2,3 or 4) in a contained facility.

Schedules provide a means of tiering the information requirements to the type and extent of introduction.

Micro-organism schedules: anywhere in Canada, in one ecozone, indigenous or not indigenous, with confinement, with containment, experimental field study, same site.

All other organisms schedule: anywhere in Canada

Notifiers must provide information as required by the regulations; EC and HC commit to completing the assessment in a pre-determined period which is also in the regulation.

Transitional organisms are those that were first imported or manufactured between 1987 and June 30, 1994. This group of organisms may be notified as late as January 1, 1998.

Post-transitional organisms are a class of organisms that were (and are) imported or manufactured after July 1994; this class of organisms will need to be notified shortly after publication of the regulations in Canada Gazette part II in order for the assessment to be complete by the time the regulations come into force - otherwise import or manufacture will have to stop (but not sales, if a sufficient quantity is available prior to the date the regulations come into force).

Information Requirements in the regulations:

Information about the organism: Substantiated identity, strain history, description of any modifications, biological and ecological characteristics, patents, dispersal of traits, geographic distribution.

Manufacturing and importation information: Trade name, manufacturers, importers, vendors, identification and description of manufacturing locations, formulation, storage and disposal, quantities, method of manufacture, potential releases and control measures, procedures for dealing with wastes.

Information on the introduction (use): Intended and potential uses, history of use, natural habitat, habitat of introduction, nature of selection at site of introduction, termination procedure.

Environmental fate: Plant and animal species likely to be exposed, habitats where the organism could persist or proliferate, estimated quantities and population trends, other fate information.

Ecological effects: Test data on aquatic and terrestrial species, involvement in adverse effects, biological diversity considerations.

Human health effects: Documented involvement in human health effects, tests of antibiotic susceptibility, tests of pathogenicity, potential for immunologic reaction, estimated number of persons exposed.

Any other information: All other pertinent information available, other agencies notified, test procedures.

General Considerations

The information requirements are described openly in the regulations (nothing is hidden).

Each information requirement must be addressed in the notification.

For a few information items, test data is required. For all other information items, available information is required (published or unpublished literature).

Where test data is not required and there is little or no known information, the assessment may proceed but the importance of the 'gap' will be evaluated in the assessment.

Any information requirement may be waived but must be justified and a notice of the waiver will be made public. Justification for a waiver includes:

> The information is not needed to determine whether the substance is toxic.
>
> The substance is to be used for a prescribed purpose or manufactured at a location where the person requesting the waiver is able to contain the substance so as to satisfactorily protect the environment and human health.
>
> It is not practicable or feasible to obtain the test data necessary to generate the information.

A complete notification will be assessed in a pre-determined length of time (30 to 120 days) depending on the schedule. Incomplete or unacceptable notifications will require clarification and may be turned back

Risk Assessment

Assessment of Potential for Adverse Environmental Effects

Adverse effects include: pathogenicity, toxicity, invasiveness and other adverse effects.

Assessment of Potential Exposure

Exposure is affected by level of introduction (quantity, frequency, conditions), dispersal, persistence, proliferation.

Risk Characterization

Summarize potential for adverse effects, exposure.

Identify knowledge gaps.

Determine likelihood that an adverse effect will be realized.

Make recommendations.

Outcomes of Assessment

1. no suspicion of CEPA toxic

   In which case the import or manufacture proceeds.

2. suspicion of CEPA toxic

In which case measures to mitigate (controls) can be imposed or the import or manufacture could be prohibited. In the latter case, CEPA requires that regulations be developed within 2 years.

Consequences for Biomining Industry

Once the regulations are in force (tentatively July 1, 1997) and you import into or manufacture in Canada an organism for a use not regulated by any other federal Act, you will need to comply.

This will include micro-organisms used in: biomining, biofilters, bioremediation, to aid in oil recovery, to mitigate acid mine drainage, etc.

Contacts

Toll-free number: 1-888-693-0473

New Substances Division, Environment Canada, Place Vincent Massey, 14th floor, 351 St. Joseph Blvd., Hull, QC, K1A 0H3 attn. New Substances Notification

Web Page: http://www.ec.gc.ca/cceb1/eng/biohome.htm
(has copies of the Guidelines, Gazette Notice, a brochure, and information notes)

SUGGESTED READINGS

Canada Gazette Part I, August 17, 1996. Vol. 130, No. 33

Guidelines for the Notification of New Substances: Organisms (available from the address above)

THE ROLE OF APPLIED BIOTECHNOLOGY IN DECOMMISSIONING MINING OPERATIONS

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ABSTRACT

Biotechnological approaches to decommissioning of mine waste management areas are discussed in the context of sustainable development. Improved design of waste sites and environmental management paves the way for the application of new technological approaches. Mining wastes are better confined, effluent quantity is reduced and the quality is expected to improve in the future. The decommissioning methods discussed focus on the production of conditions inside the waste management area which confine the contaminants in the tailings and seepage collection ponds, as well as pits, which were part of the operating mine.

Biogeochemical reactions are assisted through installation of the treatment processes to take place inside the waste management areas to confine the metals on site. Fundamentally, the three treatment steps, facilitated biogeochemically, are the formation, flocculation and collection of particulates. Microbially active sediments are installed to assist particulate formation and serve as environmental sinks for metals. In deeper sediment strata, stable forms of metals are created. Biological polishing is used to collect the particulates and relegate them to the sediment.

LE RÔLE DE LA BIOTECHNOLOGIE APPLIQUÉE DANS LE DÉCLASSEMENT DES MINES

M. KALIN

Boojum Research Limited, Toronto, Ontario

RÉSUMÉ

La présente communication porte sur les approches biotechnologiques au déclassement des zones de gestion de décharges de résidus miniers dans le contexte du développement durable. L'amélioration de la conception des décharges de résidus miniers et la gestion de l'environnement ouvrent la voie à la mise en oeuvre de nouvelles approches technologiques. Les résidus miniers sont mieux confinés, la quantité d'effluents est réduite et une amélioration de la qualité est prévue dans l'avenir. Les méthodes de déclassement qui ont fait l'objet de discussions sont axées sur la production de conditions à l'intérieur de la zone de gestion des décharges qui confine les contaminants dans les résidus et les bassins d'infiltration ainsi que dans les fosses qui faisaient partie de la mine exploitée.

Les réactions biochimiques sont facilitées grâce aux procédés de traitement qui sont réalisés à l'intérieur de la zone de gestion des décharges afin de confiner les métaux sur place. En principe, les trois étapes du traitement qui sont facilitées par des procédés biogéochimiques, sont la formation, la floculation et la collecte des particules. Les sédiments microbioactifs sont utilisés pour faciliter la formation de particules et pour précipiter les métaux. Dans les strates plus profonds de sédiments, des formes stables de métaux sont créées. Le polissage biologique est utilisé pour collecter les particules et les intégrer aux sédiments.

INTRODUCTION

The role of biotechnology in decommissioning of mining waste management areas should be placed in the context of sustainable development. The concept of sustainable development as defined by the Brundtland Commission (1987) for the restoration/ reclamation of mining operations could be translated as follows: The increasing demand for the resources by the world population must be met in a manner which does not compromise the earth's environment over the long term (Brooks et al., 1995).

Mining activities alter the environment. A review of environmental changes brought about by mining in Africa and South America reveals significant environmental and socio-economic impacts associated with artisanal mining (Suttill, 1995). The changes in landscape experienced in the Sudbury district represent another example of major alteration.

Early mining activities started in 6,000 B.C., consisting of digging pits and tunnels for the exploration of flintstones. Mining of gold in Egypt commenced as early as 5,000 B.C. With the onset of the industrial age in Europe in the latter part of the nineteenth century, mining methods significantly advanced. Narrow vein mining was replaced by open pit mining in the early part of the twentieth century, leading to increases in mineral extraction, along with greater volumes of waste material generated. As wastes have accumulated, a new awareness of the mining impacts has developed over the past 30 years, generating a wealth of publications addressing mining and the environment.

Mulligan (1996) summarizes the Australian experience in his recent book, "Environmental Management in the Australian Minerals and Energy Industries, Principles and Practices". He described the progress made, mainly due to the integration of mine and waste management planning during site selection and the design stages. This strategy allows new technology and practices to be more fully integrated into mining operations to better deal with the complexity of environmental management. Applied environmental biotechnology offers a set of tools for reducing the complexity of the environmental management process, leading towards a sustainable approach to mine waste reclamation/restoration and facilitating mine decommissioning.

SUSTAINABLE AND NON-SUSTAINABLE RECLAMATION APPROACHES

The impact of mining on the environment was recognised as recently as the 1930s (Mitsch, 1988). Early waste management activities initially focused on erosion control, and progressed to slope stabilisation and effluent treatment. New mines are developed, replacing those with exhausted mineral resources, and the cumulative volume of waste materials continues to increase. The reclamation of these wastes and treatment of effluents have become an ever-increasing financial burden on the mining industry and, in cases of abandoned mine lands, on the public sector.

A brief review of the waste inventory and effluent treatment requirements in the mineral sector not only demonstrates the magnitude of this financial burden, but also further reveals that waste management and effluent treatment efforts are, according to modern environmental criteria, non-sustainable. To demonstrate, the inventory of tailings and waste rock pile areas in Canada with known acid generation potential is summarized, and an estimate of volumes of potentially contaminated effluent is derived in Table 1. The tailings and waste rock areas were derived after Lawrence and Poulin (1995), using a volume to area conversion factor reported by CANMET (1994) of 150,000 tonnes of tailings per hectare (ha) and 400,000 tonnes of waste rock per ha. These areas are in a similar order of magnitude as those reported by Monenco (1984) and are unlikely overestimates, since more sulphide wastes have been generated over the past decade. The volume of contaminated run-off from waste management areas, up to 113 million cubic metres per year (M $m^3.y^{-1}$), was estimated based on annual atmospheric precipitation (evaporation not considered).

A survey of acid mine drainage characteristics by Wilson (1994) reports measured flows of effluent streams, prior to treatment, in spring and summer for 38 mining operations in Canada. A total spring flow equivalent to 196 M $m^3.y^{-1}$ is estimated for the 38 operations, diminishing to a flow equivalent to 65 M $m^3.y^{-1}$ in summer. While the survey summarizes only a subset of all Canadian mining operations, the reported range of spring and summer flows of effluent streams prior to treatment brackets the flow of 113 M $m^3.y^{-1}$ which is presented in Table 1.

With this in mind, sludge volumes generated by treatment of run-off from sulphide waste management areas, using an effluent base flow of 113 M $m^3.y^{-1}$, may be underestimates.

The annual costs of treatment of effluents from Canadian waste rock and tailings management areas are plotted in Figure 1a, using cost estimates provided by Senes (1994). Costs estimates are given for the treatment of three levels of acidity in effluents (50, 500 and 5000 $mg.l^{-1}$ $CaCO_3$ equivalent), assuming that about 97 percent of the effluent volume is treated by conventional treatment technology and 3 percent by treatment plants generating high density sludge. Assuming that about 80 M m^3 of this water is treated annually, the Canadian mineral sector spends between 10 to 50 million dollars on effluent neutralization each year. These efforts in effluent treatment result in production of an additional waste material, sludge, at a rate of between 4 and 12 M m^3 (Figure 1b), using effluent to sludge ratio estimates also provided by Senes (1994). Meanwhile, the long term environmental stability of the ever-increasing sludge inventory is presently still under investigation.

These considerations of effluent treatment costs and resulting sludge volume accumulation demonstrate that this approach to reclamation is both economically unattractive and environmentally non-sustainable, especially for those cases where the sulphide waste management areas will require treatment in perpetuity.

MEETING THE CHALLENGE

In their review of the environmental effects of mining, Ripley et al. (1996) conclude that, while some contaminant release from pyritic wastes may be inevitable, the challenge is to eliminate release of metals to the environment. Careful design of the mining operation and implementation of effective waste management practices will reduce acid generation and lead to improved effluent characteristics in the future. This paper attempts to show that, through the integration of applied biotechnological advances and the application of new approaches to decommissioning, reductions of environmental impacts by mining are possible.

In Table 2, present site selection and design criteria which are taken into account during planning of a mine waste management facilities today are compared to those used in the past. Consideration of hydrological conditions during siting of facilities will minimize the number of drainage basins receiving contaminated run-off. In the past, siting considerations were based primarily on economic factors, such as an area's close proximity and its existing topographic features and ground conditions. Decisions based on economics alone frequently resulted in complex environmental problems later, for example, placement of a waste management area above ground, and spanning two or more drainage basins, as displayed in Schematic 1. If long term environmental considerations have been incorporated during the siting of these tailings, the most effective tailings disposal method would have utilize the single drainage basin (Schematic 1, C) encompassing the swamp (Schematic 1, light gray area). The peat in the swamp is underlain by a low permeability stratigraphic layer and provides a good natural seal against tailings seepage. The area selected for the tailings deposit (thick line, Schematic 1) resulted in the contamination of two additional drainage basins (A and B).

Until recently, several source of contaminants were not recognized as long term environmental problems. Waste rock, as well as low grade and mine development ore, were commonly placed over existing ground and left unattended. Seepage surveys of such stockpiles reveal that although relatively low volumes of water emerge as seepages from the toes of these piles, metal concentrations can range over several orders of magnitude. Today, these materials are placed on liners in order that seepage can be collected and treated. If applied, reclamation activities in the past commenced soon before or some time after the end of the working life of a mining operation, when acid generation and drainage basin contamination were well advanced. Presently, installation of vegetation covers for dust and erosion control and for slope stabilisation are part of the ongoing operations. Waste rock deposits are frequently segregated, placing high pyrite into tailings ponds or the best hydrologically confined areas. Research investigating the reduction or inhibition of the acid generation process is under way (Evangelou, 1995; Kalin et al., 1995).

Waste rock was routinely used as construction material, regardless of its pyrite content, while tailings dams were constructed from tailings and/or waste rock, in order to confine the tailings mass. Present practices include separation of waste rock such that only inert materials are used for construction, while engineered, low permeability dams are constructed from inert compacted materials for confinement of pore water as well as tailings within the waste management area. In the past, only the coarse fraction of the tailings was used as mine backfill. Currently, "clean" tailings technology included generation of thickened or high density tailings which, in some cases, can be used as mine backfill. Very recently, viable technologies have been developed whereby tailings are segregated into low and high sulphide fractions for separate disposal. The sulphide-rich tailings fraction, particularly when comprised of pyrrhotite, is deposited under water. Today, tailings management facilities are designed such that a long-term water cover will be maintained over the tailings for minimization of tailings oxidation.

While Table 2 does not include all new technologies, it outlines the major modern practices and technologies which are serving to reduce the magnitude of long term environmental problems, through confining the reactive fractions of waste materials to in well designed and managed facilities.

NATURAL CLEANSING PROCESSES: APPLIED BIOTECHNOLOGY

The involvement of bacteria in ore formation has been known since 1838, when the association of *Gallionella ferruginea* with ochreous deposits of bog iron was described. Winogradsky described in 1887 that *Beggiatoa*, a bacteria which could oxidize H_2S to elemental sulphur, and in 1888 that *Leptothrix ochracea* could oxidize $FeCO_3$ to ferric oxide (Ehrlich, 1990). These discoveries, and many more, lead in 1950 to the identification of acidophilic, iron oxidizing bacteria in acid mine drainage. Through the work of Bryner et al. in 1954, the first industrial application of geomicrobiology in metal leaching was utilized for copper extraction at the Bingham Canyon open pit mine in Utah (Ehrlich, 1990). From examinations of the biogeochemistry of iron since 1960, it has been elucidated that microbes not only assist in oxidative reactions, but are also involved with a wide variety of reductive processes. Reductive reactions driven by microbes counteract oxidative reactions, and thus present the natural tool to the environmental problems associated with mine waste oxidation and release of metals.

Microbially-mediated reductive reactions generally take place at the water-sediment interface, where oxygen diffusing into the sediment is consumed (anoxic conditions), or in deeper sediment strata free of oxygen (anaerobic conditions). Sediments serve as environmental sinks for particulates formed in overlying waters. Biomass produced by plants and algae assist the production of particulates, organic colloids and complexes. Upon flocculation of these substances, settleable particles ultimately reach the sediment.

These three stages, particulate formation, flocculation and settling, comprise microbially-assisted processes which can be used for waste water treatment. Therefore, the biotechnological approach to decommissioning involves the installation of environments which support primary productivity and microbial reductive processes, promoting the formation and flocculation particulates and their deposition in the sediment. For example, the installation of microbially-active sediments in tailings ponds and open pits, as part of a decommissioning plan, will transform the abiotic tailings pond or flooded pit into a biologically active water body. While, in principle, this approach appears simple, from an environmental management perspective, difficult questions arise with respect to how to specifically design and implement such measures?

THE DECOMMISSIONING APPROACH

In Table 3, the three phases required to develop the decommissioning approach and the design criteria for a biological/geochemical remediation restoration process are outlined. In the first phase, the physical site lay-out determines which 'facilities' exist in the waste management area which can be used for the treatment to be implemented. For example, the lay-out of a mine site, depicted in Schematic 2, is comprised in part of a waste rock pile surrounded by a ditch system. During the mining operation, the ditches direct ARD to a pond, from which effluent is pumped to the treatment plant. The collection pond could serve as a 'facility' for biological treatment processes. In the mine lay-out, the pit is located near the collection pond and could serve as a second 'facility' for further treatment and flocculation. A sediment layer is installed in the collection pond and the pit conditions are modified to promote primary productivity assisting flocculation of contaminants.

When deriving decommissioning approaches, the interactions between surface and ground water and their seasonal fluctuations are important characteristics of the waste management area which determine, in part, the contaminant load generated on an annual basis. The contaminant loads, in turn, determine the sequence of the processes to be used. Seasonal variation in chemical characteristics of effluents will determine which of the precipitation processes is most suitable for contaminant removal. Thus in the first phase, effluent flow volumes and the geochemical reactions, such as iron oxidation and hydrolysis, need to be determined.

These rates will indicate the physical dimension required or, practically, the changes in the lay-out of the site required, through ditching or pond construction. The characteristics of the existing waste management ecosystem also needs to be identified in phase I, including the primary productivity, the organic compounds in the effluents as well as the characteristics of inorganic suspended solids. This information facilitates the selection of the likely flocculation processes which can be enhanced or induced. The result of the information gathering and compilation in phase I will result in a proposed decommissioning approach.

PHASE II: ON-SITE TESTING

During phase II, the proposed decommissioning approach is tested through field and laboratory work. The tests are carried out mainly on site for determination of design criteria for implementation of the decommissioning approach. Phase II should be continued for at least 2 to 3 years such that seasonal differences are well understood and defined.

At the end of phase II, the treatment/remediation approach can be defined with respect to contaminant reductions which can be achieved and the time frame in which this reduction can be expected. Biological systems require time to develop and, once established, continue to change as the remediation process improves the conditions of the site.

The changes which take place can resemble stages of ecological succession which occur in normal ecosystems. For example, communities of attached algal species which initially served to adsorb metals and collect the precipitates/flocculants in polishing ponds may be replaced over time by aquatic moss communities. The consequence of these ecological changes need to be evaluated by a ecologist familiar with the geochemical and microbial requirements of the effluent treatment process. Prediction of these successional changes in waste site ecosystems is difficult, and slowing or modifying them is, at our present level of understanding, virtually impossible. This represents, from the perspective of the engineer, the most complex aspect of application of biotechnology in environmental management. The design criteria for restoration are based on the original conditions of the waste site, and may have to be modified as environmental conditions of the site improve. A full scale system will therefore require monitoring for at least five years and must include parameters which define the health of the ecosystem.

AVAILABLE PROCESSES

The implementation of the biotechnological decommissioning approach has been discussed with respect to the information needed and the necessary approach. Table 4 outlines that information gathered during the first phase of developing a decommissioning scenario which is now related to available processes which could be implemented. Biological polishing agents, the living surfaces of organisms used to collect the particulates and produce organic matter, are selected based on the chemistry of the effluent and the precipitate formation mechanisms which can be utilized at the site. In one case, brush cuttings may be used, while at another site, demolition material from buildings was available as substrate of biological polishing agents. In this process, surfaces area has to be provided for the growth of attached algae and moss. Alternately, floating structures supporting the submerged root mass of floating wetland vegetation (e.g. cattail) are used. All these surfaces serve to collect particulates formed in the 'facility', for instance, the contaminated lake, the tailings pond or the flooded pit.

The residence time of water in a polishing pond is considered a key criterion for the design of polishing systems (Table 4). During this period, necessary reactions and processes must be completed, such as oxidation, precipitate formation, flocculation and particulate settling. Sufficient time must also be available for adequate primary productivity supporting biological polishing or microbial processes. The rates of these processes have to be understood in order to optimize the process for an specific effluent flow. Seasonal differences in the effluent can influence these design parameters and limit performance of the process during certain periods of the year. This has to be dealt with in the same manner as classical engineered treatment plants, when conditions exceed the design criteria of the treatment plant and performance is compromised. Cases may arise where seasonal chemical additions, such as phosphate, are required to assist system performance.

Particulate formation can be assisted by microbially-active sediments. Existing sediment can be used or new sediments created using carbon-rich waste materials. For example, Mud Lake (Schematic 1) was contaminated through the discharge of contaminated ground water originated from beneath a tailings management area. This lake's sediments are classical Gyttja semi-solids several metres in thickness. When these sediments are supplemented with organic carbon, microbially activity increases, oxygen is consumed, and nitrate, iron and sulphate are reduced in sequence, and metal sulphide precipitation and settling ensues. The supply of organic matter initially added during the implementation stage will be replaced by the floating wetland vegetation being installed over the lake. Depending on site conditions, both biological polishing and microbial treatment using sediment reductive processes are used.

PHASE III: IMPLEMENTATION

The foregoing discussion outlined decommissioning approaches, the concepts behind biotechnological/ecological systems and the information required to implement decommissioning strategies. Table 5 summarizes the status of the field implementations of the processes developed for the decommissioning approach. The ARUM process (Acid Reduction Using Microbiology) has been tested in several enclosed systems described in detail by Kalin et al. (1996, in press). Removal rates ranging from 0.1 $g.m^{-3}.d^{-1}$ to 0.3 $g.m^{-3}.d^{-1}$ have been measured. A biological polishing system comprised of a series of ponds is treating 20 $l.s^{-1}$ of circumneutral mine effluent. Zinc concentrations are reduced from 20 $mg.l^{-1}$ to 2 $mg.l^{-1}$ during the ice-free season. In its present configuration, the system's winter performance is wanting, as oxidation of iron is not taking place beneath the ice cover. Particle formation mechanisms are currently being studied in detail, as this understanding could be applied to improving winter performance.

A lake containing 1 M m^3 of pH 3.5 water was gradually supplemented with approximately 250 truck loads of cut brush to provide substrate for the attached algal community serving as a biological polishing system for zinc removal. It is estimated that about 30% to 40% of the zinc input from the drainage basin is retained in the lake per annum by this process. At another mining operation, an underwater meadow of a species of rooted algae, known for its high affinity for ^{226}Ra, was introduced to a lake receiving run-off from uranium mine waste rock piles. It is estimated than about 60% of the ^{226}Ra load is retained in the lake per annum.

Floating vegetation mats established from seed have been installed over flooded open pits for removal of suspended solids prior to effluent discharge. After four years, these mats were buoyant and no longer required the original support structures. Scale-up of these mats for coverage of lakes, requiring several hundred floating structures, is currently a major challenge.

For each decommissioning approach, the sequence in which the processes are utilized will differ, as the chemical and physical conditions vary from site to site. In Schematic 2, the sequence of processes is conceptually depicted for a waste rock pile, seepage collection pond and pit. Flocculation and settling of metal precipitates takes place in the first cell of the seepage collection system, followed by two or three cells equipped with microbially active sediment (ARUM) for further precipitation and settling of metals from the effluent. Water containing residual particulates is directed to the flooded pit, where remaining dissolved metals are adsorbed/precipitated onto biological surfaces and flocculated particulates settle. Enhancement of biological polishing may require adjusting the nutrient status of the pit water for support of primary productivity, depending on the limnological characteristics of the flooded pit. Strong chemoclines frequently develop in flooded pits, depending on surface-ground water interactions and the morphology of the basin. Further biological polishing capacity can be established downstream over the flooded pit discharge path, if required.

Schematic 3 presents, conceptually, a decommissioning approach developed for a tailings management facility. Deposition of tailings is here envisaged over a gradual slope. Construction of simple internal berms will create a series of ponds over the tailings surface. When milling ceases, ARUM sediments and floating vegetation covers are installed in the ponds. Semiaquatic vegetation will colonize any shallow or emergent sections of the tailings. These conceptual decommissioning approaches are intended to bring the ecological/biotechnological solutions closer to the mine waste management area.

CONCLUSION

Biotechnological applications in decommissioning require a detailed knowledge of geochemical, hydrological and ecological data regarding the entire drainage basin encompassing the waste management area. A holistic view of the drainage basin as a waste site ecosystem facilitates the use of remediation approaches to initiate ecosystem development. As research on inhibition of the acid generation by pyritic wastes progresses, these biotechnological approaches will lead the way in the interim to sustainable environmental management in the mineral sector.

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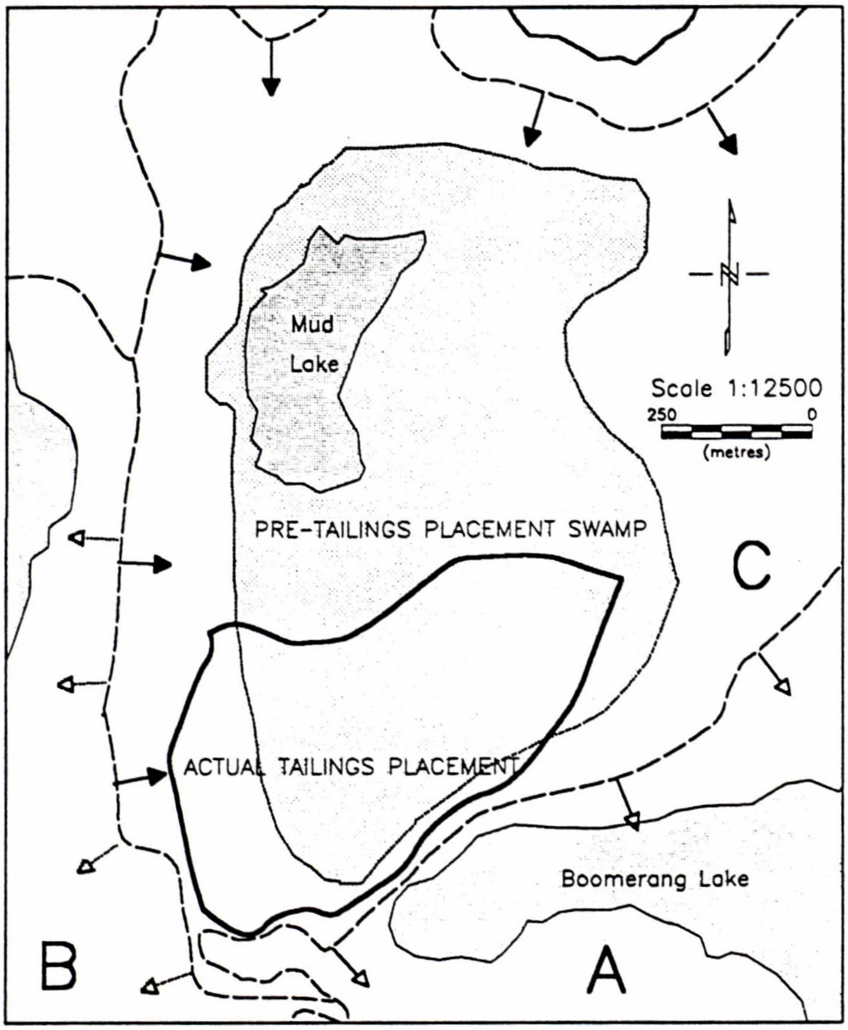
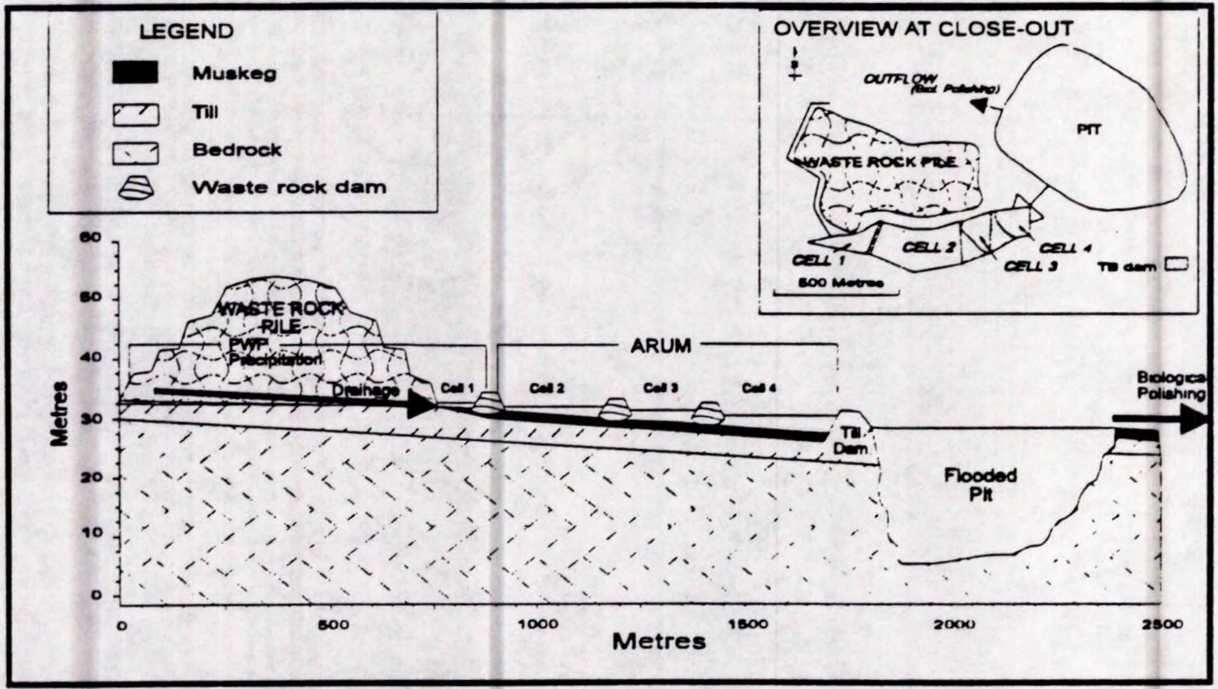
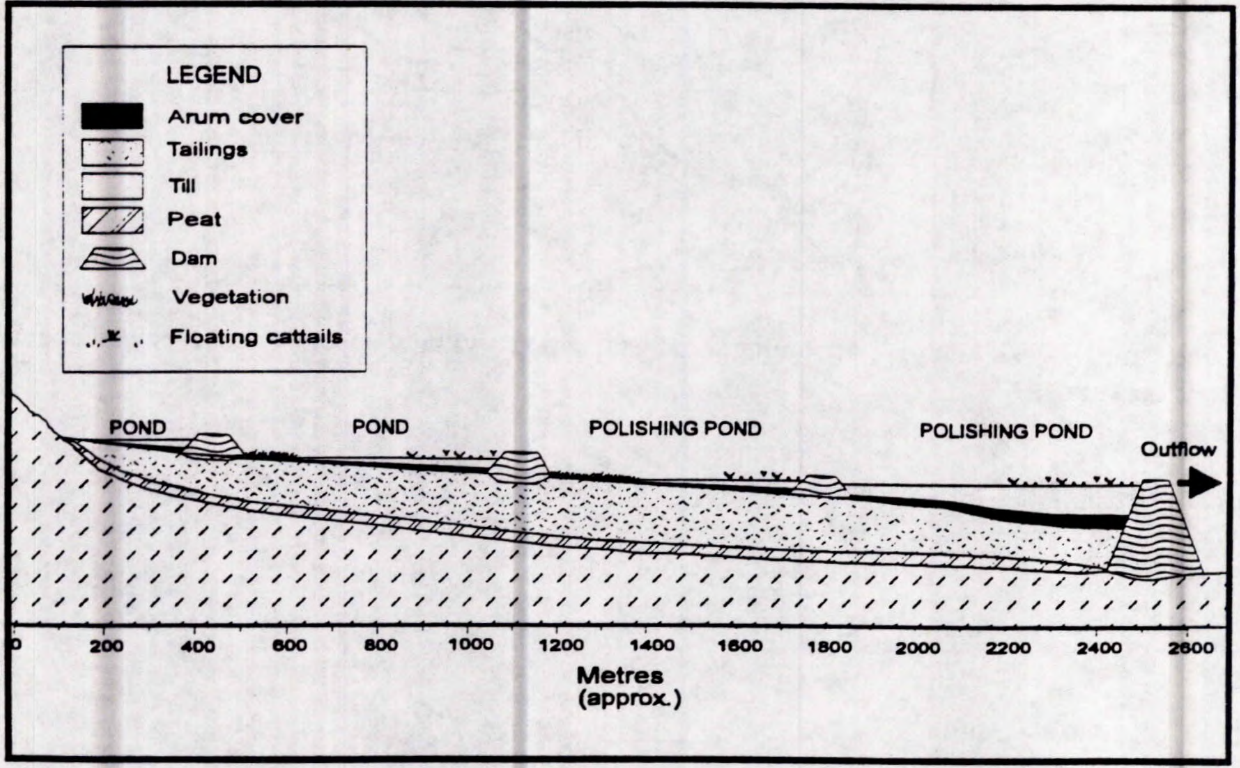


Schematic 1: Example of tailings deposit siting without present day environmental considerations.



Schematic 2: Conceptual biotechnological approach to decommissioning waste rock seepage utilizing adjacent flooded pit.



Schematic 3: Conceptual decommissioning design for tailings pond use biotechnological approach.

Table 1: Estimated Areas of, and Base Flows From, Sulphide Tailings and Waste Rock in Canada (from Lawrence & Poulin, 1995. CANMET Report 95-029)

Province/Territory	Precipitation mm	Tailings ha	Waste Rock ha	Total Area ha	Base Flow* $10^6\ m^3.y^{-1}$
British Columbia	1016	1280	1053	2333	24
Saskatchewan	508	440	50	490	2
Manitoba	550	1333	173	1506	8
Ontario	780	6560	200	6760	53
Quebec	762	1693	175	1868	14
New Brunswick	889	513	65	578	5
Nova Scotia	1016	73	90	163	2
Newfoundland	762	200	3	203	2
Yukon & NWT	711	427	43	469	3
Total					113

* maximum possible(no evaporation); actual values will be less.

Table 3: Four Phases of Biological Treatment System Development and Application.

PHASE		DESCRIPTION
Phase 1:	Site Characterization	- site history: mine waste management area - physical layout - climate, hydrology, ground and surface water quality - contaminant loadings - waste mineralogy, geochemistry contaminant paths and fate. - process selection - existing terrestrial and aquatic ecosystems - biological system selection
Phase 2:	Field Testing of Treatment Strategy	- geochemical and biological reaction rates - define site-specific design criteria for treatment strategies. - assess strategies' feasibility based on experimental data. - decision proceed to Phase 3 or address missing aspect of site conditions.
Phase 3:	Scale-up of Treatment System	- full-scale design, construction and monitoring of treatment approach. - modify if necessary; fine tune system

Table 2: Comparison of Past and Present Mining Waste Management.

PRESENT	PAST
SITE SELECTION AND DESIGN FOR WASTE ROCK AND TAILINGS	
Site selection for waste rock and tailings with hydrological and economic considerations	Economic considerations only (e.g. proximity to mine).
Ore stockpiles placement and exposure	Not considered
Run-off drainage systems isolated from contaminated flows.	Sometimes considered
Progressive reclamation of site during operations.	Not considered
General mine closure plan considered	Not considered
Strict design criteria for storage facilities for chemicals and fuel	Sometimes considered
Segregation and stockpiling of rock types according to acid generating potential	Unsegregated waste rock piles
Improved dam design including liners and leak detection systems	Dams constructed from coarse tailings, overburden or wasterock
Thickened tailings; Underwater tailings management facilities	Above ground tailings management facilities, no thickening
Tailings cleaning - sulphide separation.	Not available
Tailings: high density paste backfill	Not available
Highly acid generating material used as backfill	Conventional backfilling, using only coarse fraction of the tailings

Table 4: Design Criteria for Biologically-Mediated processes.

PROCESS	DESIGN CRITERIA
Biological Polishing	- contaminant concentrations and loads - water chemistry (pH, acidity, alkalinity, etc.) - precipitate formation and settling characteristics. - sediment/substrate biogeochemistry. - seasonal, long term variation in water quality. - effluent volume, retention time in waste management area - retention structure surface area and depth; ice-free and winter volume.
Microbial Treatment Using Sediment Processes	In addition to above criteria: - effluent stream-specific Fe, Al, metal geochemistry and precipitate formation and settling characteristics - local hydrogeology; ground-surface water interactions.

Table 5: Biological Processes Used to Reduce/Prevent Acidic Loadings In Mining Waste Management Areas.

PROCESS	STATUS	FUNCTIONS
ARUM Acid Reduction Using Microbiology	-Process demonstrated in field system treating AMD from Ni and coal tailings. -Tested in several field enclosures.	Utilization of constructed sediments for removal of acidity and metals through promoting bacterial activity, metal precipitation and alkalinity generation.
Biological Polishing Processes	-Full scale system installed in flooded pit and ponds constructed to treat effluent from Zn-Cu mine (20 $L.s^{-1}$).	Utilization of attached algae/moss for the removal of metals from mine waste waters (metal complexation, adsorption, precipitation).
	-Full scale system being built gradually in lake receiving AMD from Cu-Zn tailings.	Moss and primary productivity utilized to remove Zn.
	- Installed in drainage basin to remove ^{226}Ra in run-off from uranium waste rock piles.	The algae *Characeae* concentrate ^{226}Ra on cell walls and decay to the sediment.
Floating Wetland Vegetation Covers	-Covers in place for 6 years over flooded pit, self-buoyant.	- production of organic carbon for microbial processes
	- Cover over ARUM test system operating for 4 years.	- reduction in wind-driven re-suspension of particulates and oxygenation
	-Scale-up over pH 2.8 lake in progress at Cu-Zn mine.	- collection of precipitates and nitrogen removal.

Figure 1a: Estimated Costs of Treating Base Flow From Canadian Waste Rock and Tailings for One Year

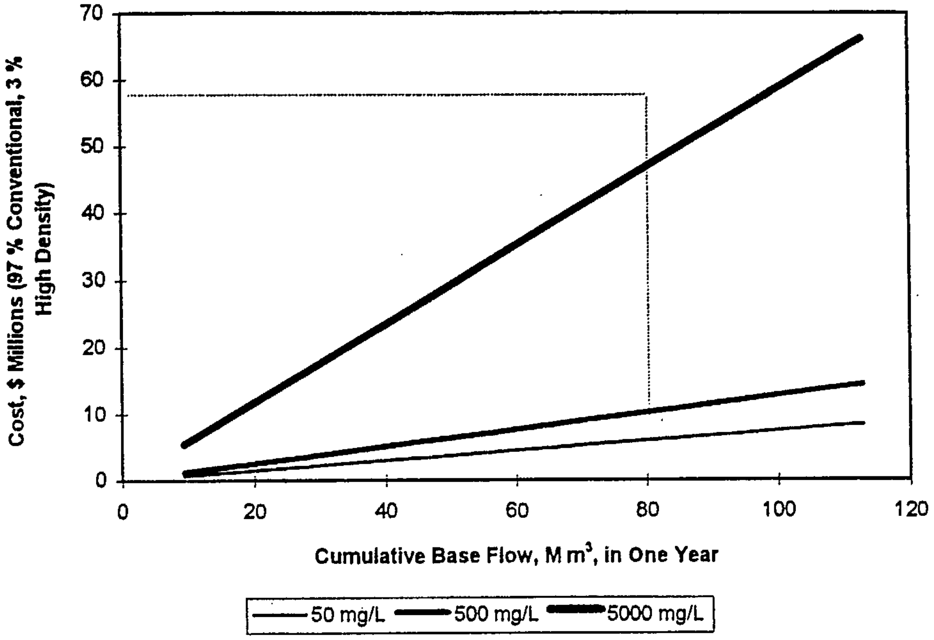


Figure 1b: Estimated Cumulative Production of Sludge From Treatment of Base Flow From Canadian Waste Rock and Tailings, 1 Year