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Selection of Reactive Mixtures for the Prevention of
Acid Mine Drainage using Porous Reactive Walls

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Title

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Abstract

Porous, permeable, geochemically-reactive walls present a promising passive treatment alternative for remediating metal-contaminated water. These walls are installed *in situ* in the path of the migrating contaminated groundwater by excavating the aquifer material and replacing it with a suitable reactive mixture. Contaminants are removed from the groundwater as a result of chemical reduction, and the subsequent precipitation of sparingly soluble compounds. This process is mediated by sulphate reducing bacteria (SRB), which reduce SO_4^{2-} to HS^- using solid-phase organic carbon as a carbon source. In designing a reactive wall, both the reactivity and the permeability of the reactive mixture must be considered. Batch tests were conducted using simulated mine-drainage water to assess the reactivity of several different organic mixtures. The permeability of the mixtures was measured using a falling-head permeameter test. Results obtained from these studies indicate levels of reactivity and permeability of the organic mixture suitable for remediating tailings impacted groundwater can be obtained.

Management Perspective

Permeable reactive walls are an alternative *in situ* technique for remediating contaminated groundwater. These reactive walls are installed by excavating aquifer material and replacing it with reactive media to passively remove contaminants from flowing groundwater. This paper describes a series of laboratory tests to evaluate mixtures for remediating tailings-derived groundwater using reactive wall technology. The mixtures evaluated in the laboratory study were selected to induce sulfate reduction and metal sulfide precipitation reactions to remove sulfate, dissolved metals and to increase alkalinity. Laboratory batch and column tests were conducted to evaluate the effectiveness of a variety of organic carbon sources at promoting sulfate reduction and metal sulfide precipitation reactions. Batch experiments using different combinations of organic carbon sources, including composted sewage sludge, leaf mulch, wood chips, sawdust and composted sheep manure, all resulted in efficient removal of sulfate and dissolved metals. Based on the results of the batch experiments, optimal reactive mixtures were selected for use in laboratory column experiments to evaluate their potential for remediating mine drainage water under dynamic flow conditions. To date, good treatment has been observed in the column experiments. The results of the laboratory experiments were used as a basis for selecting a reactive mixture for a field scale trial of this technology which is currently underway at the Nickel Rim mine site near Sudbury, Ontario.

SELECTION OF REACTIVE MIXTURES FOR THE PREVENTION OF ACID MINE DRAINAGE USING POROUS REACTIVE WALLS¹

K.R. Waybrant², D.W. Blowes² and C.J. Ptacek^{3,2}

Abstract: Porous, permeable, geochemically-reactive walls present a promising passive treatment alternative for remediating metal-contaminated water. These walls are installed *in situ* in the path of the migrating contaminated groundwater by excavating the aquifer material and replacing it with a suitable reactive mixture. Contaminants are removed from the groundwater as a result of chemical reduction, and the subsequent precipitation of sparingly soluble compounds. This process is mediated by sulphate reducing bacteria (SRB), which reduce SO_4^{2-} to HS^- using solid-phase organic carbon as a carbon source. In designing a reactive wall, both the reactivity and the permeability of the reactive mixture must be considered. Batch tests were conducted using simulated mine-drainage water to assess the reactivity of several different organic mixtures. The permeability of the mixtures was measured using a falling-head permeameter test. Results obtained from these studies indicate levels of reactivity and permeability of the organic mixture suitable for remediating tailings impacted groundwater can be obtained.

Key Words: acid mine drainage, prevention, sulphate-reducing bacteria, sulphate reduction, metal-sulphide precipitation.

Introduction

The mining and milling of sulphidic ore deposits generate large quantities of sulphide-rich waste rock and finely crushed mill tailings. These tailings are deposited within impoundments which are generally active for 10-25 years, depending upon the size of the deposit, the size of the tailings area and the rate of deposition. During the active deposition period the tailings impoundment remains near water saturation. Upon decommissioning however, an unsaturated zone develops as the original mill process water drains naturally through the underlying geologic material. Atmospheric oxygen diffuses throughout the unsaturated zone, at a more rapid rate than through the saturated zone, and is consumed through oxidation reactions.

Oxidation of sulphide-bearing minerals, within the unsaturated zone of mill-tailings impoundments, results in low-quality drainage waters characterized by low pH and high concentrations of sulphate, ferrous iron and base metals such as lead, zinc, cadmium, copper and nickel. This water, termed acid mine drainage (AMD), may eventually make its way into the groundwater system and ultimately discharge into

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surface water bodies potentially damaging aquatic and terrestrial ecosystems. The release of tailings impacted water is the single most important environmental concern facing the mining industry today (1).

Current techniques for controlling or treating mine drainage include minimizing sulphide oxidation, collection and treatment of the acidic water, and controlling the migration of tailings pore water. These techniques are often costly and impractical. Researchers at the University of Waterloo are currently looking at an alternative, passive approach using porous, permeable, geochemically-reactive walls which are installed below the ground surface in the path of migrating tailings-derived water (Fig. 1). These geochemically engineered walls are designed to enhance biological sulphate reduction through the addition of reactive solids (2, 3).

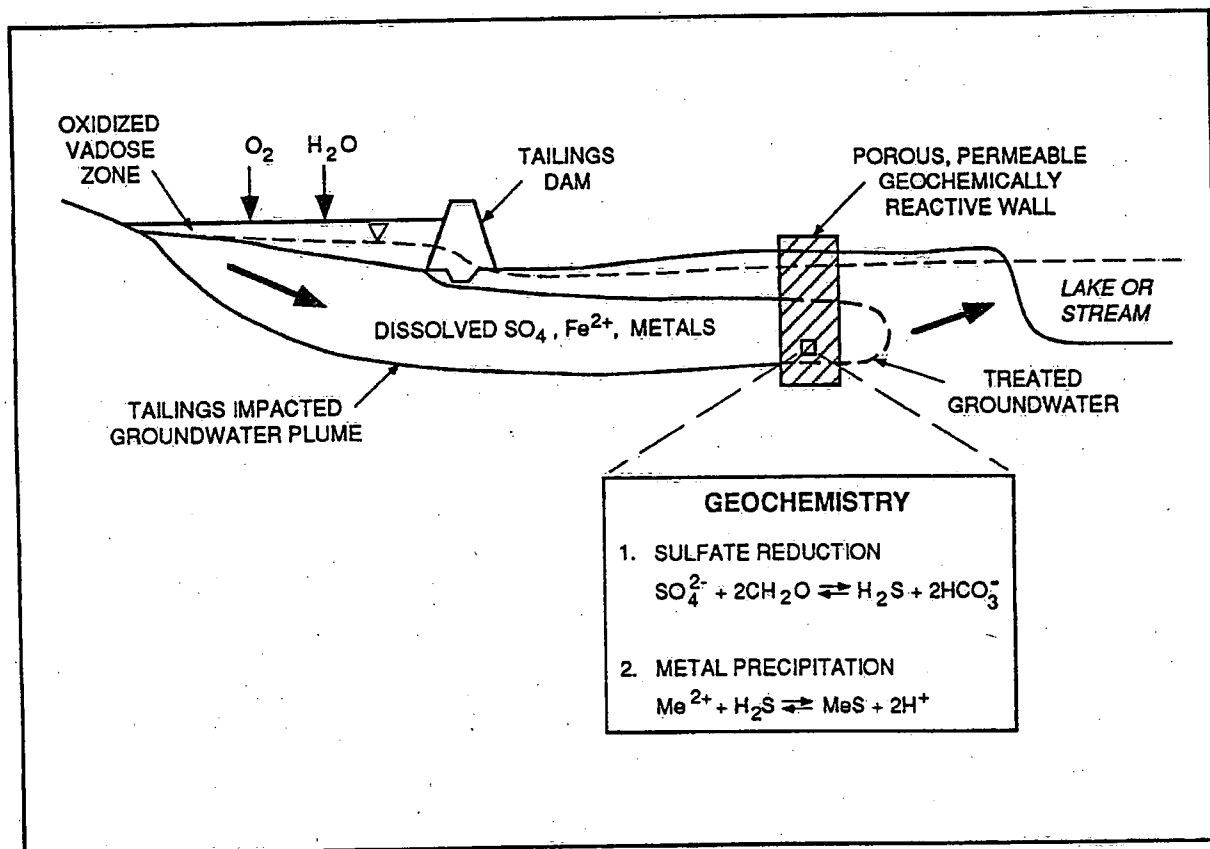
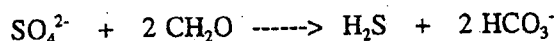


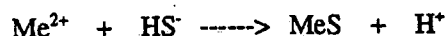
Figure 1: Schematic of a porous, permeable geochemically reactive wall at a mine tailings site.

Under appropriate conditions sulphur-reducing bacteria (SRB) convert sulphate to sulphide by catalyzing the oxidation of organic carbon coupled with the reduction of sulphate:



where "CH₂O" represents a simple organic carbon. Sulphate reduction reactions consume SO₄, produce H₂S and result in an increase in alkalinity and pH (4). Increases in pH enhance the precipitation of

dissolved metals. Increasing HS^- concentrations accelerates the precipitation of metals as metal sulphides:



where Me^{2+} denotes a metal such as Cd, Fe, Ni, Cu, Co and Zn.

Tuttle et al. (4) observed sulphate reduction, accompanied with increases in pH, in mine discharge water after passage through a wood dam. Since then numerous authors have reported AMD mitigation using various organic sources such as straw (5), hay (6), peat (7), mushroom compost (8, 9) and solid municipal waste (10).

The focus of this research is batch reaction studies to determine optimal reactive mixtures for use in geochemically-reactive walls based primarily upon reactivity and permeability of the mixture but also considering availability and cost.

Methods

Laboratory batch experiments, using simulated tailings-derived water based upon field data from the Nickel Rim minesite near Sudbury, Ontario (11), were conducted to assess the potential for a single organic source or mixture of different sources to promote sulphate reduction. Five different organic sources were studied including: leaf mulch, sawdust, wood chips, composted sheep manure and composted municipal sewage sludge. A sixth organic source, delignified waste cellulose from E.B. Eddy is currently being assessed. The source of SRB used for these batch studies was collected from the anaerobic zone of a local creek. The presence of SRB was assured by the odour of H_2S gas and the rich black colour of the sediment. There are some advantages of using creek sediment over pure cultures: the creek sediment will contain a consortium of bacteria, some of which facilitate the development of reducing conditions and the degradation of organic polymers into low-molecular weight compounds. It is also readily available, and very easy and inexpensive to collect. Agricultural limestone was also added to ensure optimum pH conditions for the bacteria. The reactive organic carbon mixtures (Table I), plus creek sediment, limestone and simulated tailings leachate were placed in well-sealed, glass reaction flasks. Anaerobic conditions were maintained throughout the experiments, as indicated by low Eh values and production of a sulphate-reduction product, H_2S gas.

Table I: Volume percentages of the organic sources present in each mixture.

Batch Mixture	Sewage Sludge	Leaf Mulch	Wood Chips	Sheep Manure	Sawdust
#1	100%	-	-	-	-
#2	-	-	-	100%	-
#3	-	100%	-	-	-
#4	-	24%	-	39%	37%
#5	8.5%	15%	42%	8.5%	26%

Sampling

The reaction flask contained two ports from which substances could be removed or added by piercing the teflon lined septum on the port with a syringe. Samples were obtained by withdrawing an aliquot of sample from one of the ports, while simultaneously injecting N₂ or Ar gas in the other port. This procedure ensured that anaerobic conditions were maintained throughout the experiment. The batch experiments were sampled as a function of time and under a closed system environment.

Measurements of pH, Eh and alkalinity were determined immediately upon sampling. The pH and Eh were measured on unfiltered samples in sealed vials and a filtered sample was used for determining the alkalinity. Samples were filtered through a 0.45 µm cellulose acetate filter paper and both acidified and unacidified samples were collected and stored at 5°C until analyses of SO₄, Fe, Mn, Zn, Ni, Ca, K, Na, Mg, and DOC were completed. Analyses were conducted by Fenwick Laboratories in Nova Scotia and the Water Quality Lab at the University of Waterloo within 30 days of sampling.

The permeability of the most promising organic mixtures was measured using falling-head permeameter cells at the University of Waterloo.

Results and Discussion

Reactivity

The reactivity of the mixture is a measure of the lability or availability of carbon. An ideal mixture would contain a solid-phase carbon source which is sufficiently reactive to promote sulphate reduction, yet stable enough to remain a continuous carbon source for an economically viable amount of time. Sulphate-reducing conditions developed rapidly after an initial acclimation period in all mixtures (Table I) except in the batch mixture containing composted sheep manure (Fig. 2). The acclimation periods ranged from 2 days to 14 days with sewage sludge being the most rapid. In mixture #4, the SO₄

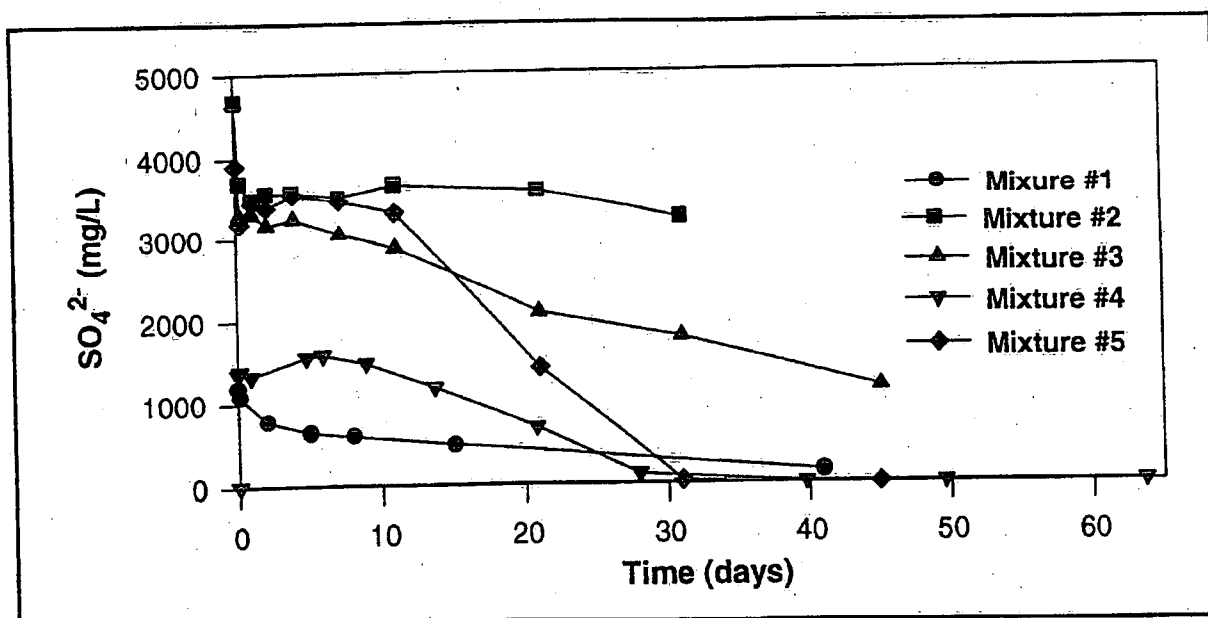


Figure 2: Sulphate concentrations *versus* time for various organic mixtures.

concentration decreased from 1200 mg/L to < 10 mg/L in 26 days; for batch mixture #5, SO_4 concentrations decreased from 3300 mg/L to < 35 mg/L in 20 days.

Under closed, anoxic systems rates of bacterial sulphate reduction are approximately the same as sulphate removal rates (12). Other processes such as adsorption to ferric oxyhydroxides and acclimation periods will affect measured sulphate concentrations. The sulphate reduction rates were compared using linear least-squares analysis, disregarding data from early acclimation periods and initial loss of sulphate due to adsorption (Table II). Reactive mixtures containing several organic sources had sulphate reduction rates considerably greater than mixtures containing a single organic source. In addition to high sulphate reduction rates, these multiple organic source mixtures contain carbon with varying degrees of lability. Wood chips and sawdust contain more complex organic compounds and will therefore take longer to decompose than simpler organic matter such as composted

Table II: Regressed sulphate reduction rates and correlation coefficients.

Mixture	No. Samples	Sulphate Reduction Rate (mg/L/d)	Correlation Coefficient
#1	5	-22.5	0.913
#2	-	-	-
#3	6	-43.9	0.978
#4	4	-72.3	0.998
#5	4	-154.4	0.986

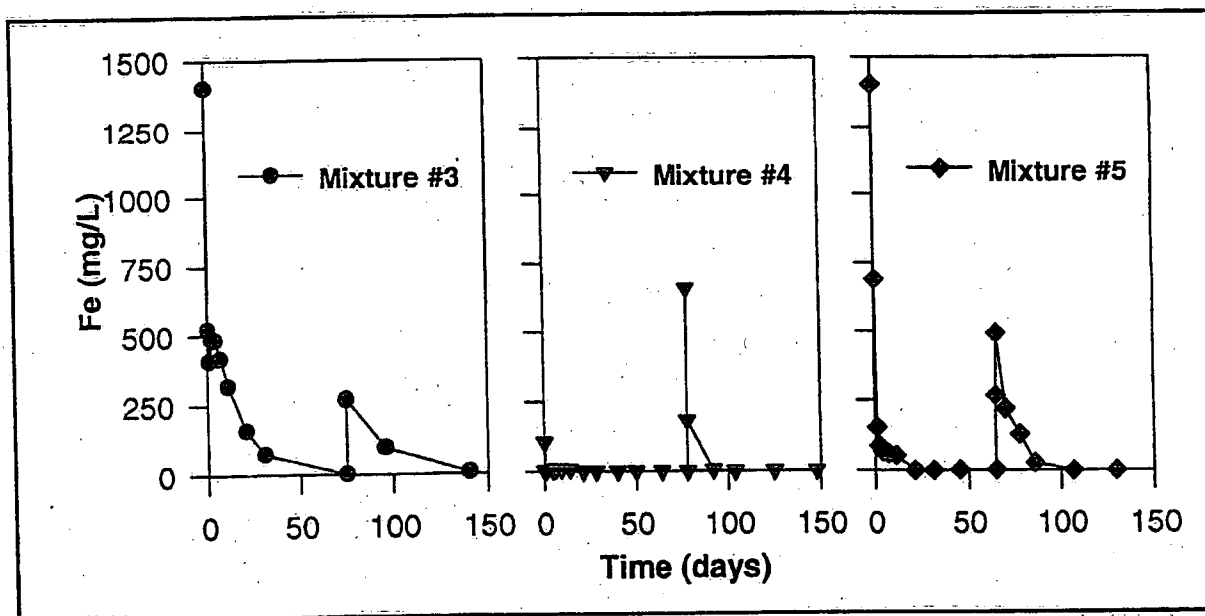


Figure 3: Iron concentrations as a function of time for reactive mixtures #3, #4 and #5. Reaction flasks were spiked with additional Fe(II) and SO_4 on Day 78.

sheep manure and sewage sludge. Thus, reactive mixtures containing a variety of organic matter types have the potential to serve as a long-term source of carbon.

Metal concentrations were assessed in all the reactive mixtures except the mixture containing 100% composted sheep manure. Sheep manure was eliminated from further studies due to low reactivity. Results showed metal concentrations decreased rapidly, this decrease was sustained in all of the mixtures assessed except pure sewage sludge. The pure sewage sludge showed concentrations of nickel increasing with time to values more than three times the initial input concentration. Due to this observation this reactive mixture was eliminated from further testing. Subsequent additions of sulphate, iron and other metals were added to the remaining three mixtures, resulting again in rapid and sustained removal although at a lower sulphate reduction rate (Table 3 and Figure 3, 4 and 5).

Table III: Regressed sulphate reduction rates and correlation coefficients for mixtures: #3, #4 and #5 after subsequent additions of metals and sulphate.

Mixture	No. Samples	Sulphate Reduction Rate (mg/L/d)	Correlation Coefficient
#3	6	-24.27	0.988
#4	4	-41.53	0.976
#5	5	-62.18	0.984

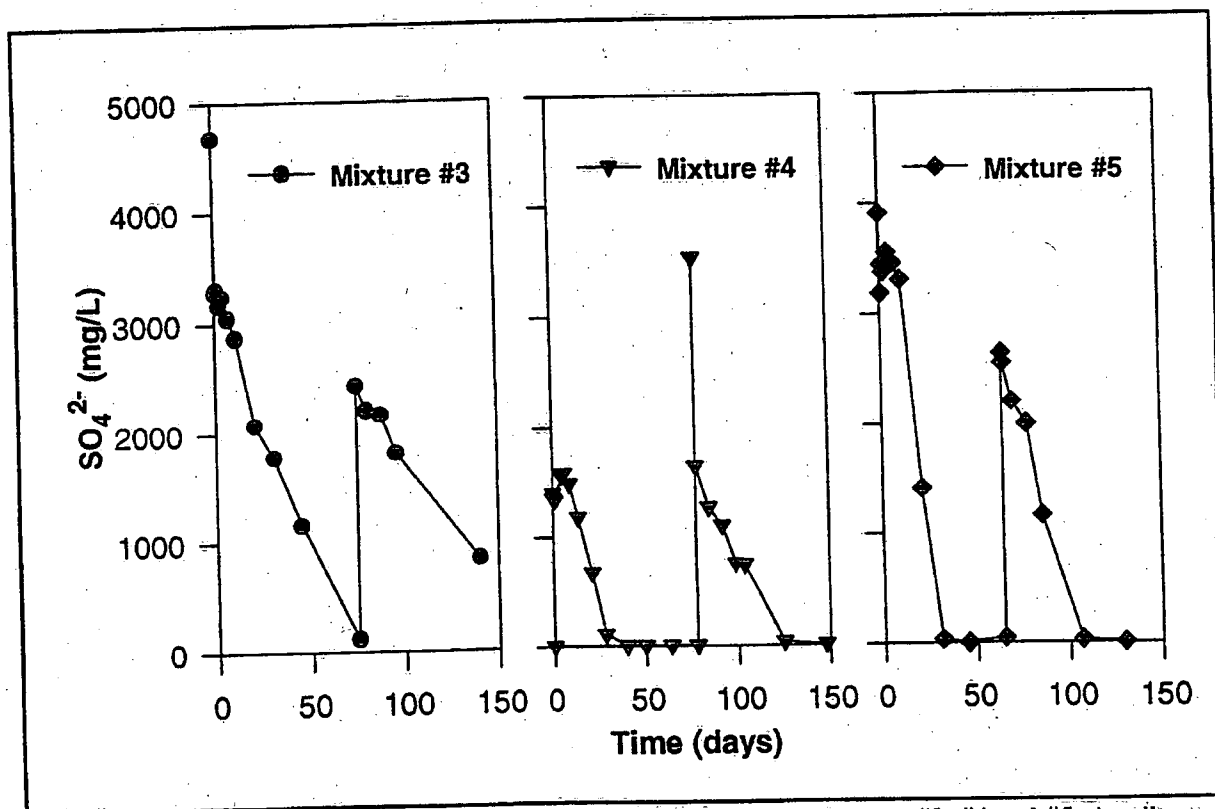


Figure 4: Sulphate concentrations as a function of time for reactive mixtures: #3, #4 and #5. A spike was introduced to each of the reaction flasks at day 78.

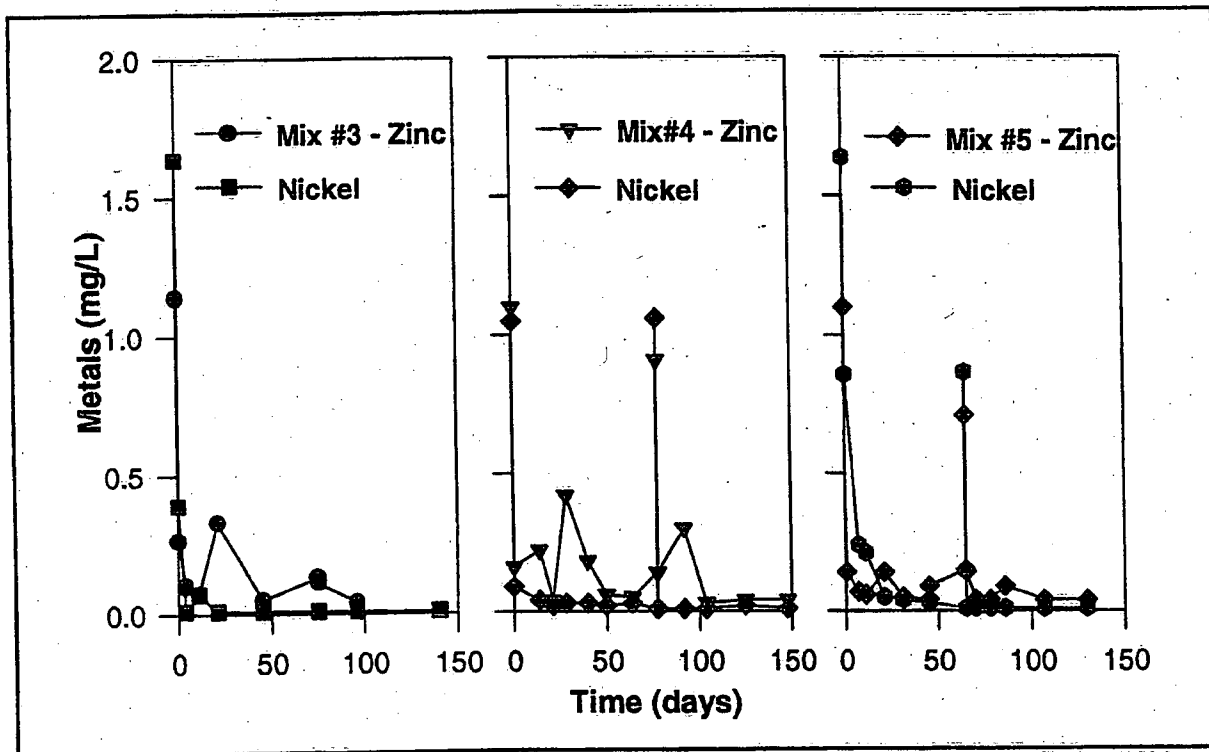


Figure 5: Metal concentrations as a function of time for reactive mixtures: #3, #4, and #5. Reaction flasks were spiked with additional metals on Day 78.

Permeability

The permeability of the reaction mixture is an important parameter which must be considered when designing a reactive wall. The reactive mixture must be sufficiently permeable to ensure that the groundwater flows through the wall and not substantially alter the groundwater flow path. Thus, mixtures should be designed such that the permeability is the same or slightly higher than that of the surrounding aquifer material. For our studies we used field data from the Nickel Rim site near Sudbury, Ontario which has a permeability of $< 10^{-3}$ cm/s (11).

The permeability of the optimal reaction mixtures are shown in Table 4. Required permeabilities greater or lower than those listed can easily be modified through altering mixture ratios, grain size and through the addition of pea gravel.

Table IV: Measured permeabilities of reactive mixtures: #3, #4, and #5, using falling-head permeameters.

Mixture	Permeability
#3	$< 10^{-2}$ cm/s
#4	$> 10^{-3}$ cm/s
#5	$> 10^{-3}$ cm/s

Conclusions

The laboratory results show that mixtures containing multiple sources of organic matter appear to be the best candidates for use in reactive walls because they have a higher sulphate reduction rate

compared to the single source mixtures, and they offer potential for long-term effectiveness by containing a variety of carbon sources with differing decomposition stabilities.

Reactive mixtures based on the findings of these batch tests are currently being tested under dynamic flow conditions using continuous flow-through columns. Permeability of reactive mixtures was generally greater than 10^{-3} cm/s and could easily be adapted to areas with higher and lower aquifer permeabilities. Results from these studies will be simulated using geochemical reactive/transport computer models to assess the overall effectiveness of the organic-carbon mixtures for use in the treatment of mine drainage using reactive walls.

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