

**Studies on the Use of Depyritized Tailings, Gold Tailings, Sewage
Incinerator Ash and Granulated Slag as Cover Alternatives for the
Reclamation of Sulphide Tailings**

by

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A Thesis

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of the requirements for the Degree of
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Abstract

The Thickened Tailings Disposal Method, implemented at Kidd Creek in 1973, disposes of tailings at 60-65% solids, and yields a relatively stable, erosion-resistant deposit. Tailings oxidation, and thus metal and acid release, are limited by maintaining high moisture levels. Depyritized and gold tailings, and other waste materials such as sewage incinerator ash and granulated slag, are being considered as cover materials on thickened pyritic tailings, to aid in site closeout and revegetation. This study revealed normal seed germination of Redtop (*Agrostis gigantea* Roth.) in all cover materials, and superior seedling establishment and sustained growth in incinerator ash and gold tailings. Plants in incinerator ash and gold tailings showed strong positive responses to a 6-24-24 (NPK) fertilizer, and no increase in shoot metal concentrations, except for Mn. The addition of fertilizer significantly increased shoot Mn concentrations. Shoot concentrations of Cu, Mn, Ni, and Zn were higher than values reported for grasses in non-metal-contaminated substrates, but were similar to published values for grasses grown in metal-contaminated substrates. Shoot Cr and Fe concentrations were higher than levels reported elsewhere for grasses in metal contaminated substrates. Fertilizer increased shoot metal content of Fe, Mn, Ni and Zn per gram of root, indicating either better exploitation of the substrate by roots, or increased translocation from root to shoot. A column leach test showed that the amount of iron leached from the columns was elevated under a cover of gold tailings, sewage incinerator ash or slag. However, gold tailings, sewage incinerator ash and slag lowered the amount of Cd, Co, Mg, Mn, Ni, Se, and Zn leached from the columns. These findings were attributed to the ability of the cover materials to limit iron sulphide oxidation in the underlying tailings by maintaining the tailings at a higher water content and thereby slowing the diffusion of atmospheric oxygen.

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1. INTRODUCTION

Mine tailings are the waste materials that are discarded after the ore has been separated by milling and flotation (Peters, 1995), and are generally unfavourable substrates for vegetation establishment because of low fertility, poor moisture retaining properties, lack of organic matter and microorganisms, and the occurrence of toxic quantities of metals (Peterson & Nielson, 1973; Hunter & Whiteman, 1974; Shetron, 1976; Watkin, 1988; Taylor & Schuman, 1988).

Watkin (1988) lists three major approaches that can be undertaken to establish vegetation on tailings:

- 1) direct seeding of the tailings or other wastes following the addition of a soil amendment such as limestone, fertilizer or organic matter.
- 2) seeding and/or planting of native or indigenous species having a high tolerance to adverse conditions present on a site.
- 3) Isolation of conditions by covering with one or more capping materials (eg. topsoil, overburden, waste rock) and seeding or planting with native or agricultural species.

However, oxidation of sulphides near the surface of pyritic tailings normally leads to acidification, and the acid water percolating through the waste is able to dissolve and transport a wide variety of materials in the leachate water (Doepker, 1988). Not only do a portion of these dissolved constituents remain on-site, where they become part of the ion balance of the soil water and possibly affect plant establishment and growth (Gentry *et al.*, 1992), but they also exert an effect on surrounding areas, through addition to groundwater and surface runoff. Thus, the establishment of a perpetual vegetation cover directly on tailings is often very difficult, and may require enormous quantities of limestone (or other suitable neutralizing agents) as a means of controlling both the existing acidity and the potential acidity (from further oxidation of sulphides). A good initial vegetative cover may be subsequently "killed" by reacidification of the treated tailing surface caused by depletion of the neutralizing reagent reserve (Hawley, 1972).

The Falconbridge Ltd. (Kidd Creek Division) metallurgical site is situated twenty-six kilometres east of Timmins, Ontario. It is mainly a copper-zinc milling complex, and because of the sulphidic nature of the ores, the tailings are potentially acid-generating.

When covering materials are placed on potentially acid-generating and metalliferous tailings, they perform a dual purpose. On one hand they assist in achieving the aesthetic and ecological benefits of revegetation by acting as a substrate for plant growth. At the same time they limit the accessibility of oxygen to the pyritic material through diffusion, and control the infiltration and runoff of water, thus limiting the oxidative weathering of pyrite and retarding or eliminating the production of acid (Hoving and Hood, 1984).

Winterhalder (1992) demonstrated, on a field experiment level, the effectiveness of gravel and/or loam covers on the oxidized sulphide tailings of the Kam-Kotia site, also in Timmins. However, the Kidd Creek tailings pond comprises an area of approximately 1200 hectares, and this extremely large area makes it unfeasible to use conventional and expensive cover materials such as gravel and loam. Thus, attention was also turned to other readily available, relatively inexpensive and potentially non-phytotoxic, non-polluting waste products such as gold tailings, sewage incinerator ash and granulated slag as cover materials.

Making use of waste products in the revegetation of mine tailings is not only economical, but it also eliminates the need for storage of these materials on a site of their own. The concern, however, is that these waste materials often themselves contain potentially toxic substances that may inhibit plant growth, may concentrate in the plant material, or may leach into the surrounding environment, and thus may only serve to worsen the problem of metal contamination.

In 1973, Falconbridge Ltd. (Kidd Creek Division) adopted the Thickened Tailings Disposal (TTD) System for its tailings pond, on the recommendation of E.I. Robinsky Associates Ltd. The TTD system involves the deposition of tailings at 60-65% solids, producing a cone-shaped tailings deposit. Unlike conventional methods, in which the tailings are deposited at 30-35% solids and usually undergo extensive particle segregation, thickened tailings are deposited in slurry form, and do not undergo particle segregation. This results in a much more stable and

erosion-resistant tailings mass than the conventional version because the homogenous nature of the deposit and the sloped surface allow rapid surface runoff and drainage (Robinsky, 1978; Salvas, 1989). A direct consequence of the homogeneous nature within the thickened tailings deposit is the development of a shallow water table and high capillarity, which result in near-saturated conditions to surface throughout much of the cone (Robinsky *et al.*, 1991). Therefore, the TTD methods attempts to maintain the tailings near moisture saturation, limiting oxidation, metal release and acid drainage.

An advantage of the TTD approach is that it allows the progressive reclamation of the tailings during the active life of the operation (discussed further in section 1.2), so that reclamation activities can proceed ideally on relatively fresh, unoxidized (neutral) tailings. According to Hammack and Watzlaf (1990), once bacterially-mediated sulphide oxidation has been established, the oxygen partial pressure would have to be maintained below 1% to realize any reduction in oxidation rate. In general, no cover materials that are capable of maintaining these low oxygen values, other than water, are currently available or economically feasible, although in recent years, the use of fine-grained materials to develop multiple-layer saturated cover designs has been commanding increased attention from mine reclamation researchers (Nicholson *et al.*, 1991; Yanful, 1991; Sydor, 1992). The principle behind such a design is based on a sufficient textural contrast between the tailings and a cover layer, such that the overlying fine material will be resistant to drainage into the underlying coarse layer and will thus tend to remain saturated. This technology is recognized as exhibiting excellent potential for the prevention of oxidation and subsequent acidification of reactive sulphide tailings and waste rock, and is thought to be generally comparable to underwater disposal. However, the application of multiple-layer covers over large tailings disposal areas remains very cost prohibitive and requires extensive quantities of borrow materials.

Hammack and Watzlaf (1990) also report that if bacteria are inhibited, any reduction in oxygen partial pressure from atmospheric will result in a proportional decrease in the pyrite oxidation rate. Therefore, the application of a suitable cover on fresh tailings may prevent or at least delay their oxidation and subsequent enhanced metal release, so long as the pH remains high enough to prevent oxidation by *Thiobacillus ferrooxidans*, which can use ferric iron as an oxidizing agent under near-anoxic conditions below pH 4.

The initial goal of this project was to determine whether the addition of a layer of depyritized tailings as a relatively inert cover at the final stage of spigotting would be economically-feasible, and amenable to revegetation. Because the physical nature of depyritized tailings is essentially the same as that of pyritic tailings, the depyritized layer could be spigotted as thickened tailings in similar fashion to the pyritic tailings. It later became evident that the depyritization of the final run of tailings might not be economically feasible, and attention was also turned to other potentially inexpensive and effective covers.

A preliminary objective of this study was to investigate the feasibility of establishing a grass cover directly in the pyritic Cu-Zn tailings via the surface incorporation of limestone, fertilizer, marl and sewage incinerator ash as amendments. While limestone and fertilizer are amendments which are routinely used in attempts to establish vegetation on tailings, marl was chosen for its acid neutralizing capability and its fairly close proximity to Timmins, while incinerator ash was chosen because it was felt that its high nutrient content might stimulate grass growth in nutrient-deficient tailings. Because the establishment of vegetation directly in the pyritic tailings was expected to have little or no effect on decreasing oxidation in the tailings, this study was abandoned in favour of the application of covers.

Thus, the primary objective of this study was to evaluate and compare the effects of four cover materials; depyritized Cu-Zn tailings, gold tailings, sewage incinerator ash, and granulated slag applied over thickened pyritic Cu-Zn tailings.

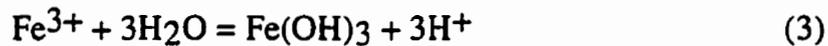
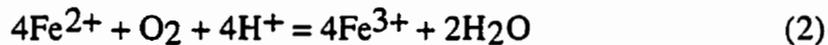
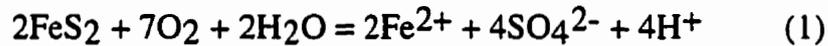
The specific effects investigated were:

- i) the success of germination and establishment of *Agrostis gigantea* Roth.
- ii) metal uptake in *Agrostis gigantea* Roth.
- iii) the degree and rate of oxidation of the pyritic tailings, as indicated by the leachate characteristics

1.1 Sulphide Oxidation

Pyrite (FeS_2), its dimorph marcasite, and pyrrhotite (Fe_{1-x}S) are the most problematic and common minerals found in mining and mineral processing wastes, occurring in both sulphide ores and in coal (Doyle and Mirza, 1990). When oxidized in the presence of water, these minerals release sulphuric acid, dissolved iron, sulphate, and heat, all of which can be deleterious to the environment (Doyle and Mirza, 1990).

Numerous reaction pathways and mechanisms have been proposed for the oxidation processes. Using pyrite as an example, the overall reactions are summarized, based on descriptions by Kleinmann *et al.* (1981), Carrucio *et al.* (1988) and Skousen (1995).



In reaction 1, iron sulphide is oxidized to sulphate with the release of ferrous iron and acidity. Upon dissolution, ferrous iron may oxidize to form ferric iron (reaction 2). Reactions 1 and 2 proceed rather slowly at pH's above 4.5. However, under aerobic conditions, as pH approaches 4.5 these reaction rates can be increased by five fold or more due to the activity of *Thiobacillus ferrooxidans*, which can catalyze the oxidation of sulphides, sulphur and ferrous iron (Doyle and Mirza, 1990). Ferric iron may then undergo hydrolysis, forming ferric hydroxide and acidity (reaction 3). At lower pH ranges, ferric iron may oxidize the sulphide (reaction 4), greatly increasing the rate of ferrous iron and acid formation. The rate of reaction 4 is determined by the rate of reaction 2.

The oxidation of ferrous iron by oxygen (reaction 2) is much slower than the oxidation of iron sulphides by ferric iron (reaction 4) (Carrucio *et al.*, 1988). This indicates that sulphide is oxidized initially by oxygen (reaction 1), but that once sufficient quantities of ferric iron have been generated, sulphide is oxidized by the

mechanism given in reaction 4 rather than reaction 1, and that oxygen is involved only in the regeneration of ferric iron by reaction 2 (Carrucio *et al.*, 1988, Michelutti and Wiseman, 1995).

That the role of oxygen is diminished once sufficient oxidation has occurred has serious implications with respect to the ability of a cover material to prevent or decrease the production of acid mine drainage. If a cover is applied over oxidized tailings, sulphide oxidation by ferric iron would be expected to continue, resulting in the continued degradation of tailings drainage until the ferric iron had been washed out of the tailings (Michelutti and Wiseman, 1995). In essence, this would limit the role of a soil cover solely to that of a growth medium.

The oxidation of pyrite leads to two main environmental problems; 1) an environment that is too toxic for plant growth, and 2) the production of acid mine drainage, consisting of low pH water with elevated metals (especially iron) and sulphate.

1.2 Thickened Tailings Disposal System

The thickened tailings disposal method was conceived, tested and developed by E. I. Robinsky in 1965, and implemented in 1973 for the Texasgulf Canada Ltd., Kidd Creek Mine of Timmins, Ontario. Since that time, the system has been operating at a daily tailing discharge of approximately 7500 dry tons (Robinsky, 1978).

The primary goal of thickened tailings disposal is to eliminate high and potentially expensive tailings dams, and also to eliminate slimes ponds and decant systems. This goal is attained by depositing the tailings in a cone-shaped hill, which is one of the most stable and erosion-resistant shapes found in nature (Robinsky 1978).

Because the TTD system allows greater control than conventional methods over placement of the tailings (as described below), a tailings impoundment can basically be filled in "sections". Thus, once a particular section is filled, spigot lines can be moved and deposition continued in another section. In this way, reclamation activities, if initiated soon after deposition ceases, can proceed on relatively fresh, unoxidized (neutral) tailings. With conventional tailings

deposition methods, reclamation activities are generally not possible until all deposition has ceased and the site has been properly contoured. Contouring is usually necessary to provide adequate drainage for vegetation to establish. The time interval between initiation of tailings deposition and reclamation activities with conventional disposal, causes extensive oxidation of the exposed tailings (especially the more coarse and dry areas), resulting in increased difficulty in establishing vegetation. This difficulty extends to both vegetation establishment in a cover material and growth directly in the tailings.

A more extensive description of the TTD method is outlined below, and provides details of the principles behind this method.

Salvas (1989) described the depositional behaviour of the tailings in terms of the relationship between the slope formed and the water content of the tailings at the time of deposition. In the mining industry, the consistency of the tailings is usually described using the percent solids by mass.

Figure 1 shows laboratory data for a range of depositional slope vs. percent solids by mass curves, with each individual tailings having its unique curve (Salvas, 1989). Curve 1 represents fine tailings, curve 2 represents coarser tailings, and curve 3 represents tailings that are intermediate between those of curves 1 and 2. The shape and position of the curve depends mainly on the size gradation of the tailings ie. the finer the tailings the less thickening is required to obtain a given slope, though other factors such as specific gravity, particle shape and roughness, pH and density of the fluid, and the temperature of the slurry at deposition all exert an influence (Salvas, 1989).

Curve 3 of Figure 1 is typical for tailings from a base metals operation similar to that of Kidd Creek Ltd. and will be used as an example. In this case, the tailings slurry normally exits the mill at between 30 and 35 percent solids, where it behaves as a mixture of both fluids and solids, and is kept in motion by turbulent flow. If the flow is reduced or stopped, then segregation by particle size occurs very quickly. This is illustrated by the portion of the curve from A to B.

The behaviour of the tailings changes to a homogeneous stabilized slurry at point B. Because the quantity of fluids has been decreased, the particles are so close

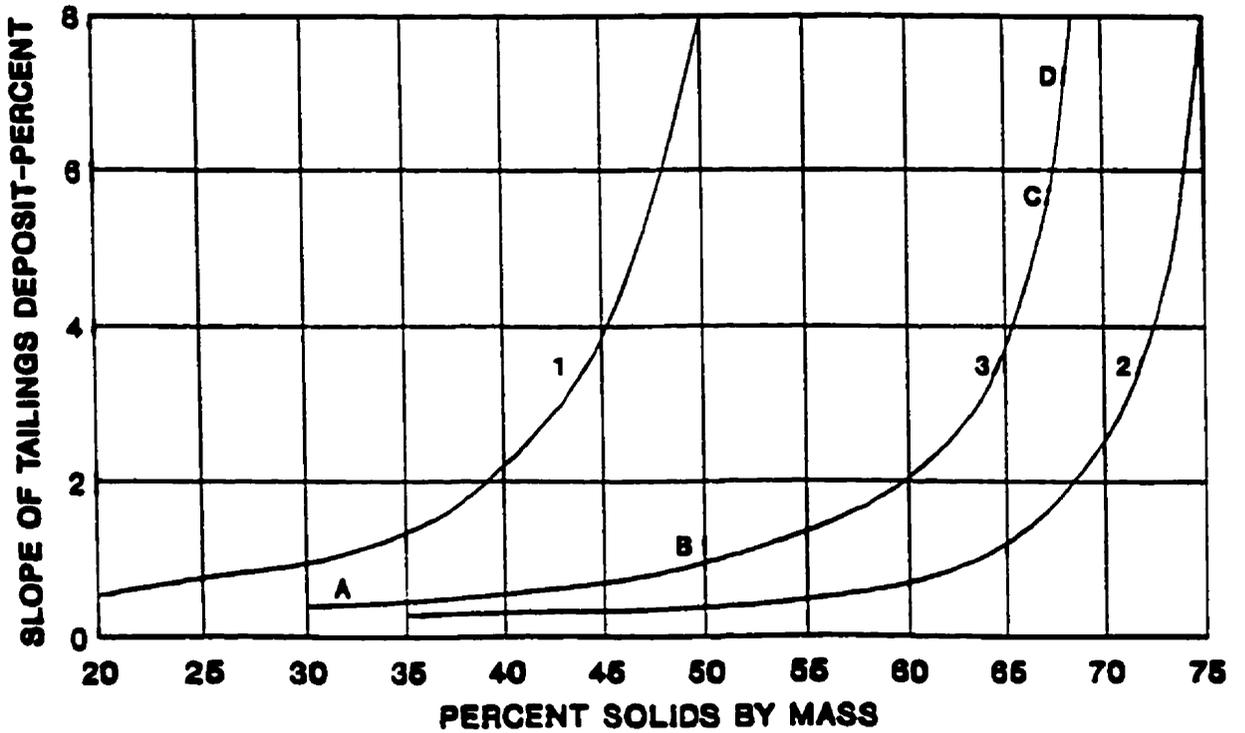


Figure 1: Laboratory deposition curves showing the relation between depositional slope and percent solids for fine tailings (curve 1), coarse tailings (curve 2) and intermediate tailings (curve 3) (after Salvas, 1989).

together that they cannot separate and settle individually. As the slurry flows downslope from the discharge point, it begins to slow as the slope decreases and eventually stops as a homogeneous deposit.

Consolidation due to self weight begins immediately, and as it progresses, fluid seeps from the deposit, increasing the percent solids and thus increasing stability.

Point C in Figure 1 represents the suggested upper limit of deposition for thickened tailings from the base metals operation given in this example. Point C for this mine would occur at 67.5 percent solids, and would result in a slope of 6%. This level of thickening (67.5% solids) allows the slurry to be pumped to the discharge points, whereas a higher percent solids may require the use of trucks or a conveyor.

At some point (D) on the curve, the tailings slurry reaches a sufficiently high percent solids or bulk density to begin to behave as a soil. The particles are in intimate contact with each other and the slope is governed largely by inter-particle friction. Beyond point D, the tailings do not behave as a slurry and will not flow (Salvas, 1989).

The preferred slope of the tailings mound is not greater than 6%, as this value provides safe stability, good surface drainage for future vegetation, and a topography that blends in with the surrounding terrain (Robinsky, 1978).

Initially, the solids to water ratio is controlled at a minimum slurry consistency, which permits the tailings to spread all the way to the 'toe' of the conical deposit (Figure 2). As the tailings build-up, the solids to water ratio is increased progressively, thus steepening the cone, but maintaining its 'toe' at the same place. If full thickening is allowed from the start, the tailing deposit will build up quickly at the point of discharge, making it necessary to raise the tailing line ramp immediately (Robinsky, 1978).

With the thickened tailings, only a small dam is required to contain the effluent and the small quantities of fines washed out by the run-off. The conical shape of the deposit tends to disperse the run-off, thus minimizing its erosive capability (Robinsky, 1978).

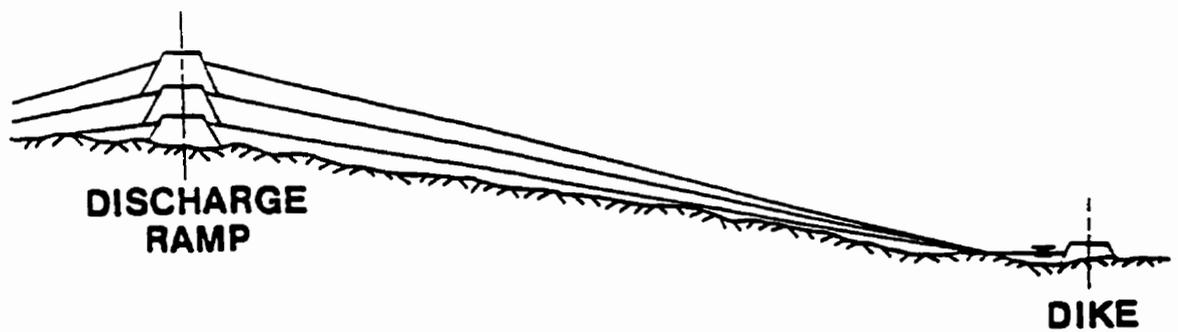


Figure 2: Schematic section showing progressive build-up of depositional slopes with the Thickened Tailings Discharge Method (after Salvas, 1989).

At the commonly used tailing concentration of 25 - 35 percent solids, segregation is rapid. The material at this low percent solids behaves like a mixture, each particle settling at its own rate, dependant primarily on its size and specific gravity, and the temperature and velocity of the transporting liquid. The coarser material settles out close to the discharge point. Progressively finer material settles out farther from the discharge, and most of the slimes (extremely fine particles) are invariably carried to the slimes pond. The slope of the major portion of the deposit is usually less than one percent and is generally concave in shape. This description of depositional behaviour is typical for conventional tailings ponds. Particle segregation is used to advantage to supply a coarser material at the perimeter of the pond with which to build the tailing dam. The flat depositional slopes are of little concern, and the creation of a slimes pond is accepted as an undesirable, but inevitable, feature (Robinsky, 1978).

Field studies have confirmed that when the tailing is thickened adequately, particle segregation does not occur. Grain-size analyses were performed on tailing samples obtained from the disposal area of Kidd Creek Mine in Timmins. Samples were collected at 250-foot intervals from the point of discharge to a radial distance of 3680 feet, and it was shown that very little grain-size segregation had occurred (Robinsky, 1978).

Robinsky (1989) suggests that, even if no attempt were made to revegetate the tailings surface, the surface layer of a thickened tailings deposit would be progressively leached-out by alternating runoff and high capillary suction. Capillary suction would cause the generated acids and soluble salts to rise to the surface, to be subsequently washed off by the next rain. In this manner, the upper layers would be progressively cleared of the sulphides. Furthermore, he anticipated that the surface would be artificially neutralized (limestone/fertilizer) to a depth of approximately 0.2-0.3 metres to permit vegetation to establish.

Thus, in the long term, it is anticipated that the sulphides will slowly leach out through the surface, and eventually environmental pollution (acid generation) will cease (Robinsky, 1989). The slow leaching of acid and metal contaminated water is generally not viewed as being an environmentally or economically acceptable alternative (even with water treatment facilities) because, depending on the size of

the impoundment and geology of the tailings, the production of acid, metal-contaminated drainage may continue for decades or even centuries.

2. DESCRIPTION OF MATERIALS

All materials were air-dried and thoroughly mixed prior to storage. Because of consolidation during drying, pyritic, depyritized and gold tailings were reduced to their original size range after drying by grinding lightly, but they were not sieved. Incinerator ash and granulated slag were passed through a 2 mm sieve without grinding.

2.1 Pyritic Tailings

This material was obtained fresh, directly from the thickeners at the Kidd Creek mill site. Robinsky (1989) has indicated that the capillary rise in this material is expected to be over two metres because of the fine texture, and analysis (Lakefield Research, 1990) has found that the tailings possess a net acid-producing potential of 139 kg/tonne.

A size analysis performed on representative tailings samples indicated that 91.7% of the pyritic tailings were minus 200 mesh (75 μ m) (Lakefield Research, 1990). Particle size was also tested at Laurentian University, by means of the hydrometer method (Appendix 1), which indicated that under the U.S. Department of Agriculture classification system, these tailings consisted of 0.6% clay, 36.5% silt, and 63% sand, and were classified as sandy loam (Table 1). Robinsky (1989) indicated that, based on the effective grain size ($D_{10} = 0.003$ mm), the pyritic tailings would be classified as a fine silt. The saturated hydraulic conductivity was determined to be 3.6×10^{-4} cm/s (Table 1).

2.2 Depyritized (Desulphurized) Tailings

These tailings were obtained from the Kidd Creek mill, but had been stored in pails prior to shutdown of a temporary depyritization circuit. Because the depyritizing circuit had been shut down and dismantled for some time, the tailings, while stored in a water cover and therefore subjected to minimal oxidation, were not fresh samples. The depyritized tailings show only a slight acid-producing potential of approximately 3 kg/tonne (Lakefield Research, 1990).

Table 1: Particle Size Analysis, Saturated Hydraulic Conductivity and pH of Potential Cover Materials.

Material	% Clay (<.002mm)	% Silt (<.05mm)	% Sand (<2mm)	USDA Classification	*Hydraulic Conductivity (cm/s)	pH
Gold Tails	2	4.7	94.3	Sand	1.8×10^{-3}	8.06
Incin. Ash	4.5	14.1	81.5	Loamy Sand	6.2×10^{-3}	7.46
Depy. Tails	1.5	40.2	58.3	Sandy Loam	3.4×10^{-5}	7.38
Pyritic Tails	0.6	36.5	63.0	Sandy Loam	3.6×10^{-4}	5.77
Slag	-	-	-	-	0.1	7.09

* Analysis courtesy of Dr. David Blowes of the University of Waterloo Centre for Groundwater Research.

The reduced sulphur content combined with the potential ability to spigot this material in thickened form (as for pyritic tailings) make it appealing as a potential cover. However, costs of establishing a depyritizing circuit on an operational scale would have to be addressed, should this material prove worthwhile.

Size analysis (Lakefield Research, 1990) indicated that 87.4% of the depyritized tailings were minus 200 mesh, whereas the hydrometer method indicated that the tailings were composed of 1.5% clay, 40.2% silt, and 58.3% sand, also classifying them (under the USDA system) as a sandy loam (Table 1). The saturated hydraulic conductivity was determined to be 3.4×10^{-5} cm/s (Table 1). Thus the depyritized tailings used in the forthcoming experiments appeared to be very similar to the pyritic tailings, though perhaps slightly more fine, as they conducted water 10 times more slowly than the pyritic tailings (Table 1).

2.3 Gold Tailings

The gold tailings were obtained from a gold mine (Royal Oak) adjacent to Kidd Creek, and are therefore readily available for large-scale applications. They are neutral or near neutral when deposited, and analysis shows a net acid-consuming potential of approximately 14 kg/tonne (Lakefield Research, 1990). The source of the alkalinity was thought to be due to carbonate content, although this was not determined. Material Safety Data Sheets indicated that these tailings were relatively inert and low in heavy metals, which, combined with their acid-consuming ability, offer very good potential for use as a cover material over acid-generating mill tailings, both as an acid buffer and growth medium.

These tailings were coarser than either the pyritic or depyritized tailings, with only 27.4% less than 200 mesh (Lakefield Research, 1990). Similar findings were obtained by the hydrometer method, which yielded 2% clay, 4.7% silt, and 94.3% sand, classifying the gold tailings as a sand (Table 1). The saturated hydraulic conductivity was found to be 1.8×10^{-3} cm/s (Table 1). The material is therefore able to conduct water faster than either pyritic or depyritized tailings.

2.4 Sewage Incinerator Ash

The sewage incinerator ash is a by-product of a Toronto sewage treatment plant, in which the sludge removed during the treatment process is burned. It was obtained from Mr. Pat Sheridan of Timmins, Ontario, who maintained a small stockpile under Ministry of Environment permission. Preliminary discussions with Ontario Ministry of the Environment personnel indicated that the ash appeared to be a good growth media, but that a high inherent metal content had raised concerns regarding potential toxicity problems due to leaching of heavy metals.

The hydrometer method indicated that the incinerator ash was composed of 4.5% clay, 14.1% silt, and 81.5% sand, leading to the classification of a loamy sand (Table 1). The saturated hydraulic conductivity was 6.2×10^{-3} cm/s (Table 1), comparable to gold tailings, but higher than pyritic or depyritized tailings.

2.5 Granulated Slag

Granulated slag is a by-product of copper refining at Kidd Creek, and therefore is also readily available on a fairly large scale. Because of its coarse physical nature, this material is unlikely to be a good growth medium. However, it may have a potential function as a capillary break between the tailings and a cover material. It is currently stored on the Kidd Creek tailings, and used in the construction of access roads and spiggoting ramps. Thus it was deemed necessary to explore its potential impact on the tailings and surrounding environment, in terms of metal leaching, and its ability to support vegetation.

Because of its obviously coarse nature, granulated slag was not subjected to particle size analysis by the hydrometer method, but instead it was subjected to a

sieve analysis. The results indicated that 8.9% by weight was > 1.4 mm, 77.8% was between 0.42 and 1.4 mm, and 10.8% was < 0.42 mm.

2.6 Marl

Marl was obtained from a small stockpile in the Pup lakes (formerly Twin lakes) area in west-central Thorneloe township, district of Temiskaming. It is composed chiefly of calcium carbonate or dolomite intermingled with clay, in variable proportions (Pirsson, 1908), and as such offered excellent potential for use as an acid-neutralizing agent.

While marl was used as a tailings amendment in the first experiment, because of the rather small stockpile and expected difficulty in obtaining larger volumes of this material, no further analyses were conducted.

2.7 Seeds

The seeds used in the initial pot experiment were an early version of the "Sudbury seed mixture", and had the following composition by weight:

<i>Agrostis gigantea</i> Roth.	Redtop	10%
<i>Festuca arundinacea</i> Schreber	Tall Fescue	30%
<i>Phleum pratense</i> L.	Timothy	20%
<i>Poa compressa</i> L.	Canada Bluegrass	10%
<i>Poa pratense</i> L.	Kentucky Bluegrass	20%
<i>Trifolium hybridum</i> L.	Alsike Clover	10%

For subsequent experiments it was decided that it would be better to concentrate on one grass species. Redtop was selected as the test grass because it is currently utilized in many revegetation seed mixtures, it has demonstrated an ability to withstand a wide range of adverse growing conditions, and has exhibited metal tolerance (Hogan *et al.*, 1977a & b; Hogan & Rauser, 1979; Rauser & Winterhalder, 1985; McLaughlin & Crowder, 1988).

Redtop seeds were obtained by Mr. Tony Spires (M.Sc. 1975, Laurentian Univ.) in 1974 from a seed supply house, and stored in sealed jars. Germination tests conducted immediately prior to initiation of the forthcoming experiments indicated that approximately 75% of the seeds were still viable; thus, their use was deemed acceptable.

2.8 Chemical Analysis of Materials

Each potential cover material was subjected to metal analyses. In some cases different batches of material were used, or the materials were used after an extended period of storage. Therefore, the range in metal levels among materials was quite high at times.

Means and ranges for total, water soluble, and dilute acid extractable elements are shown for potential cover materials in Tables 2, 3, and 4 respectively.

All materials were analyzed for total element content by Inductively Coupled Argon Plasma (ICP) Spectrophotometry at the Geoscience Laboratory of the Ontario Ministry of Northern Development and Mines in Sudbury, Ontario, following nitric-perchloric-hydrochloric acid digestion. Dilute-acid extractable metals were measured by ICP, following extraction with 0.05N hydrochloric acid. Water-soluble metals were measured by ICP after extracting with distilled water. Also, an analysis of the coarse ash (> 2 mm), was included to determine whether any significant quantities of metals were contained in the larger particles. Complete methods are presented in Appendix 1.

2.8.1 Total Element Concentrations

It was notable that for total element concentrations (Table 2), at least one potentially phytotoxic element was present at a concentration of greater than 1000 $\mu\text{g/g}$ in each of these materials. Specific examples include aluminum, iron and sulphur in all materials, chromium and copper in the ash, and zinc in all but the gold tailings. All of the materials were high in total calcium and magnesium, with incinerator ash also having a high phosphorus content. No substantial differences were found between the sieved incinerator ash (< 2mm) and the coarse incinerator ash (> 2mm).

Table 2: Total Element Concentrations of Potential Cover Materials ($\mu\text{g/g}$ material unless otherwise stated).

	^a Pyritic		^b Depyritized		^b Gold		^a Ash		^c Coarse Ash		^a Slag	
	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
Ag	11.4	0.3 - 24.6	1.4	0.4 - 2.7	0.4	nd - 0.4	296	267 - 349	295	290-298	5.8	0.4 - 11.9
*Al	2.20	1.7 - 2.8	2.58	2.1 - 3.5	0.81	0.7 - 1.0	2.83	2.5 - 3.2	2.50	2.4 - 2.6	1.98	1.9 - 2.1
As	328	115 - 461	98.5	3.8 - 212	146	96 - 204	119	3.5 - 211	114	108 - 119	336	3.9 - 501
Ba	40.5	15 - 72	40.1	17 - 77	28.3	12 - 53	1267	1159-1467	1076	1051-1094	502	328 - 583
*Ca	1.47	1.1 - 1.9	1.12	1.0 - 1.5	2.42	2.1 - 2.8	6.99	6.8 - 7.2	7.77	7.7 - 7.9	3.35	3.2 - 3.7
Cd	49.4	42 - 58	12.7	5.7 - 19.9	4.1	1.9 - 6.3	62.1	43 - 74	46.0	43 - 50	41.3	15 - 55
Co	133	104 - 169	53.5	40 - 66	17.4	14 - 21	62.9	26 - 122	31.5	31 - 33	580	513 - 611
Cr	24.3	12 - 45	22.5	14 - 34	37.9	28 - 46	1413	745 - 2012	822	783 - 863	80.5	48 - 180
Cu	1417	1252-1533	375	345 - 400	27.4	20 - 48	2519	1959-3237	2196	2140-2260	9044	*0.8 - 1.3
*Fe	10.3	9.4 - 10.6	7.2	6.7 - 7.9	3.4	3.2 - 3.6	15.0	12 - 18	14.9	14 - 15	34.0	32 - 36
K	1611	800-3200	1990	1100-4400	905	500-1500	2421	2300-2600	1921	1800-2100	2592	1300-3500
*Mg	1.53	1.3 - 1.7	1.70	1.5 - 1.9	1.37	1.3 - 1.4	1.07	0.8 - 1.2	1.35	1.3 - 1.4	0.87	0.8 - 0.9
Mn	875	715 - 979	966	923 - 1004	680	627 - 726	653	602 - 719	641	629 - 654	657	596 - 699
Mo	16.0	0.5 - 25.2	11.0	0.6 - 23.4	7.4	0.6 - 12.7	41.4	38 - 46	33.9	31 - 35	57.1	14 - 82
Na	761	622 - 882	429	304 - 708	194	119 - 326	2735	2413-3141	2493	2455-2519	7140	6751-7294
Ni	48.2	37 - 64	23.5	17 - 30	57.1	54 - 64	183	156 - 226	153	147 - 162	76.0	58 - 85
P	148	62 - 228	118	38 - 172	558	489 - 663	*6.2	*5.1 - 6.8	*7.1	*6.8 - 7.5	1130	241 - 4641
Pb	778	625 - 1018	106	48 - 165	19.5	6 - 32	730	683 - 787	357	347 - 371	829	713 - 887
*S	5.24	4.6 - 6.1	0.74	0.7 - 0.8	0.28	0.2 - 0.4	0.15	0.1 - 0.2	0.11	0.1 - 0.12	0.48	0.4 - 0.6
Se	308	0.9 - 1047	245	1.0 - 712	124	1.0 - 380	328	0.9 - 792	458	95 - 679	391	0.9-1166
*Zn	0.66	0.6 - 0.7	0.15	0.1 - 0.2	0.04	0.01-0.09	0.52	0.4 - 0.8	0.25	0.2 - 0.3	3.64	3.5 - 3.8

* indicates % a: N=9 b: N=6 c: N=3 nd=not detectable

2.8.2 Water Soluble Element Concentrations

Overall, water soluble element concentrations were generally quite low, with the exception of cadmium, nickel and zinc in the pyritic tailings, aluminum in pyritic and depyritized tailings and incinerator ash, and copper in slag (Table 3). These are all present at potentially phytotoxic concentrations.

There was virtually no difference in sulphur content between water soluble and dilute acid extractable fractions (Table 4) for the three tailings samples. These fractions represent the sulphate sulphur, and the low levels indicate that the tailings are relatively unweathered, since most of the sulphur remains in sulphide form. In incinerator ash, soluble sulphur represents approximately 50% of the total sulphur. This is likely in the form of metal sulphates, with solubility determined by the associated metal.

Water soluble metal levels in the sieved incinerator ash were generally equal to or higher than those in the coarse ash, with the exception of copper (Table 3).

2.8.3 Dilute Acid-Extractable Element Concentrations

Dilute acid-extractable analyses, which were carried out to determine which of the elements were soluble or likely to become soluble under plant growth conditions, led to an interesting contrast between pyritic and depyritized tailings. Although the pyritic tailings contained similar levels of aluminum and much more total copper than depyritized tailings, the depyritized tailings had more of these metals in soluble or plant-available form, as evidenced by the higher acid-extractable values (Table 4). In addition, while pyritic tailings contained much higher total levels of sulphur than depyritized tailings, acid-extractable levels were quite similar.

For copper, Blowes¹ (personal communication) has indicated that in pyritic tailings, copper is co-precipitated on sulphide surfaces as CuS (covellite). If the sulphide is removed (during the depyritization process), the potential for copper binding is reduced and it will be more readily leached. As explained previously,

¹ Dr. David W. Blowes, Waterloo Centre for Groundwater Research, University of Waterloo, Waterloo, Ontario, Canada.

Table 3: Water-Soluble Element Concentrations of Potential Cover Materials ($\mu\text{g/g}$ material)

	aPyritic		bDepyritized		bGold		aAsh		cCoarse Ash		aSlag	
	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
Al	7.4	6.1 - 8.1	8.1	7.4 - 8.8	1.0	0.6 - 1.3	4.7	4.0 - 5.5	3.65	3.0 - 4.4	0.71	0.6 - 1.3
As	0.23	0.20-0.24	0.24	0.23-0.24	0.23	0.22-0.24	0.24	0.24	0.35	0.2 - 0.6	0.22	0.2 - 0.24
Ca	2786	1819-3588	3520	2646-4493	77.1	66 - 83	728	432 - 1322	122	112 - 141	26.0	19.3-32.6
Cd	1.75	0.2 - 4.6	0.10	0.05 - 0.2	0.05	0.05	0.05	0.05	0.05	0.05	0.07	0.04 - 0.2
Co	1.59	0.3 - 3.2	0.23	0.08 - 0.4	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Cr	0.06	0.05-0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.05
Cu	0.07	0.05 - 0.2	0.05	0.05	0.05	0.05	0.05	0.05	2.47	2.4 - 2.6	2.26	0.9 - 3.9
Fe	0.11	0.1 - 0.17	0.15	0.1 - 0.2	0.10	0.1 - 0.2	0.60	0.3 - 1.0	0.46	0.2 - 0.7	0.30	0.2 - 0.5
K	25.9	19.5-31.8	32.0	20.2 - 51	26.8	24.8-30.6	11.8	5.2 - 23.0	5.37	4.2 - 6.7	1.73	1.0 - 5.2
Mg	259	134 - 435	210	206 - 216	24.3	23.8-26	80.2	54.7-105	34.7	33 - 38.1	1.39	1.1 - 1.8
Mn	43.4	18.3 - 80	9.8	7.3 - 12.5	0.05	0.01 - 0.1	0.02	0.01-0.06	0.01	0.01	0.06	0.01 - 0.3
Na	66.4	34.9 - 115	88.0	82 - 96	24.2	21.1 - 30	44.6	29.8-77.8	16.9	14.9-18.6	4.22	2.5 - 7.6
Ni	1.4	0.3 - 3.9	0.29	0.29	0.29	0.29	0.29	0.29	0.30	0.30	0.28	0.25 - 0.3
P	0.63	0.5 - 0.8	0.54	0.4 - 0.6	0.25	0.25	6.5	4.3 - 9.0	6.6	5.5 - 8.6	0.24	0.22-0.26
Pb	0.53	0.51-0.55	0.55	0.55	0.54	0.52-0.55	0.55	0.55	0.56	0.56	0.52	0.5 - 0.6
S	2745	1684-3512	3151	2409-3962	58.1	55.3-62.9	641	394 - 1127	105	94 - 125	17.8	14 - 21.7
Se	0.91	0.7 - 1.2	0.89	0.8 - 1.2	0.74	0.72-0.76	0.76	0.76	0.77	0.77	0.72	0.65-0.77
Zn	201	18.4 - 558	4.9	0.9 - 11.1	0.08	0.08	0.10	0.08 - 0.3	0.08	0.08	5.57	4.7 - 9.4

a: N=9 b: N=6 c: N=3

Table 4: Dilute Acid-Extractable Element Concentrations of Potential Cover Materials ($\mu\text{g/g}$ material)

	aPyritic		bDepyritized		bGold		aAsh		cCoarse Ash		aSlag	
	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
Al	52.7	11.4 - 133	102.9	37.9 - 169	10.2	9.1 - 11.1	9.9	4.3 - 13.4	3.8	3.1 - 4.5	205.4	191 - 219
As	0.41	0.2 - 0.6	0.32	0.3 - 0.4	0.23	0.2 - 0.3	1.24	0.3 - 2.5	0.37	0.3 - 0.6	3.96	3.7 - 4.3
Ca	5366	4701-6268	5585	5244-6172	2113	2048-2215	2954	465 - 4762	126	115 - 145	442	406 - 471
Cd	7.6	5.3 - 8.8	3.2	3.0 - 3.4	0.06	0.05 - 0.1	0.76	0.05 - 1.4	0.05	0.05	0.29	0.2 - 0.3
Co	4.4	2.3 - 7.0	8.2	5.0 - 11.5	0.60	0.55 - 0.7	0.16	0.07 - 0.3	0.07	0.07	5.5	5.0 - 6.0
Cr	0.07	0.06 - 0.1	0.19	0.1 - 0.4	0.06	0.05-0.06	0.06	0.05-0.06	0.06	0.06	0.07	0.05 - 0.1
Cu	23.7	0.05 - 73	50.8	6.9 - 95.4	0.1	0.05 - 0.3	0.9	0.05 - 1.7	0.13	0.05 - 0.3	102	89 - 124
Fe	375	4.6 - 1156	372	152 - 565	809	722 - 861	0.93	0.3 - 1.5	0.48	0.2 - 0.7	3001	2749-3287
K	35.4	27 - 45	65.7	59 - 71	34.5	32 - 37	28.2	8.1 - 54.8	5.5	4.4 - 6.9	48.1	46 - 51
Mg	408	249 - 548	487	407 - 580	646	619 - 672	361	56 - 658	36	34 - 39	98	90 - 106
Mn	119	90 - 145	91	84 - 101	56	53 - 59	7.23	0.01 - 12	0.01	0.01	8.76	8 - 10
Na	69.7	39 - 124	107.6	96 - 122	29.0	26 - 33	69.2	33 - 116	17.4	15 - 19	99.5	92 - 107
Ni	10.9	5.9 - 16.2	1.41	1.0 - 1.7	0.61	0.5 - 0.79	0.55	0.3 - 0.96	0.31	0.3 - 0.31	0.28	0.27 - 0.3
P	0.74	0.5 - 1.0	0.67	0.5 - 0.9	0.25	0.2 - 0.3	235	4.4 - 457	6.8	5.7 - 8.8	2.03	1.7 - 3.2
Pb	15.8	0.6 - 47.1	1.04	0.5 - 2.0	0.53	0.51-0.54	0.55	0.5 - 0.6	0.57	0.57	8.67	8.0 - 9.2
S	2664	1667-3264	2928	2239-3808	51.4	44 - 62	659	419 - 1109	108	97 - 129	19.6	14 - 29
Se	0.76	0.75-0.76	0.74	0.71-0.76	0.73	0.70-0.75	0.76	0.72-0.79	0.79	0.79	0.74	0.71-0.76
Zn	940	596 - 1146	387	373 - 417	3.04	0.7 - 6.6	5.11	0.1 - 13.5	0.08	0.08	456	417 - 493

a: N=9 b: N=6 c: N=3

the measured sulphur is probably in the form of residual sulphate, and the low level indicates the relatively unoxidized status of both the pyritic and depyritized tailings at the time of analysis. However, after repeating the acid extractions, it was discovered that the acid extractions were occurring at a lower pH in depyritized tailings and slag than in pyritic and gold tailings and incinerator ash (Table 5), and would thus be expected to release more metals. This was not surprising for the granulated slag, which was low in buffering materials such as calcium and magnesium (and carbonates), but was not expected from depyritized tailings, because they contain roughly the same levels of calcium and magnesium (and presumably carbonates) as pyritic tailings. Therefore it is probably a combination of binding effects and extraction at lower pH that explains the observed difference between metal levels in pyritic and depyritized tailings.

Extractions of this nature (acid extractions) would be more accurate if the samples were extracted at the same pH, in order to account for different acid-buffering capabilities between materials, and could be accomplished by varying the volume of acid used.

In general, substantial increases were observed in the concentrations of Al, Cu, Fe, Mn, Zn, Pb, and Ni when extracted with a dilute acid as compared to water extractions (Tables 3 & 4). This was totally expected, because many metals become more soluble at lower pH's.

Table 5: Mean pH \pm S.D. and Median of Filtrate for Cover Materials Extracted With Dilute Hydrochloric Acid.

<u>Material</u>	<u>Mean pH \pm S.D.</u>	<u>Median</u>	<u>n</u>
Pyritic Tailings	5.06 \pm 0.57	5.17	12
Depyritized Tailings	3.83 \pm 0.82	3.61	7
Gold Tailings	4.94 \pm 0.15	4.96	6
Sewage Incinerator Ash	4.74 \pm 0.12	4.71	8
Granulated Slag	2.41 \pm 0.18	2.41	8

Note: Mean pH values are arithmetic means of the pH values and have not been calculated from $[H^+]$.

Acid extractable metal levels were higher in the sieved incinerator ash fraction than in the coarse ash fraction, except for slightly increased copper in the coarse ash (Table 4). These results, combined with the water soluble and total data, indicate that no substantial quantities of metals were lost by discarding the coarse ash fraction.

From the point of view of plant nutrition, the high total phosphorus content of the incinerator ash was encouraging, though the water soluble levels indicated that comparatively little was available for use by plants (Tables 2-4). Phosphorus solubility did, however, increase substantially under mildly acidic conditions (Table 4). Cole (1994), found that it was desirable to mix acidic peat with incinerator ash to release phosphorus for plant use. Acidification may, however, result in an increase in the release of some metals.

2.9 Historical Leachate Information

As part of the background information, data were obtained from Kidd Creek pertaining to possible metal dissolution from the pyritic, depyritized and gold tailings. The "Legislation 309 Leachate Extraction" procedure was performed (analyses by Lakefield Research), with leachates analyzed for the elements specified in schedule 4 of regulation 309. The results are summarized in Table 6.

Regulation 309 required that if the concentrations of any of the elements (outlined in schedule 4 of Regulation 309) in the leachate were below ten times the "quality criteria", the waste product was not registerable or hazardous. If the concentrations of any of the elements were between ten and one hundred times the "quality criteria", the waste was registerable but not hazardous, and if the concentrations were above one hundred times the "quality criteria" the waste was registerable and hazardous. Based on these criteria, all of the elements were below the level which defines the wastes as either registerable or hazardous, except for cadmium in the pyritic and depyritized tailings, which would make these materials registerable but not hazardous.

However, the leachate 309 procedure was performed on fresh tailings, and does not take into account the evolving nature of the tailings as they oxidize, which may result in much higher extractable metal levels.

Table 6: Elemental Concentrations (mg/L) in Leachate of Pyritic, Depyritized and Gold Tailings Obtained under the Legislation 309 Leachate Extraction Procedure.

Element (mg/L)	Pyritic Tailings	Depyritized Tailings	Gold Tailings	Quality Criteria
Ag	< 0.03	< 0.03	< 0.03	0.05
As	< 0.05	< 0.05	< 0.05	0.05
B	< 5.0	< 5.0	< 5.0	5.0
Ba	0.05	0.09	< 0.02	1.0
Cd	0.23	0.081	< 0.005	0.005
Cr	< 0.02	< 0.02	< 0.02	0.05
Hg	< 0.001	< 0.001	< 0.001	0.001
Pb	0.15	< 0.05	< 0.05	0.05
Se	0.02	< 0.01	< 0.01	0.01

3. GROWTH STUDIES

3.1 Introduction

Heavy metals contained in soils may influence vegetation growth in two fundamental ways, by influencing germination and initial seedling establishment, and also by reducing long term biomass production through accumulation of these metals to potentially phytotoxic levels. To simply state that heavy metals inhibit vegetation growth is generally not sufficient, because it gives no indication of possible mechanisms that are responsible for seedling mortality. Much is known about the physiology and mechanisms involved in metal toxicity in plants. However, primary evaluations of possible growth substrates must first attempt to determine whether metal toxicity is likely to be a problem, and secondly must determine the growth stage at which the problem becomes apparent.

Therefore, the purpose of the growth studies was to provide an evaluation of the relative abilities of pyritic, depyritized and gold tailings, sewage incinerator ash and granulated slag to support vegetation. The experiments were designed a) to compare growth in the germination and establishment phase by conducting germination and early growth tests in Petri dishes, and b) to examine longer term (sustained) biomass production through pot experiments.

3.2 A Note on Statistical Analyses

Throughout the growth studies presented in this chapter, the reader will find that there has been a rather consistent lack of normal distribution and homogeneity of variance. Because of this, it was felt that an explanation of the general statistical methods and the rationale for their use should be given.

Statistical analyses have generally proceeded according to the following sequence: 1) test of normality 2) parametric analysis and check of homogeneity of variance 3) data transformations as necessary 4) parametric analysis of transformed data and check of homogeneity of variance 5) nonparametric analysis.

Where data transformations resulted in improvement of the data such that violations of assumptions were minimized, the transformed data was used.

However, nonparametric analyses were used in all cases to confirm the findings of the parametric tests, and generally yielded very similar interpretations. Thus, even though small violations of the assumptions for a particular parametric test (ANOVA) may have been present, statistical analysis proceeded through the use of parametric tests with confirmation by nonparametric tests.

Green (1979) indicated that one of the most serious violations of assumptions for statistical tests is heterogeneity of variance. However, Cochran (1947), as stated in Green (1979) argues that, overall, F-tests (such as ANOVAs) are probably affected the least. Crovello (1970), as indicated in Green (1979), argues for the use of as many methods as possible at any given stage of analysis. He emphasizes that this is not to find a method that gives the desired results, but rather that if the different models (based on different assumptions) lead to similar results, then a robust theorem exists which is relatively independent of the details of the statistical model. Green (1979) suggests that researchers who resort to nonparametric versions of ANOVA because of slight non-normality of within-group error distributions are being unnecessarily fastidious, and that the price paid for a slight increase in robustness is a loss of power in the test and a loss of information in descriptive presentation of the results.

Lastly, Green (1979) indicates that nonparametric tests are rarely necessary, while Harris (1975), as stated in Green (1979), indicates that violations of a particular assumption for a test does not invalidate the test since the test may be quite robust under violation of the assumptions used to derive it. He notes that there is much strong evidence that most univariate normal distribution-based statistical tests are extremely robust under such violations.

3.3 Germination and Early Growth (Petri Dish Experiments)

3.3.1 General Method

The method used to assess germination and early growth was a technique developed by Archambault (1991). Similar methods have been used by Wilkins (1957) and Bradbeer (1989).

Ten holes were drilled into the bottom half of a 9 cm plastic Petri dish for drainage. A glass microfibre filter paper was then placed in the bottom of the Petri dish in order to retain the materials used. The appropriate air-dried material plus any required amendment were thoroughly mixed prior to being added to the Petri dish. A second glass microfibre filter paper was placed on top of the material, and the plastic Petri dishes were then placed in larger glass Petri dish bottoms to which water had been added (Figure 3). This method allowed water to move up through the holes in the bottom of the plastic petri dishes, through the 'soil', wetting the upper filter paper.

Fifty seeds of Redtop (*Agrostis gigantea* Roth.) were counted out under a dissecting microscope and placed on the top filter paper. Seeds were added at the same time, once enough had been counted for all dishes.

Distilled water was added as necessary so as to maintain a slight reservoir in the glass Petri dishes but not to over-saturate the upper filter paper. The plates were kept under dark conditions and examined twice daily until germination was initiated (usually about 2 days), as indicated by the protrusion of the radicle through the seedcoat, and were then placed either on a well-lighted bench in the laboratory or in the greenhouse.

Harvesting of the seedlings was initiated when the seedlings appeared to be constrained by the lid of the plastic Petri dish, usually after approximately one week of growth. Harvesting permitted the determination of percent germination, measurement of root and shoot length, and the calculation of a root:shoot ratio.

Data were then analyzed using the SPSS package on the VAX computer system.

3.3.2 Experiment 1: Amendments to Pyritic and Depyritized Tailings

3.3.2.1 Purpose

This experiment was conducted to determine the effect of the addition of limestone, fertilizer, marl, and sewage incinerator ash as amendments to pyritic and depyritized tailings on germination, root and leaf growth of Redtop (*Agrostis gigantea* Roth.).

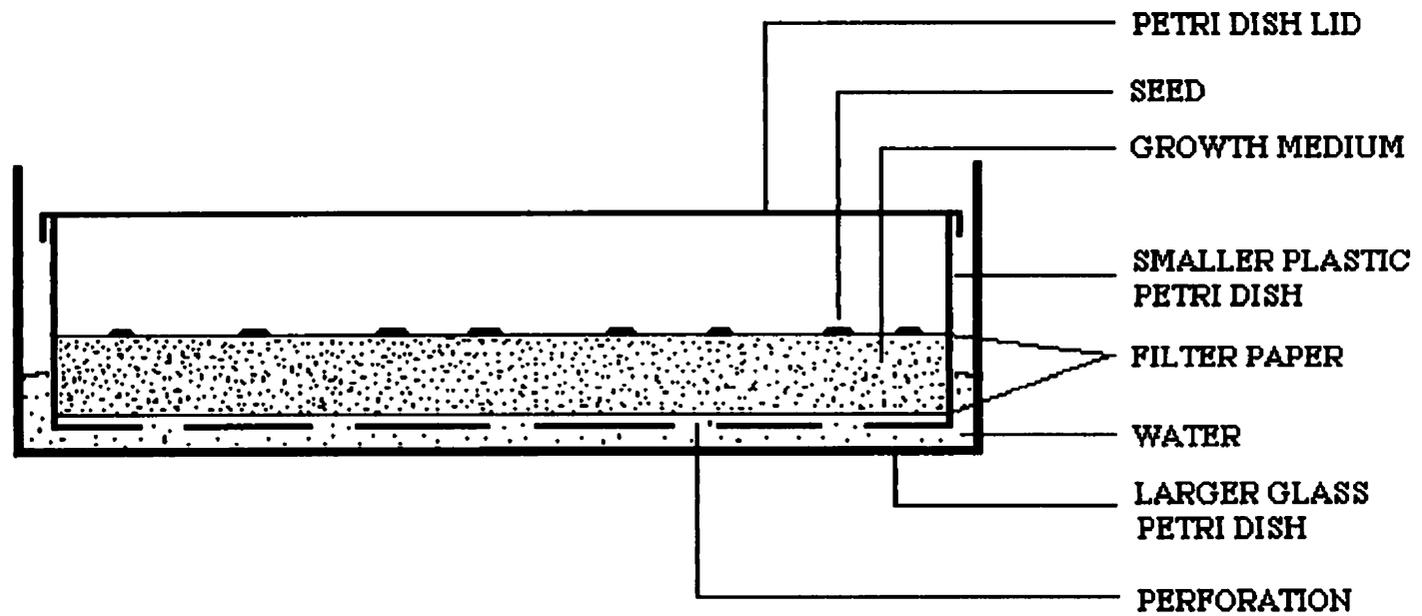


Figure 3: Design of Petri Dish Apparatus Used in the Measurement of Germination and Early Growth.

The hypothesis tested was that germination and early growth would be significantly better on depyritized tailings than on pyritic tailings, and further, that the addition of amendments would promote germination and early growth.

3.3.2.2 Methods and Materials

Approximately 20 grams of either pyritic or depyritized tailings were mixed with 0.2 grams of dolomitic limestone, fertilizer (6-24-24 NPK), marl or incinerator ash (the 1:100 ratio was equivalent to a field rate of approximately 6T/ha, incorporated to a depth of 10 cm) and added to the Petri dishes. Two control treatments were also present, in which no amendments were added. Fifty seeds of *Agrostis gigantea* were counted out and added to the top filter paper. All Petri dishes were then placed in the dark for a period of approximately 2 days, by which time the majority of seeds had germinated. The Petri dishes were then placed in the greenhouse in a randomized block design (Heath, 1970) with three replicates. The grass seedlings were allowed to grow for approximately one week. At completion, root and leaf lengths were measured and % germination and root/shoot ratios were calculated.

A gravelly soil obtained from Willisville, Ontario was used to compare growth in a gravelly substrate. Seeds were also germinated on filter paper alone, as a comparison of growth based only on nutrients contained in the seed endosperm. Both the gravel and filter paper treatments were included in the randomized block design (with 3 replicates). However, because no amendments were added to these materials, they were omitted from the statistical analysis.

Normality of the data was tested using the Kolmogorov-Smirnov test, and homogeneity of variance using Bartlett-Box 'F' test (under the 1-way ANOVA command). A 2-way Analysis of Variance (ANOVA), 1-way ANOVAs and Scheffé's Multiple Range Tests were employed to analyze the data. Sources of interactions, where encountered, were identified by computing all possible variable combinations and subjecting them to statistical analyses. Findings were verified via Kruskal-Wallis and Mann-Whitney non-parametric tests, which make no assumptions of normal distribution or homogeneity of variance. Differences were deemed significant at $p < 0.05$ unless specified otherwise.

3.3.2.3 Results and Discussion

While some statistics were computed using \log_{10} transformed data, for ease of interpretation all results are presented in their original format. Where transformed data were used, significant differences indicated in the forthcoming Figures are based on statistical analyses of the transformed data.

No differences were found in mean germination rates between any of the treatments, as shown in Figure 4.

A Kolmogorov-Smirnov test indicated that the germination data were not normally distributed ($z=6.0$, $p<0.001$), even after data transformations were attempted.

A 2-way Analysis of Variance on the original data indicated that germination was not affected by treatment (none, limestone, fertilizer, marl or ash) [$F(4,20)=0.59$, $p=0.67$; $\eta^2=0.27$] when added to either substrate (pyritic or depyritized tailings) [$F(1,20)=3.53$, $p=0.08$; $\eta^2=0.33$], with an r^2 of 0.186. Identical results were obtained using \log_{10} transformed data. In addition, germination on amended tailings was not significantly different from that on the filter paper and gravel controls, averaging approximately 75%. These results, and homogeneity of variance were confirmed using 1-way ANOVA's.

Therefore, any toxic qualities that the pyritic and depyritized tailings possessed, under any of the treatments, did not influence germination. Similar results were obtained by Blundon (1984), who found that the addition of limestone and/or fertilizer to oxidized tailings did not significantly affect the germination of various grasses. In contrast, Plass (1976), as stated in Maddox *et al.* (1977), indicated that the seed coat of some grass species may be permeable to specific toxic ions (zinc in pyritic tailings for example), and therefore the seed may also be susceptible to damage. Further, acidity caused by the addition of some fertilizers can also damage seeds (Plass, 1976).

The effect of fertilizers on germination may be species dependent; Maddox *et al.* (1977) found that the addition of triple superphosphate increased germination in Redtop, while ammonium nitrate depressed germination in all species tested except Redtop. It was suggested that high ionic strength fertilizers may create an

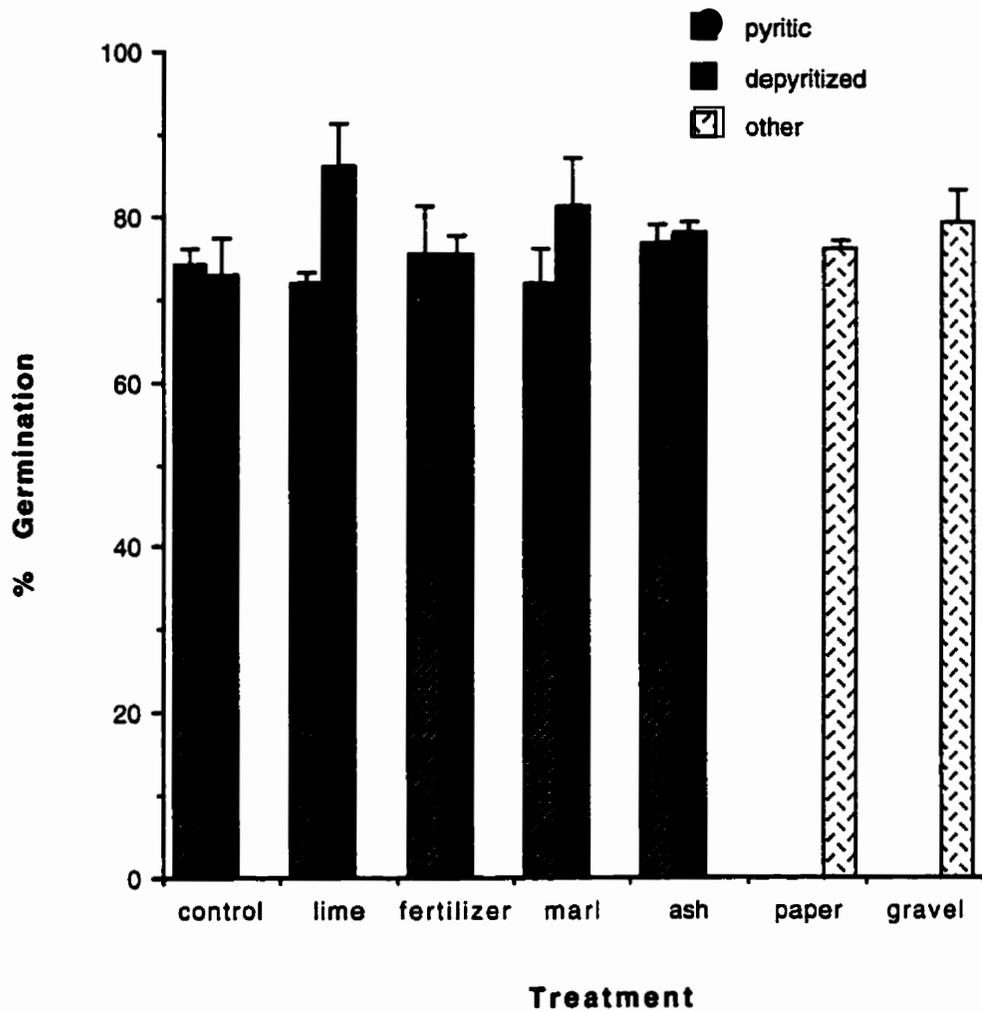


Figure 4: Mean germination rates (+ S.E. ; n=3) of Redtop grass seeds germinated on paper, gravel, unamended (control) tailings and four amended tailings, for two tailings types (Experiment 1).

osmotic condition that inhibits moisture imbibition.

Turner (1988) found that a lower pH decreased percent germination, and also decreased the time until germination occurred in *Paulownia tomentosa*. Although the seeds germinated more quickly, primary root growth was slowed. Thus Turner suggested that lower soil pH may impede root development, increasing the probability of desiccation. This is a very important consideration in establishing vegetation directly on tailings.

Overall, root growth was significantly better on depyritized tailings than on pyritic tailings for all treatments (Figure 5). Fertilizer was the only treatment that had a significant effect on root growth, exhibiting an inhibitory effect. Root growth on depyritized tailings was similar to that on gravel, except where fertilizer was applied, while growth on pyritic tailings was, at best, half as good as on gravel. Growth on filter paper alone was far better than that on the pyritic, depyritized and gravel treatments, and may simply be a reflection of the growth-restricting metals present in each of the waste materials tested, and generally poor nutrient status of the gravel.

A Kolmogorov-Smirnov test indicated that the root data were not normally distributed [$z=31.01$, $p<0.001$], even after data transformations were attempted.

A 2 way ANOVA on the original root data indicated significant substrate and treatment main effects, but subsequent 1-way ANOVAs (Bartlett-Box F) on substrate and treatment effects indicated a lack of homogeneity of variance. A 2-way ANOVA on \log_{10} transformed data produced a substrate x treatment interaction [$F(4,1138)=34.4$, $p<0.001$] in addition to substrate [$F(1,1138)=288.2$, $p<0.001$; $\eta^2=0.36$] and treatment [$F(4,1138)=149.2$, $p<0.001$; $\eta^2=0.52$] main effects. Both effects combined accounted for 41.4% ($r^2=0.414$) of the observed variance in the data. It should be noted that the degrees of freedom differ from those of the germination data because the germination values were calculated on a per plate basis, while root lengths were obtained on an individual basis ie ~ 40-50 per Petri dish.

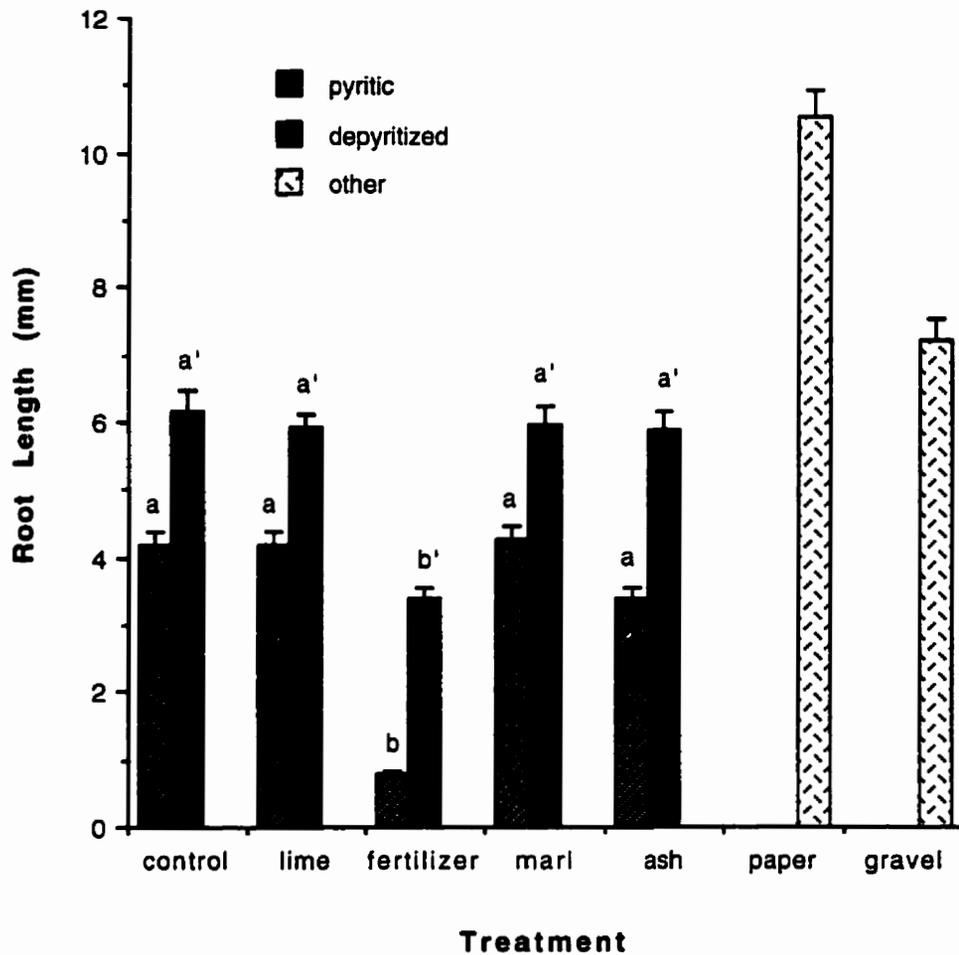


Figure 5: The effect of amendments on mean root length (+ S.E. ; n=3) of Redtop seedlings grown in pyritic and depyritized tailings, in comparison with a control (unamended), paper and gravel (Experiment 1). Different superscripts, both between pairs and within treatments, indicate significant differences in a Scheffé multiple range test ($p=0.05$) following \log_{10} transformation.

A 1-way ANOVA carried out on the substrate x treatment combinations for the \log_{10} transformed data, indicated significant differences among groups [$F(9,1138)=115.4$, $p<0.0001$], although heterogeneity of variance was still indicated. A Scheffé multiple range test ($p=0.05$) indicated that fertilizer significantly decreased growth when added to both pyritic and depyritized tailings relative to the control (Figure 5). However, it decreased growth on pyritic by 82%, but by only 45% on depyritized tailings. Thus, the source of the interaction appears to be the relative effect of the fertilizer amendment. Because heterogeneity of variance was indicated, Kruskal-Wallis and Mann-Whitney non-parametric tests were employed to confirm these findings, and they yielded identical conclusions.

Fertilizers that contain ammonium, or otherwise can form ammonia in the soil, tend to increase soil acidity through oxidation to nitric acid (Brady, 1990). Shetron (1976) attributed plant mortality on iron tailings following the application of fertilizer to an increase in soluble salt content. The observed root growth differential between pyritic and depyritized tailings is probably due to enhanced metal solubility and therefore toxicity in the pyritic tailings, as a result of the drop in pH normally associated with fertilizer applications, combined with an increase in soluble salt content. Curtin and Smillie (1986) indicated that the likelihood of plant metal toxicities increases very greatly when soil pH declines to values less than 5. While not measured, it is entirely possible that the pH of the pyritic tailings dropped from an initial value of 5.77 (Table 1) to near 5, but is less likely for the depyritized tailings, which had an initial pH of 7.38. Therefore, metal toxicity was more of an immediate problem in pyritic tailings than in depyritized tailings.

Differences in shoot length between substrates and amendments were minimal (Figure 6).

A Kolmogorov-Smirnov test indicated that the shoot data were not normally distributed ($z=36.61$, $p<0.001$), even after transformations were attempted. A 2-way ANOVA on the original data produced a significant substrate effect [$F(1,1138)=17.05$, $p<0.001$; $\eta^2=0.12$], but no treatment effect. In addition to the substrate effect, the 2-way ANOVA also yielded a substrate x treatment interaction

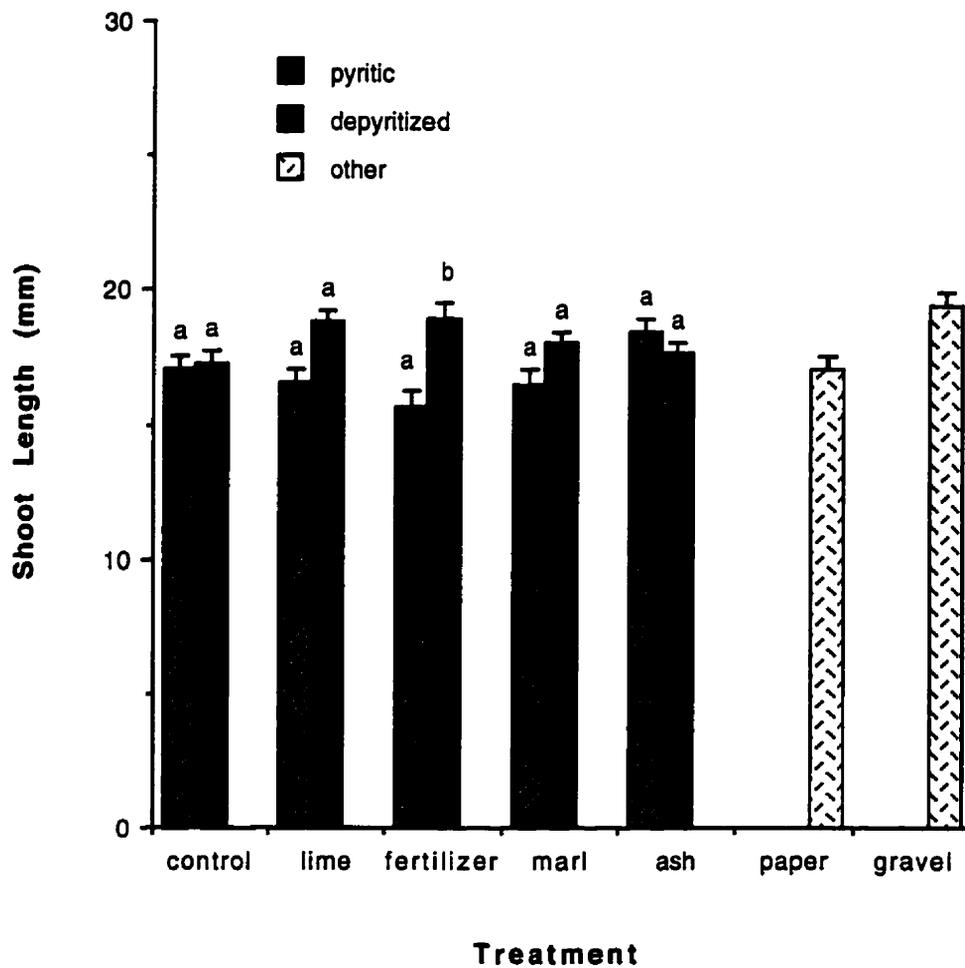


Figure 6: The effect of amendments on mean shoot lengths (+ S.E. ; n=3) of Redtop seedlings grown in pyritic and depyritized tailings, in comparison with controls (Experiment 1). Different superscripts indicate significant differences within pairs at $p=0.05$.

[F(4,1138)=5.25,p<0.001]. Overall, the two variables accounted for 1.8% ($r^2=0.018$) of the variability, representing statistically weak effects.

A 1-way ANOVA on the computed interactions, although indicating slight heterogeneity of variance, showed significant differences by group [F(9,1138)=4.75, p<0.0001]. A Scheffé Multiple Range Test (p=0.05) showed that shoot growth in depyritized tailings was significantly better than in pyritic tailings for the fertilizer treatment only (Figure 6). This is likely a reflection of the much poorer root growth exhibited in pyritic tailings with the addition of fertilizer (Figure 5). The interaction was confirmed by nonparametric Mann-Whitney tests.

Analysis of the \log_{10} transformed shoot data also showed a significant substrate effect in addition to a substrate x treatment interaction, although the interaction effect was smaller than for the original data. Subsequent analysis of the \log_{10} transformed interactions via 1-way ANOVA indicated no differences and greater heterogeneity of variance than obtained with the original data. Thus, analysis of the original data was deemed appropriate.

Root:shoot ratios were calculated but are not shown. They were essentially a reflection of the root data, since by far, the greatest treatment effects were exhibited by the roots, with only minor differences in the shoots. Roots, being in direct contact with the growth medium, usually react in a more sensitive fashion than shoots during early seedling growth, and hence they are the most commonly used indicators of toxicity as pioneered by Wilkins (1957).

Overall, these results indicate that while germination was unaffected, early root growth was definitely better on depyritized tailings. This appeared to be due to root inhibition by toxic levels of metals in the pyritic tailings, such as water soluble Cd, Co, Mn, Ni and especially Zn (Table 3). The limiting factor during the early stages of growth is root development. After successful germination, developing seedlings must produce a healthy root system in order to support and provide nutrients for above ground growth. Smith and Bradshaw (1972) state that heavy metal toxicity frequently causes the complete inhibition of root growth. They attributed plant mortality on heavy metal contaminated soils to the susceptibility of plants to droughtiness as they lack sufficient root development.

Patterson and Olson (1983), in looking at the effects of metals on pine and spruce seed germination and growth, found that the major effect appears to be the reduction in radicle elongation at relatively low metal concentrations, with seed germination being relatively unaffected. In agreement with Smith and Bradshaw (1972), Patterson and Olson further state that metals are not only toxic by themselves, but can increase the likelihood of seedling mortality from other environmental stresses such as moisture stress.

Carter (1978) found that the major cause of plant mortality in four tree species was related to zinc, as seedlings took up increasingly more zinc from the soil as the concentration of zinc increased in the soil, and White *et al.* (1979) indicated that zinc did not affect seed germination in soybean, but that plants at the seedling stage or older were adversely affected by zinc toxicities.

Surprisingly, the addition of neutralizing agents (limestone, marl, ash) were not effective at increasing root growth in pyritic tailings. This was probably due to the already near-neutral pH of the pyritic tailings (Table 1). Since little oxidation (and drop in pH) of the pyritic tailings likely occurred, the neutralizers were of no benefit over such a short time frame.

Therefore, it seems that in the short term, the addition of amendments (at levels used in this experiment) were not helpful in seedling establishment.

Because the establishment of vegetation directly on tailings is often considered to be ineffective in preventing/decreasing oxidation of fresh tailings (Veldhuizen *et al.*, 1987), the use of these materials as amendments to tailings was not considered further. Instead, attention was focused on their use as cover materials, which might inhibit tailings oxidation.

3.3.2.4 Summary of Findings

- 1) None of the materials tested produced a significant effect on germination of Redtop.
- 2) Root growth of Redtop in depyritized tailings was significantly better than in pyritic tailings for all treatments tested.

3) Fertilizer was the only amendment that produced a significant effect on root growth in Redtop, causing a decrease in length in both pyritic and depyritized tailings.

4) Leaf growth in depyritized tailings was superior to that on pyritic tailings for the fertilizer treatment only.

3.3.3 Experiment 2: Comparison of Germination and Early Growth in Waste Materials

3.3.3.1 Purpose

This experiment was conducted in order to compare germination and early growth of Redtop seedlings on sewage incinerator ash, gold tailings, granulated slag and a gravel reference material (Willisville) for use as potential cover materials.

3.3.3.2 Methods and Materials

All substrate samples were air dried for approximately 24 hours prior to being used. Twenty grams each of sewage incinerator ash, granulated slag, gold tailings and gravel (control) were placed between filter papers in plastic Petri dishes, with each treatment replicated five times. Fifty seeds of Redtop (*Agrostis gigantea* Roth.) were counted out under a dissecting microscope and placed on the upper filter paper of each plate.

The plates were kept under darkened conditions until seed germination was initiated, then were placed on a well-lighted benchtop in the lab for a period of approximately one week. Root and shoot lengths were then measured and the percent germination determined.

Normality of the data was tested using the Kolmogorov-Smirnov test and homogeneity of variance using Bartlett-Box 'F' test. Oneway ANOVA's and Scheffé's Multiple Range Tests were used to analyze the data. Data were log₁₀ transformed in an attempt to improve normality and reduce heterogeneity of variance, and re-analyzed as above. Where assumptions of normality and homogeneity of variance were violated, findings were verified using Kruskal-Wallis and Mann-Whitney non-parametric tests.

3.3.3.3 Results and Discussion

Results of this experiment, with the exception of germination, are presented in Figures 7-8. While some statistics were computed using log₁₀ transformed data, for ease of interpretation all results presented are of the original data. Where

transformed data were used, significant differences are indicated based on the statistical analysis of the transformed data.

A Kolmogorov-Smirnov test on the germination data indicated that the data were not normally distributed ($z=7.03$, $p<0.001$).

A 1-way ANOVA indicated that there was no significant difference in percent germination for any of the substrates [$F(3,16)=0.91$, $p=0.46$], averaging approximately 70-75%. Although there was heterogeneity of variance, identical findings were obtained by ANOVA with \log_{10} transformed data, and a nonparametric Kruskal-Wallis rank sum test

Mean root lengths were found to be significantly different among all four substrates tested (Figure 7).

A Kolmogorov-Smirnov test indicated that the root data were not normally distributed ($z=22.62$, $p<0.001$) even after transformations were attempted.

A 1-way ANOVA on the untransformed root data indicated a strong substrate effect, and a subsequent Scheffé's Multiple Range Test ($p=0.05$) showed that all four substrates were significantly different from each other. However, extreme heterogeneity of variance was indicated. A \log_{10} transformation provided homogeneity of variance, and a oneway ANOVA yielded a strong substrate effect [$F(3,719)=293.5$, $p<0.0001$]. A Sheffé Multiple Range Test ($p=0.05$) indicated that root growth in all substrates was significantly different (Figure 7). A Kruskal-Wallis rank sum test confirmed this interpretation ($\chi^2=356.8$, $p<0.0001$), and significant differences were located using Mann-Whitney tests.

The gold and ash treatments showed a slight inhibitory effect on root growth compared to the gravel control, while root growth in the slag substrate was severely inhibited.

The extremely poor root growth in slag can likely be attributed to a relatively high level of water soluble copper, combined with low nutrient levels (Table 3). Similar findings have been demonstrated Hogan and Rauser (1979) who, in looking at the relative toxicity of Co, Cu, Ni, and Zn to *A. gigantea*, found that Cu

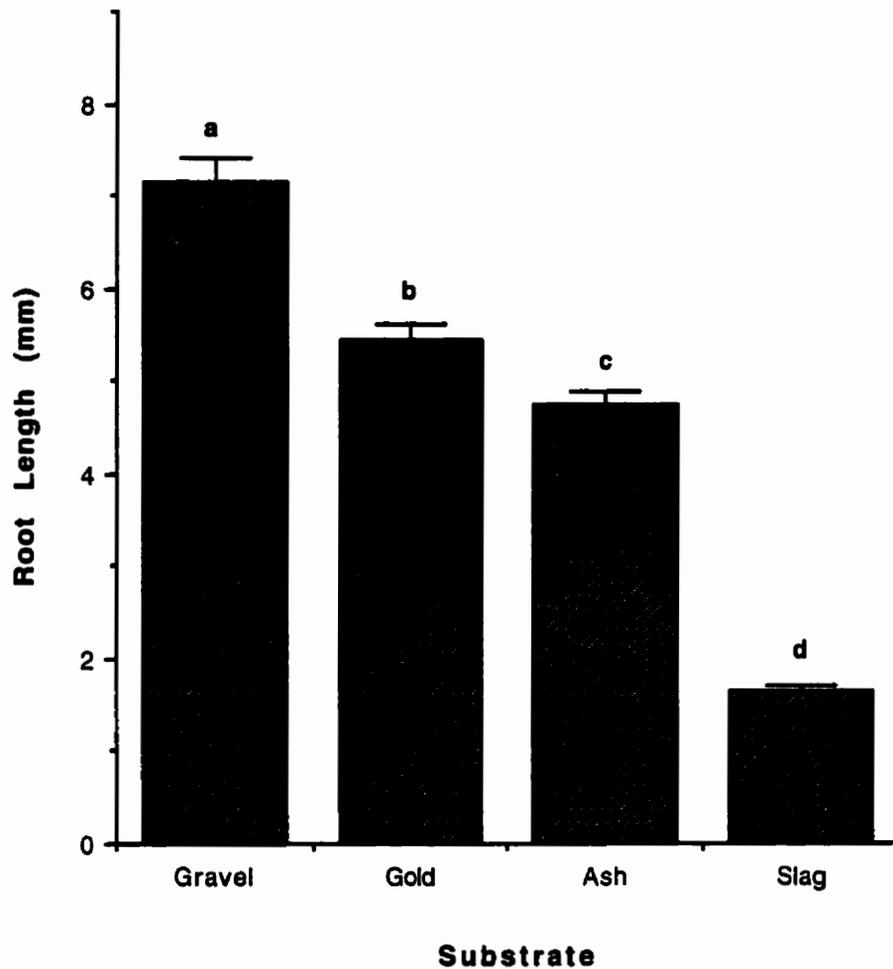


Figure 7: Mean root length (+ S.E. ; n=5) for seedlings of *A. gigantea* grown in waste materials and a gravel control (Experiment 2). Different superscripts indicate significant differences at p=0.05.

was most toxic (as measured by reduced root growth), followed by Ni, Co, and Zn. Similar results were also found by Rauser and Winterhalder (1985) for *A. gigantea*, Jowett (1958) for *A. tenuis*, Wong and Bradshaw (1982) for *Lolium perenne*, and Whitby and Hutchinson (1974) for tomato plants.

Mean shoot (first leaf) lengths were found to be higher in gravel and incinerator ash, as shown in Figure 8.

A Kolmogorov-Smirnov test indicated that the shoot data also had a non-normal distribution ($z=26.56$, $p<0.001$) even after transformations were attempted. A 1-Way ANOVA of the original data yielded a significant substrate effect [$F(3,719)=8.6$, $p<0.0001$], though showed heterogeneity of variance. A Scheffé's Multiple Range Test ($p=0.05$) indicated that shoot growth in incinerator ash was not significantly different from shoot growth in the gravel control, but that both were different from shoot growth in gold tailings and slag (Figure 8). This slightly increased shoot growth in incinerator ash can likely be attributed to elevated soluble phosphorus levels (Table 3), an effect not seen in the roots because of inhibition of roots by metals in the ash.

Analysis of the \log_{10} transformed data yielded no significant differences, although it resulted in an increase in heterogeneity of variance. A Kruskal-Wallis rank sum test indicated significant differences by substrate ($\chi^2=40.8$, $p<0.0001$), and Mann-Whitney tests confirmed the findings of the Scheffé test for the original data. Thus, the analysis of the original data was accepted.

Because there was very little difference in shoot lengths amongst substrates, root:shoot ratios were a reflection of the variation which occurred in the root data, and are not presented.

3.3.3.4 Summary of Findings

- 1) None of the materials tested produced a significant effect on the germination of Redtop.

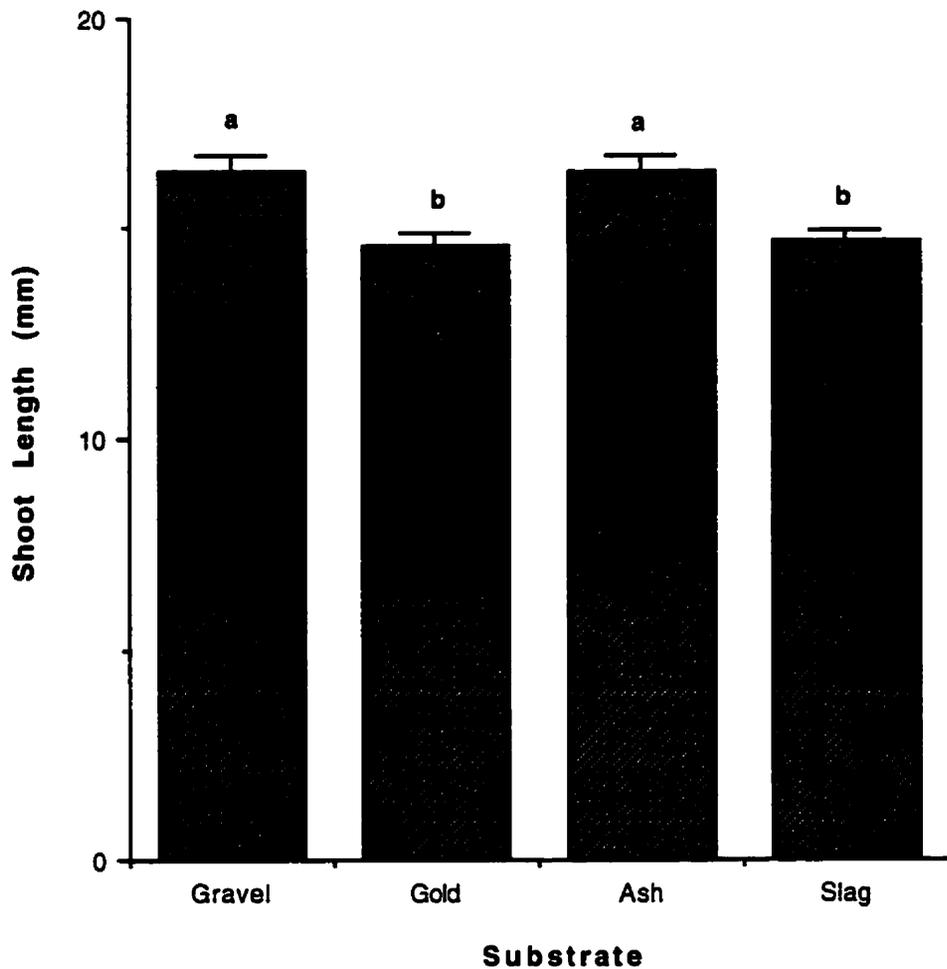


Figure 8: Mean shoot length (+ S.E. ; n=5) for seedlings of *A. gigantea* grown in waste materials and a gravel control (Experiment 2). Different superscripts indicate significant differences at $p=0.05$.

2) The best root growth of Redtop occurred on the gravel control, followed by gold tailings, incinerator ash and slag. The extremely poor root growth in slag was hypothesized to be caused by water soluble copper and low nutrient levels.

3) Leaf length of Redtop was greatest on the gravel control and incinerator ash, though these differences were small and are not likely of biological consequence at this stage of growth.

3.3.4 Experiment 3: Comparison of Germination and Early Growth in Waste Materials with the Addition of Limestone

3.3.4.1 Purpose

This experiment tested the effect that each of the potential cover materials, with and without the addition of dolomitic limestone, had on germination and early root and leaf growth. This was essentially the same as the previous experiment, except that pyritic and depyritized tailings were included for the sake of comparison, and the effect of limestone was tested. The addition of limestone was originally included to combat what was supposed to be low pH in the granulated slag (~3.7). However, at termination of the experiment it was determined that the pH of the original slag was actually much higher than originally thought (~6.4), and that the initial reading of approximately 3.7 was erroneous.

3.3.4.2 Methods and Materials

Twenty grams of pyritic tailings, depyritized tailings, incinerator ash, granulated slag or gold tailings respectively, with and without the addition of 0.2 grams (1:100, equivalent to a rate of ~6T/ha incorporated to a depth of 10 cm) of ground dolomitic limestone, were placed between filter papers in plastic Petri dishes. Fifty seeds of *Agrostis gigantea* (Redtop) were placed on the top filter paper. All treatments were replicated five times in a randomized block design (Heath, 1970);

i.e. 5 materials x 2 treatments x 5 replicates = 50 plates.

The plates were kept mainly under darkened conditions until germination occurred, then were subjected to normal daylight conditions for a period of 8 days. Root and shoot growth were measured to the nearest millimetre, % germination determined, and root:shoot ratios calculated. Finally, the surface pH of each material was measured.

Normality of the data was tested using the Kolmogorov-Smirnov test and homogeneity of variance using Bartlett-Box 'F' test. Two-way ANOVA's, 1-way ANOVA's and Scheffé's Multiple Range Tests were employed to analyze the data.

Data were \log_{10} transformed to correct/reduce normality and heterogeneity of variance problems whenever necessary, and re-analyzed as above. Where interactions were indicated, all possible variable combinations were computed and subjected to a 1-way ANOVA and Scheffé's Multiple Range Test to determine the source of the interaction. These results were then verified using Kruskal-Wallis and Mann-Whitney non-parametric tests.

3.3.4.3 Results and Discussion

While some statistics were computed using \log_{10} transformed data, for ease of interpretation all results presented are of the original data. Where transformed data were used, significant differences are indicated based on the statistical analysis of the transformed data.

Germination rates were not affected by any of the treatments or by the addition of limestone.

A Kolmogorov-Smirnov test indicated that the germination data were not normally distributed ($z=7.07$, $p<0.001$).

A 2-way ANOVA on the original germination data showed no significant differences by either substrate or limestone on percent germination. A 2-way ANOVA on the transformed data also failed to show any significant differences in germination, as did a non-parametric Kruskal-Wallis test. Germination averaged approximately 70-75%.

Mean root length was greatest in gold tailings and depyritized tailings, and was found to increase with the addition of limestone in slag only (Figure 9).

The root data were not normally distributed as shown by a Kolmogorov-Smirnov test ($z=35.3$, $p<0.001$). A 2-way ANOVA on the \log_{10} transformed root data revealed a strong substrate effect [$F(4,1827)=455.9$, $p<.001$; $\eta^2=0.71$], a small limestone effect [$F(1,1827)=4.42$, $p=0.04$; $\eta^2=0.03$], and a substrate x limestone interaction [$F(4,1827)=3.31$, $p=0.01$], with the two variables (substrate and limestone) accounting for 49.8% of the variance ($r^2=0.498$). A 1-way ANOVA of the substrate-limestone combinations revealed a significant group effect

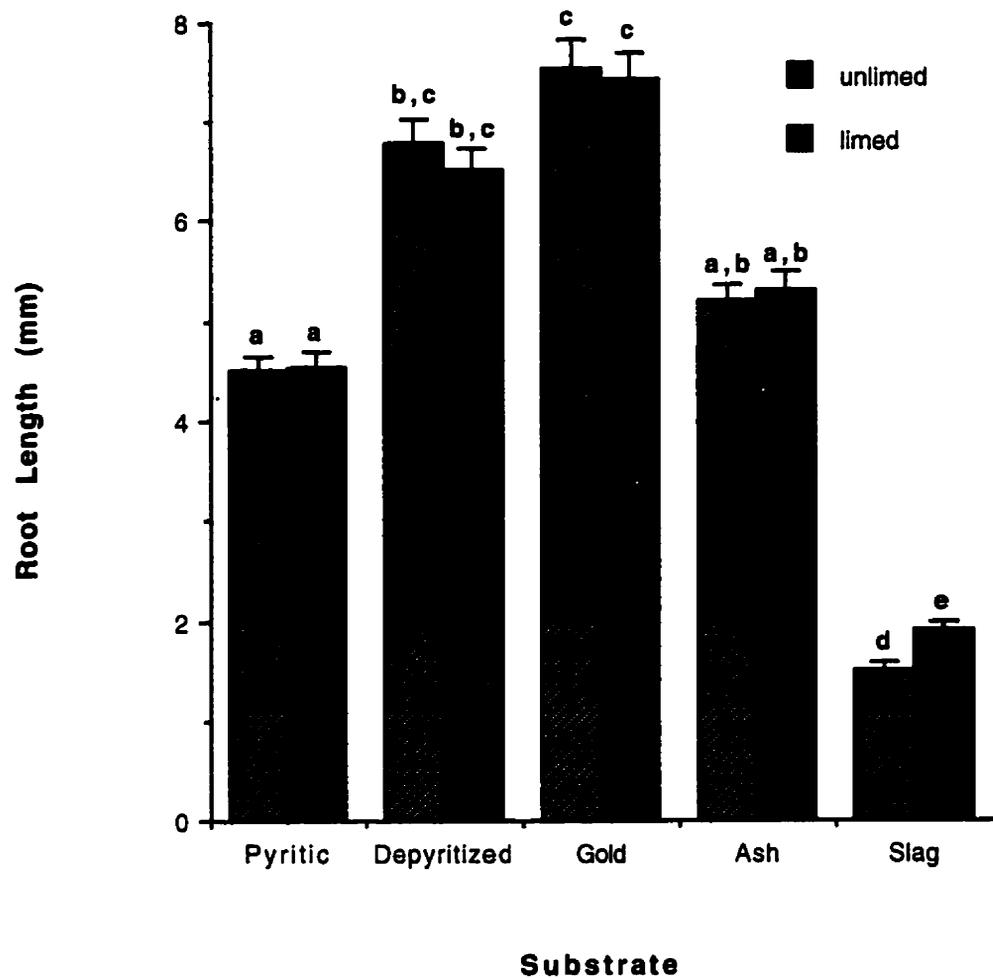


Figure 9: Mean root length (+ S.E. ; n=5) for seedlings of *A. gigantea* grown in waste materials in comparison with growth in pyritic tailings (Experiment 3). Different superscripts indicate significant differences at $p=0.05$.

[F(9,1827)=204.5, $p<0.0001$] and a Scheffé multiple range test ($p=0.05$) revealed that root length was greatest in gold tailings and poorest in slag. In addition, limestone produced significantly better root growth in slag, but not in any of the other substrates, and represents the source of the observed interaction (Figure 9).

As in the previous experiment, root growth was severely inhibited when grown in slag, and was attributed to higher water soluble copper and low nutrient levels. The addition of limestone produced slightly better root growth in slag due to metal binding, in particular copper. This is in agreement with the findings of Winterhalder (1996), who found that the addition of dolomitic limestone was effective at decreasing water-soluble copper levels in contaminated soils.

The addition of limestone had no effect on mean shoot length, but small differences were found in shoot lengths between substrates (Figure 10).

A Kolmogorov-Smirnov test indicated that the shoot data were not normally distributed ($z=42.2$, $p<0.001$).

A 2-way ANOVA on the \log_{10} transformed shoot data indicated that there was a significant substrate effect [F(4,1827)=19.48, $p<0.001$; $\eta^2=0.20$], but that limestone had no effect. The two variables accounted for 4.1% of the variance ($r^2=0.041$), indicating a rather weak statistical effect.

A 1-way ANOVA on the shoot data indicated a significant substrate effect [F(4, 1836)=19.27, $p<0.0001$] though slight heterogeneity of variance was indicated. A Scheffé's test ($p=0.05$) showed that growth in incinerator ash was significantly better than growth in all other materials, and that growth in slag was significantly less than in pyritic tailings (Figure 10). Once again, better growth in incinerator ash was likely due to greater soluble phosphorus levels.

Analysis by nonparametric Mann-Whitney tests confirmed the above findings, but also indicated that growth in pyritic tailings was significantly higher than in depyritized and gold tailings, and that growth in gold tailings was significantly higher than in slag.

Root:shoot ratios were calculated, but as differences in shoot length were rather

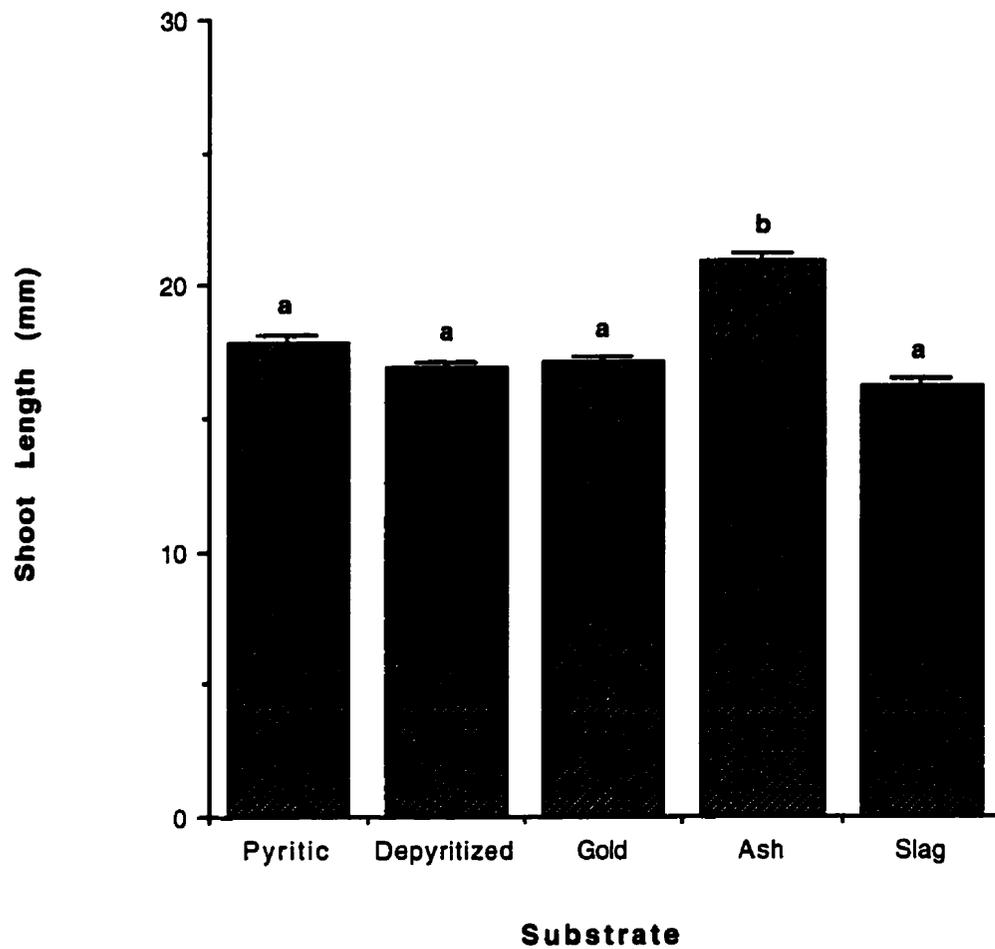


Figure 10: Mean shoot length (+ S.E. ; n=5) for seedlings of *A. gigantea* grown in waste materials in comparison with growth in pyritic tailings (Experiment 3). Different superscripts indicate significant differences at $p=0.05$.

small, are not presented because they were essentially a reflection of the variation occurring in the root data.

It was originally thought that the poor root growth on slag observed in the second germination study (Experiment 2) was primarily due to low pH (3.71) initially measured on the original material, and therefore increased metal toxicity. The surface pH of the slag after the experiment was found to be 6.83, and upon retesting, the pH of the original material was found to be 6.40. The reason for this error in pH measurement is unknown.

The principal role of limestone is to reduce acidity, which decreases the concentration of soluble metals that are potentially toxic to plants, especially during germination and early growth (establishment). The application of limestone to materials that are already neutral or circumneutral would be expected to have little effect (Chaney *et al.*, 1977; Carrucio *et al.*, 1988; Brady, 1990). However, because limestone also plays a role in binding metals (Chaney *et al.*, 1977; Curtin and Smillie, 1986), thereby decreasing metal phytotoxicity, the experiment was not totally unwarranted. Winterhalder (1996) indicated that calcium and magnesium ions in dolomitic limestone may be involved in the competitive exclusion of metal ions from the exchange complex of root-hairs, and that calcium may also play a role in improving membrane integrity.

A Kolmogorov-Smirnov test indicated that the pH data were not normally distributed ($z=7.07$, $p<0.001$).

In this case, a 2-way ANOVA indicated that the addition of limestone did not produce a significant pH response in any of the substrates (therefore the data were pooled), but that there was a significant difference between substrates [$F(4,40)=83.7$, $p<0.001$; $\eta^2=0.94$]. The combination of both variables (limestone and substrate) accounted for 89.1% of the variance ($r^2=0.891$). A 1-way ANOVA revealed a significant substrate effect [$F(4,45)=91.6$, $p<0.0001$] and a Scheffé test indicated that pH was highest in the gold tailings and incinerator ash, followed by depyritized tailings, slag and pyritic tailings (Table 7). These results were confirmed by nonparametric Mann-Whitney tests.

While the initial purpose of this experiment (response to limestone) was questionable, it did provide a comparison of germination and early growth on pyritic and depyritized tailings to the other materials, and also confirmed the general findings of the previous experiment.

Table 7: Final pH (n=5) of Potential Cover Materials at Completion of a Petri Dish Study (Experiment 3). Materials with the Same Superscript were Not Significantly Different at p=0.05).

Media	pH
Pyritic Tailings	d 6.45
Depyritized Tailings	b 7.41
Gold Tailings	a 8.05
Sewage Incinerator Ash	a 7.97
Granulated Slag	c 6.90

3.3.4.4 Summary of Findings

- 1) Limestone had no effect on germination, root or shoot length of Redtop for any of the materials tested.
- 2) Gold tailings and depyritized tailings produced the best root growth of Redtop, followed by incinerator ash and pyritic tailings, with slag producing very little root growth.
- 3) Incinerator ash produced slightly better shoot growth of Redtop than the other substrates, possibly due to elevated phosphorus, while no significant differences were found between the remainder of the materials.

3.4 Sustained Growth (Pot Bioassays)

3.4.1 Experiment 4: Addition of Limestone and Fertilizer to Pyritic and Depyritized Tailings

3.4.1.1 Purpose

This experiment was designed to determine the effect of dolomitic limestone and fertilizer, singly and in combination, on the productivity of a grass mixture grown on pyritic tailings, depyritized tailings and a 50-50 mix of the two.

3.4.1.2 Methods and Materials

The experiment was based on a randomized block design with 5 blocks, i.e. 3 growth substrates (pyritic, depyritized and 50/50 mix) x 4 (2 x 2 factorial) treatments x 5 replicates = 60 pots. Treatments were based on ~15T/ha limestone and ~3T/ha fertilizer (incorporated to a 10 cm depth), as follows:

Treatment 1 - Control (no limestone or fertilizer)

Treatment 2 - 12 g limestone per pot (1:100)

Treatment 3 - 3 g fertilizer per pot (0.25:100)

Treatment 4 - 12 g limestone + 3 g fertilizer per pot

Twelve hundred grams of tailings, with the addition of the appropriate amendment, were thoroughly mixed in a small plastic bag before being placed in a 9 cm square pot. A number 3 Whatman filter paper had been placed in the bottom of each pot in order to retain the tailings. After thoroughly wetting each pot, 0.2 grams of Sudbury seed mixture were sown at a depth of approximately 0.25 cm.

The experiment was set up in a greenhouse, and watered regularly with demineralized water for approximately 3 months, at which time the resulting vegetation was harvested. Harvesting began with the clipping of the above ground portions at the tailings surface and placing them in small paper envelopes. The pH of the tailings surface was determined, and the roots were carefully washed out of the tailings and placed in small paper envelopes. All samples were then oven-dried at 70-80°C, and the dry weight determined.

Normality of the data was tested using Kolmogorov-Smirnov tests and homogeneity of variance using Bartlett-Box 'F' test. Statistical analysis then proceeded through the use of 3-way ANOVAs followed by 1-way ANOVAs and Scheffé's Multiple Range Tests. Where an interaction was found, all combinations were calculated and analyzed via 1-way ANOVA and Scheffé's Multiple Range Tests. The data were square root transformed to correct/improve heterogeneity of variance where necessary. Where assumptions of normality and homogeneity of variance were violated, findings were verified through Kruskal-Wallis and Mann-Whitney nonparametric tests.

3.4.1.3 Results and Discussion

While some statistics were computed using square root transformed data, for ease of interpretation all results presented are of the original data. Where transformed data were used, significant differences are indicated based on the statistical analysis of the transformed data.

Square root transformations produced homogeneity of variance for all variables except root/shoot ratios and pH, for which homogeneity of variance was already present in the original data.

Overall, root growth was best in depyritized tailings, followed by the 50/50 mixture and pyritic tailings respectively (Figure 11). In addition, fertilizer increased root growth in pyritic tailings and the 50/50 mix, but not in the depyritized tailings. Limestone had no effect on root growth.

A Kolmogorov-Smirnov test indicated that the root data were not normally distributed ($z=3.90$, $p<0.001$).

A 3-way analysis of variance (substrate, limestone, fertilizer) on the square root transformed root data yielded a substrate effect [$F(2,48)=142.0$, $p<0.001$; $\eta^2=0.85$], a fertilizer effect [$F(1,48)=46.3$, $p<0.001$; $\eta^2=0.34$] and a substrate x fertilizer interaction [$F(2,48)=4.38$, $p=0.02$]. Because limestone failed to show a significant statistical effect, either on its own or in combination with other variables, the limestone data were subsequently pooled. The three variables accounted for 83.9% ($r^2=0.839$) of the variance. A subsequent 1-way ANOVA on

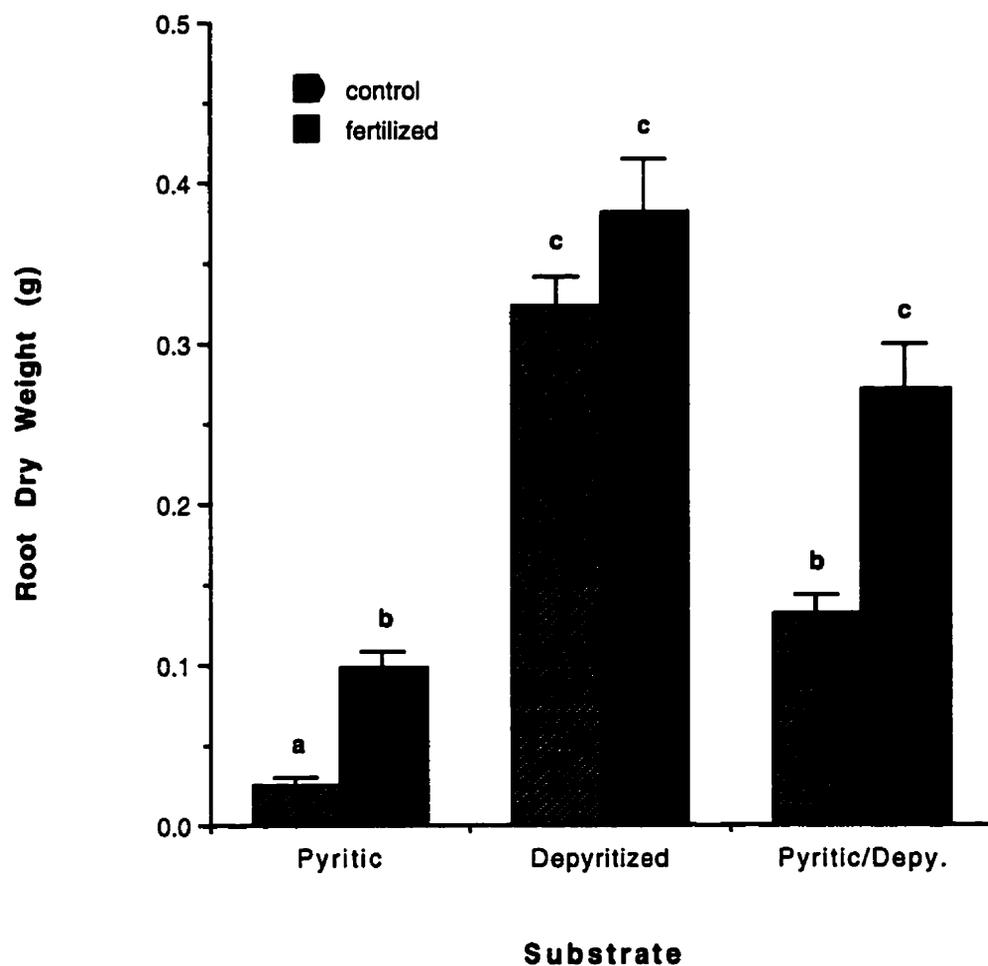


Figure 11: Mean root weight per pot (+ S.E. ; n=10) for a grass-legume seed mixture grown in pots in pyritic tailings, depyritized tailings and a 50/50 mixture (Experiment 4). Different superscripts indicate significant differences at p=0.05.

the computed interactions indicated a significant group effect [$F(5,54)=65.98$, $p<0.0001$], and a Scheffé multiple range test determined that fertilizer significantly increased root growth in the pyritic tailings and the 50/50 mix, but not in the depyritized tailings (Figure 11). This differential in root growth represents the source of the observed interaction.

In addition, without fertilizer, root growth was significantly different among all three substrates, being highest in the depyritized and lowest in the pyritic tailings. With fertilizer, root growth was significantly higher in depyritized tailings and the 50/50 mix than in pyritic tailings, although the former were not significantly different from each other.

These results were confirmed by a nonparametric Kruskal-Wallis rank sum test ($\chi^2=48.5$, $p<0.0001$), with specific differences identified by Mann-Whitney tests. The findings were identical, except that a significant difference was indicated between fertilized depyritized tailings and the fertilized 50/50 mix. Since homogeneity of variance was not violated, the parametric tests were deemed most appropriate.

While overall growth was expected to be poorer in pyritic tailings because of increased soluble levels of such metals as Cd, Co, Mn, Ni and Zn, a significant response to fertilizer in the pyritic tailings but not in the depyritized tailings was unexpected. This is also in contrast to the findings of the first germination experiment, where fertilizer decreased early growth in both pyritic and depyritized tailings. Perhaps nitrogen residues were present in the depyritized tailings as a result of the depyritization process, in which organic chemicals are used in a flotation process to remove sulphides. Both phosphorus and potassium are already present in similar quantities in water soluble form (Table 3) in both the pyritic and depyritized tailings, suggesting that nitrogen may be responsible for the observed difference in growth. Ebelhar *et al.* (1982) found that the application of nitrogen significantly increased dry matter yields of Common Bermudagrass grown on coal spoils, while phosphorus and potassium had no effect on yield.

Shoot growth was significantly different in all three substrates, and was increased by the addition of fertilizer (Figure 12).

A Kolmogorov-Smirnov test indicated that the shoot data were not normally distributed ($z=3.89$, $p<0.001$).

A 3-way ANOVA (substrate, limestone, fertilizer) on the square root transformed shoot data revealed significant substrate [$F(2,48)=67.8$, $p<0.001$; $\eta^2=0.74$] and fertilizer [$F(1,48)=59.0$, $p<0.001$; $\eta^2=0.49$] effects. Because limestone failed to show a significant statistical effect, either on its own or in combination with other variables, the limestone data were subsequently pooled. The three variables accounted for 78.5% ($r^2=0.785$) of the variance. While the data displayed identical trends to those of the root data, no measurable statistical interaction was observed.

A subsequent 1-way ANOVA indicated a significant substrate effect [$F(2,57)=34.2$, $p<0.0001$] and a Scheffé test revealed that shoot growth on all three materials were significantly different, with growth best on depyritized tailings (a function of increased root growth and the possible presence of nitrogen) and worst on pyritic tailings (Figure 12a). A 1-way ANOVA also indicated that shoot growth was significantly better with the addition of fertilizer [$F(1,58)=18.1$, $p=0.0001$] (Figure 12b). The increase in shoot growth was simply a reflection of the low levels of nitrogen and phosphorus in the tailings. Identical results were obtained using a Kruskal-Wallis rank sum test for substrate ($\chi^2=31.8$, $p<0.0001$) and fertilizer ($\chi^2=12.5$, $p=0.0004$), with specific differences located by Mann-Whitney tests.

Mean root:shoot ratios were higher for seedlings grown in depyritized tailings than in either pyritic tailings or the 50/50 mix, and were decreased by the application of fertilizer (Figure 13).

A Kolmogorov-Smirnov test indicated that root:shoot data were not normally distributed ($z=5.91$, $p<0.001$).

A 3-way ANOVA (substrate, limestone, fertilizer) of the original root:shoot ratios indicated significant substrate [$F(2,48)=19.6$, $p<0.001$; $\eta^2=0.61$] and fertilizer [$F(1,48)=9.3$, $p=.004$; $\eta^2=0.30$] effects, but no interaction. Because limestone failed to show a significant statistical effect, either on its own or in combination with other variables, the limestone data were subsequently pooled. Overall, the

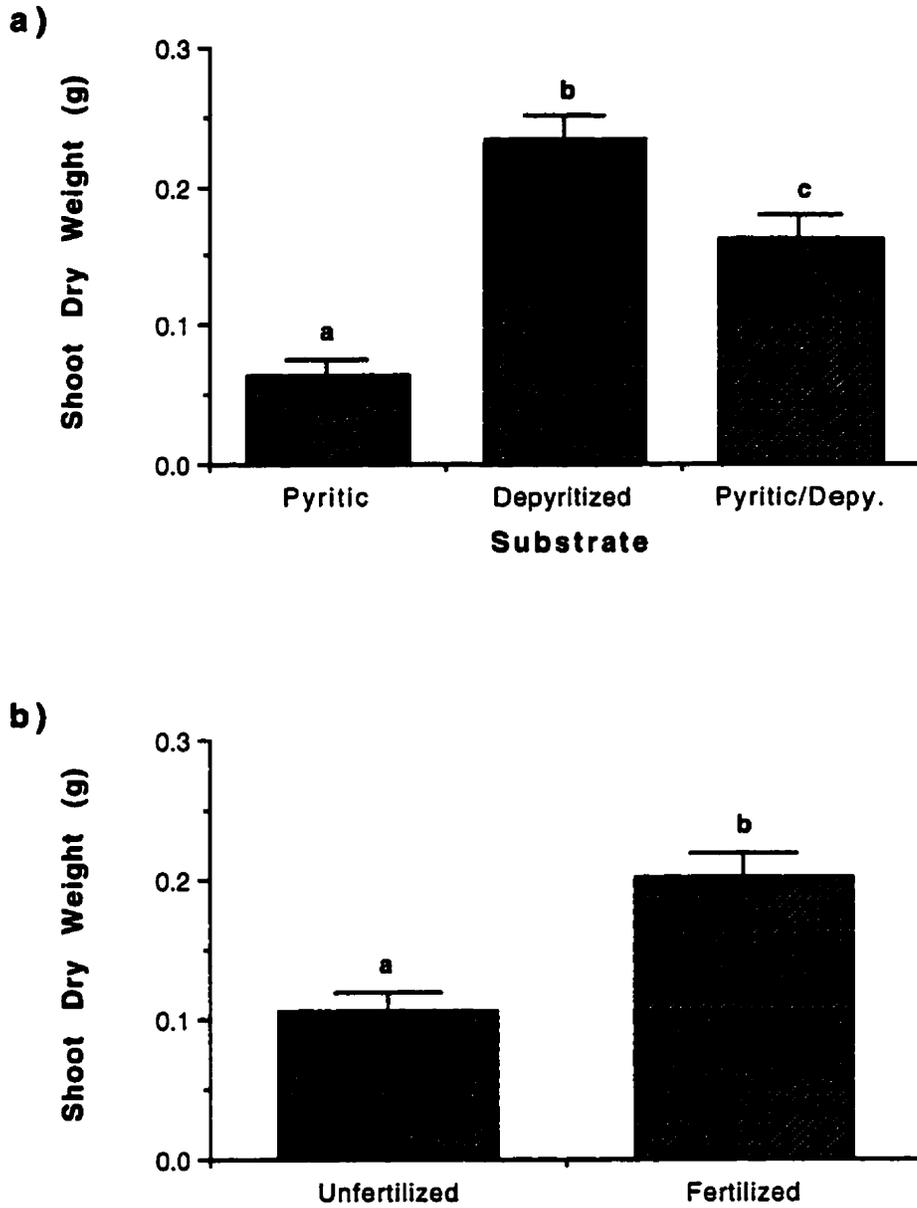


Figure 12: Mean shoot weight (+ S.E.) by a) substrate (n=20) and b) fertilizer (n=30), for a grass-legume seed mix grown in pots in pyritic tailings, depyritized tailings, and a 50/50 mixture (Experiment 4). Different superscripts indicate significant differences at p=0.05.

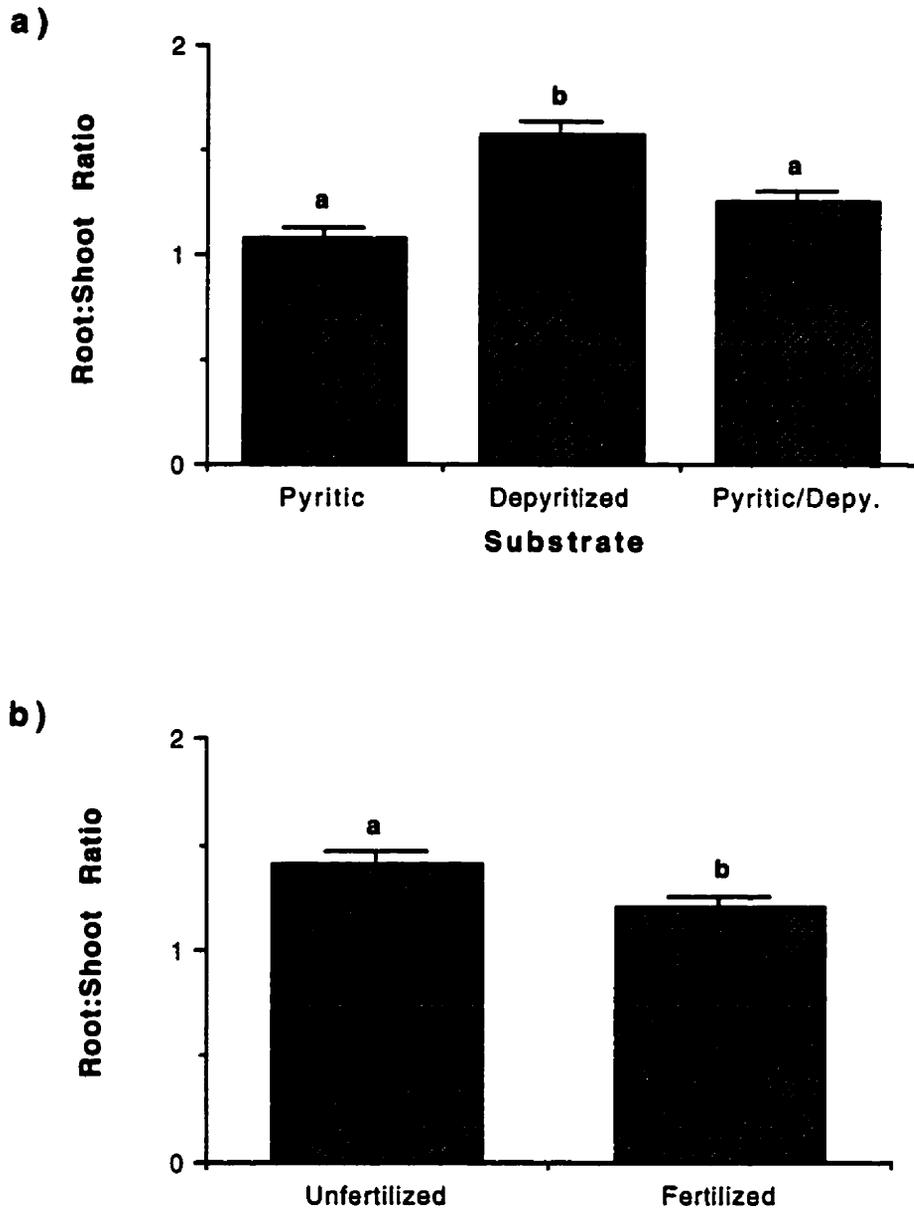


Figure 13: Mean root:shoot ratios based on dry mass (+ S.E.) by a) substrate (n=20) and b) fertilizer (n=30), for a grass-legume seed mix grown in pots in pyritic tailings, depyritized tailings, and a 50/50 mixture (Experiment 4). Different superscripts indicate significant differences at $p=0.05$.

three variables accounted for 46.9% ($r^2=0.469$) of the variance.

A subsequent 1-way ANOVA indicated a significant substrate effect [$F(2,57)=17.07$, $p<0.0001$] and a Scheffé test ($p=0.05$) determined that root:shoot ratios obtained in the depyritized tailings were significantly higher than in pyritic tailings or the 50/50 mix (Figure 13a). That the mean value for plants grown in the depyritized tailings was greater than 1, indicates that these plants were utilizing more of the available resources for root development. The remaining two treatments had root:shoot ratios of approximately 1, and were therefore dividing their available resources equally between roots and shoots. This implies decreased root toxicity in the depyritized tailings as the roots were able to better exploit the substrate in search of nutrients.

A subsequent oneway ANOVA also indicated a significant fertilizer effect [$F(1,58)=5.65$, $p=0.021$] and a Scheffé test ($p=0.05$) revealed that the addition of fertilizer decreased the root:shoot ratios (Figure 13b). This was simply due to the effect of fertilizer on promoting shoot growth. In the absence of fertilizer, the seedlings must allocate more resources to their roots as they search for very limited available nutrients. With the addition of fertilizer, nutrients are quite readily available, allowing plants to devote comparatively more energy into shoot production.

The pH of the tailings surface was measured as an indicator of whether the tailings were oxidizing and therefore generating acid, and also to measure the effect of limestone and fertilizer on this process. This would give some indication of whether oxidation was a contributing factor to the poorer plant growth observed in pyritic tailings throughout the experiment. It was found that pH was lower in pyritic tailings, and with the application of fertilizer (Figure 14), although these differences were very small.

A Kolmogorov-Smirnov test on the pH data indicated that the data were not normally distributed ($z=7.75$, $p<0.001$).

A 3-way ANOVA on the original pH data yielded significant substrate [$F(2,48)=39.8$, $p<.001$; $\eta^2=0.71$] and fertilizer [$F(1,48)=24.8$, $p<.001$; $\eta^2=0.40$] effects. Because limestone failed to show a significant statistical effect, either on

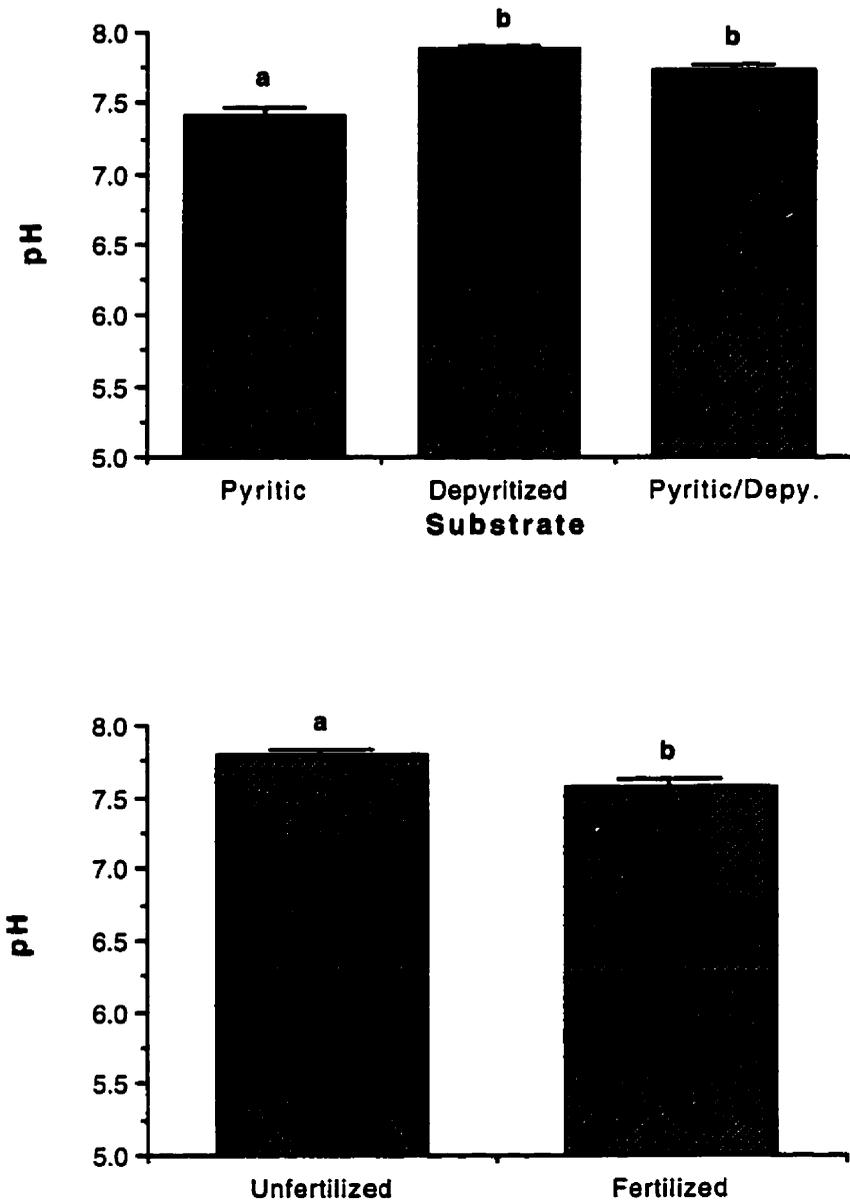


Figure 14: Mean surface pH (+ S.E.) by a) substrate (n=20) and b) fertilizer (n=30), for a grass-legume seed mixture grown in pots in pyritic tailings, depyritized tailings, and a 50/50 mixture (Experiment 4). Different superscripts indicate significant differences at $p=0.05$.

its own or in combination with other variables, the data were subsequently pooled. Overall, the three variables accounted for 67.7% ($r^2=0.677$) of the variability.

Subsequent 1-way ANOVA's and Scheffé tests ($p=0.05$) of the substrate and fertilizer effects indicated that the pH of the pyritic tailings was significantly [$F(2,57)=29.76$, $p<0.0001$] lower than for the other two materials (Figure 14a), and that fertilizer significantly [$F(1,58)=10.98$, $p=0.002$] decreased the pH of the tailings (Figure 14b). The decrease in pH with the application of fertilizer is a common occurrence, normally associated with the addition of nitrogen (in the form of ammonium) fertilizers (Brady, 1990). All pH measurements were in the 7.5-8.0 range. Thus, the pH differences between treatments and with the addition of fertilizer, while being statistically significant, were small enough that they were not considered to have had a significant effect on growth.

That substrate surface pH was higher at the end of the experiment than in the original tailings material (Table 1) is likely due to leaching of hydrogen ions from the tailings. As the materials were contained in free-draining pots, much of the acidity that was present could be freely washed from the pots with each successive watering.

Identical findings were obtained using Kruskal-Wallis rank sum tests for substrate ($\chi^2=32.4$, $p<0.0001$) and fertilizer ($\chi^2=8.9$, $p=0.0028$) effects, with specific mean differences revealed through Mann-Whitney tests where appropriate.

The addition of limestone had no effect on either pH or growth. This was not really surprising, as even the control pots (no limestone or fertilizer) showed little visual sign of oxidation during the three month period of operation. This was due to the natural buffering ability of the tailings and/or leaching of hydrogen ions. Also, the addition of limestone was found to have no effect on pH or early growth during previous germination experiments.

3.4.1.4 Summary of Findings

- 1) Limestone had no effect on any of the parameters considered in this experiment.

- 2) Root growth in depyritized tailings was significantly greater than in pyritic tailings or the 50/50 mix, and was unaffected by the addition of fertilizer, which significantly increased root growth in the pyritic tailings and the 50/50 mix.
- 3) Shoot growth was significantly higher in depyritized tailings followed by the 50/50 mix and pyritic tailings respectively. All three substrates produced significantly better shoot growth with the addition of fertilizer.
- 4) Root:shoot ratios in depyritized tailings were significantly higher than in pyritic tailings and in the 50/50 mix, and fertilizer significantly decreased the ratios in all three materials.
- 5) The pyritic tailings had a significantly lower pH than the depyritized and the 50/50 mix, and the addition of fertilizer significantly lowered pH. While these effects were statistically significant, they were not considered to be of any real biological consequence.

3.4.2 Experiment 5: Waste Materials Applied as Covers to Pyritic Tailings

3.4.2.1 Purpose

This experiment was carried out to simulate a simple tailings cover design, in which each of the materials was applied as a cover to fresh, unoxidized Kidd Creek tailings. Since the pots were free-draining, unsaturated conditions were present in the underlying tailings and the experiment followed the same experimental design as the subsequent column leaching experiment.

This was a longer term growth experiment which tested the ability of the cover materials to support vegetation when placed in direct contact with tailings.

In addition, the shoot metal content was measured to provide insight into the possible uptake of phytotoxic levels of metals from the waste materials.

3.4.2.2 Methods and Materials

The experiment was based on a randomized block design with 5 blocks, i.e. 5 cover materials x 4 (2 x 2 factorial) treatments x 5 replicates = 100 pots.

Treatments were based on ~15T/ha limestone and ~3T/ha fertilizer (incorporated to a 10 cm depth), as follows:

- Treatment 1 - Control (no limestone or fertilizer)
- Treatment 2 - 7.0 g limestone per pot
- Treatment 3 - 1.75 g fertilizer per pot
- Treatment 4 - 7.0 g limestone + 1.75 g fertilizer per pot

Pots were constructed of 22 cm lengths of 7.5 cm (I.D.) P.V.C. pipe. A 10 cm square base, in which ten small holes had been drilled was glued to each section of pipe. A #42 Whatman filter paper was then added to each.

All pots were first loaded with a pyritic tailings base, consisting of 700g of dried tailings added as a slurry (approx. 3:1 tails:water), representing a depth of

approximately 10 cm. An attempt was made to dislodge air bubbles and promote uniform packing by tapping the pots with a brass bar.

Cover materials were added by dry weight so as to obtain a depth of approximately 10 cm. Thus, an additional 700g of pyritic tailings were added to the control (in order to maintain a constant total depth), while 650g depyritized, 750g gold tailings, 400g incinerator ash and 900g granulated slag were utilized in their respective pots. The pyritic and depyritized tailings covers were added as a slurry to simulate deposition methods, while the gold tails, ash and slag were added in dry form.

The treatments were produced by mixing the limestone (agricultural grade) and/or ground fertilizer (6-24-24 NPK) as required, into each cover material in a 1L beaker before adding it to the pyritic base. The pots were then thoroughly watered, and tapped again to remove excess air bubbles and promote uniform packing.

Fifty seeds of Redtop (*Agrostis gigantea* Roth.) were added to each pot and pushed just under the surface. The pots were then covered for 4-5 days until germination began and were then placed in a greenhouse.

The experiment was harvested after approximately 12 weeks. Harvesting consisted of cutting the above ground portion at surface level and washing in distilled water. The pH of the soil surface was then determined and the roots washed from the soil. The roots and shoots were then placed into separate bags and set out to dry in an oven at 80°C.

The above ground biomass from the incinerator ash, gold tailings and granulated slag was cut into small pieces (except where the entire sample was used). A subsample was digested for total metal content (Appendix 1) and analyzed for cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead and zinc by Atomic Absorption Spectrophotometry. Approximately 0.1 g of sample was analyzed for all incinerator ash treatments and those receiving fertilizer and both limestone and fertilizer in the gold tailings. For the remainder of the samples, approximately 0.02 g of sample was used, except for slightly over half of the slag samples, where less than 0.01 g of sample was available. All of the samples at

0.02 g or less were digested using half volumes of acids and were diluted to 50 ml instead of the standard 100ml.

3.4.2.3 Results and Discussion

3.4.2.3.1 Plant Growth

Table 8 shows the mean and standard deviation for root and shoot mass and root:shoot ratios, revealing poor growth in the pyritic and depyritized tailings and granulated slag, and the error associated with these measurements.

While growth parameters for the pyritic and depyritized tailings and granulated slag covers have been included in Table 8 for comparison purposes, they have been excluded from the statistical analysis, because of the very low levels of growth obtained in these treatments. The few seeds that managed to germinate only produced about 2-3 cm of growth in approximately 3 months time, probably because of nutrients contained in the endosperm. Further, it was rather questionable as to whether these seedlings were actually still alive. The exception to this occurred in slag, with the addition of both limestone and fertilizer, where 2 of 5 replicates produced biomass similar to that in the gold tailings control and limed treatments. However, the other three replicates approached an order of magnitude lower. In some cases the recorded biomass was due to the survival of only one seedling.

Where no growth (or measurable dry weight) could be obtained, a value of 0.0001g was used in place of zero. However, this resulted in a complete lack of variability in the data, often producing false interactions and unduly complicated statistics. In addition, the large differences in scale between biomass production in the incinerator ash, gold tailings and the remaining three materials resulted in extreme heterogeneity of variance and non-normal distribution which could not be corrected or significantly improved through data transformations. Therefore, because growth was so severely reduced for all treatments within the pyritic, depyritized and slag covers, statistical analysis was superfluous. This was felt to be further justified by considering that the marginal biomass produced under greenhouse conditions would most certainly not have survived under field conditions.

The only variable not excluded was the pH of the surface at termination of the experiment, which was measured and analyzed for all growth media.

Table 8: Root and Shoot Mass, Root/Shoot Ratio and Substrate Surface pH (\pm S.D. ; n=5) for *Agrostis gigantea* grown in each substrate when applied as a cover (Experiment 5).

<u>Substrate</u>	<u>Root Wt. (g)</u>	<u>Shoot Wt. (g)</u>	<u>Rt/St Ratio</u>	<u>Surface pH</u>
Ash				
Control	0.349 \pm 0.039	0.283 \pm 0.025	1.24 \pm 0.16	7.30 \pm 0.14
Limestone	0.352 \pm 0.036	0.290 \pm 0.019	1.22 \pm 0.12	7.26 \pm 0.18
Fertilizer	1.864 \pm 0.125	3.218 \pm 0.312	0.59 \pm 0.08	7.04 \pm 0.15
Lime/Fertilizer	1.713 \pm 0.270	3.063 \pm 0.371	0.56 \pm 0.03	7.08 \pm 0.08
Gold Tailings				
Control	0.025 \pm 0.004	0.024 \pm 0.003	1.08 \pm 0.27	8.07 \pm 0.22
Limestone	0.021 \pm 0.006	0.020 \pm 0.004	1.07 \pm 0.24	8.15 \pm 0.18
Fertilizer	0.554 \pm 0.271	1.244 \pm 0.420	0.43 \pm 0.11	7.23 \pm 0.25
Lime/Fertilizer	0.479 \pm 0.222	1.056 \pm 0.409	0.45 \pm 0.12	6.93 \pm 0.26
Slag				
Control	NG	NG	NG	NG
Limestone	0.008 \pm 0.004	0.019 \pm 0.005	0.39 \pm 0.10	8.47 \pm 0.18
Fertilizer	0.001 \pm 0.001	0.003 \pm 0.001	0.20 \pm 0.22	8.11 \pm 0.24
Lime/Fertilizer	0.007 \pm 0.010	0.022 \pm 0.022	0.20 \pm 0.17	8.25 \pm 0.30
Depyr. Tail.				
Control	0.003 \pm 0.003	0.002 \pm 0.001	1.18 \pm 0.64	7.87 \pm 0.05
Limestone	0.004 \pm 0.003	0.002 \pm 0.002	1.54 \pm 0.51	7.93 \pm 0.09
Fertilizer	0.0003 \pm 0.001	0.001 \pm 0.001	0.61 \pm 0.44	6.24 \pm 0.15
Lime/Fertilizer	0.001 \pm 0.000	0.001 \pm 0.000	1.00 \pm 0.00	6.49 \pm 0.51
Pyritic T.				
Control	0.002 \pm 0.002	0.002 \pm 0.002	1.09 \pm 0.47	7.17 \pm 0.07
Limestone	0.001 \pm 0.001	0.001 \pm 0.001	1.32 \pm 0.58	7.26 \pm 0.08
Fertilizer	0.001 \pm 0.000	0.001 \pm 0.000	1.00 \pm 0.00	6.80 \pm 0.05
Lime/Fertilizer	0.001 \pm 0.000	0.001 \pm 0.000	1.00 \pm 0.00	6.76 \pm 0.07

NG: No Growth

Root and shoot data for all treatments in the incinerator ash and gold tailings covers were log₁₀ transformed. While this transformation did not necessarily yield homogeneity of variance, heterogeneity of variance was markedly improved. Surface pH was the only variable not transformed as it already exhibited homogeneity of variance, although it did show a non-normal distribution.

Although some statistics were computed using \log_{10} transformed data, for ease of interpretation all results presented are of the original data. Where transformed data were used, significant differences were indicated based on the statistical analysis of the transformed data.

Mean shoot weight in incinerator ash and gold tailings was influenced by both substrate and fertilizer (Figure 15).

A Kolmogorov-Smirnov test indicated that the shoot data were not normally distributed ($z=4.95$, $p<0.001$).

A three-way Analysis of Variance (substrate, limestone, fertilizer) for the transformed shoot data indicated significant substrate [$F(1,30)=629$, $p<0.001$; $\eta^2=0.49$] and fertilizer [$F(1,30)=1719$, $p<0.001$; $\eta^2=0.81$] effects, and a substrate by fertilizer interaction [$F(1,30)=99.3$, $p<0.001$]. Because limestone failed to show a significant statistical effect, either on its own or in combination with other variables, the limestone data were subsequently pooled. All three variables (substrate, limestone, fertilizer) accounted for 95% of the variability ($r^2=0.95$), although limestone on its own accounted for only a very small portion.

A oneway ANOVA on the computed substrate-fertilizer combinations indicated significant differences between groups [$F(3,35)=904$, $p<0.0001$]. A Scheffé multiple range test ($p=0.05$) revealed that shoot growth was significantly different for all four groups, being highest in the fertilized incinerator ash, followed by fertilized gold tailings, unfertilized ash and unfertilized gold tailings respectively (Figure 15). While shoot growth was increased by the application of fertilizer for both incinerator ash and gold tailings, the effect was much greater in gold tailings, with growth increased by approximately 1000% (~10 fold) in the incinerator ash, compared to approximately 5000% (~50 fold) in the gold tailings. This probably represented the source of the observed interaction.

A Kruskal-Wallis Rank Sum test verified the substrate-fertilizer interaction ($\chi^2=35.6$, $p<0.0001$), with identical significant differences indicated via Mann-Whitney tests.

No toxicity symptoms were noted in the shoots, except for a pale green color of

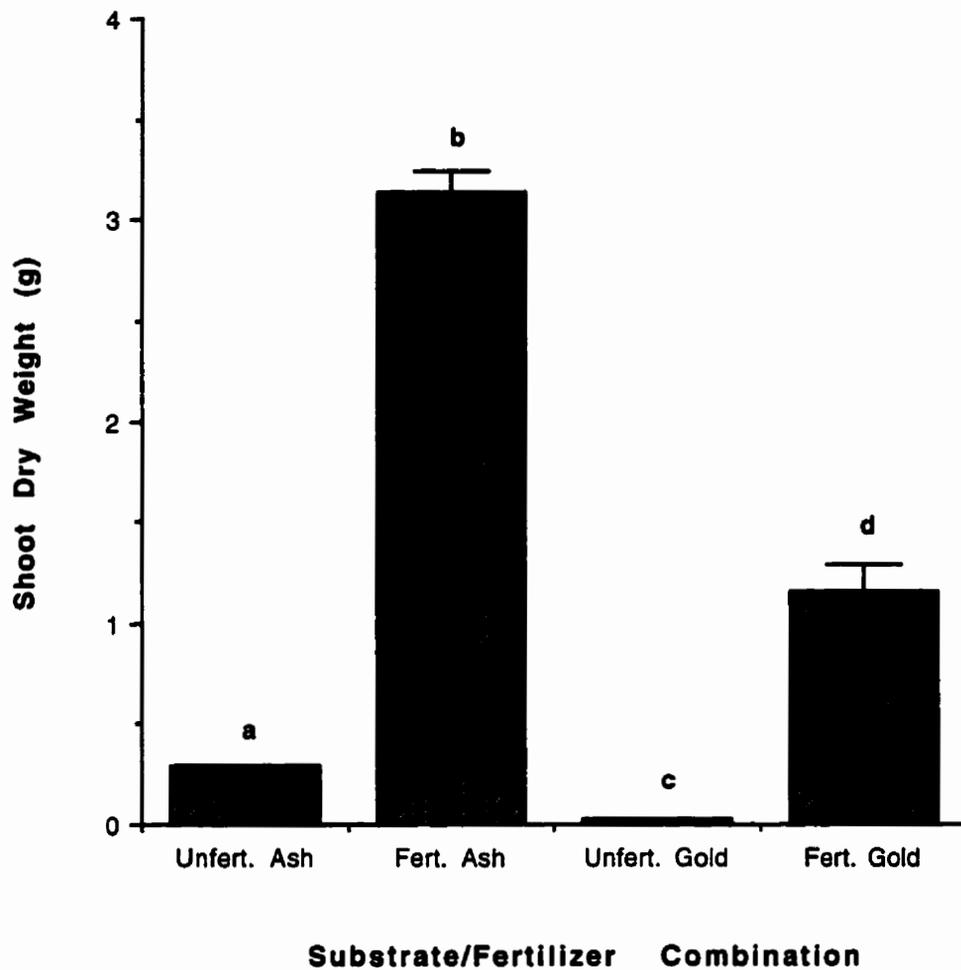


Figure 15: The effect of fertilizer on mean shoot weight (+ S.E. ; n=10) for *Agrostis gigantea* grown in pots in incinerator ash and gold tailings (Experiment 5). Different superscripts indicate significant differences at p=0.05.

shoots grown without the addition of fertilizer, indicating a nitrogen deficiency in both incinerator ash and gold tailings.

Mean root weight in incinerator ash and gold tailings was influenced by both substrate and fertilizer (Figure 16).

A Kolmogorov-Smirnov test indicated that the root data were not normally distributed ($z=4.95$, $p<0.0001$).

A 3-way ANOVA (substrate, limestone, fertilizer) on the \log_{10} transformed root data indicated significant substrate [$F(1,30)=446$, $p<0.001$; $\eta^2=0.63$] and fertilizer [$F(1,30)=525$, $P<0.001$; $\eta^2=0.69$] effects and a significant substrate by fertilizer interaction [$F(1,30)=46.6$, $p<0.001$]. Because limestone failed to show a significant statistical effect, either on its own or in combination with other variables, the data were pooled. The combination of media, limestone and fertilizer accounted for 93% of the variance ($r^2=0.93$), although the contribution from limestone was extremely small.

A oneway ANOVA on the computed substrate-fertilizer combinations indicated significant differences between groups [$F(3,35)=396.1$, $p<0.0001$]. A Scheffé multiple range test ($p=0.05$) indicated that root growth was significantly greatest in fertilized incinerator ash, that there was no difference between unfertilized incinerator ash and fertilized gold tailings, and that root growth was poorest in unfertilized gold tailings (Figure 16). As occurred in the shoot data, root growth was increased by the application of fertilizer in both incinerator ash and gold tailings, but relative growth was higher in gold tailings. Fertilizer increased root growth in the incinerator ash by approximately 410% (~ 5 fold) and by approximately 2000% (~20 fold) in the gold tailings, and probably represents the source of the observed interaction.

A Kruskal-Wallis Rank Sum test also indicated significant group differences for the substrate-fertilizer interaction ($\chi^2=33.0$, $p<0.0001$), with identical significant differences indicated via Mann-Whitney tests.

That the fertilizer effect was greater in gold tailings may be a reflection of the generally better nutritional status of the incinerator ash, which contains higher

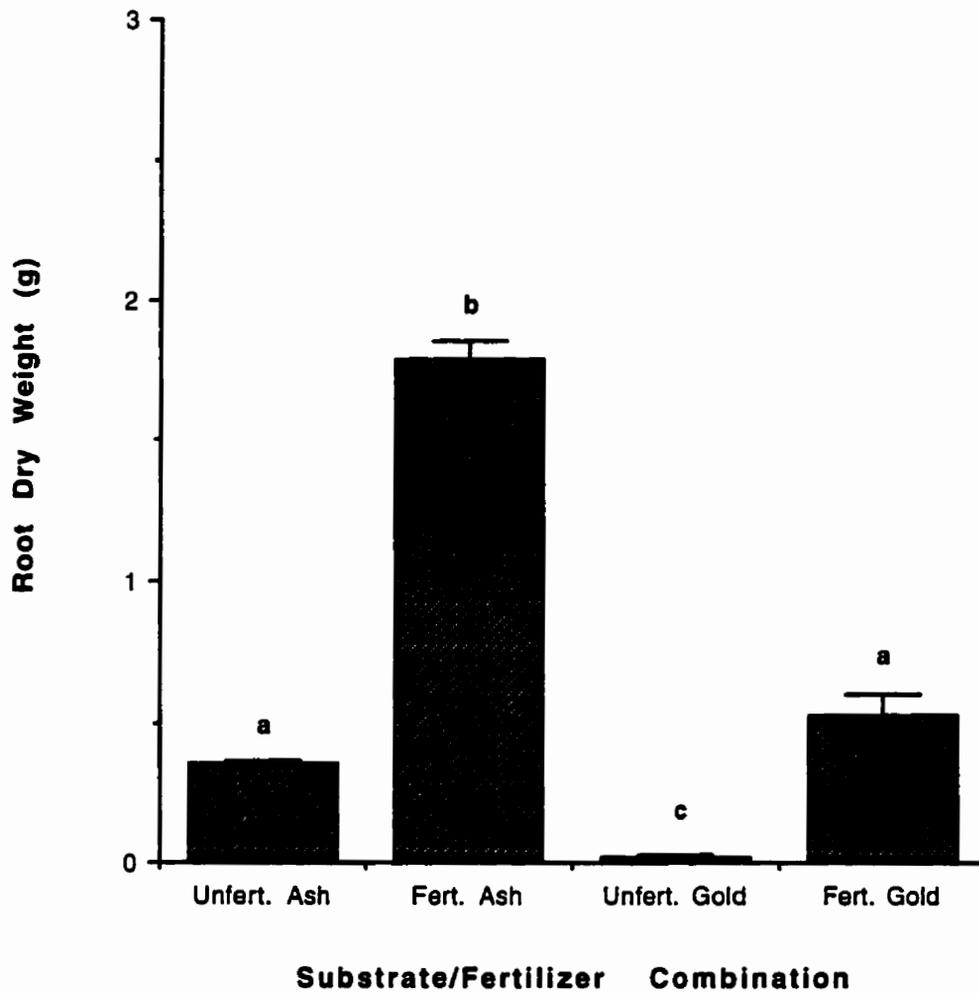


Figure 16: The effect of fertilizer on mean root weight (+ S.E. ; n=10) for *Agrostis gigantea* grown in pots in incinerator ash and gold tailings (Experiment 5). Different superscripts indicate significant differences at $p=0.05$.

levels of water soluble Ca, Mg, and P, although it has lower K (Table 3). Thus the addition of fertilizer would be expected to have a decreased effect on vegetation grown in incinerator ash.

The roots of seedlings grown in unfertilized gold tailings generally only penetrated to a depth of approximately 5 cm, whereas with the addition of fertilizer, roots generally grew to the bottom of the pot, although only along the sides. In incinerator ash, roots generally grew to the bottom of the pots, although much greater root masses were found at the bottom of the pot when fertilizer was added. Roots did not show any proliferation or significant penetration into the tailings under covers of either incinerator ash or gold tailings, except occasionally within cracks.

Overall, presumably because of the inherent Ca, Mg, and P content, growth in incinerator ash was superior to that in gold tailings.

Mean root:shoot ratios were affected by both substrate and fertilizer (Table 9).

Table 9: Mean Root:Shoot Ratios (n=20) for *Agrostis gigantea* Grown in Pots Containing Incinerator Ash and Gold Tailings, With and Without the Addition of Fertilizer (Experiment 5).

<u>Treatment</u>	<u>Mean</u>	<u>Standard Deviation</u>
Unfertilized	^a 1.15	0.21
Fertilized	^b 0.51	0.11

Different superscripts indicate significant differences at p=0.05.

A Kolmogorov-Smirnov test indicated that the root:shoot ratio data were not normally distributed (z=5.26, p<0.001).

A 3-way ANOVA of the log₁₀ transformed root/shoot ratios indicated significant substrate [F(1,31)=10.5, p=0.003; eta=0.23] and fertilizer [F(1,31)=153.2, p<0.001; eta=0.89] effects, but no interaction. Because limestone failed to show a significant statistical effect, either on its own or in combination with other variables, the data were pooled. The combination of substrate, limestone and

fertilizer accounted for 83.4% of the variance ($r^2=0.834$), with fertilizer by far the dominant variable.

Subsequent oneway ANOVAs indicated that there was no significant difference between substrates (ash and gold), but that the addition of fertilizer significantly [$F(1,37)=131$, $p<0.0001$] decreased the root:shoot ratio (Table 9). Identical results were obtained through nonparametric Mann-Whitney tests.

The decrease in the root:shoot ratios was presumably due to an increase in the allocation of energy to shoot growth as a result of better nutritional status. Since nutrients were more readily available with the addition of fertilizer, emphasis was placed on establishing shoots for increased photosynthesis. However, while increases in both shoot and root mass were observed with the addition of fertilizer, shoot mass increased at a greater rate. Thus the root:shoot ratios dropped from slightly greater than 1 in the unfertilized treatment, where slightly greater emphasis was placed on root growth, to approximately 0.5 with the addition of fertilizer. In this latter case, much greater emphasis was placed on shoot production.

Lane and Associates (1990) found that the addition of a high phosphorus fertilizer, both singly and in combination with limestone, significantly increased the growth rate of Redtop in gold tailings. The addition of a high nitrogen fertilizer either had no effect or even depressed growth rates. Limestone was effective in this case, because the gold tailings were of a lower pH than those used in the present study.

Surface pH values were influenced by both substrate and fertilizer (Figure 17).

A Kolmogorov-Smirnov test indicated that the pH data were not normally distributed ($z=9.9$, $p<0.001$).

A 3-way ANOVA of the original surface pH data (all 5 substrates) indicated significant substrate [$F(4,78)=147.2$, $p<0.001$; $\eta^2=0.70$] and fertilizer [$F(1,78)=311.8$, $p<0.001$; $\eta^2=0.51$] main effects, and a significant substrate-fertilizer interaction [$F(4,78)=44.1$, $p<0.001$]. Because limestone failed to show a significant statistical effect, either on its own or in combination with other variables, the data were pooled. The combination of substrate, limestone and

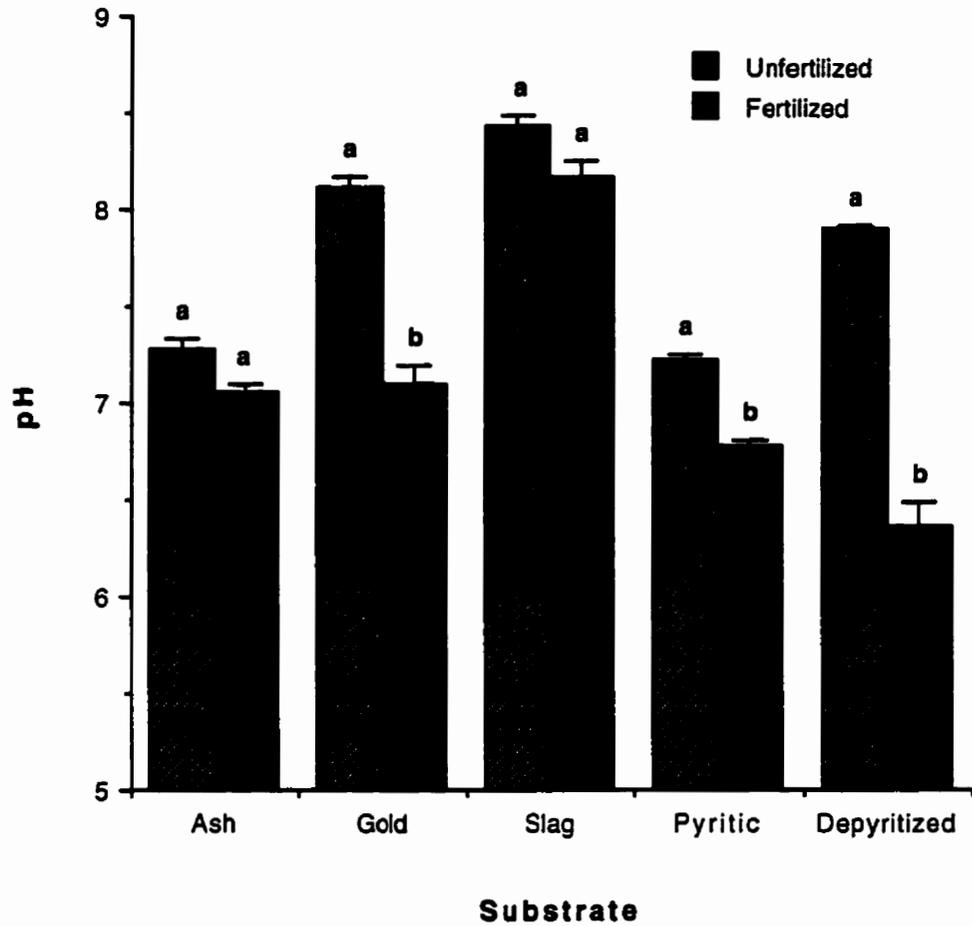


Figure 17: The effect of fertilizer on mean surface pH (+ S.E. ; n=10) of the cover materials from pots seeded with *Agrostis gigantea* (Experiment 5). Different superscripts indicate significant differences at p=0.05.

fertilizer accounted for 77.6% of the variance ($r^2=0.776$), with limestone having had virtually no contribution.

A oneway ANOVA of the computed substrate-fertilizer combinations indicated a significant group effect [$F(9,89)=115.4$, $p<0.0001$] and a Scheffé multiple range test ($p<0.05$) revealed that fertilizer significantly lowered pH in pyritic, depyritized and gold tailings, but not in incinerator ash or slag (Figure 17). The group differences were confirmed via a Kruskal-Wallis Rank Sum test ($\chi^2=88.0$, $p<0.0001$). However, Mann-Whitney tests indicated that fertilizer significantly lowered pH in all materials.

While fertilizer may have decreased pH, the reaction remained neutral or near-neutral in all materials, and should not have had a serious effect on seedling growth.

A major problem associated with the application of a cover to potentially acid generating tailings is the production of water soluble salts as (and if) the tailings oxidize. These salts are toxic to most vegetation, and tend to migrate to the surface layers where they become concentrated, thus contaminating the cover material.

Hawley (1972) indicated that the migration of toxic salts to the surface can be arrested by applying even a thin layer of coarse material over the surface of the tailings. Since migration occurs through capillary action, the larger pore spaces of the coarse material act as a capillary break. This was confirmed by Spires (1975) and Ames (1981), who demonstrated that the application of a gravel layer between tailings and a cover prevented the migration of salts into the cover.

It was expected that the underlying pyritic tailings in the present experiment would eventually have a negative impact on the cover material, which would be reflected in poor vegetation performance. However, no visible signs of this were observed. This was attributed to the fact that the experimental pots were free-draining and maintained in a greenhouse at high humidity. Thus, the leaching processes would be expected to be dominant over evaporation, with little or no effect on the cover. In addition, fresh tailings were used in the experiment, which did not show any

visible symptoms of oxidation because insufficient time (3 months) was allowed for acid generation to overcome inherent neutralizing reactions.

Tisch (1996) demonstrated that a 5 cm layer of granulated slag was effective in preventing the upward migration of acid and metals from oxidized sulphide tailings to covers of both incinerator ash and depyritized tailings, when a water table was maintained in the sulphide tailings. Without a capillary break, the incinerator ash and depyritized tailings were rapidly acidified. Thus, in the short term, incinerator ash and gold tailings covers will support vegetation, but a capillary barrier is likely to be necessary for long term maintenance, depending on evaporative and leaching conditions within the system.

3.4.2.3.2 Metal Uptake to Shoots

3.4.2.3.2.1 Metal Concentrations

Metal analyses of shoot material grown in pyritic tailings, depyritized tailings and slag were omitted because insufficient material (biomass) was produced. While analysis of the shoots grown in slag was attempted, the data were considered unreliable because of the very low sample weights and missing data. In all of the fertilized slag and in 2 of 4 limestone and fertilizer treatments, sample weight ranged from 0.003 - 0.008 g., approximately 10-35 times less than the 0.1 g used in incinerator ash and gold tailings. In terms of missing data, no data were available for the slag control (no growth), while the slag limestone and limestone + fertilizer treatments were based on 4 out of 5 replicates and the slag fertilized treatment was based on 3 out of 5 replicates. In addition, sample weight in three of these treatments was based on growth of only one (of 100 seeded) seedlings, while in three others the sample weight was based on growth from less than ten seedlings. As a result, slag data have been included in Table 10 for comparison purposes, but were not submitted to statistical analysis.

The means and standard deviations for the shoot metal concentration for grasses grown in incinerator ash, gold tailings and slag are shown in Table 10, illustrating the rather erratic and sometimes extreme values associated with slag. The metal concentrations for all analyses in which limited growth was observed, and therefore lower sample weights were used (gold-control, gold-lime, slag-lime,

Table 10: Mean Concentration ($\mu\text{g/g}$) and S.D. of Metals in Shoot Tissue of *A. gigantea* (n=5, except where noted).

Media	Chromium	Copper	Iron	Manganese	Nickel	Zinc
Ash						
Control	55.6 \pm 37.7	68.0 \pm 23.9	1007 \pm 513	77.8 \pm 9.0	39.1 \pm 15.5	162.5 \pm 24.6
Lime	95.4 \pm 90.0	80.3 \pm 44.1	2262 \pm 3120	72.0 \pm 28.4	66.2 \pm 44.1	159.3 \pm 78.8
Fertilizer	53.6 \pm 12.6	48.0 \pm 6.4	1134 \pm 362.3	252.3 \pm 17.5	45.7 \pm 6.5	192.0 \pm 13.6
Lime/Fert.	63.7 \pm 14.3	53.9 \pm 9.0	1602 \pm 591.4	267.9 \pm 26.3	54.5 \pm 14.5	188.2 \pm 37.9
Gold						
Control	209.6 \pm 86.5	292.8 \pm 93.5	4594 \pm 2137	707.2 \pm 412.4	286.7 \pm 234.1	327.8 \pm 289.7
Lime	291.3 \pm 91.3	416.5 \pm 264.5	7024 \pm 1335	787.4 \pm 78.1	259.6 \pm 110.9	188.3 \pm 108.2
Fertilizer	64.3 \pm 41.5	39.4 \pm 5.3	1020 \pm 530.9	378.1 \pm 52.5	61.4 \pm 12.9	141.0 \pm 31.7
Lime/Fert.	73.0 \pm 77.5	44.7 \pm 8.8	1175 \pm 1222	388.1 \pm 29.0	96.0 \pm 38.7	176.8 \pm 42.9
Slag						
Control	NG	NG	NG	NG	NG	NG
Lime ¹	213.9 \pm 146.0	315.1 \pm 231.8	3072 \pm 3989	106.0 \pm 70.8	184.4 \pm 148.4	910.1 \pm 1506
Fertilizer ²	1756 \pm 155.2	3227 \pm 769.2	9239 \pm 3969	215.6 \pm 95.5	1079 \pm 188.4	1218 \pm 553.3
Lime/Fert. ¹	332.7 \pm 223.3	1223 \pm 1190	5932 \pm 4912	84.2 \pm 45.6	269.1 \pm 162.1	735.0 \pm 608.6

NG: No Growth 1: n=4 2: n=3

fertilizer, lime/fert.), were generally much higher than those in which good growth was obtained and higher sample weights used. This suggests that the metals are concentrated in the shoot tissue because of the limited growth. However, it is also possible that these values may be artifacts, caused by very low sample weight used in the metal analyses. These effects cannot be separated with the present data.

All statistical analyses for metal data obtained from growth in incinerator ash and gold tailings were performed on \log_{10} transformed data, which either established homogeneity of variance or greatly improved upon it.

Cadmium, cobalt and lead were analyzed, but concentrations were below detection limits in all cases, and are not reported.

Mean metal concentrations are shown in Figures 18 - 20.

Normality was tested using Kolomogorov-Smirnov tests, which showed that none of the metal concentrations were normally distributed ($z \sim 7.0$, $p < 0.001$).

A 3-way ANOVA (substrate, limestone, fertilizer) of the logged metal concentrations yielded significant substrate and fertilizer main effects, and a substrate by fertilizer interaction for all metals (Cu, Cr, Fe, Mn, Ni) except zinc, which showed no significant effects. Summary statistics for these effects are shown in Table 11.

Limestone did not produce a significant effect, so the data were pooled. Brady (1990) states that zinc availability is reduced drastically by magnesium-containing limestone, and that this phenomenon may be caused by interactions between the two cations either in the soil or in the plant. Wear (1956) found that an increase in soil pH from 5.7 to 6.6 significantly decreased the shoot zinc concentration in sorghum. This was expected to be of significance in acid soils, but showed no effect in this study.

Oneway ANOVAs on the substrate-fertilizer combinations indicated significant group differences for all five metals, as did Kruskal-Wallis Rank Sum tests. Summary statistics for these effects are displayed in Table 12.

Table 11: Summary statistics of the shoot metal concentration effects and interactions for Experiment 5.

Effect	F -value	D.F.	P-value	Eta	Explained Variance
Cu					
substrate	39.2	(1,31)	< 0.001	0.40	-
fertilizer	103.7	(1,31)	< 0.001	0.66	62%
subst. x fert	59.8	(1,31)	< 0.001	-	-
Cr					
substrate	14.2	(1,31)	0.001	0.42	-
fertilizer	15.4	(1,31)	< 0.001	0.44	40.2%
subst. x fert	15.8	(1,31)	< 0.001	-	-
Fe					
substrate	8.3	(1,31)	0.007	0.33	-
fertilizer	13.0	(1,31)	0.001	0.41	31.3%
subst. x fert	21.2	(1,31)	< 0.001	-	-
Mn					
substrate	120.9	(1,31)	< 0.001	0.74	-
fertilizer	10.6	(1,31)	0.003	0.22	59.0%
subst. x fert	56.7	(1,31)	< 0.001	-	-
Ni					
substrate	40.9	(1,31)	< 0.001	0.64	-
fertilizer	9.8	(1,31)	0.004	0.31	54.4%
subst. x fert	14.2	(1,31)	0.001	-	-

Table 12: Summary statistics for oneway analysis of the substrate-fertilizer interaction for shoot metal concentration in Experiment 5.

Element	F-value	D.F.	P-value
Cu	73.4	(3,35)	< 0.0001
Cr	16.1	(3,35)	< 0.0001
Fe	15.1	(3,35)	< 0.0001
Mn	64.8	(3,35)	< 0.0001
Ni	22.3	(3,35)	< 0.0001

Scheffé multiple range tests ($p=0.05$) revealed that no significant differences were observed in chromium, copper, and nickel (Figure 18), and iron (Figure 19) shoot concentrations among fertilized incinerator ash, unfertilized incinerator ash, or fertilized gold tailings, except for copper between unfertilized ash and fertilized gold tailings. Shoot concentrations of Cr, Cu and Ni generally ranged between 50 - 100 $\mu\text{g/g}$ for these treatments, while Fe was much higher at 1000 - 1500 $\mu\text{g/g}$.

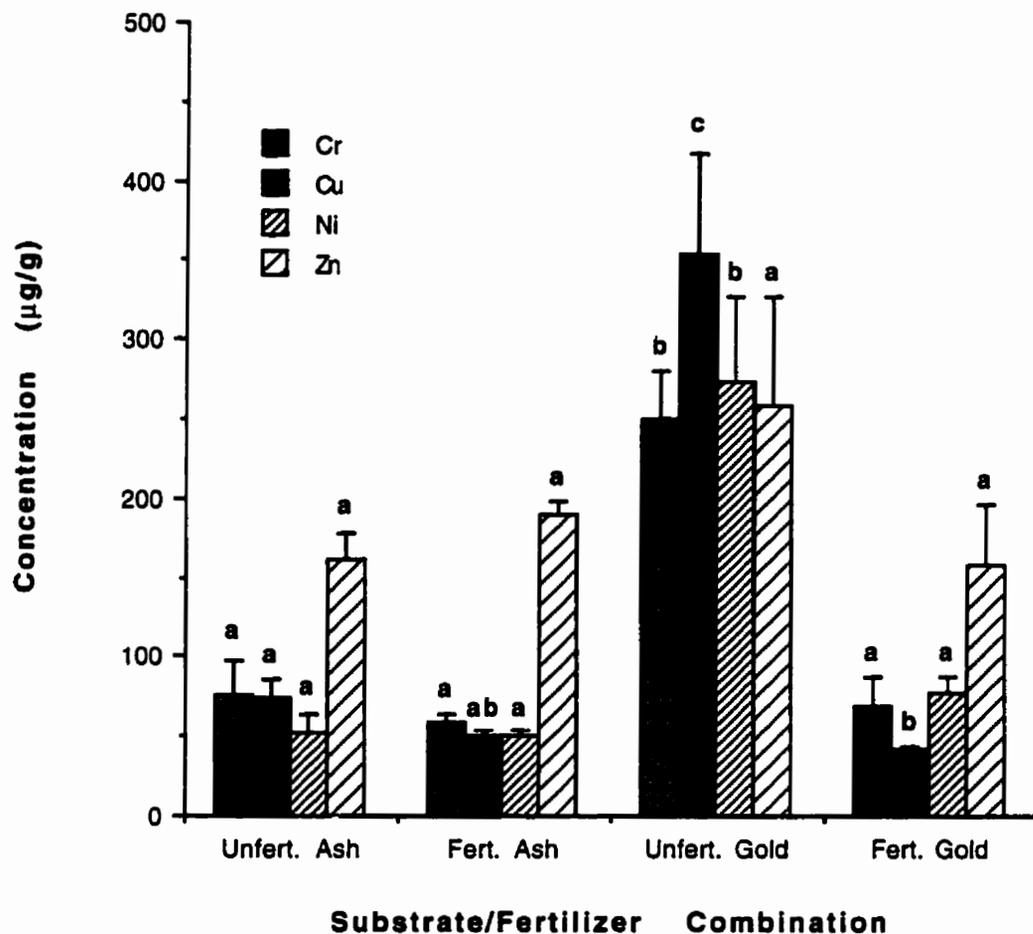


Figure 18: The effect of fertilizer on metal concentration (+ S.E. ; n=5) in shoots of Redtop (Experiment 5). Different superscripts within each metal represent significant differences at p=0.05.

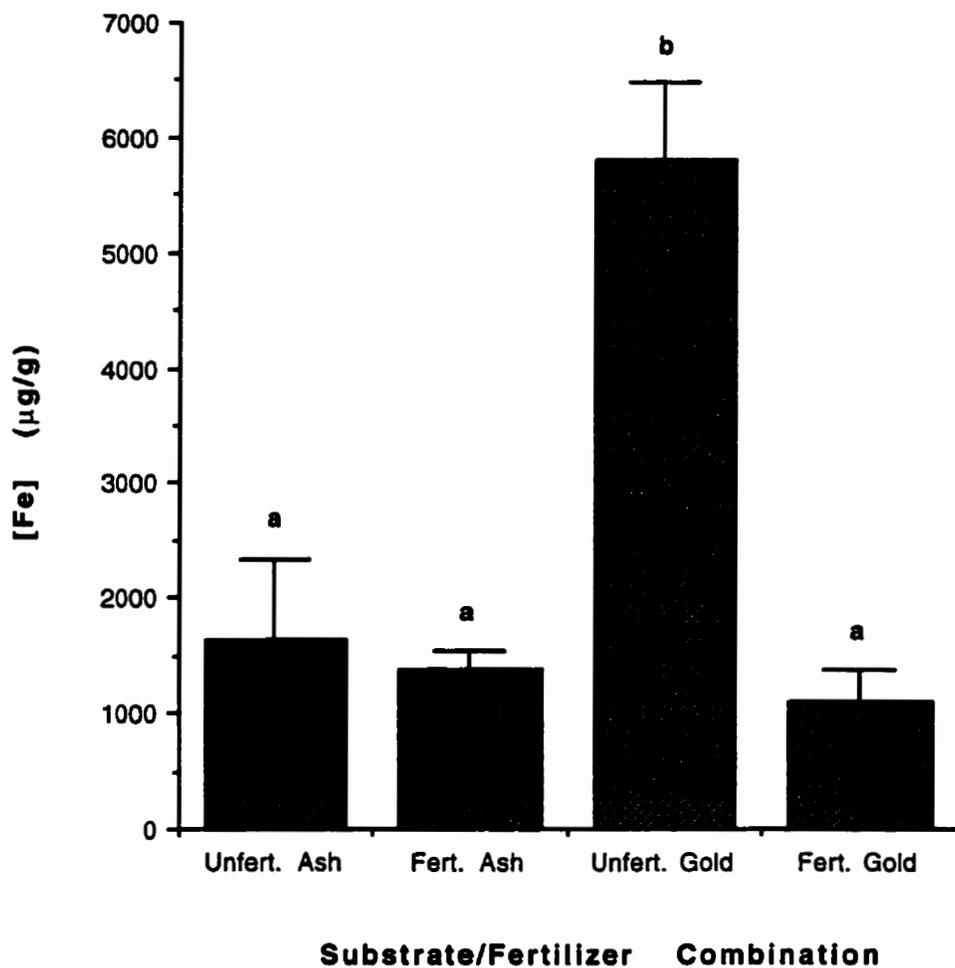


Figure 19: The effect of fertilizer on iron concentration (+ S.E. ; n=10) in shoots of Redtop (Experiment 5). Different superscripts represent significant differences at p=0.05.

Shoot concentrations of Cr, Cu, Fe and Ni were significantly higher in unfertilized gold tailings than in the other three substrate/fertilizer combinations, ranging between 250 - 350 $\mu\text{g/g}$ for Cr, Cu and Ni, and at nearly 6000 $\mu\text{g/g}$ for Fe. This difference represents the source of the observed substrate-fertilizer interactions. The increased concentration of metals in the shoot tissue of seedlings grown in unfertilized gold tailings can be explained by the relative effect of fertilizer on the growth of seedlings. In incinerator ash, the addition of fertilizer resulted in an increase in shoot growth of approximately 10 fold, while fertilizer increased shoot growth in the gold tailings by approximately 50 fold. Therefore, the concentration effect is more pronounced when grown in gold tailings *ie* metal dilution is greater in seedlings grown in incinerator ash. Sutcliffe and Baker (1974) indicate that the initial phase of rapid vegetative growth is accompanied by a large increase in salt content, with absorption declining as growth slows. In the early stages of seedling growth, salt content will often rise more rapidly than dry matter. However, the situation reverses, so that even though total salt content continues to rise, the amount expressed in ppm of dry matter, declines (Sutcliffe and Baker, 1974).

In incinerator ash, manganese was the only metal analyzed which showed a significant increase in shoot concentration with the addition of fertilizer (Figure 20). This effect was not observed in gold tailings, probably because it was masked by the concentration effect discussed above.

Growth is stimulatory to ion uptake in that the synthesis of new carrier molecules and the incorporation of additional inorganic ions into the cell constituents are required. Cell expansion results in a greater surface area of membrane across which ion uptake can occur. When growth slows down, the internal ionic concentration rises and uptake declines (Sutcliffe and Baker, 1974). Thus the increased uptake of manganese with increasing growth may be due to an increased metabolic demand. That a similar response was not observed for Cu, Fe, Ni or Zn may be due to a lower metabolic requirement, although this is uncertain.

The metabolic importance of iron, and its tendency to remain in the cell once elaborated into a molecule, mean that a growing plant has a continuing demand for this element (Jeffrey, 1987). However, while overall levels of iron were high, fertilizer (and enhanced growth) had no effect on shoot iron concentrations.

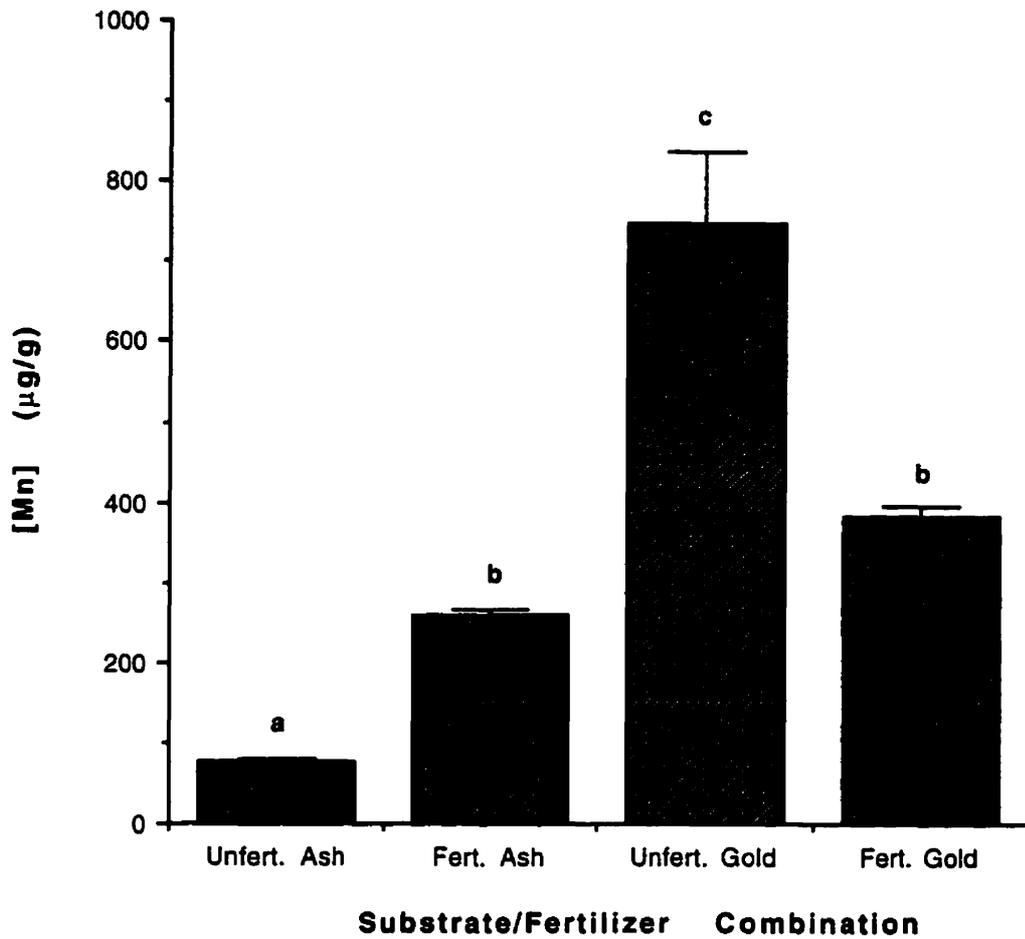


Figure 20: The effect of fertilizer on manganese concentration (+ S.E. ; n=10) in shoots of Redtop (Experiment 5). Different superscripts represent significant differences at p=0.05.

Given that all other factors are non-limiting, a plant will respond exponentially to increments of ion supply until, eventually, further uptake no longer produces growth (Jeffrey, 1987). Further uptake is referred to as luxury consumption which, if it continues, will usually begin to cause decreases in shoot production.

While both gold tailings and incinerator ash contain similar total (~650 µg/g) and water soluble (0.05 µg/g) quantities of manganese (Tables 2 & 3), gold tailings release more than incinerator ash (~56 µg/g versus ~7 µg/g) under dilute acid conditions (Table 4). Thus it might be expected that more manganese would be taken up from gold tailings under the slightly acidifying conditions caused by the addition of fertilizer and the resulting enhanced root growth. Curtin and Smillie (1986) found that fertilization caused a reduction in pH and brought about large increases in soil solution concentrations of Mn, Al and Zn. Although the addition of fertilizer resulted in a slight decrease in pH in incinerator ash (Figure 17), this decrease was not statistically significant, and it is unlikely to be the reason for the increased manganese uptake. Also, the addition of fertilizer resulted in a drop in surface pH of approximately 1 unit in gold tailings, but resulted in a decrease in shoot manganese in comparison with unfertilized gold tailings. However, this effect has probably been masked by the concentration effect discussed previously. It is also possible that the difference in pH between fertilized and unfertilized treatments were at a minimum at the time of measurement (3 months after being added), as the pH of fertilized soils tends to rise slowly again as the fertilizer salts are removed by plants or by leaching (Adams, 1981).

Sutcliffe and Baker (1974) state that some elements, such as iron and manganese, are taken up less readily at high pH due to the conversion of easily-absorbed ferrous (Fe^{2+}) and manganous (Mn^{2+}) ions to more highly oxidized, less available ferric (Fe^{3+}) and manganic (Mn^{3+}) ions.

Jeffrey (1987) indicated that the behaviour of manganese in soil resembles that of iron, but in the plant it resembles that of calcium and magnesium. It is involved in the activation of enzymes, and to some extent replaces magnesium. Thus, elevated levels of available Ca and Mg (as in incinerator ash) may inhibit the uptake of manganese by plants in the incinerator ash, and may be responsible for the relatively high levels observed in gold tailings.

Henriques and Fernandes (1991) found that *Juncus conglomeratus* prevented metals that were in excess (Fe, Cu, Pb) from reaching toxic levels in shoots, while selectively absorbing Mn from the Mn-deficient substrate and accumulating it in the shoots.

The addition of fertilizer to incinerator ash resulted in much greater root growth around the underlying tailings, providing greater access to a substrate with higher water soluble Mn. This may partially explain the increase in Mn with the addition of fertilizer, although this did not occur with zinc. Thus it appears that the increase in Mn may be caused by a combination of both the effect of fertilizer on seedling growth and its effect on soil pH.

Hawley (1984) carried out an in-depth study of the levels of metals found in vegetation growing on various tailings types. He listed mean metal concentrations in above-ground vegetation for numerous species, although grasses were generally not divided into species. These figures, along with ratios of vegetation metal concentrations:soil metal concentrations and background values (not affected by tailings), are summarized in Table 13. Similar vegetation:soil ratios were expressed by Hodgson (1970).

Table 13: Metal Levels (ppm) Found in Grasses Growing in Mineral Tailings and Control Sites (Background) in Ontario (after Hawley, 1984).

<u>Metal</u>	<u>Mean</u>	<u>Range</u>	<u>Background</u>	<u>Veg.:Soil</u>
Cu	33.4	5.2 - 51	7.0	0.08
Cr	2.73	1.2 - 5.22	0.86	0.03
Fe	480.3	92 - 900	120	0.01
Mn	243.6	217 - 285	320	0.63
Ni	31.2	<2.7 - 88	0.71	0.3
Zn	345.1	23 - 966	42	0.3

In comparison with the background values obtained by Hawley (1984), shoot metal concentrations in the present study were elevated for all metals except manganese. They were, however, very similar to the mean values reported by Hawley for tailings, and also to values reported by numerous other authors for

metal contaminated sites (Freedman & Hutchinson, 1980; Sheets *et al.*, 1982; Stanley *et al.*, 1982; Hazlett *et al.*, 1983; Winterhalder *et al.*, 1984; McLaughlin *et al.*, 1985 and Lane & Associates, 1990)

The ratio of metals in the shoots to total metals in the soil are shown in Table 14. It can be seen that the ratios are quite consistent between treatments for the incinerator ash, except for manganese. The control and limestone treatments are higher in the gold tailings, once again, a reflection of the limited growth and low sample weight used in the plant metal analyses, as discussed previously.

Table 14: Ratios of Metal Concentration in Vegetation to Total Metal in Soil for Plants Grown in pots of Sewage Incinerator Ash and Gold Tailings (Experiment 5).

Substrate	Cr	Cu	Fe	Mn	Ni	Zn
Ash						
Control	0.04	0.03	0.01	0.12	0.21	0.03
Limestone	0.07	0.03	0.02	0.11	0.36	0.03
Fertilizer	0.04	0.02	0.01	0.39	0.25	0.04
Limestone/Fert.	0.05	0.02	0.01	0.41	0.30	0.04
Gold						
Control	5.53	10.69	0.14	1.04	5.02	0.82
Limestone	7.69	15.20	0.21	1.16	4.55	0.47
Fertilizer	1.70	1.44	0.03	0.56	1.08	0.35
Limestone/Fert.	1.93	1.63	0.04	0.57	1.68	0.44

It is interesting to note, however, that the ratios are generally much higher in all treatments in the gold tailings than in the incinerator ash. Thus, while there was little difference in the actual tissue metal concentrations, plants growing in gold tailings are taking up proportionately more metal. Although total metal levels are generally much higher in incinerator ash (Table 2), there is little difference in the water soluble metal concentrations between incinerator ash and gold tailings. Since uptake of metals occurs in soluble forms only, it is not surprising that tissue concentrations are nearly identical. It appears that the grass seedlings have accumulated sufficient quantities of metals for metabolism, and that further accumulation would simply be luxury consumption.

Total metal levels will not really be an important factor until pH declines, at which time plant available concentrations of metals should be much higher in incinerator ash. This has not been shown (Table 4), as most metals are present at generally similar concentration in the ash and gold tailings when extracted at a pH slightly less than 5 (Table 5). However, incinerator ash still maintains the potential to release significantly higher concentrations of metals if the pH drops even lower.

The total elemental content of soils includes ions within the crystal lattices of clay, as well as in silt, sand and gravel particles, which are not immediately usable by plants. Total concentrations, therefore, are poor indicators of plant availability. A better value would be the amount of each ion available during the plant's growing season, although availability is often undefinable because ion uptake by plants varies so greatly with plant variety and growth conditions, as well as with soil chemistry. Differences in ion uptake or availability due to plant factors are usually small compared to the differences due to soil chemical reactions (Bohn *et al.*, 1979). Hazlett *et al.* (1983) found that tissue metal concentrations for *Agrostis scabra* could best be correlated with the total soil metal concentration, together with soil pH and organic matter content.

Chang *et al.* (1992) describe phytotoxicity as an intoxication of living plants by substances present in the growth medium, when these substances are taken up and accumulated in plant tissues. Metals may induce phytotoxicity by altering plant water relations, causing water stress and wilting; they may increase permeability of roots, thus causing them to become less selective in the extraction of constituents from the growth medium; they may inhibit photosynthesis and respiration; or they may adversely affect metabolic enzymes (Chang *et al.*, 1992). The inhibition of root growth is also very characteristic of phytotoxicity (Smith and Bradshaw, 1972).

The uptake of metals from the soil to plant tissues is usually dependant both on the available concentrations found in the soil and the form of the metal. This is largely dependant on the pH, moisture, organic matter and redox conditions in the soil (Brady, 1990), activity of microorganisms, and discrimination by the plant root during ion uptake (Bohn *et al.*, 1979). However, plant species and age, organ sampled, and health of the plant can also have a major influence (Hawley, 1984).

Therefore, it is not surprising that a great deal of variation may be found between reported metal concentrations.

In addition to pH effects on the availability of individual ions, various nutrients often interact with respect to their effects on plant growth. Some such interactions may arise from similarities in uptake mechanisms for different nutrients, but others may arise from precipitation or immobilization of ions near the plant root or within the plant itself. Chemically similar ions also may compete with each other for adsorption or absorption sites on the plant root surface (Bohn *et al.*, 1979).

Tissue metal concentrations in this study were generally in the range of those reported by Hawley (1984), except for Cr, which was approximately 10-20 times higher in this study. Chromium, which is present in soils as an anion, differs from other micronutrients (including Cu, Fe, Mn, Ni, and Zn) in that its availability decreases with increasing acidity (Bohn *et al.*, 1979). Values reported by Hawley (1984) were generally for plants found on acidic tailings, and would therefore yield chromium levels at lower concentrations than those grown in incinerator ash or gold tailings at circumneutral pH. Bohn *et al.* (1979) indicated that Cr, Ni, Cd, Hg and Pb are toxic to organisms, and Holub (1987) reported that Pb, Zn, Cd and Cr decreased cellulolytic activity in the soil. Thus, it appears that chromium toxicity may represent a potential problem, especially when plants are grown in incinerator ash, because of the high total Cr content.

Several papers have been published which indicate that some clones of *Agrostis gigantea* exhibit tolerance to such metals as cobalt, copper, nickel and zinc (Hogan, 1975; Hogan *et al.*, 1977a & b; Hogan & Rauser, 1979; Rauser & Winterhalder, 1985), while others have demonstrated metal tolerance in other members of the genus *Agrostis* (Walley *et al.*, 1974; Gartside & McNeilly, 1974; Wu *et al.*, 1975 a & b; Archambault, 1991).

Metal tolerances have been demonstrated in clones of Redtop found on more toxic regions of Sudbury tailings, and were generally not found in individuals thriving in less toxic sites (McLaughlin and Crowder, 1988). Further, Hogan & Rauser (1979) found that a clone derived from supply house seed lacked tolerance to any of the metals tested. Therefore, as an aside, it is recommended that future studies

involving survivability and metal uptake by vegetation include a component which establishes the metal tolerance of the clone under study.

Plants can exhibit tolerance in several ways: through their ability to concentrate or exclude elements from the roots, through their ability to alter the root environment, through the effect of nutrient interactions and nutrient stress, and through dilution of elemental concentrations in plant tissues resulting from plant growth (Hodgson, 1970).

Metal tolerance in plants has been linked to metallothioneins, and Rauser and Curvetto (1980) report that copper-thionein occurred in the roots of a clone of *A. gigantea* tolerant to excess copper.

Hawley (1984) indicated: that Cu, Ni and Zn are routinely elevated in plant tissue grown on tailings, and represent potential environmental problems; that Fe and Mn, while commonly elevated in plants grown on tailings do not represent environmental hazards because of their innocuous nature; and that Cr levels in plants growing on tailings are not environmentally significant. In similar fashion, Webber (1975) suggested that mercury, lead and chromium were unlikely to cause serious crop quality or production problems because there is little translocation of these elements to the edible portions of crops. However, this is likely to be species specific, and the translocation of lead and chromium to the above-ground portions of vegetation was not found in this study. Webber further suggested that zinc, copper and nickel in soils cause severe crop production problems because of reduced yields, and that crop quality is not a serious problem because yields are reduced before metal content is high enough to be toxic to most animals. This seems to be in agreement with the findings of the present study.

3.4.2.3.2.2 Absolute Shoot Metal Levels

Absolute metal levels are essentially a reflection of the amount of biomass produced (concentration x biomass), and represent the total amount of metal potentially available during consumption by herbivores of the entire plant(s), ie total metal per pot.

The mean and standard deviation of all metals analyzed for all three substrates are shown in Table 15, illustrating the extreme variation exhibited in the shoots grown in granulated slag.

Kolmogorov-Smirnov tests revealed that none of the absolute metal data were normally distributed ($z \sim 7.0$, $p < 0.001$).

A 3-way ANOVA of the \log_{10} transformed absolute shoot metal data indicated significant substrate and fertilizer main effects for chromium, copper, iron, manganese and nickel. A significant substrate x fertilizer interaction was present in addition to the substrate and fertilizer main effects for zinc. Limestone did not produce a significant effect; therefore the data were pooled. Summary statistics for these effects are presented in Table 16.

Oneway ANOVAs of the substrate main effects for Cr, Cu, Fe, Mn and Ni revealed significant differences (Table 17), and Scheffé multiple range tests indicated that while all absolute shoot metal levels were higher when grown in incinerator ash than in gold tailings, only chromium, copper and iron were significantly different (Table 18). Nonparametric Mann-Whitney tests indicated that all five metals were significantly higher in the incinerator ash plants. Because there was generally very little difference in shoot metal concentrations between incinerator ash and gold tailings, the higher absolute metal levels in the shoots grown in incinerator ash were simply a reflection of the better overall growth which occurred in this material.

Oneway ANOVAs of the fertilizer main effects for Cr, Cu, Fe, Mn and Ni revealed that absolute shoot metal content was significantly higher in both incinerator ash and gold tailings treated with fertilizer. Summary statistics for these effects are presented in both Tables 17 and 19, with identical results obtained via Mann-Whitney tests. As occurred with the substrate effect above, the fertilizer effect was also simply due to greatly enhanced shoot growth.

A oneway ANOVA of the computed substrate-fertilizer combinations for the total zinc data revealed a significant group difference [$F(3,35)=211.96$, $p < 0.0001$]. A Scheffé Multiple Range Test ($p=0.05$) indicated that all four treatments were significantly different from each other (Figure 21). Identical results were obtained

Table 15: Mean (\pm S.D. ; n=5 except where noted) Total Metal Levels (μg) in Shoots of *A. gigantea* Grown in a Pot Experiment (Experiment 5).

Media	Chromium	Copper	Iron	Manganese	Nickel	Zinc
Ash						
Control	15.79 \pm 10.82	19.15 \pm 6.52	280.0 \pm 122.7	21.94 \pm 2.06	11.25 \pm 4.98	46.00 \pm 7.82
Lime	27.32 \pm 24.96	23.35 \pm 12.56	642.7 \pm 860.7	20.91 \pm 8.01	19.09 \pm 12.51	46.17 \pm 21.97
Fertilizer	174.0 \pm 50.2	154.4 \pm 24.0	3639 \pm 1154	815.2 \pm 124.3	146.7 \pm 23.2	617.1 \pm 65.7
Lime/Fert.	191.8 \pm 31.1	163.4 \pm 23.7	4769 \pm 1369	820.6 \pm 119.9	164.1 \pm 34.8	570.9 \pm 109.9
Gold						
Control	4.75 \pm 1.63	6.71 \pm 1.41	106.5 \pm 49.7	15.82 \pm 8.34	6.46 \pm 5.28	7.27 \pm 6.21
Lime	5.56 \pm 0.75	7.51 \pm 2.85	138.2 \pm 27.0	15.71 \pm 3.65	4.84 \pm 1.06	3.47 \pm 1.25
Fertilizer	68.90 \pm 18.54	49.22 \pm 18.37	1369 \pm 813	470.9 \pm 179.9	74.67 \pm 21.69	172.8 \pm 52.1
Lime/Fert.	83.14 \pm 88.50	45.21 \pm 15.17	1321 \pm 1394	411.0 \pm 169.8	98.6 \pm 51.6	179.5 \pm 68.7
Slag						
Control	NG	NG	NG	NG	NG	NG
Lime ¹	4.09 \pm 2.51	6.14 \pm 4.17	55.47 \pm 65.69	2.16 \pm 1.58	3.49 \pm 2.56	15.87 \pm 25.15
Fertilizer ²	5.68 \pm 1.02	10.30 \pm 2.31	28.50 \pm 7.43	0.69 \pm 0.30	3.43 \pm 0.31	3.76 \pm 1.08
Lime/Fert. ¹	4.08 \pm 0.25	13.47 \pm 7.46	66.35 \pm 21.22	1.24 \pm 0.49	3.59 \pm 0.75	9.02 \pm 3.51

NG: No Growth 1: n=4 2: n=3

Table 16: Summary Statistics for a 3-way ANOVA of the Absolute Shoot Metal Data in Experiment 5.

Effect	F -value	D.F.	P-value	Eta	Explained Variance
Cr					
substrate	38.3	(1,31)	< 0.001	0.40	-
fertilizer	166.4	(1,31)	< 0.001	0.83	86.4%
Cu					
substrate	107.2	(1,31)	< 0.001	0.48	-
fertilizer	325.9	(1,31)	< 0.001	0.83	93.2%
Fe					
substrate	24.1	(1,31)	< 0.001	0.40	-
fertilizer	90.0	(1,31)	< 0.001	0.78	78.2%
Mn					
substrate	249.5	(1,31)	< 0.001	0.14	-
fertilizer	725.8	(1,31)	< 0.001	0.96	95.8%
Ni					
substrate	27.5	(1,31)	< 0.001	0.28	-
fertilizer	284.5	(1,31)	< 0.001	0.90	90.5%
Zn					
substrate	147.1	(1,31)	< 0.001	0.48	-
fertilizer	428.5	(1,31)	< 0.001	0.82	92.9%
substrate x fert	13.3	(1,31)	< 0.001	-	-

Table 17: Summary Statistics for 1-Way ANOVAs of the Absolute Shoot Metal Data in Experiment 5.

Element	F-value	D.F.	P-value
Cu			
substrate	12.16	(1,37)	0.001
fertilizer	14.85	(1,48)	0.0003
Cr			
substrate	7.95	(1,37)	0.008
fertilizer	23.41	(1,48)	< 0.0001
Fe			
substrate	8.08	(1,37)	0.007
fertilizer	12.66	(1,48)	0.001
Mn			
substrate	1.08	(1,37)	0.31
fertilizer	10.59	(1,48)	0.002
Ni			
substrate	3.80	(1,37)	0.06
fertilizer	25.74	(1,48)	< 0.0001

Table 18: Mean (\pm S.D. ; n=20) Absolute Metal Levels in Shoots of *Agrostis gigantea* Grown in Pots Containing Incinerator Ash or Gold Tailings (Experiment 5). Different Superscripts Across Rows Indicate Significant Differences at $p=0.05$.

Element	Sewage Incinerator Ash		Gold Tailings	
	Mean (μg)	S.D.	Mean (μg)	S.D.
Cr	a102.23	88.32	b38.35	51.96
Cu	a90.07	72.67	b26.21	23.36
Fe	a2332.65	2169.16	b702.68	931.14
Mn	a419.65	416.20	a218.76	246.55
Ni	a85.29	75.04	a43.38	47.91

Table 19: Mean (\pm S.D. ; n=20) Absolute Metal Levels in Shoots of *Agrostis gigantea* Grown in Pots With and Without the Addition of Fertilizer (Experiment 5). Different Superscripts Across Rows Indicate Significant Differences at $p=0.05$.

Element	Unfertilized		Fertilized	
	Mean (μg)	S.D.	Mean (μg)	S.D.
Cr	a11.81	14.68	b97.67	84.30
Cu	a12.84	9.68	b80.8	66.66
Fe	a252.45	424.33	b2096.85	2032.46
Mn	a15.86	8.54	b486.63	352.08
Ni	a9.26	8.43	b90.26	67.60

via a Kruskal-Wallis Rank Sum test and Mann-Whitney tests.

The source of the interaction appears to be a relatively greater increase of approximately 33 fold (3273%) in the gold tailings versus a 13 fold (1289%) increase in the incinerator ash, with the addition of fertilizer. This differential was simply a function of the increased biomass production observed in Figures 15 and 16 with the addition of fertilizer.

The presence of an interaction for zinc but not the other metals was attributed to the higher concentrations found in the unfertilized gold tailings treatment in all metals except zinc. These high concentrations resulted in elevated total metal levels for Cr, Cu, Fe, Mn and Ni in the unfertilized gold tailings, so that the ratio of metal levels in unfertilized gold to fertilized gold tailings was decreased and

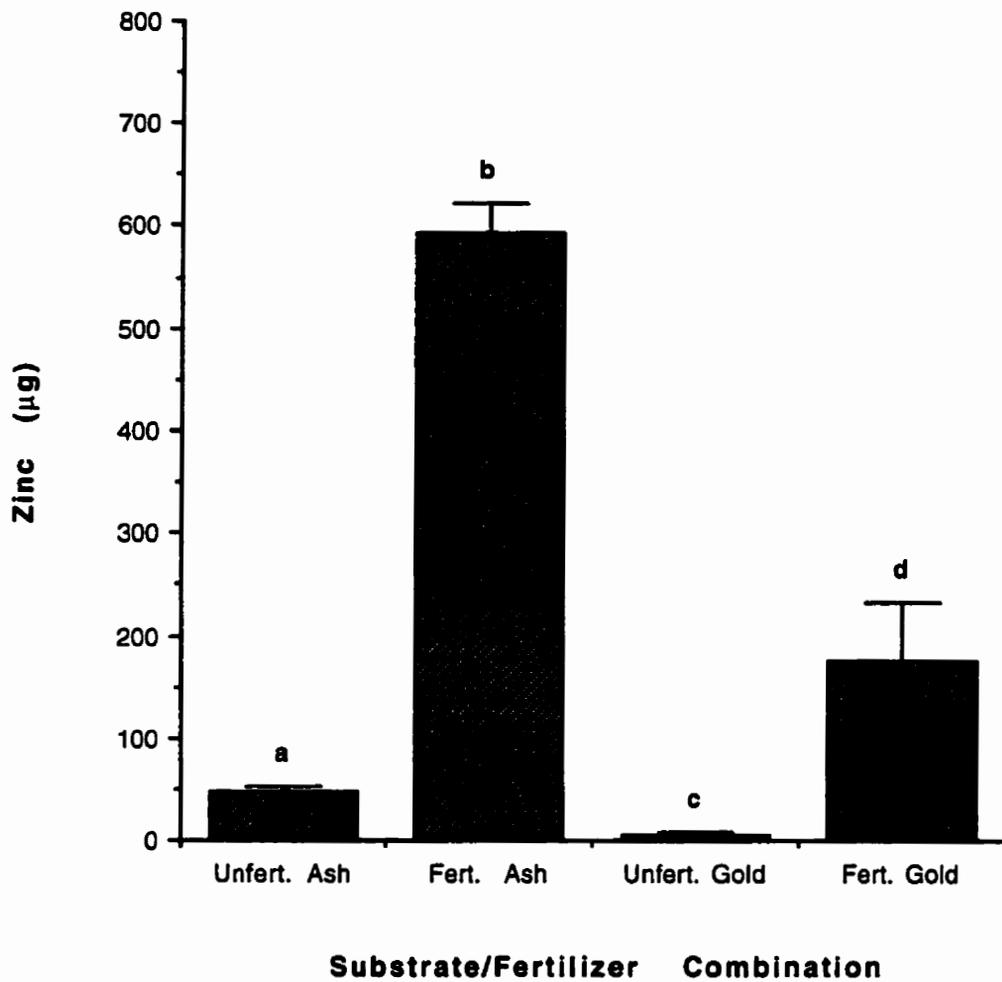


Figure 21: The effect of fertilizer on mean absolute shoot zinc content (+ S.E. ; n=10) in seedlings grown in pots in sewage incinerator ash and gold tailings (Experiment 5). Different superscripts represent significant differences at p=0.05.

was also very similar to the ratio observed for the ash treatments. This was not the case with zinc.

Overall, absolute metal levels were generally higher in the shoots grown in incinerator ash, and in treatments containing fertilizer. This was due mainly to the production of more biomass.

3.4.2.3.2.3 Metal Content of Shoots per Gram of Root

While the addition of fertilizer resulted in increases to both root and shoot biomass (Figures 15 and 16), the proportion of these increases were not the same. The addition of fertilizer caused roughly twice as much shoot growth as it did root growth, as can be seen in the root:shoot ratios in Table 9. Therefore, an alternate way of displaying shoot metal content is to express the mass of metal contained in the shoot material on the basis of the root mass. This was accomplished by simply expressing the absolute weight of a particular metal (μg) in the shoots on a per gram of root basis.

Because the roots are the organs that control the uptake of metals from the growth media, this may be a more appropriate measure of metal accumulation. Sutcliffe and Baker (1974) state that there is a close relationship between root surface area and ion uptake. Thus it was felt that this method might allow the determination of whether the shoot metal content is influenced by the size of the root mass, *ie* does greater root surface area result in enhanced metal uptake into the shoots? Further, the expression of shoot metal content as a function of root mass should provide a comparison of the ability of roots to exploit the growth medium and/or translocate metals from the roots to the shoots. Winterhalder (1996), indicated that control of translocation from the root to shoot lies in the root, and that the application of limestone reduces metal uptake through improved membrane integrity and competitive exclusion of toxic ions.

The mean and standard deviations for the shoot metal contents on a per gram of root basis for all three media are shown in Table 20, and illustrate the extreme range and variability exhibited by the data from granulated slag.

Table 20: Mean Metal Concentration per Gram of Root ($\mu\text{g/g}$) \pm S.D. (n=5, except where noted) in Shoots of *A. gigantea* Grown in Pots (Experiment 5).

Media	Chromium	Copper	Iron	Manganese	Nickel	Zinc
Ash						
Control	46.32 \pm 33.72	56.46 \pm 22.84	833.6 \pm 444.1	63.31 \pm 6.37	32.75 \pm 15.57	134.2 \pm 31.6
Lime	81.87 \pm 78.87	68.71 \pm 42.03	1905 \pm 2666	60.14 \pm 25.46	56.92 \pm 41.08	132.3 \pm 67.9
Fertilizer	94.89 \pm 33.09	83.57 \pm 16.54	1967 \pm 630	441.0 \pm 89.6	79.57 \pm 17.27	333.4 \pm 51.7
Lime/Fert.	115.4 \pm 31.0	97.13 \pm 19.03	2886 \pm 1080	482.1 \pm 60.8	98.04 \pm 26.25	340.2 \pm 81.4
Gold						
Control	187.1 \pm 52.9	274.8 \pm 66.5	4167 \pm 1646	601.2 \pm 277.9	252.0 \pm 200.5	287.3 \pm 244.4
Lime	277.1 \pm 77.8	381.7 \pm 171.7	6856 \pm 2186	753.8 \pm 110.4	246.8 \pm 90.6	169.2 \pm 63.3
Fertilizer	159.2 \pm 101.1	99.2 \pm 40.7	2477 \pm 1293	928.7 \pm 282.5	159.7 \pm 89.7	354.8 \pm 219.9
Lime/Fert.	167.3 \pm 178.8	106.1 \pm 36.2	2652 \pm 2720	913.8 \pm 253.8	225.4 \pm 96.9	405.5 \pm 113.5
Slag						
Control	NG	NG	NG	NG	NG	NG
Lime ¹	547.1 \pm 426.4	788.8 \pm 671.8	8451 \pm 12152	255.9 \pm 180.8	452.7 \pm 336.4	2602 \pm 4521
Fertilizer ²	*21.4 \pm 21.2	*41.0 \pm 40.4	*149 \pm 193	2630 \pm 2345	*15.0 \pm 17.6	*19.9 \pm 26.3
Lime/Fert. ¹	*12.8 \pm 21.3	*65.1 \pm 118.3	*260 \pm 446	2895 \pm 4700	*11.0 \pm 19.1	*35.1 \pm 62.4

NG: No Growth * (mg/g) 1: n=4 2: n=3

Kolmogorov Smirnov tests indicated that the shoot metal contents on a per gram of root basis were not normally distributed ($z \sim 7.00$, $p < 0.001$).

Results of a three-way analysis of variance on the \log_{10} transformed shoot metal data on a per gram of root basis were quite similar to those obtained for the shoot metal concentrations. All metals other than zinc showed significant substrate main effects and substrate by fertilizer interactions, with copper and manganese also exhibiting a fertilizer main effect. Zinc showed a fertilizer effect only. Limestone did not produce a significant effect for any of the metals; therefore the data were pooled. Summary statistics are presented in Table 21

Table 21: Summary statistics for a 3-way ANOVA of the shoot metal content (per gram of root) data in Experiment 5.

Effect	F -value	D.F.	P-value	Eta	Explained Variance
Cu					
substrate	50.47	(1,31)	< 0.001	0.63	-
fertilizer	5.93	(1,31)	0.021	0.22	45.8%
substrate x fert	38.36	(1,31)	< 0.001	-	-
Cr					
substrate	22.77	(1,31)	0.001	0.58	-
substrate x fert	12.02	(1,31)	0.002	-	35.4%
Fe					
substrate	14.51	(1,31)	0.001	0.47	-
substrate x fert	18.05	(1,31)	< 0.001	-	24.8%
Mn					
substrate	209.3	(1,31)	< 0.001	0.70	-
fertilizer	131.61	(1,31)	< 0.001	0.55	77.5%
substrate x fert	62.13	(1,31)	< 0.001	-	-
Ni					
substrate	55.56	(1,31)	< 0.001	0.74	-
substrate x fert	10.37	(1,31)	0.003	-	59.3%
Zn					
fertilizer	30.30	(1,31)	< 0.001	0.68	49.5%

Oneway ANOVAs on the substrate-fertilizer combinations revealed significant group differences for all metals, as did Kruskal-Wallis Rank Sum tests, with summary statistics indicated in Table 22.

Table 22: Summary statistics for 1-way ANOVAs of the substrate-fertilizer interaction for shoot metal concentration on a per root basis (Experiment 5).

Element	F-value	D.F.	P-value
Cu	34.36	(3,35)	< 0.0001
Cr	12.04	(3,35)	< 0.0001
Fe	11.24	(3,35)	< 0.0001
Mn	133.88	(3,35)	< 0.0001
Ni	23.34	(3,35)	< 0.0001

Scheffé Multiple Range Tests ($p=0.05$) revealed that in the incinerator ash, manganese (Figure 22), nickel (Figure 23), and iron (Figure 24) were significantly higher in the fertilized treatment than in the unfertilized treatment. This is in contrast to the concentration values, where except for manganese, no differences were indicated. No significant differences were observed for copper or chromium when expressed on a per root basis (Figure 23). These findings are identical to the results for the concentration data.

For gold tailings, Scheffé Multiple Range Tests ($p=0.05$) indicated that in contrast to the concentration data, levels of manganese (Figure 22), nickel (Figure 23) and chromium (Figure 23) were no longer significant. However, levels of copper and iron were still significantly different and similar to the results of the concentration data (Figures 23 and 24 respectively).

High metal levels in shoots from unfertilized gold tailings can once again be traced to the limited growth and small sample weight analyzed.

A oneway ANOVA of the fertilizer effect for zinc indicated significant differences by group [$F(1,48)=10.28$, $p=0.0024$], while a Scheffé test ($p=0.05$) revealed that shoot metal content per gram of root was significantly higher in the shoots grown with the addition of fertilizer (Figure 25).

Overall, the application of fertilizer to incinerator ash caused seedlings to accumulate more Fe, Mn, Ni and Zn per gram of root, and although the effect was not statistically significant for Cu and Cr, the general trend was identical. Thus, while the addition of fertilizer results in substantially better growth, it also causes increased extraction of metals from the soil by the roots, and/or increased

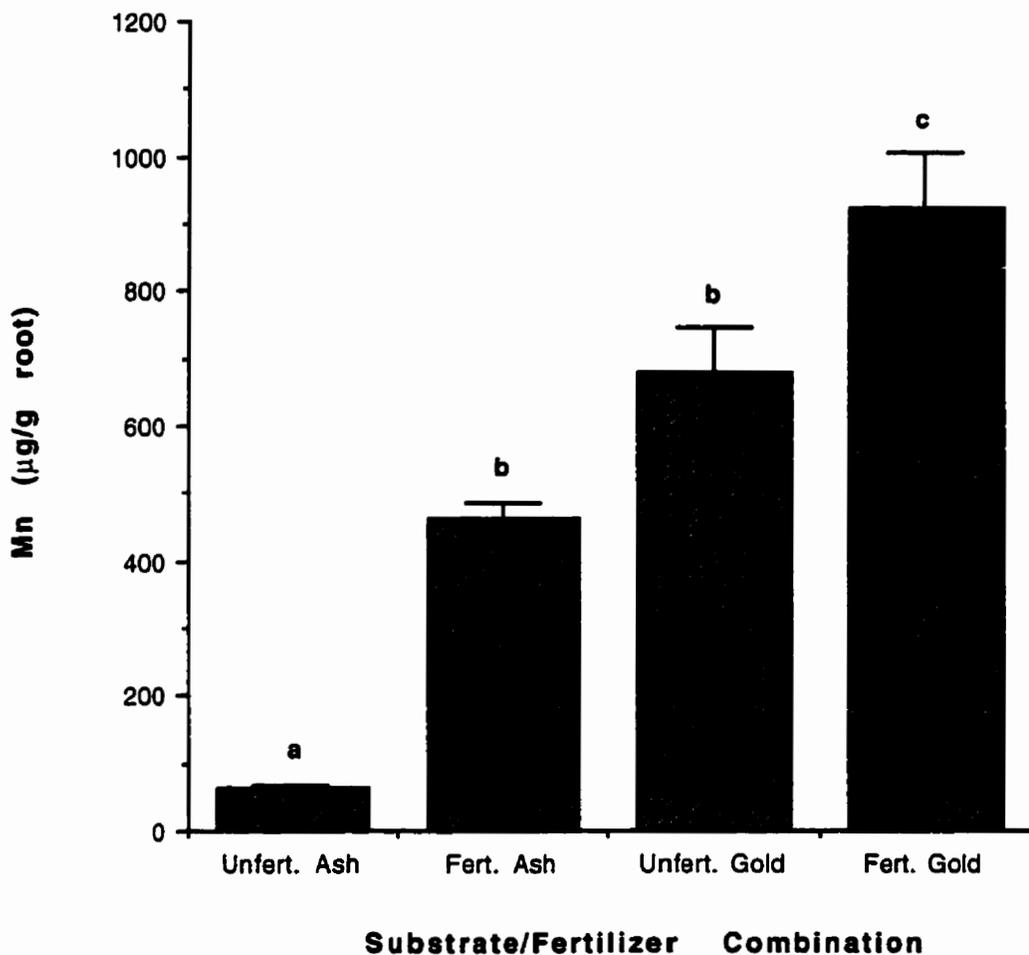


Figure 22: The effect of fertilizer on mean shoot manganese content per gram of root (+ S.E. ; n=10) for Redtop seedlings grown in pots containing incinerator ash or gold tailings (Experiment 5). Different superscripts represent significant differences at p=0.05.

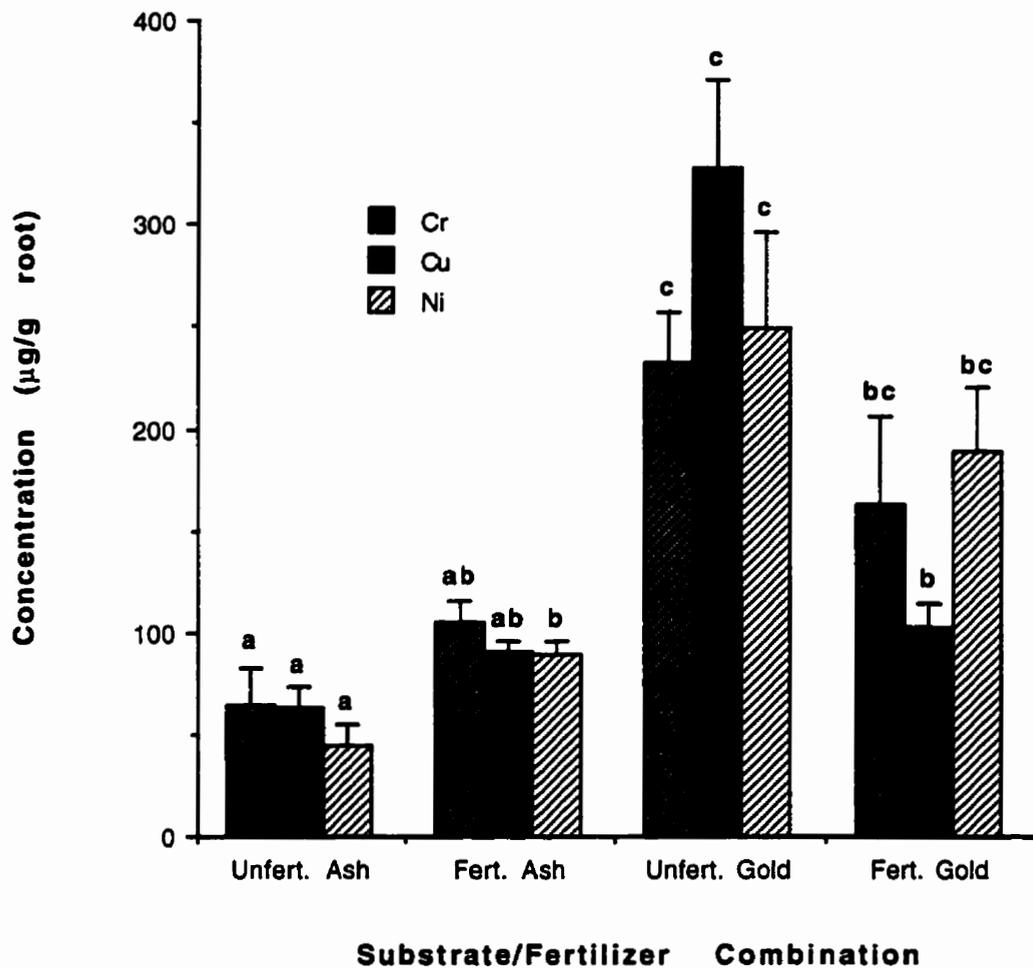


Figure 23: The effect of fertilizer on mean shoot chromium, copper and nickel per gram of root (+ S.E. ; n=10) for Redtop seedlings grown in pots containing incinerator ash or gold tailings (Experiment 5). Different superscripts within each metal represent significant differences at $p=0.05$.

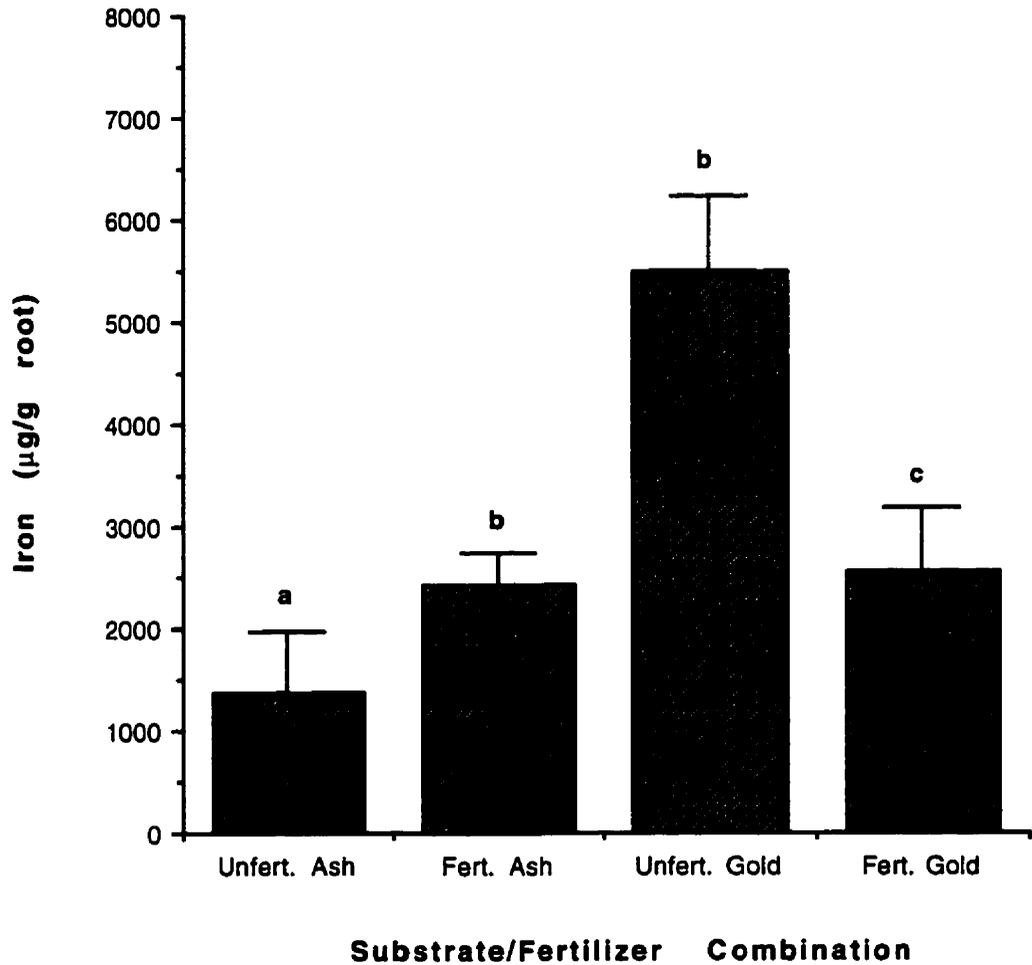


Figure 24: The effect of fertilizer on mean shoot iron per gram of root (+ S.E. ; n=10) for Redtop seedlings grown in pots containing incinerator ash or gold tailings (Experiment 5). Different superscripts represent significant differences at p=0.05.

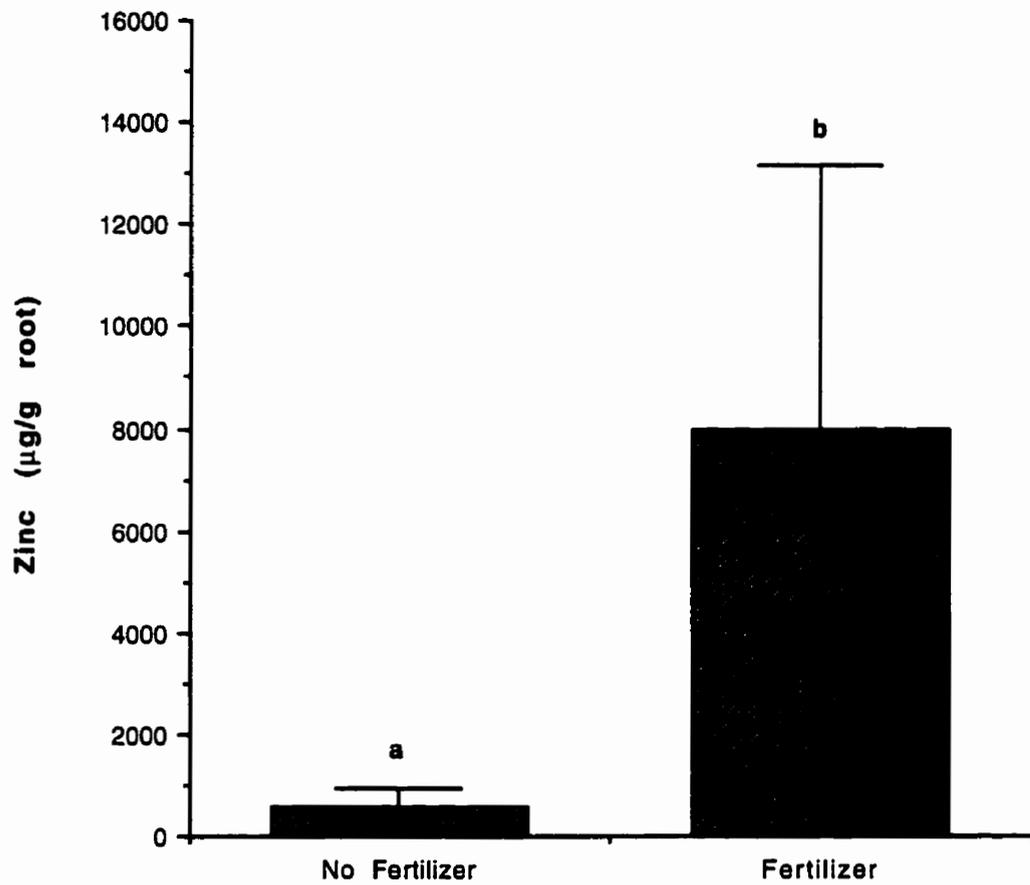


Figure 25: The effect of fertilizer on mean shoot zinc per gram of root (+ S.E. ; n=20) for Redtop seedlings grown in pots containing incinerator ash or gold tailings (Experiment 5). Different superscripts represent significant differences at $p=0.05$.

translocation of metals from the soil to the shoots. This may be of concern in situations where growth occurs in metal-contaminated soil such as tailings, because it may lead to higher concentrations of metals near the surface as the vegetation decomposes. However, translocation may be influenced by a variety of factors. For example, Wu *et al.* (1975b) found that the roots of *Agrostis stolonifera* accumulated more copper than the leaves, and that more copper was accumulated by tolerant clones than non-tolerant clones. Further, as the concentration of copper in solution increased, copper moved into the leaves of non-tolerant clones more readily than the leaves of tolerant clones.

3.4.2.4 Summary of Findings

- 1) The best growth (both roots and shoots) was obtained in incinerator ash, followed by gold tailings. Vegetation established in depyritized tailings, pyritic tailings and granulated slag was minimal to nil.
- 2) The application of fertilizer significantly increased both shoot and root growth, and while overall growth was significantly higher in incinerator ash, fertilizer caused proportionately more growth in gold tailings.
- 3) No toxicity symptoms were noted in the shoots, except for possible nitrogen deficiency without the addition of fertilizer. This effect was present in both incinerator ash and gold tailings.
- 4) The addition of fertilizer decreased root:shoot ratios, with no difference indicated between incinerator ash and gold tailings.
- 5) The addition of fertilizer significantly decreased pH in pyritic, depyritized and gold tailings, but not in incinerator ash or granulated slag.
- 6) There was no evidence of upward salt migration into the covers as a result of oxidation of the underlying tailings.
- 7) Shoot concentrations of cadmium, cobalt and lead were below detection limits in all cases.

- 8) The addition of fertilizer resulted in increased shoot manganese concentration, an effect not seen in the other metals studied.
- 9) In comparison with reported background values from uncontaminated sites, shoot metal concentrations were elevated for all metals except manganese. Shoot metal levels were, however, similar to mean values reported for metal-contaminated sites.
- 10) Ratios of metal concentration in the vegetation to total metals in the soil were higher when plants were grown in gold tailings than when grown in incinerator ash. No difference was noted between control treatments and with the application of lime or fertilizer.
- 11) Shoot chromium concentrations for seedlings grown in incinerator ash and gold tailings were approximately 10-20 times higher than values reported in the literature.
- 12) Absolute (per pot) shoot metal levels were generally higher when grown in incinerator ash than in gold tailings, and increased with the addition of fertilizer.
- 13) The application of fertilizer to incinerator ash caused leaves of grass seedlings to accumulate more Fe, Mn, Ni, and Zn on a root weight basis. This effect was not apparent in gold tailings because of magnified metal levels in unfertilized gold tailings, caused by low biomass production.
- 14) Limestone had no statistical effect on any of the parameters measured.

3.5 Conclusions From Growth Studies

Phytotoxic effects associated with high metal levels in a particular substrate can be manifested in germination and early development phases of seedling development, primarily through a reduction or inhibition of root growth. Alternatively, the effect of metals on early growth may not be severe enough to prevent growth, but may significantly affect long term development.

Germination tests indicated that seed germination was not affected by any of the materials tested, and was generally similar to germination obtained in gravel controls. Early seedling establishment was most seriously impaired in pyritic tailings and granulated slag, with the effect most noticeable in root development. Roots, because they are in intimate contact with the growth substrate, are usually impacted most by increased metal levels. Seedling establishment was found to be best in depyritized tailings, gold tailings and incinerator ash.

Longer term growth experiments revealed that the best growth was obtained in incinerator ash and gold tailings, and that both materials showed a strong response to fertilizer. Contrary to the findings of the germination experiments in which the best initial growth was found in depyritized tailings, longer term growth in depyritized tailings was severely impaired. This may have been more a function of the inability of roots to penetrate the tailings than a response to phytotoxic metal levels.

An analysis of shoot metal concentrations for seedlings growing in incinerator ash and gold tailings revealed that seedling metal uptake from the two materials was similar. However, values were generally higher than background values reported in the literature, but were similar to values reported for metal-contaminated sites. Unfortunately, due to lack of growth, no shoot metal data were available for seedlings grown directly in the pyritic tailings. Therefore, no comparison could be made between metal concentrations that could be expected in vegetation growing in the existing tailings versus concentrations in the potential cover materials.

The addition of fertilizer to pots containing incinerator ash or gold tailings resulted in an increase in shoot concentration for manganese only. This increase in manganese was attributed to a combination of both the effect of fertilizer on seedling growth (greater metabolic demand), and possibly increased availability as a result of a decrease in pH associated with the addition of fertilizer. However, elevated shoot manganese concentrations are not thought to represent an environmental hazard. Shoot chromium concentrations were found to be approximately 10-20 times higher in the present study than in reported literature values. The availability of chromium increases at higher pH's, and is thought to be the reason for increased accumulation in shoots. Chromium is reportedly toxic to organisms, and remains a potential hazard in establishing vegetation in incinerator ash.

Absolute (per pot) shoot metal levels were higher for incinerator ash than for gold tailings, and increased with the addition of fertilizer. These higher levels were a reflection of the greater shoot growth in incinerator ash and with the addition of fertilizer.

For incinerator ash, shoot contents of Fe, Mn, Ni and Zn expressed on a root weight basis were higher with the addition of fertilizer. Thus, while fertilizer increased growth in the incinerator ash, it also increased the proportion of these metals accumulated in the shoots. Therefore, the roots were better able to exploit the metal-contaminated soil and/or translocate metals to the shoots, which may eventually lead to higher concentrations of metals near the ground surface as the vegetation decomposes.

The addition of limestone did not have an effect on any of the growth or metal uptake parameters measured. This was not surprising, as most of the potential cover materials maintained circumneutral pH's. Even the longer term growth experiments (~3 months) did not provide sufficient time for acid produced through sulphide oxidation to overcome the inherent acid neutralizing capacity of the pyritic tailings, the most potentially acid -producing material tested.

4. COLUMN STUDY

4.1 Introduction

Column studies are one example of the many tests that are currently being utilized to predict the chemical quality of drainage generated within tailings. In their simplest form, columns consist of a container of tailings which are subjected to leaching, generally by introducing a leachant into the top of the column and collecting the leachate from the bottom of the column.

The design of the columns can vary greatly in complexity, and can be used simply to determine whether a particular tailing sample can be expected to oxidize and generate acidic drainage, and also, by adding different materials, can be used to evaluate various treatment options. Because column tests can predict changes in leachate chemistry over time, they are termed *kinetic* tests, as opposed to *static* tests, which generally make predictions based on one-time measurements.

4.2 Literature Review of Test Protocols for the Prediction of Acid Mine Drainage

4.2.1 Static Testing versus Kinetic Testing

Laboratory tests aimed at predicting the occurrence of acid mine drainage (AMD) from tailings can be divided into two main categories; static tests and kinetic tests.

Lawrence (1990) described static tests as an attempt to define the balance between the potentially acid producing sulphide minerals and the acid consuming (typically carbonate) minerals. This definition was expanded upon by Bradham and Carrucio (1991), who described static tests as the use of whole rock analyses to predict mine drainage quality, and are based on the assumption that the specific minerals comprising the mine waste/overburden will react with water to produce varying degrees of alkalinity and acidity. Lawrence (1990) further stipulated that the results of static tests should be used with some judgement since complete reaction of both sulphide and carbonates is assumed, with no consideration to kinetics or chemical equilibria.

Kinetic tests attempt to predict the longer term weathering characteristics of a waste material as a function of time (Lawrence, 1990), and empirically determine leachate quality by subjecting the tailings samples to simulated weathering conditions while monitoring the quality of the effluent produced (Bradham and Carrucio, 1991). These tests are usually carried out only if preliminary static testing indicates the potential for AMD. In addition to providing confirmation of AMD potential indicated by static test conditions, kinetic tests might also provide an assessment of the rates of sulphur oxidation, acid generation, depletion of neutralization capacity, and metal concentrations in the drainage. In addition, different waste deposition and control scenarios can be evaluated by varying the conditions under which the tailings are weathered (Lawrence, 1990).

Lawrence (1990) suggested that, although several of the static and kinetic tests could provide an accurate prediction of whether AMD would be generated from specific samples of waste, one test alone might not provide a definitive assessment of the potential of many wastes, and a combination of procedures would provide greater certainty. This sentiment was echoed by Morin & Hutt (1994) who stated that static and kinetic tests should be performed as one suite of testwork, because each relies on information from the other for proper interpretation.

Within the broad categories of static and kinetic tests, a variety of analytical techniques are available, each possessing advantages and disadvantages relative to the others. The most common techniques used in both Canada and the United States include simulated weathering chamber tests (columns and humidity cells), Soxhlet reactors (infrequently used), biological confirmation tests (commonly referred to as B.C. Bacterial tests), whole rock analyses (acid-base accounting; used extensively in coal fields), and B.C. Research Initial tests, which are used extensively for base metal and gold mines in Canada and the Western United States (Bradham & Carrucio, 1991). The advantages and disadvantages of several of these tests are summarized in Table 23.

Sobek *et al.* (1978) indicated that the most widely used static test was the acid-base account (ABA), as did Lawrence (1990), who stated that on the basis of cost and simplicity, acid base accounting is the preferred static method, but recommended using the modified acid-base accounting procedure. This method follows the same principles as Sobek *et al.* (1978), but differs in that the acid

Table 23: Most Commonly Used Mine Waste Analytical Techniques
(after Bradham & Carrucio, 1991).

Method	Advantages	Disadvantages
Static Tests		
-Acid/Base Accounting (Sobek <i>et al.</i> 1978)		
Whole rock analyses completed on a pulverized sample. Acid potential related to sulphur content, NP ¹ determined by hot acid digestion with HCl.	Simple to perform, quick turn-around time. Useful in areas that are acid or alkaline prone. Relatively inexpensive.	Does not relate to kinetic data. Assumes parallel release of acidity and alkalinity.
Dynamic (Static) Tests		
-Soxhlet Reactor (Renton <i>et al.</i> 1988)		
Leachate generated from a pulverized sample which is cycled in a soxhlet reactor. During interim, sample is stored at 105°C.	Easy to perform. Quick turn-around time, purported kinetic data.	Expensive apparatus, extremely aggressive oxidation of sample.
-Humidity Cells (Carrucio 1968)		
Crushed rock is placed in humidified atmosphere and leached periodically. Volume and character of leachate related to rock weight to produce alkaline/acid production potential.	Produces kinetic data. Rates of acidity per unit weight of sample obtained, approximates field conditions.	Long time required, large data base generated. Relatively expensive.
-Column Weathering Test (Hood and Oertel 1984)		
Field sample placed in large columns and leached periodically. Leachate is analyzed and related to rock weight.	Best approximator of field conditions.	Same as above. In addition, large volume of samples required. Channelization problem encountered.

I: Neutralization Potential

digestion step is carried out under milder conditions than the boiling specified by the method of Sobek. This advice was confirmed by Lapakko (1992), who found that the acid production potential and the neutralization potential determined by the Modified Acid Base Accounting were more accurate than the corresponding values determined by Sobek's Acid Base Account. The acid potential (AP) of the waste is usually calculated from the sulphur content of the material, while the acid consuming capacity or neutralization potential (NP) is determined by experimentally measuring the quantity of acid consumed by a finely ground sample of the material. The waste is considered to be a potential producer of acid if the acid potential exceeds the neutralization potential (Lawrence, 1990).

Lapakko (1994), further refined the B.C. Research initial test by titrating to pH 6 instead of pH 3.5. He reasoned that the neutralization potential available above this pH represents the amount of acid that a mine waste could neutralize while maintaining drainage pH in a range that meets water quality standards. This method was more accurate than the standard ABA, modified ABA and B.C. Research initial test in predicting neutralization potential.

Calow *et al.* (1995) evaluated the B.C. Research Initial and the EPA Acid-Base Accounting procedures, and found that quite different results were obtained, depending on the source of the waste material. They recommended that the B.C. Research method be adopted as a universal standard AMD predictive static test.

For the evaluation of the longer term weathering characteristics of a waste material, Lawrence (1990) recommended the use of humidity cells.. This is essentially a column design for which air flow, temperature and moisture are controlled. This method allows for the removal of oxidation products through leaching, in order to determine the onset of AMD, mass loads, and the concentration of metals and other species as a function of time.

Michalovic and McGee(1984) concluded that properly conducted leach tests are able to produce data that can be correlated with the leachate characteristics of the parent waste piles, and that they can reproduce the acid production mechanisms occurring in the field. In addition, they stated that "the laboratory leach test can also be used to predict acidic runoff and may have utility as an experimental test

bed where chemical and physical treatments to mitigate acid production can be evaluated".

The disadvantages associated with leaching tests are the long time frame, the amount of laboratory space and the apparatus required for the analyses. However, leaching tests provide empirically derived data, eliminating the error in interpreting static tests such as acid-base accounting. The ability of a sample to produce acidic or alkaline leachates can be easily discerned and identified using kinetic tests (Caruccio and Geidel, 1994). Further, cumulative acid production can be plotted versus time, permitting an estimate of the time required for a particular tailings sample to produce acidic drainage under a given set of conditions.

Carrucio and Geidel, (1986) stated that column tests best approximated the quality of the leachate derived from large scale field tests, and Bradham and Carrucio (1990) found that column tests utilizing well-sorted, coarse-grained samples (>0.5 cm), most accurately resembled field conditions. However, they indicated that fine-grained particles (<1 mm) may afford the sample with a large water-holding capacity (specific retention) which, because the diffusion of oxygen through water is slow, may create an airlock that effectively inhibits the transfer of oxygen required to oxidize pyrite and restrict acid production to the exterior of the surface. They also indicated the possibility of the formation of channels, through which the leachate may preferentially travel, especially when a dry cycle is included. The result of this would be a shorter leachant retention time, which may produce leachate that is not representative of chemical conditions within the column.

In terms of predicting whether tailings would produce acidic or alkaline leachates, Bradham & Carrucio (1990) found that column tests appeared to be the worst of the four methods tested, though they were still 80% accurate (predicting 8 out of 10 samples tested), with the two incorrect classifications attributed to air-locks.

The column test protocols appear to have the ability to distinguish potentially reactive tailings from benign tailings, but do not necessarily reflect the extent to which potential reactivity is realized in the natural setting of the tailings themselves (Doepker and O'Connor, 1990a).

Erickson & Hedin (1988) found that neither acid-base accounting nor simulated weathering studies were effective in predicting drainage quality. Acid-base accounting was able to predict strongly acidic or basic leachates, but a grey area remained for intermediate samples. The weathering procedure used (humidity cells) suggested that pyrite oxidation could be mimicked, but that the alkalinity-generating processes were not mimicked. They suggested that neutralization reactions that occur in the field can be simulated in the laboratory if the neutralizing strata were exposed to leachate from acidic strata.

The studies reviewed above, when taken together, suggested that kinetic tests provided a more detailed examination of tailings oxidation and the release of metals, both from the tailings and potential cover materials. In addition, kinetic tests may provide some insight into the mechanisms responsible for the rate of acid production and metal release.

4.2.2 Evaluation of Test Protocols for Leaching Columns

A variety of leaching columns have been used by numerous researchers to study the weathering of tailings, beginning mostly with efforts to determine the factors that influence pyrite oxidation.

While the following is intended to provide background material on the evolution of column design, methodology and results, it is by no means exhaustive, and is aimed at illustrating some of the means by which column tests have been used to assess tailings oxidation.

Hood and Oertel (1984) used leaching columns as a method for predicting the effluent quality from surface mines. They constructed the columns from glass tubing 122 cm. long by 3.5 cm. wide (I.D.), with a two-hole rubber stopper fitted into the bottom and secured with tape. One hole provided drainage into a catch bottle, while the other was connected to the mouth of a 250 ml. polyethylene bottle from which the bottom had been removed. The bottle, attached mouth downward, was a reservoir for the distilled water used to leach the sample. A wad of glass wool was placed in the bottom of the column to prevent clogging, and a piece of tygon tubing, open at both ends and perforated every 2-3 cm. was inserted into the

centre of the column, extending from below the glass wool to the top of the column. The columns were then packed with 1 kilogram of crushed overburden (coal). This study produced several relevant conclusions. First, they found that the duration of the leaching cycle made little difference in the quality of the effluent. Therefore, the leaching experiments were designed to fit into a convenient laboratory schedule. The cycle length that was selected was a compromise between the desire to have a realistically long aeration cycle and the need to complete the experiment in a practical length of time. Thus a one-week total cycle time, using a two day rock-water contact time, was selected. Second, relationships among the important chemical constituents were very similar to those present in actual mine drainage waters, but the overall concentrations of ions were more dilute in the leachates. Multiplying the leachate concentrations by a factor of 4.5 gave values similar to mine waters. From this, they suggested that each of the leaching cycles represented about three years of natural weathering, thus providing the evolution of the mine drainage water over a time span of about 36 years.

Michalovic and McGee (1984) conducted a column study to develop a technique to assess coal waste leachate. The columns were constructed of 63.5 cm lengths of 8.9 cm (I.D.) PVC tubing, loaded to a depth of 38.1 cm. with coal waste of a particle size less than 0.95 cm. Gaps between the sample and the inside walls of the column were minimized by lightly tamping the material as it was added to the columns. The coal waste samples were retained by a polypropylene Büchner funnel with an inside diameter of 9.2 cm, fitted onto the bottom of the column and held in place by an O-ring seal. A glass wool plug was placed between the funnel and the sample, and the leachate collected in 1000 ml polypropylene bottles. Two leaching cycles were utilized; 1) 2 inches of "rain" for 5 consecutive days followed by a 10 day dry period before repeating. 2) 2 inches of rain for 5 consecutive days followed by a 3 day dry period. The leachates were collected until just before the next "rainfall". They found that the extended drying period resulted in increased conductivity and iron in the leachate.

Shellhorn and Rastogi (1984), in a study to determine the effects of bactericides on the production of acid mine drainage, used glass columns 45 cm long with an inside diameter of 6 cm. The columns were sealed at the bottom with a rubber stopper which had a coiled drain tube to act as a trap and prevent back-flow. A layer of silica glass beads was sandwiched between stainless steel screens at the

base of the column, which was then packed with 1 kg of coal refuse. The refuse was leached weekly over a 10 week period and the leachate was analyzed for acidity, pH, conductivity, Eh, and bacterial activity. They found that sodium lauryl sulphate was effective in decreasing bacterial populations, resulting in decreased oxidation and release of associated byproducts.

Bradham and Carrucio (1990), conducted a comparison of acid/base accounting, weathering cells, columns, and soxhlet reactors for their efficiency in predicting leachate quality. They used several tailings samples possessing a variety of Neutralization Potential/% Sulphur ratios. While specific details for column methodology were not provided, they found that particle size plays a major role in acid production, with acid loads varying inversely with particle size.

Hammack and Watzlaf (1990) utilized both small and large columns to weather pyrite at room temperature, with a constant humidity of 88% and oxygen partial pressures between 0.5 and 21%. The small columns were 40 cm in length and 2.54 cm in diameter, and were filled with 5 g of pyrite dispersed in 100 g of 30-60 mesh acid-washed silica sand. Glass wool at the base of each column prevented the sample from washing out of the column. These columns were designed to allow pyrite to weather under unsaturated conditions in known oxygen atmospheres. The columns were leached weekly with 200 ml of 16 megaohm deionized water, and the leachate monitored for bacteria by using the most probable number type of bacterial enumeration, and for sulphate by ion chromatography.

The large columns were constructed using 1.92 m lengths of 0.29 m diameter cast acrylic. For these columns, three room temperature experiments were carried out;

- a) a comparison of two applied oxygen partial pressures during unsaturated leaching,
- b) a comparison of four unsaturated leaching frequencies
- c) a comparison of unsaturated leaching with water saturated leaching

Deionized water was added through the top of the columns for all leaching and flushing tests. The tops of the columns remained open to the atmosphere for tests b) and c), but were closed for a). During all unsaturated leaching tests, the valve on the final leachate collection system remained open with the end of the tube kept

under water to prevent oxygen inflow. During flushing tests, the columns remained saturated with water with a constant water level maintained at 0.15 m. above the surface of the shale. Twenty litres of water were added and withdrawn simultaneously to maintain this water level.

The results of these column tests indicated that initial abiotic oxidation of fresh pyrite surfaces was independent of oxygen partial pressures above 10%, and was proportional to the oxygen partial pressures below 10%. With bacteria present, the rate of pyrite oxidation was found to be independent of oxygen partial pressures above 1%. Below 1% oxygen, the reaction rate was proportional to oxygen partial pressures, and the rates of abiotic and biotic pyrite oxidation were not significantly different at oxygen partial pressures above 15%. Lastly, they indicated that the role of bacteria was to sustain high oxidation rates at low oxygen partial pressures. Thus, in order to be effective at reducing pyrite oxidation, oxygen levels must be maintained below 1%. In general, these results indicated that current oxygen impermeable or consumptive barriers (except water) would not be effective at limiting pyrite oxidation without bacterial inhibition.

In evaluating the effect of leaching frequency, four leaching schemes were followed; a) 1L every day b) 7 L every 7 days c) 14 L every 14 days and d) 21 L every 21 days, and it was found that there was very little variance between treatments (Hammack and Watzlaf, 1990). Two possible explanations were offered: first, that the build up of weathered products did not retard pyrite oxidation or, secondly, that the solubilization of sulphate minerals under these conditions may be slower than pyrite oxidation. Therefore, leaching frequency tests may only be indicative of the rate of oxidation product solubilization rather than pyrite oxidation.

Thus, overall, the results showed that under unsaturated conditions, pyrite oxidation can only be reduced by bacterial inhibition in conjunction with an oxygen-consumptive or oxygen-impermeable barrier.

A series of column experiments were conducted by Doepker (Doepker, 1988; Doepker & O'Connor, 1990a; Doepker & O'Connor, 1990b; Doepker, 1991a; Doepker, 1991b) to determine the dissolution characteristics of metal from various tailings types.

Columns were constructed of 61 cm or 122 cm lengths of 7.6 cm (ID) PVC tubing, and were equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed. A 9 cm borosilicate glass fibre filter was placed on the perforated plate before installation of the bushing. Approximately 1.75 kg of tailings were placed in the 61 cm columns and 7.0 kg in the 122 cm columns. Leachant was introduced to the columns drop by drop from a 1 litre polypropylene bottle through tygon tubing fitted with a screw clamp. The volume of leachant used depended on an experimentally determined pore volume. Pore volume was generally estimated as the difference between the leachant and leachate volumes, representing the volume of water held by the pores of the sample. These experiments generated many relevant conclusions regarding the oxidation of tailings and the resultant dissolution of metals, which are summarized over the next several pages.

Considerable differences in leachate concentrations were observed when fresh tailings were compared to well-oxidized tailings because secondary minerals may be more or less soluble than primary sulphide minerals. The effects of sample location and depth on leachate concentrations may be related to the degree of oxidation that has occurred and the composition of the undeveloped samples.

Leachate metal concentrations from well oxidized tailings will slowly decrease with continual leaching, and will not be influenced by drying and/or temperature variations. Oxidizable sulphidic tailings will generally react similarly if the tailings are maintained at or near saturation, since under these conditions, the rate of oxidation is slow. Destructive oxidation of tailings will occur in the unsaturated zone, requiring both water and atmospheric oxygen, and resulting in decreased leachate pH and enhanced metal release.

Basic tailings with large acid-buffering capabilities may still produce acid leachates as a result of the oxidation of sulphides (pyrite) within the tailings. Enhanced metal release as a result of the oxidation of unsaturated tailings may follow, even when leachate pH remains near normal.

Two conditions are necessary for enhanced metal dissolution from tailings containing reactive sulphides: that oxygen be available and that pore water evaporate. The rate of metal release from tailings depends on the local

environment of the system, that is, pH and total ionic strength of the leachant, chemical composition of the host rock, formation rates of secondary minerals, and the oxidation potential of the locality. In addition, increased metal dissolution was observed through the formation of acetate complexes, and it was suggested that this may become important with the addition of organic matter to tailings.

High sulphate production is more commonly associated with high metal concentrations, and is indicative of tailings that are susceptible to atmospheric oxidation.

Tailings that produce acid leachates appeared to be sulphate driven, that is, sulphate was present in the sample from mobile metal sulphate complexes. It was suspected that the use of biocides and other treatment measures may have little effect on metal dissolution until this "excess" sulphate is eluted. Sulphate formation seemed to be more related to the rate of pore water evaporation than to leachate residence time. This indicated that the rate of sulphide oxidation by oxygen must have been tightly controlled by the distribution of water and oxygen on the sulphide surface.

In general, high sulphate yields initially observed through leaching procedures flag potentially oxidizable tailings, but may be the result of past activity as opposed to present activity. Due to enhanced solubility of metal-sulphate complexes, leachates containing large amounts of sulphate may also exhibit high metal loading. A reduced oxygen atmosphere may be the only method to stabilize metal dissolution from tailings at an acceptable level.

The production of sulphate can be directly related to the percent of pore water loss (the more pore water lost, the more sulphate produced). Therefore it may be reasonable to adjust the leachant volume in order to standardize the leachate volume.

Tailings that produce acidic leachates often produce relatively small changes (less than one order of magnitude) in metal concentrations with dry cycles, while tailings that normally produce basic leachates may demonstrate enhanced metal dissolution of one to two orders of magnitude.

Leachate concentrations from packed columns of 6 to 12 inches produced observable wet/dry cycle effects, while longer columns (approx. 40 inches) revealed little observable metal enhancement from unsaturated conditions. The high leachate sulphate and metal concentrations initially observed in air-dried tailings, followed by rapidly falling concentrations with subsequent leachings, appeared to reflect oxidative reactivity and/or highly oxidized tailings samples.

In general, Doepker also found that leachate metal concentrations from longer columns were higher than concentrations from shorter columns for the same tailings in any one leaching. However, on a pore volume to pore volume comparison, they were similar. The leachate metal concentrations from columns of air dried metal-mine tailings peaked within 1 to 3 pore volumes, and then decreased with each subsequent leaching.

A four-fold increase in tailings depth (40" compared to 10") did not greatly increase the leachate metal concentrations when near-saturation was maintained in the columns. However, if unsaturated conditions occur and the tailings are subject to oxidation, the shorter column may produce much increased leachate metal concentrations, while a much smaller increase may be observed from the longer columns.

Certain sulphidic tailings produced enhanced metal dissolution when leaching occurred after an extended drying period. This enhanced metal mobility (if present) was evident only when the column depth was 30 cm or less. The longer columns, when leached with a fraction of the pore volume, appeared relatively insensitive to enhanced metal mobility. Doepker surmised that dilution and leachate residence time were major factors in the apparent insensitivity. The longer columns maintained at constant room temperatures appeared to be relatively insensitive to dry cycles.

Doepker also found that saturated conditions existed in freely draining columns containing 22 to 26 cm of tailings where pore water evaporation was prevented. On the other hand, drainage must be restricted in order to maintain saturation if columns are to be 90 cm deep. Even covering the columns with a plastic wrap did not eliminate oxygen diffusion, but was effective at reducing oxygen diffusion under constant temperatures. If daily temperatures changed, the availability of

oxygen was enhanced through simple expansion and contraction (thermal pumping) of air. It is reasonable to expect that where the rate of oxidation depends on oxygen, oxidation will be increased through any mechanism that increases oxygen availability. Therefore, longer, free-draining columns might be expected to produce leachates of higher than predicted metal concentrations (higher than equivalent short, free-draining columns) if the tailings are reactive to oxidation. The percent of saturation at the long column is less than that of the short column, and therefore more prone to oxidation.

In the case of submerged metal-mine tailings, Doepker and Drake (1991c) found that the total amount of waste material influences metal concentrations over the short term, but not when long-term contact is considered (approx. 520 days in this case). In general, surface area has a minimal effect on initial metal concentrations, but as the contact time becomes greater, the rate of metal dissolution becomes directly proportional to contact surface area.

Gentry, Willis and Halverson (1992) constructed their columns from polyethylene, 20.3 cm in length and 10.4 cm in diameter. They added 1.5 kg of spoil to the column, which was retained by an inert fibreglass mat at the bottom of each cylinder. Each of 3 replications was irrigated weekly with 2.54 cm of water and allowed to drain freely. The leachate was collected in a new polyethylene bottle each week. The columns were covered with a watchglass between irrigations to prevent excessive drying of the spoil.

The treatments consisted of leaching the spoil (156 weekly wet/dry cycles) with artificial precipitation with pH adjusted to 5.6, 5.0, 4.6, 4.2, and 3.8, respectively. Approximately 50 ml of solution was required to restore the spoil to field capacity prior to leaching. Channel formation during percolation was prevented by a second fibreglass pad used to distribute the irrigation water over the spoil surface. The columns were located in a climate controlled environment to remove any effects of temperature changes. Samples were analyzed for 18 different ions, plus acidity, alkalinity, pH and specific conductance, the day after collection. In addition, total dissolved solids (TDS) was determined by adding the mass of all ions that were measured.

The results of this study showed that readily available ions quickly leached from fresh spoil into the ground water. As time passed, the percent of readily available ions greatly decreased but ions continued to be leached, coming from the weathering and breakdown of the spoil. The chemistry of the leachate produced by simulated acid precipitation was different from that produced by distilled water. Although the study did not show which parameter caused the difference, it did indicate that it was not pH. The spoil seemed to have a high buffering capacity which resulted in the pH of the leachate being constant for a long period of time and at a very different pH than that of the leachant.

Leaching columns have not only been used to determine the factors that affect the oxidation of iron sulphides, but also to evaluate the effect of the addition of various cover materials over tailings in preventing tailings oxidation. This has often necessitated the construction of more complex column designs, so that such parameters as % moisture, porewater pH, Eh, metals etc. can be evaluated *in situ*.

Hoving & Hood (1984) used column tests to look at the effect of different thicknesses of limestone and soil over pyritic material on leachate quality. The columns were constructed of 3 inch diameter polyvinyl chloride (PVC) pipe, ranging from 4 - 6 feet high, open on top and capped on the bottom. The caps were drilled and fitted with T-connectors and tygon tubing for drainage, and glass wool was placed in the bottom of the column to prevent clogging of the T-connector. The columns were packed with 18 inches of pyritic material and leached each week for 12 weeks, with leachate collected in 1 litre polyethylene bottles. They found that limestone generally had no impact on the rates of acid generation in the underlying pyritic material, and that compared to uncovered wastes, a five-fold decrease was obtained using soil covers.

Reardon and Moddle (1985), in determining the suitability of peat as an oxygen interceptor over uranium tailings, used 4.4 cm (I.D.) plexiglass columns 185 cm in length. Each column was fitted with a jacket of thick polyethylene plastic, to reduce the possibility of oxygen diffusion through the walls of the plexiglass. Two holes were drilled into the end-plate, one (effluent port) to obtain the leachate sample and the other (a flushing port) used to remove air bubbles that periodically became trapped in the end-plate during unsaturated-flow experiments. Quartz sand (25 - 35 mesh) was packed into the bottom of each column to a height of 10

cm in order to prevent possible clogging of filter paper which had been placed on the end-plate. Water flow rates were controlled in this experiment through the use of a multichannel peristaltic metering pump.

Samples of the column effluent were stored in 20 ml plastic scintillation vials. Cation analysis was performed on acidified samples, while dissolved organic carbon and total carbon were determined on unacidified samples.

They derived a relationship which allowed the prediction of a diffusion coefficient for oxygen at temperatures near 25 degrees Celsius. This coefficient was used to evaluate the design characteristics of a uranium tailings close-out scheme which involved the placement of a peat layer between uranium tailings below and depyritized tailings above. They found that the cover material must be efficiently packed at the time of deposition, so as to minimize the total porosity of the material, if a sufficiently low diffusion coefficient is to be achieved. The minimum thickness of both peat and cover layer required to provide for a thousand years' exclusion from pyrite oxidation was calculated to be 20 cm, assuming permanent water saturation conditions for the cover layer.

Jackson *et al* (1993) used columns to determine the influence of fly ash, topsoil, limestone and rock-P on the quality of drainage from coal refuse. The columns were constructed of 20 cm diameter, smooth bore plastic drainage pipe, with perforated end caps to retain 36 kg of coal refuse. A HDPE funnel was sealed with silicon to the bottom of the column and packed with glass wool to wick the leachate from the bottom of the column. The columns were leached weekly with 2.5 cm of simulated rain, and analyzed for pH, conductivity, Fe, Mn and B. This study determined that fly ash may prove to be a viable alternative to conventional topsoil/limestone treatments to control AMD, if adequate alkalinity is present in the ash/refuse mixture.

Ames (1981) used plexiglass columns, 85 cm in height with an inside diameter of 15 cm, to monitor the movement of acid and metals from oxidized tailings to overlying cover media. Porewater samples were collected from several depths within the columns via porcelain cups 9 cm in length, inserted horizontally into the columns. Solutions were extracted through the use of 20 ml pre-vacuumed, acid-

washed vacutainers. A water table was maintained approximately half-way up the tailings material for the duration of the experiment.

Each column consisted of 30 cm of tailings and 45 cm of overburden. The columns were vibrated with each increment of tailings added in order to reduce later cracking, swelling and slumping of the tails. This also helped obtain a fairly uniform bulk density of the tailings in all of the columns. Once the tails were added, they were allowed to settle for a day before the overburden was added.

Extractions were collected monthly through the addition of 1L of distilled water to monitor chemical changes in the columns as a guide to the progress of the experiment. It was felt that the extractions were useful in indicating the presence of small concentrations of contaminants in the overburden originating from the tailings, which were predicted to be masked by the dilution effects of the chemical analysis carried out on the "soil" samples removed from the split columns. In addition, these liquid samples were analyzed directly, without interferences or influences of extraction solutions, solubilizing agents or the effects of destructive sampling. Further, it was felt that the monthly solutions would be useful in allowing the recognition of metals moving at different rates. These facts would not be recognized through the soil analysis alone.

Metal movement into the gravel overburden appeared to occur rapidly within the first three months of the experiment, after which the rate of movement was negligible or zero. The exception was zinc, which continually increased in concentration in the overburden with time.

Pierce *et al.* (1994) used leaching columns constructed from 185 cm lengths of 10 cm (O.D.) acrylic tubing to evaluate the application of composted municipal solid waste (MSW) to tailings. The columns were maintained in a nitrogen environment and small samples of tailings and compost were taken periodically from the columns and analyzed for gas content, Eh (under nitrogen environment), and metal concentrations. Results indicated that MSW not only maintained a high degree of saturation, and offered resistance to water conduction, but developed reducing conditions in the tailings immediately below the MSW layer. While this should eventually result in the conversion of sulphates to sulphides, accompanied by the precipitation of metals as metal sulphides, higher concentrations of iron and

sulphate were initially observed. It was felt that this was possibly a transient condition, and that mobilization of trace metals and sulphate would occur with the development of strong reducing conditions.

Several researchers have used heavily-instrumented columns to predict the ability of a cover material to remain saturated when placed above the water table (Nicholson *et al.*, 1991; Yanful, 1991; Sydor, 1992; Aachib *et al.*, 1994)).

These studies used plexiglass columns 100 cm long with an inside diameter of 10.8 cm, and were used to study the hydrological properties of a coarse layer overlain by a fine layer. The columns were fitted at several depths through the profile with tensiometers to measure pressure changes, and with Time Domain Reflectometry (TDR) probes to monitor moisture content.

In general, it was found that a fine layer placed over a coarse layer can maintain near-saturated conditions for up to 100 days (Yanful, 1991), when the coarse layer drains to its residual water content.

The preceding studies have demonstrated the range in test conditions under which column studies have been used. The results generated have confirmed the ability of a column study to accurately predict tailings oxidation, and its usefulness as a tool in evaluating measures aimed at decreasing oxidation.

4.3 Experiment 6: The Effect of Potential Cover Materials on Oxidation and Metal Release From a Column of Pyritic Tailings

4.3.1 Introduction

On the basis of the variety of conditions under which column leach tests have been successfully utilized, it was determined that column tests would be an acceptable method for evaluating the influence of the waste materials, applied as covers, on oxidation and metal release from fresh sulphidic tailings.

Humidity cells are recognized as having several advantages over standard column tests, especially in the weathering time required. However, it was recognized that humidity cells would be very difficult to manage, given the large number of

columns needed for this study. Humidity cells require strict control of air flow and humidity levels, which would be difficult to standardize for a large number of columns. In addition, the cost associated with humidity cells is much higher than for column tests. Therefore, a simple column test was undertaken to determine not only the effect of the potential cover materials on the dissolution of metals from the pyritic tailings, but also the release of metal contaminants from the cover materials themselves.

4.3.2 Purpose

A column leaching experiment was carried-out to determine the influence of depyritized and gold tailings, sewage incinerator ash and granulated slag, applied as covers with and without limestone, on the oxidation and dissolution of metals from a column of pyritic tailings.

4.3.3 Methods and Materials

The column experiment consisted of the following components:

$$5 \text{ covers} \times 2 \text{ treatments} \times 5 \text{ replicates} = 50 \text{ columns}$$

Leach columns (fig. 26) were constructed of 47 cm lengths of 10 cm (I.D.) PVC pipe. A 10 cm sewer cap was glued to the bottom end of each column and sealed with silicone. Prior to gluing, each cap had been heated and moulded into a funnel-like shape to facilitate drainage. A drain was created by drilling a hole into the cap, and inserting half of a plastic tubing connector, which was then glued in place. The tubing connector had been cut and sanded so as to be flush with the inside bottom of the cap. The outside of the drain was also sealed with silicone to provide further support and to prevent leakage. Plastic mesh and a glass fibre filter paper were then added to retain the tailings.

The columns were placed on a wooden table and seated on a styrofoam pad. Holes had been drilled through the table to facilitate the positioning of the drain. The drain was then connected to 500 ml plastic sample bottles located under the table *via* a piece of Tygon tubing. This was achieved by drilling a hole through the lid

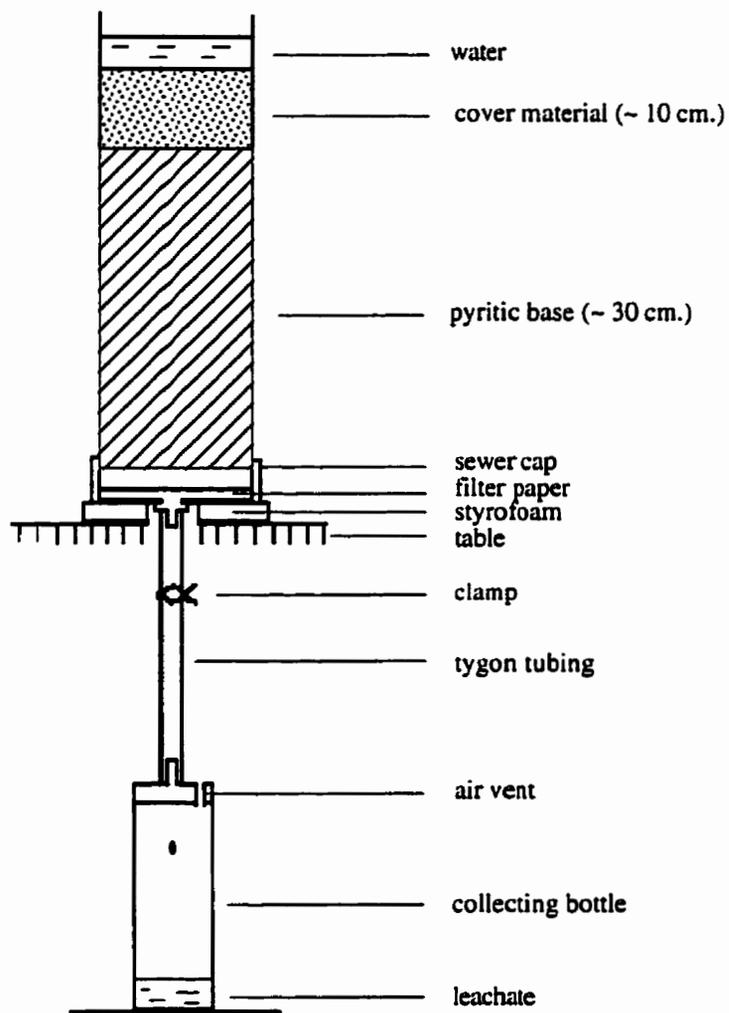


Figure 26: Design of Leaching Columns Used to Evaluate the Effect of Cover Materials on Oxidation and Metal Release From Pyritic Tailings (Experiment 6).

of the sample bottle and inserting the other half of the plastic tubing connector. When drainage had ceased, the sample bottles were simply unscrewed from the lid and then sealed with an intact lid. Between leaching cycles, movement of air through the Tygon tubing to bottom of the column was prevented by a plastic clamp.

All columns were first loaded with identical samples of pyritic tailings. Four kilograms of dried tails were mixed with distilled water and added in slurry form in 1 kg increments (approx. 70% solids by weight), representing a depth of approximately 30 cm. An attempt was made to dislodge air bubbles and promote uniform packing by tapping the outside of the columns with a brass bar after each 1 kg addition of tailings.

Cover materials were added by dry weight to a depth of approximately 10 cm. Thus an additional 1300 g of pyritic tailings were added to the control, while 1200 g of each of depyritized and gold tailings, 750 g of sewage incinerator ash, and 1600 g of granulated slag were utilized in their respective columns. The pyritic and depyritized covers were added as a slurry, while the gold tails, ash and slag were add in dry form.

The lime treatment was achieved by mixing 12 g of dolomitic limestone into each cover material in a 1000 ml beaker before adding it to the top of the pyritic base; this represented a limestone rate of approximately 15 T/ha.

The columns were thoroughly soaked with distilled water, and tapped again to try to remove air bubbles. The clamps were opened and the columns allowed to fully drain. The clamps were left open, and leaching began with the addition of 200 ml of distilled-deionized water. The volume of leachate and the time were recorded periodically, so as to obtain an estimate of the leaching rate. When a constant leachate volume was observed, the clamps were closed and the sample bottles were taken to the laboratory, where the pH and conductivity were determined. The samples were then acidified with nitric acid to a pH of approximately 2, and placed in acid-washed vials for elemental analysis by ICP. All samples were stored in a refrigerator until analyzed.

The columns were leached weekly for the next 4 weeks, after which it was deemed that the columns were not drying sufficiently between watering, and the leaching cycle was extended to once every two weeks for the next four leaching cycles. This was further extended to once every three weeks for the final four leaching cycles. These values represented the porewater residence time, which was the time that the porewater remained in the soil voids prior to being flushed out during the next leach cycle. Thus, the columns were leached a total of 12 times over a period of six months.

Approximately 5 weeks after termination of the experiment, the columns were destructively sampled by opening the columns with a power-saw and sampling the solids at six locations; top, middle and bottom of both the tailings base and the cover material.

Prior to sampling, solids at the periphery of the column were removed in an attempt to limit contamination due to possible edge effects. This was deemed necessary as there was a layer approximately 1-2 mm thick of more oxidized material around the tailings base, likely due to greater oxygen penetration around the edge of the columns as the columns dried and contracted.

Samples were collected in plastic bags. The gravimetric moisture content was determined by measuring the change in mass after drying at 105°C. The pH was determined on a saturated paste and the samples then air-dried. A 0.5 g subsample of each layer was then digested for total metal content (appendix 1) and analyzed by ICP.

Data analyses proceeded through the use of factor analysis, MANOVA and ANOVA, with all statistics calculated using the SPSS statistical package on the VAX computer system. All variables were transformed to Z-scores $(x - \text{mean}/\text{SD}) + 50$ prior to factor analysis and MANOVA. Z-scores are standardized variables whose units are standard deviations, and in this case have a mean of 50 and a standard deviation of 1. These transformations were necessary prior to multivariate analysis because of the wide range in scale amongst the variables. In multivariate analyses such as factor analysis, larger values are more heavily weighted than smaller values, and would therefore exert an overriding influence on the analyses.

4.3.4 Results and Discussion

4.3.4.1 Element Concentrations, pH, Conductivity and Volume of Leachate

Inspection of plots of element concentrations in column leachates (Figures 27 - 34) revealed that several elements appeared to exhibit similar patterns of dissolution. Therefore, fourteen variables: Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Se, Zn, pH, con (conductivity), and vol (volume) were analyzed by factor analysis to determine the factor structure among the variables, *ie*, to identify variables which behave in the same manner, and also as a data reduction mechanism.

Factorability of the correlation matrix was assessed through the size of the correlation coefficients in the matrix, the Kaiser-Meyer-Olkin (KMO) measure and Bartlett's test of Sphericity. Although several correlation coefficients between variables were found to be over 0.30 and thus suitable for factor analysis, some instances of near-perfect correlation were found, indicating that at least two of the variables were highly correlated (Garg, 1995). However, the KMO index was 0.867 and Bartlett test of Sphericity produced significant results with $P < 0.00001$. This indicates that multicollinearity should not be a problem, and that the correlation matrix appears to be adequate for factor analysis (Garg, 1995).

Three factors were extracted, and factor loadings of the variables and their communalities are shown in Table 24. The first factor was associated with the variables Co, Mn, Zn, Cd, Ni, Mg, conductivity, Se, and pH. All variables had loadings greater than 0.60, with pH alone having a negative loading, and represent variables whose pattern of dissolution was similar. This factor had an eigenvalue of 7.498, and explained 53.6% of the total variance in the data set (Table 24), and was by far the dominant factor.

The second factor was associated with Fe, Ca and Cu. These variables showed a loading of greater than 0.60, with a negative value for copper. This factor had an eigenvalue of 1.423, and explained 10.2% of the variance (Table 24).

The third factor was associated with volume, Al and pH, and showed loadings of 0.632, 0.546 and -0.528 respectively. This factor had an eigenvalue of 1.287, and

explained 9.2% of the variance (Table 24). Although pH was found to load on both factor 1 and factor 3, the loading was higher for factor 1. Therefore, pH was most strongly associated with the variables of factor 1.

Table 24: Factor Loadings and Community of Metal Concentration Values for a Factor Analysis in Experiment 6.

Variable	Rotated Factor Loading			Community
	Factor 1	Factor 2	Factor 3	
Co	.983			.972
Mn	.979			.961
Zn	.978			.959
Cd	.958			.927
Ni	.949			.905
Mg	.914			.902
con	.817			.810
Se	.728			.541
pH	-.631		-.528	.724
Fe		.778		.633
Ca		.634		.428
Cu		-.627		.539
vol			.632	.608
Al			.546	.299
Eigenvalue	7.498	1.423	1.287	
Expl. Variance	53.6%	10.2%	9.2%	

Factor scores were calculated for all three factors, and used in a multiple analysis of variance (MANOVA) to test for statistical differences by cover, lime and leach cycle. Though leach cycle ranged from 1 to 12 cycles, statistical analysis was conducted beginning with leach cycle 4, partly because of missing data for cycle 3, but mostly because inspection of the data revealed basically identical results to at least cycle 4.

Tests of homogeneity of variance showed that the assumption was satisfied only for factor 3. The assumption of homogeneity of variance-covariance matrices was tested using Box M test, which showed that the assumption was rejected [F(390, 10358)=2.15, p<0.001]. However, this test is often ignored by researchers because MANOVA is robust with respect to modest violations of this assumption, and the

test is too sensitive to modest violations (Garg, 1995). The dependent variables were found to be significantly correlated, as tested by Bartlett's test of sphericity (71.32, $p < 0.001$), although no problem with multicollinearity was indicated.

Wilk's criterion for combined dependent variables (multivariate) showed a significant interaction for COVER x WEEK [$F(96,881)=18.8$, $p < 0.001$]. A univariate analysis of variance indicated that this effect was more noticeable on factor 1 ($F=78.4$) than on factor 2 ($F=4.1$) or factor 3 ($F=8.4$), with all three significant at $p < 0.001$.

Wilk's criterion for combined dependent variables also indicated a mildly significant COVER x LIME interaction [$F(12,778)=2.1$, $p=0.016$], although the univariate analysis of variance revealed that this interaction was not significant when each of the factors was considered alone, indicating that lime did not produce a significant effect on leachate quality.

Wilk's criterion also indicated significant WEEK [$F(24,853)=52.7$, $p < 0.001$] and COVER [$F(12,778)=218.2$, $p < 0.001$] main effects, which were simply a reflection of the COVER x WEEK interaction indicated above.

Oneway ANOVA's and Scheffé Multiple Range tests ($p=0.05$) of the cover-week combinations were then used to indicate the leach cycle where metal concentrations from columns containing a cover generally became significantly different from the control (no cover).

For factor 1 (Co, Mn, Zn, Cd, Ni, Mg, Se, con and pH), leachate quality generally became different at the ninth leach cycle, being higher in the control and depyritized cover, than in those with a gold, ash or slag cover (Figures 27-31a). No significant differences were indicated between the control (no cover) and the columns with a cover of depyritized tailings.

For factor 2 (Fe, Ca, Cu), no overall significant differences could be discerned (Figures 31b -32), although the concentration of iron from the slag-covered tailings was statistically higher than from the remaining columns at week 12 only. In general, it appears that the concentration of iron leached from the columns containing a granulated slag, gold tailings or ash cover was higher than from the

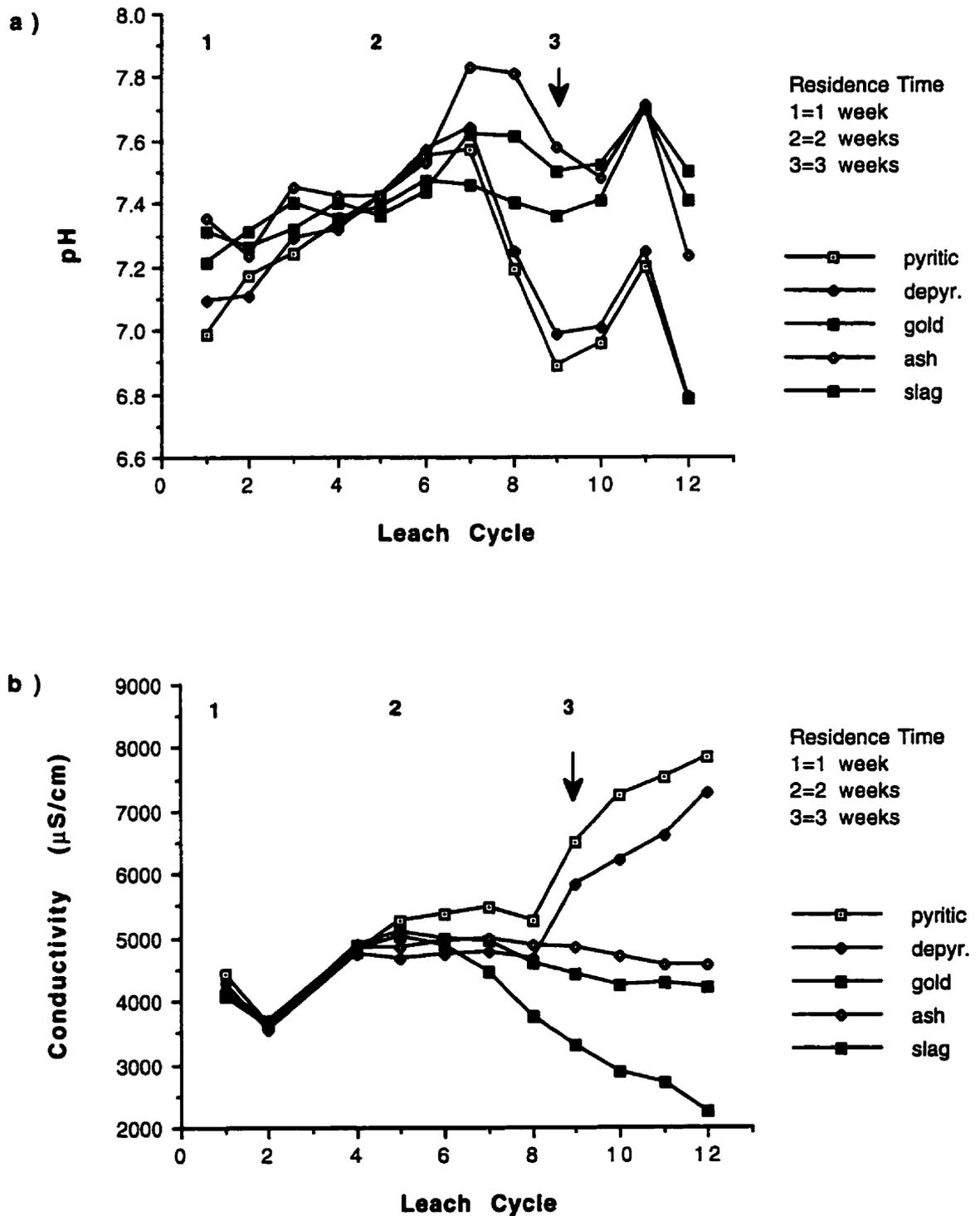


Figure 27: The effect of cover materials on (a) pH and (b) conductivity of leachates generated in a column study (Experiment 6). Arrow indicates start of significant differences.

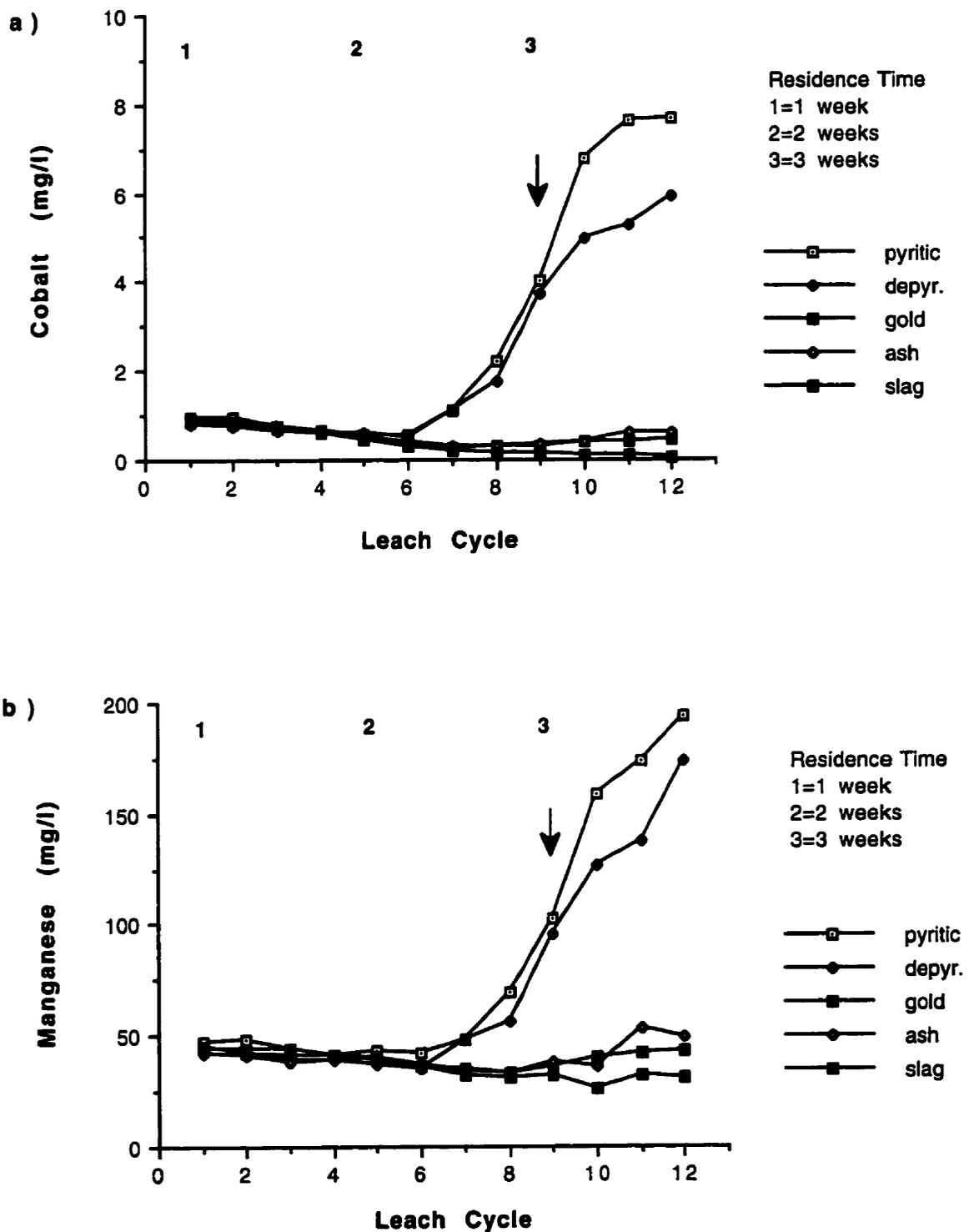


Figure 28: The effect of cover materials on (a) cobalt and (b) manganese concentration in leachates generated from a column study (Experiment 6). Arrow indicates start of significant differences.

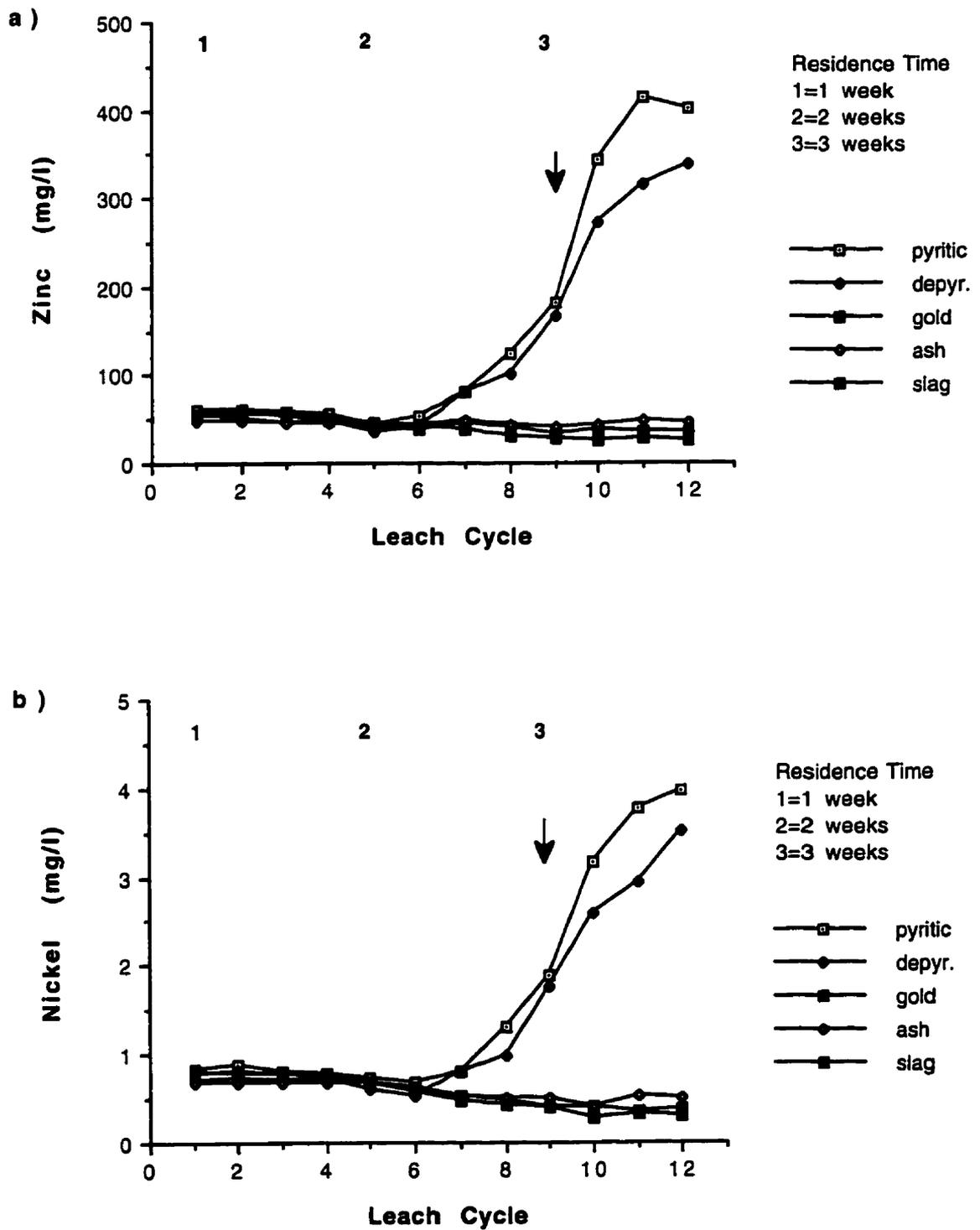


Figure 29: The effect of cover materials on (a) zinc and (b) nickel concentration in leachates generated from a column study (Experiment 6). Arrow indicates start of significant differences.

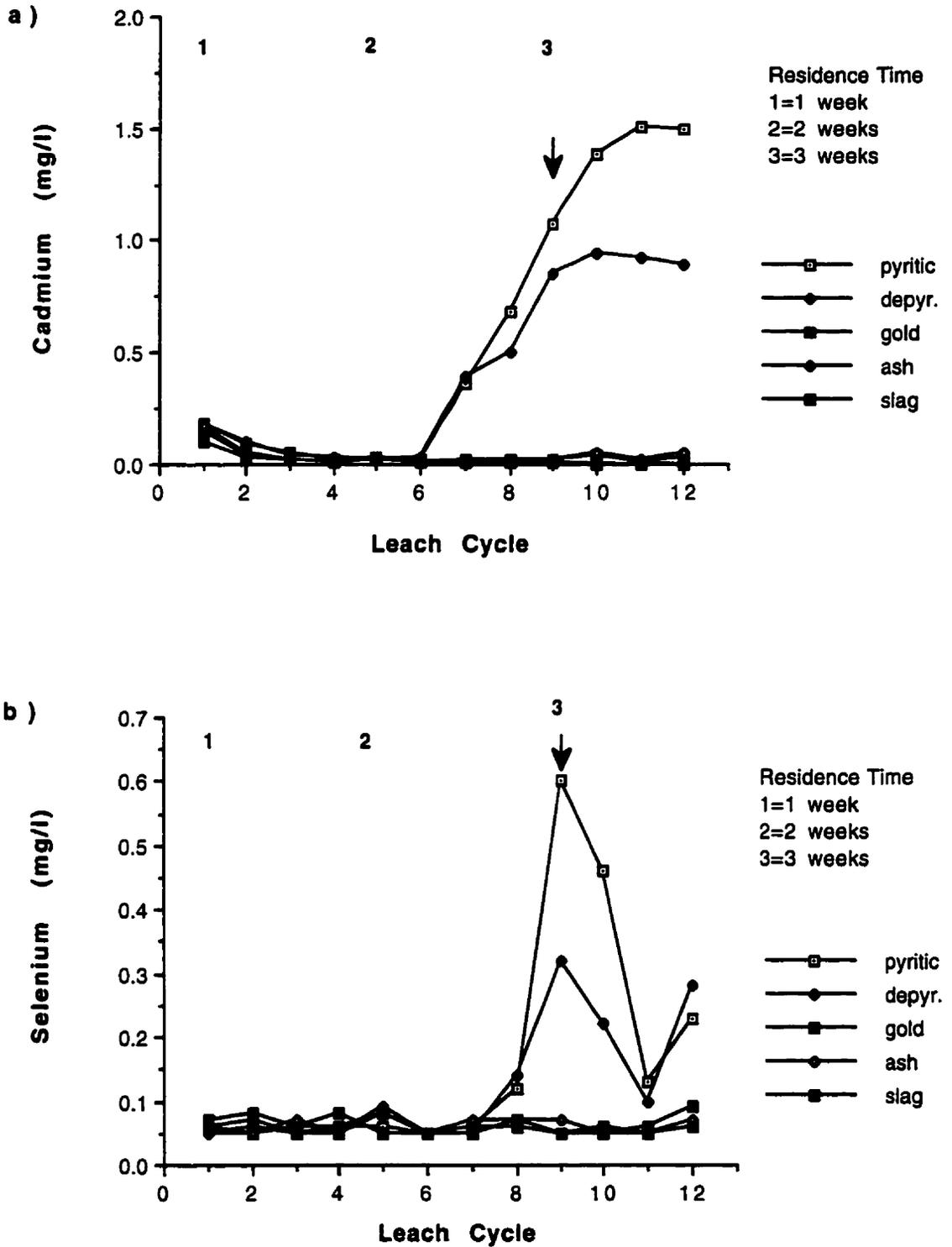


Figure 30: The effect of cover materials on (a) cadmium and (b) selenium concentration in leachates generated from a column study (Experiment 6). Arrow indicates start of significant differences.

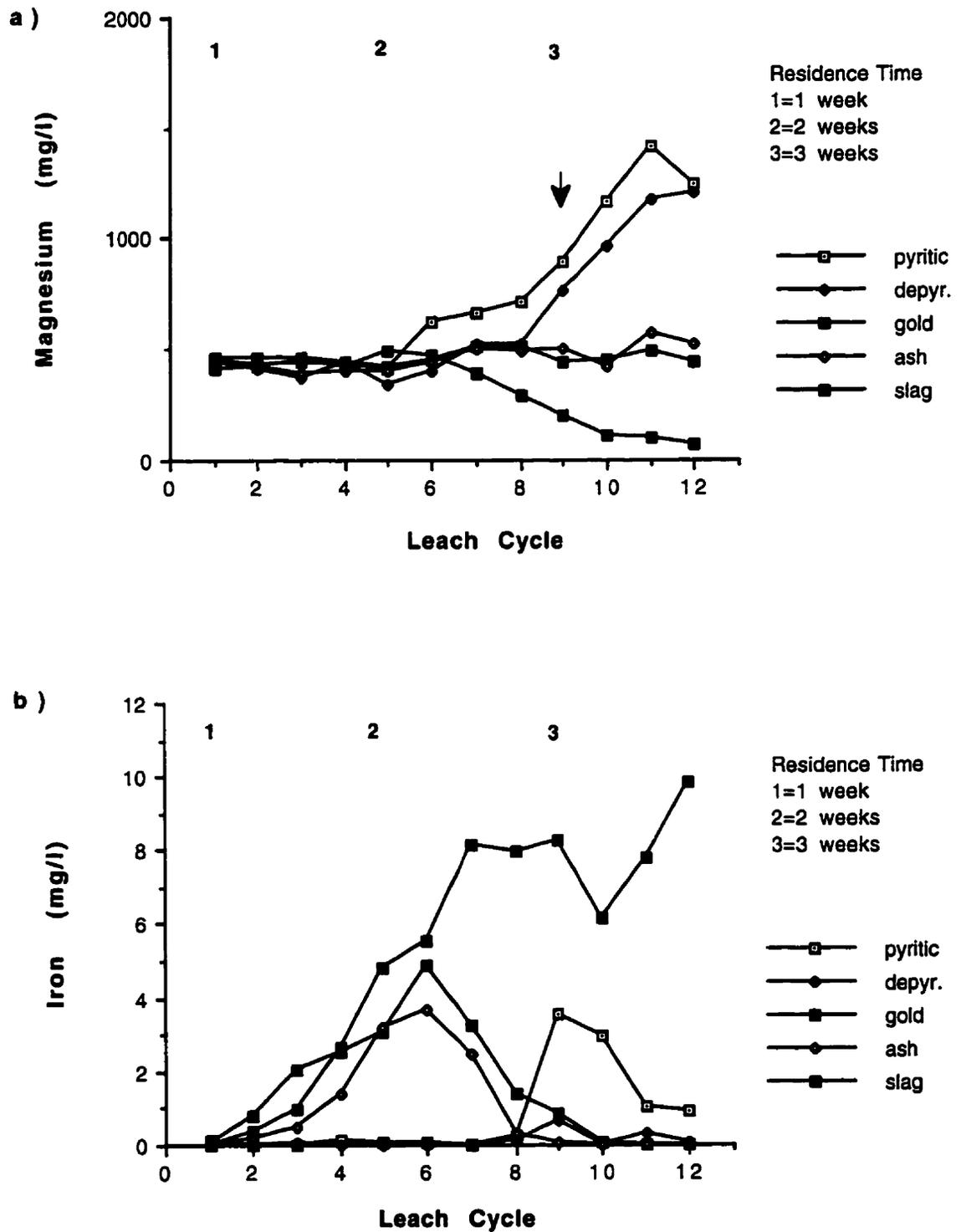


Figure 31: The effect of cover materials on (a) magnesium and (b) iron concentration in leachates generated from a column study (Experiment 6). Arrow indicates start of significant differences.

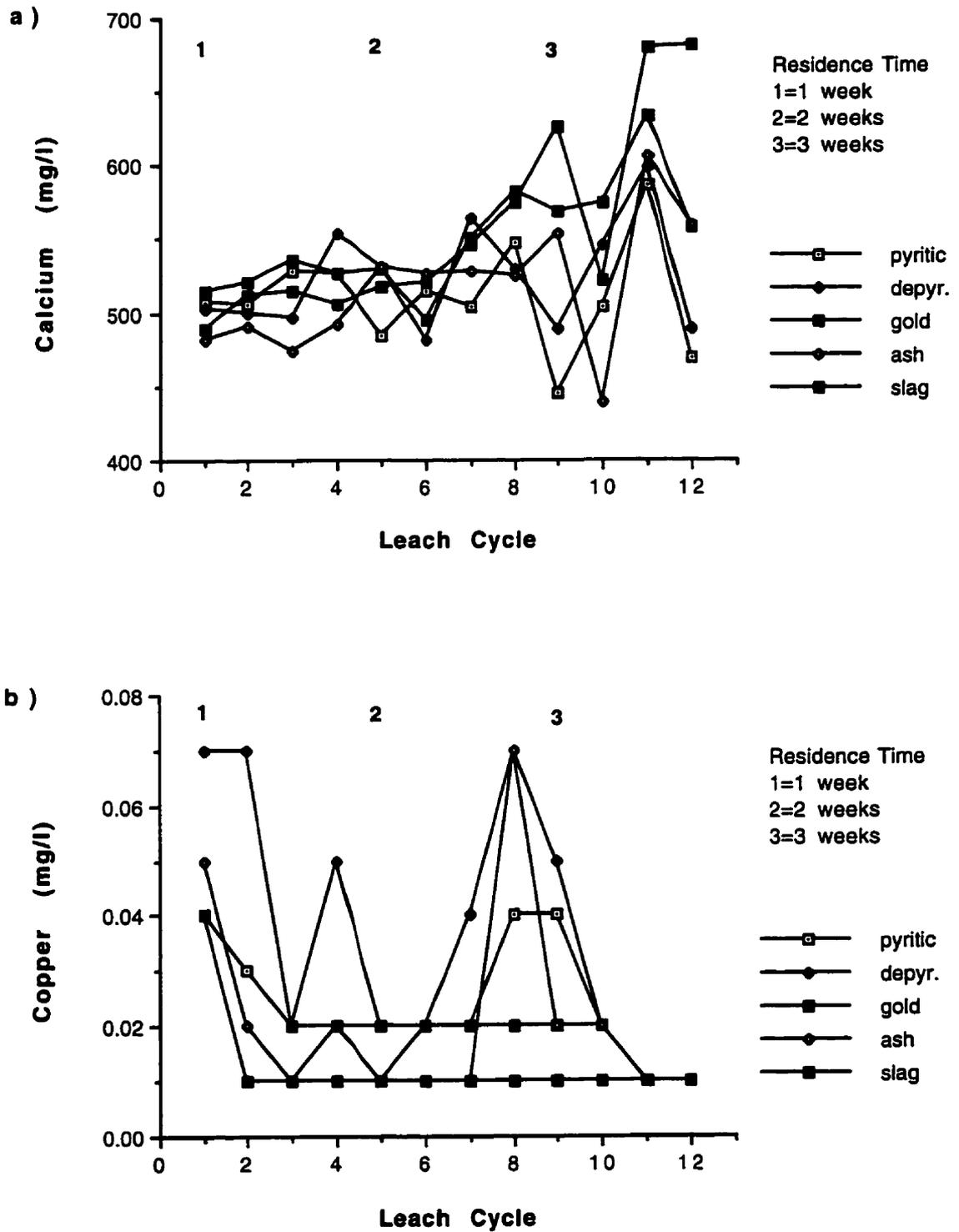


Figure 32: The effect of cover materials on (a) calcium and (b) copper concentration in leachates generated from a column study (Experiment 6).

columns with a depyritized tailings cover and the pyritic control (Figure 31b).

For factor 3 (vol, Al and pH), no statistically significant difference ($p=0.05$) was observed between the pyritic tailings control and any of the other columns (Figure 33). However, beginning at leach cycle 7, the volume of leachate produced under a cover of granulated slag was significantly higher than for the gold tailings and incinerator ash covers. This applied to volume and not aluminum, as this factor was dominated by volume (Table 24).

Sulphur data was analyzed independently of the other variables, owing to an abundance of missing data. Factor analysis excludes all cells with missing data; therefore inclusion of the sulphur data would have negated a large amount of the dataset.

A 3-way ANOVA (cover, lime, week) of the original sulphur data yielded significant COVER [$F(4,275)=139.4$, $p<0.001$; $\eta^2=0.53$] and WEEK [$F(11,275)=21.8$, $p<0.001$; $\eta^2=0.35$] main effects, and a COVER x WEEK interaction [$F(44,275)=19.6$, $p<0.001$].

A 1-way ANOVA of the computed interactions indicated a significant difference by group [$F(26,159)=42.8$, $p<0.0001$]. A Scheffé Multiple Range test ($p=0.05$) revealed that sulphur concentrations were significantly higher from the columns with the pyritic and depyritized tailings covers, after leach cycle 9. There was no significant difference between columns with a pyritic or depyritized tailings covers, or between gold tailings or incinerator ash covers. However, by leach cycle 10, sulphur from columns containing a slag cover was also significantly lower than from columns containing gold tailings and incinerator ash. (Figure 34).

While homogeneity of variance was not attained, identical results were obtained using \log_{10} transformed data.

Visual inspection indicates that sulphur appears to behave in similar fashion to the variables of factor 1, and in fact is virtually identical to magnesium, including a decline from the slag columns.

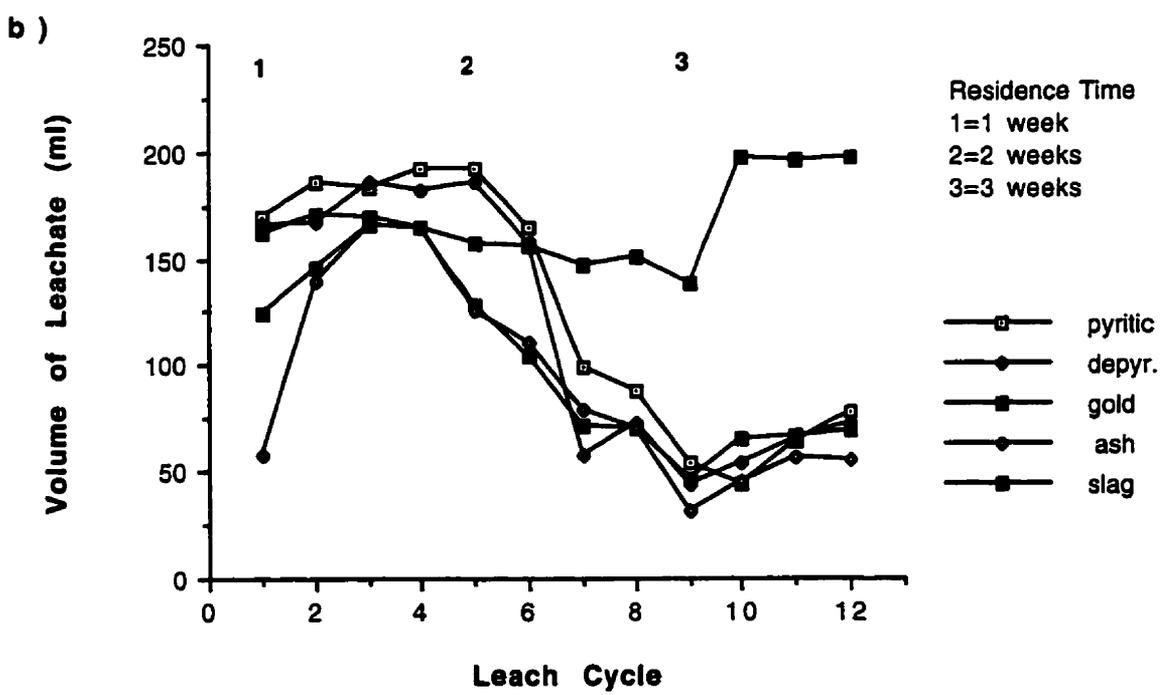
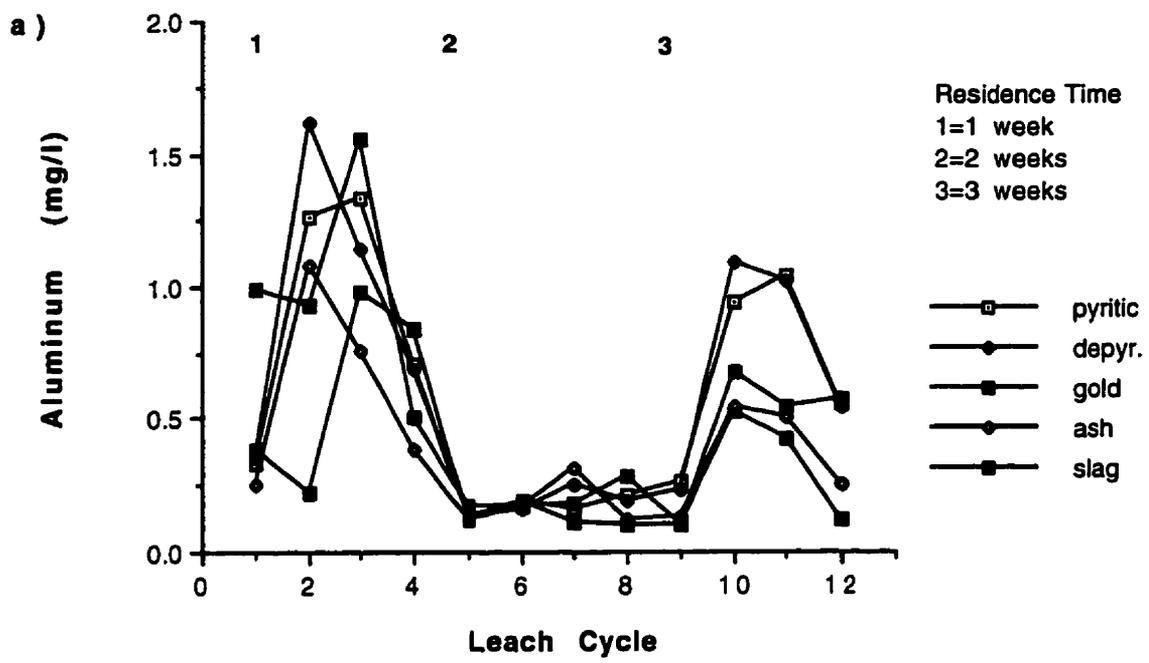


Figure 33: The effect of cover materials on (a) aluminum concentration and (b) volume of leachate generated from a column study (Experiment 6).

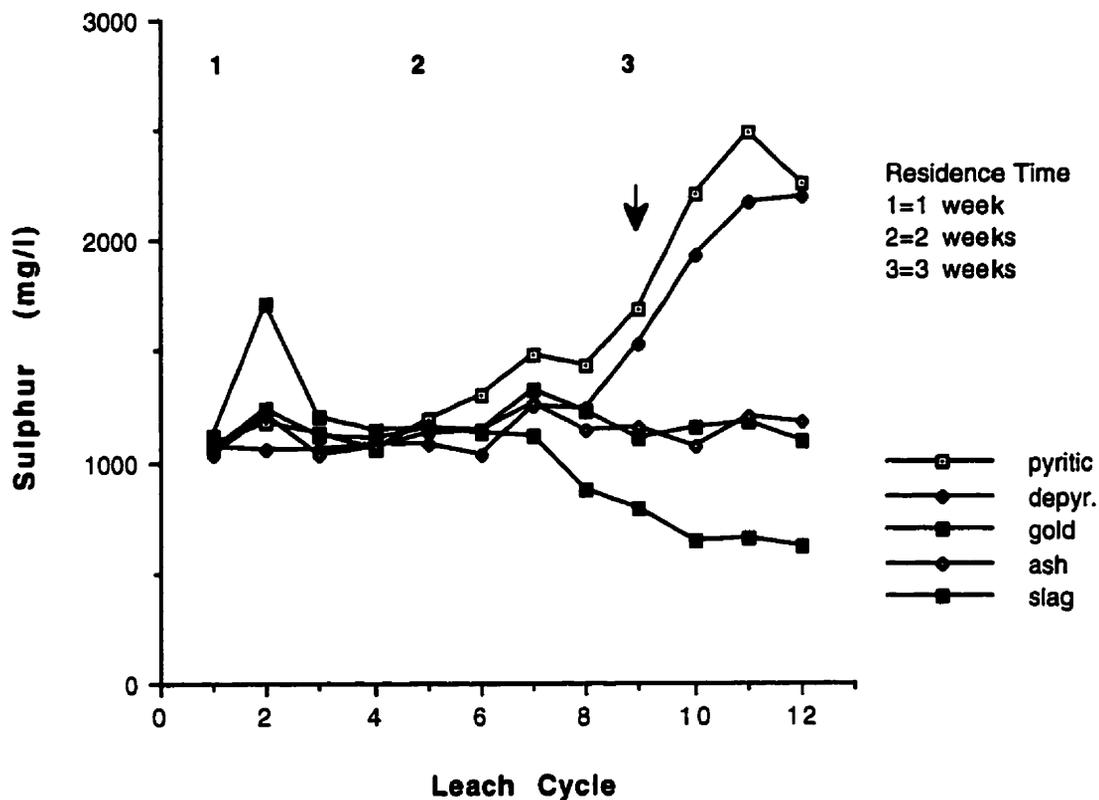


Figure 34: The effect of cover materials on the concentration of sulphur in leachates generated from a column study (Experiment 6). Arrow indicates start of significant differences.

Factor 1 variables were characterized by a decline in leachate pH and substantial increases in conductivity and metals from columns containing pyritic tailings only (control) and with a depyritized tailings cover. This suggests that sulphide oxidation was occurring more rapidly in these columns.

The oxidation of iron sulphides, through a series of reactions, produces acidic tailings porewater which can dissolve and transport a variety of metals. The most common indicators of tailings oxidation are low pH and high ferrous iron and sulphate concentrations in the drainage waters (Blowes *et al.*, 1995). Concentrations of other metals are largely dependent on the minerals present in the particular ore body that has been mined.

In general, it was expected that there would be a rather rapid release of metals over the first few leaching cycles, followed by a steady decline until a constant level was reached, as reported by Doepker & O'Connor (1990 a&b). This was thought to be due to the flushing of easily-leached metal forms from the column. Once a constant concentration of ions was obtained with successive leachings, it is assumed that the easily-leached ions have been removed, and that any ions that are still being leached are due to the weathering or decomposition of the tailings or cover (Gentry *et al.*, 1992).

That leachate pH barely dropped below 7 in these columns indicates that the experiment was terminated prior to the exhaustion of the inherent buffering capacity of the Kidd Creek mill tailings or, alternatively, that the rate of acid production had not yet exceeded the rate of carbonate mineral dissolution. In addition to the carbonate minerals naturally present in the tailings, lime is added prior to discharge to facilitate flow during the thickening process. While the trend exhibited in Figure 27a suggests that the leachate pH is beginning to decline, especially in the columns containing pyritic and depyritized tailings covers, more time was needed to overcome the inherent neutralization capacity. Jurjovek *et al.* (1995) observed a series of pH-buffering plateaus in Kidd Creek tailings, which consume hydrogen ions generated by sulphide oxidation. The reaction series consisted of carbonates (Ca, Mg, Mn, Fe) at pH=5.78-5.13, gibbsite ($\text{Al}(\text{OH})_3$) at pH=4.05-3.75, goethite at pH=1.78-1.31, and aluminosilicates at pH~ 1.3. It was indicated that dissolution of these minerals will maintain the pH at the given buffering plateau until the mineral has been depleted.

The change in leachate conductivity (Figure 27b) coincides very closely with magnesium and sulphur (probably sulphate at this pH) concentrations (Figures 31a & 34). Hydrogen ions generated through sulphide oxidation are neutralized by carbonate-mineral dissolution (Al *et al.*, 1994). If the major carbonate minerals present are dolomite and siderite (as is often the case in northern Ontario ores), this may result in an increase in the concentration of calcium, magnesium, manganese and iron, along with sulphate (from sulphide oxidation) in tailings leachate. Magnesium and manganese make up a relatively large proportion of siderite, dolomite and ankerite (Al *et al.*, 1994). Calcium and magnesium may also be used as prime indicators of sulphide oxidation, (in addition to sulphate and iron), and appear to be the major determinants of conductivity.

The increase in conductivity for the columns containing pyritic and depyritized tailings covers can also be partially explained by the slight drop in pH of the leachate from these columns. A lower pH increases the solubility and dissolution of metals, resulting in increased conductivity.

Other factors, such as the volume of leachate obtained and the degree of tailings saturation, may also affect the dissolution of metals, with a corresponding effect on conductivity.

Al *et al.* (1994) defined three geochemical zones within the Kidd Creek tailings, according to porewater metal and sulphate concentrations. In the deepest zones measured (6-10 m), concentrations of most metals and anions were below detection, and represented the mill discharge water released with the tailings. There was an intermediate zone (above 6 m), with slightly higher elemental concentrations than in the deep zone, and a surficial zone (0 - 60 cm), with high porewater concentrations.

More specifically, the surficial zone exhibited visible signs of sulphide oxidation, and was associated with increased concentrations of Mg, Fe, Zn, Pb, Cu, Ni, Co, Cd, Mn, As, Cr, Al, and SO₄. In addition, the porewater pH dropped to between 2.5 and 4.

These findings are very similar to the findings of the present study (factor 1 metals) for the pyritic tailings control, and with a cover of depyritized tailings.

However, in contrast to the findings of Al *et al.* (1994), distinctly elevated concentrations of Fe and Cu (factor 2), and Al (factor 3) were not observed, while Pb, As and Cr were below detection limits in leachates from the columns exhibiting signs of oxidation.

Al *et al.*(1994) attributed the high concentrations of magnesium and manganese to the dissolution of dolomite, and indicated that Fe, Zn, Pb, Cu, Ni, Co, and Cd are relatively soluble under low pH conditions, and were released by sulphide oxidation. Further, they indicated that where the pH decreases below 5, Al concentrations increase, probably because of pH buffering reactions involving dissolution of aluminum-silicate minerals.

Thus, it appears that Fe, Cu and Al concentrations are very dependent on pH, and that tailings pH had not declined sufficiently to cause a drastic increase in the leachate concentrations.

Signs of sulphide oxidation (elevated iron, sulphate etc.) in the leachate from the control (pyritic) columns and with a cover of depyritized tailings did not become apparent until the ninth leach cycle (Figures 27 - 31a). This was likely in response to an increase in the porewater residence time from 1 week during the initial 4 leach cycles to 2 weeks during the following 4 leach cycles and 3 weeks for the last four leach cycles. The surface of the columns were not showing any appreciable drying between leachings during the period of 1 week residence time. It was felt that the underlying tailings would remain saturated under these conditions, and thus oxidation would be minimal or nil. Therefore, the residence time was extended to two weeks in order to introduce a drying cycle. This increased drying effects, but it was felt that a 3 week residence time would be more appropriate and would represent a more harsh test of the cover systems.

The introduction of a drying cycle allows for an increase in evaporation from the cover material and fresh tailings below. As the water content drops, oxygen is able to penetrate to greater depths, causing an increase in the volume of tailings available for oxidation in the control (no cover) columns, and access of oxygen to the fresh tailings in columns containing a cover.

An increase in evaporation corresponds to a decrease in the volume of leachate obtained (assuming constant volumes of leachant are applied), as occurred in all columns except those containing a slag cover (Figure 33b). After drying, the cover materials must be brought back to field capacity before any leachate can be generated, ie we must first replace water lost through evaporation, which results in a decrease in the volume of leachate generated.

The degree to which water is lost from a material through evaporation is directly related to the particle size of the material. Finer-grained materials can lose a great deal of water through surface evaporation because of the high capillarity present in these materials, while water losses from coarse-grained materials is low because of the low capillarity, and is generally limited to water vapour. This was the case in columns containing a slag cover, where the volume of leachate obtained generally remained constant throughout the experiment. The increase in the volume of leachate obtained during the last three leach cycles was a result of an increase to 250 ml from 200 ml in the volume of leachant added (Figure 33b). This increase in leachant volume was necessary in order to obtain sufficient quantities of leachate from the remaining columns.

It is possible that the lower leachate volume observed in all columns except those containing a slag cover may have exhibited lower leachate pH's as a result of less dilution of acid that had been generated in the pyritic tailings. However, this is unlikely, as there was only a difference in leachate pH between treatments of approximately 0.6 units.

Treatment of the cover materials with lime had no significant effect on the quality of the leachate. Similar results were obtained by Hoving and Hood (1984) who, in looking at different thicknesses of limestone and soil over pyritic material, found that lime had a very limited effect on improving the quality of the effluent. This was further demonstrated by Doepker (1991a), who found that abatement treatments such as phosphate, lime and sodium lauryl sulphate were of only marginal value in improving leachate quality.

In addition to their role as a vegetation substrate, covers are added to potentially acid-generating tailings in an effort to limit pyrite oxidation by reducing the availability of oxygen to the tailings.

The application of incinerator ash, gold tailings, and granulated slag have caused reductions in the dissolution of most metals studied, over a period of approximately 6 months. Specifically, concentrations of nickel and cadmium were maintained at or below Canadian drinking water standards (Wilson, 1995), while Se was slightly higher and zinc was much higher. Without a cover (control) or with a cover of depyritized tailings, concentrations of these metals were well above guidelines.

Similar results were reported by Watzlaf and Erickson (1986), who found that a 30 cm cover of topsoil was effective in maintaining acidity and sulphate concentrations significantly below levels in barren refuse for a period of 9 months, and manganese and iron levels for 2 months and 6 months respectively.

It is anticipated that the effect demonstrated by the cover materials in the present study will decline over time, and would not be so large if the system were subjected to more taxing conditions such as temperature fluctuations and extended drought.

4.3.4.2 Absolute Metal Levels

While metal levels in the leachate were originally measured as concentrations, these were converted to absolute amounts of metal leached from each column by simply multiplying the concentration by the volume of leachate. Since the volume of leachate obtained in a single leaching event depends on the pore volume, the hydraulic conductivity of the materials, and evaporation from the column, treatments producing the same concentration of metals in the leachate may leach quite different absolute amounts of metal due to differences in the volume of leachate obtained. Thus, metal release is not only dependent on chemical alterations within the material, but also on the physical characteristics of the material itself.

Plots of absolute metal levels are shown in Figures 35 - 40

Eleven variables: absolute Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Se, and Zn were analyzed by factor analysis to determine the factor structure among the variables, in order to reduce the number of analyses required.

Factorability of the correlation matrix was assessed through the size of the correlation coefficients in the matrix, the Kaiser-Meyer-Olkin (KMO) measure and Bartlett test of Sphericity. Although several correlation coefficients between variables were found to be over 0.30 and thus suitable for factor analysis, some of the correlations were near-perfect, indicating that at least two of the variables were highly correlated (Garg, 1995). However, the KMO index was 0.765 and Bartlett test of Sphericity produced significant results with $P < 0.00001$. This indicates that multicollinearity should not be a problem, and that the correlation matrix appears to be adequate for factor analysis (Garg, 1995).

Three factors were extracted. Factor loadings of the variables and their communalities are shown in Table 25.

Table 25: Factor Loadings and Communality of Absolute Metal Values for a Factor Analysis in Experiment 6.

Variable	Rotated Factor Loading			Communality
	Factor 1	Factor 2	Factor 3	
Zn	.982			.965
Co	.969			.972
Ni	.916			.853
Mn	.894			.952
Cd	.839			.843
Mg	.676	.521		.735
Se	.556			.476
Cu		.793		.692
Ca		.666	.657	.880
Al				.135
Fe			.885	.815
Eigenvalue	5.177	1.980	1.161	
Expl. Variance	47.1%	18.0%	10.6%	

The first factor was defined by the variables Zn, Co, Ni, Mn, Cd, Mg and Se. All variables had loadings greater than 0.60, with the exception of Se (0.556), while magnesium also loaded on factor 2. As occurred in the concentration data, these are variables whose pattern of dissolution was similar, and which again clearly indicate increased sulphide oxidation from columns containing pyritic tailings only

(control) and with a cover of depyritized tailings. This factor had an eigenvalue of 5.177, and explained 47.1% of the variance (Table 25).

The second factor was composed of Cu, Ca and Mg. Copper and calcium both showed loadings of greater than 0.60, while Mg was 0.521. Because the factor loading for Mg was greater than 0.6 in factor 1, it was more strongly associated with this factor. These variables are normally associated with sulphide oxidation, but in this case did not show a clear effect for any of the covers. This factor had an eigenvalue of 1.980, and explained 18.0% of the variance (Table 25).

The third factor was composed of Fe and Ca, and showed loadings of 0.885 and 0.657 respectively. This factor had an eigenvalue of 1.161, and explained 10.6% of the variance (Table 25).

Aluminum failed to load, and the very low communality associated with aluminum (Table 25) indicates that very little of the variance associated with this variable was explained by the factor, ie aluminum had very little in common with any of the other variables, but more closely resembled those of factor 2.

Factor scores were again calculated for all three factors, and used in a multiple analysis of variance (MANOVA) to test for statistical differences by cover, lime and leach cycle. Although leach cycle ranged from 1 to 12 cycles, statistical analysis was conducted beginning with leach cycle 4, partially because of missing data for cycle 3, but mostly because inspection of the data revealed basically identical results to at least cycle 4.

Tests of homogeneity of variance showed that the assumption was not satisfied for any of the three factors. The assumption of homogeneity of variance-covariance matrices was tested using Box M test, which showed that the assumption was rejected [$F(570, 15686)=2.46, p<0.001$]. However, as stated previously, this test is often ignored by researchers because MANOVA is robust with respect to modest violations of this assumption, and the test (Box M) is too sensitive to modest violations (Garg, 1995). The dependent variables were found to be significantly correlated, as tested by Bartlett's test of sphericity (120.09, $p<0.001$), although no problem with multicollinearity was indicated.

Wilk's criterion for combined dependent variables (multivariate) showed a significant interaction for COVER x WEEK [$F(132,1242)=14.32$, $p<0.001$]. A univariate analysis of variance indicated that this effect was more noticeable on factor 1 ($F=29.0$) than on factor 2 ($F=7.3$) or factor 3 ($F=9.6$), with all three significant at $p<0.001$.

Wilk's criterion also indicated significant WEEK [$F(33,1220)=50.4$, $p<0.001$] and COVER [$F(12,1096)=196.9$, $p<0.001$] main effects, which were simply a reflection of the COVER by WEEK interaction indicated above.

Oneway ANOVAs of the computed interactions were then used to indicate the leach cycle where absolute metal levels from columns containing a cover generally became significantly different from the control (pyritic tailings cover).

For factor 1 (Zn, Co, Ni, Mn, Cd, Mg, Se), leachate quality generally became different after approximately the ninth leach cycle, being higher in the control and depyritized cover than in those with a gold, ash or slag cover (Figures 35 - 38a). No significant differences were indicated between the control (no cover) and with a cover of depyritized tailings, except at week eleven.

For factor 2 (Cu, Ca), no overall significant differences could be discerned (Figures 38b - 39). It appears that absolute calcium is higher from columns with a slag cover. This is quite similar to the response seen in iron, which is not surprising, given that calcium also loaded on factor 3 (Fe) in the factor analysis.

For factor 3 (Fe and Ca), absolute leachate levels became significantly higher from columns with a slag cover than for the rest of the covers, after week 7 (Figure 40a).

A 3-way Analysis of variance (cover, lime, week) on the original absolute sulphur data revealed significant COVER [$F(4,266)=76.2$, $p<0.001$; $\eta^2=0.44$] and WEEK [$F(11,266)=70.8$, $p<0.001$; $\eta^2=0.70$] main effects, and a COVER x WEEK interaction [$F(44,266)=4.1$, $p<0.001$]. The three variables accounted for 69.2% of the variance ($r^2=0.692$). While homogeneity of variance was not achieved, it was worsened by \log_{10} transforming the data; thus the original data was deemed most appropriate.

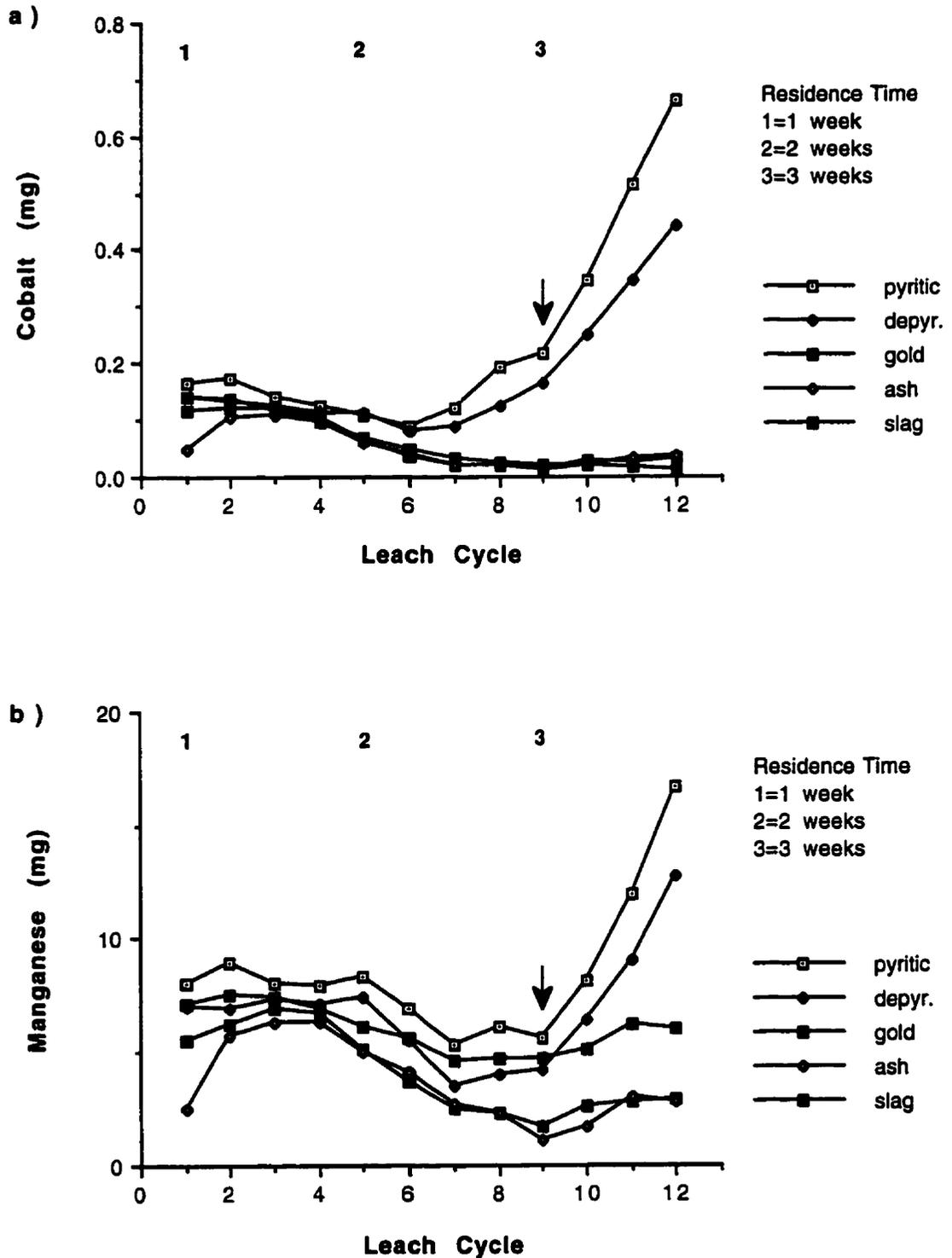


Figure 35: The effect of cover materials on absolute (a) cobalt and (b) manganese in leachate generated from a column study (Experiment 6). Arrow indicates start of significant differences.

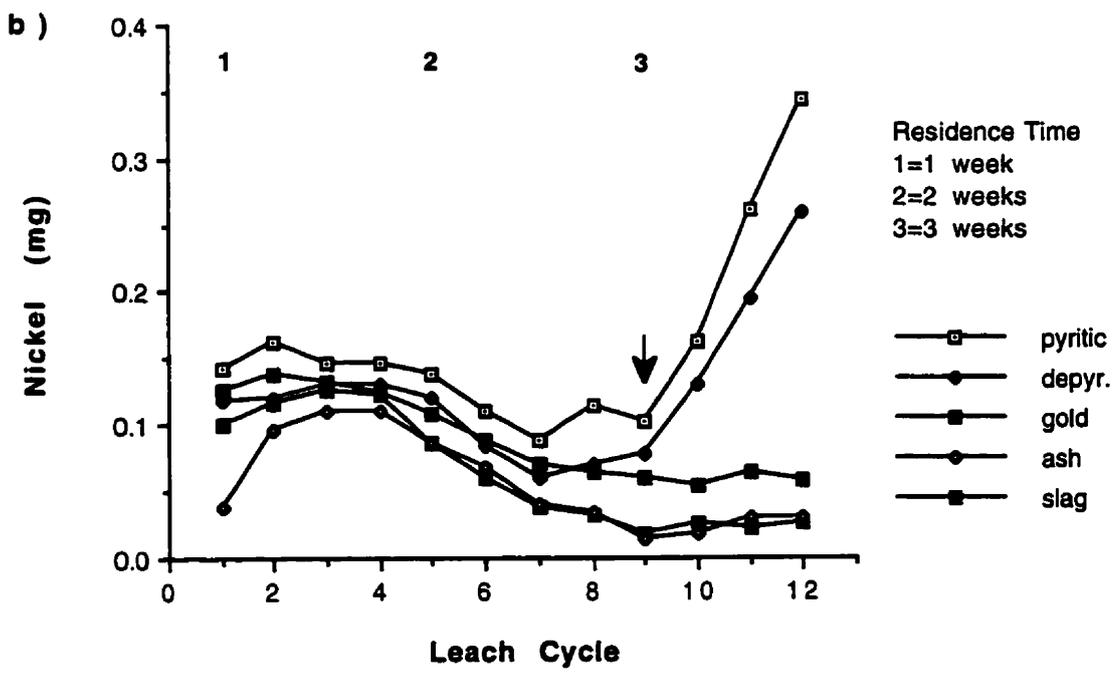
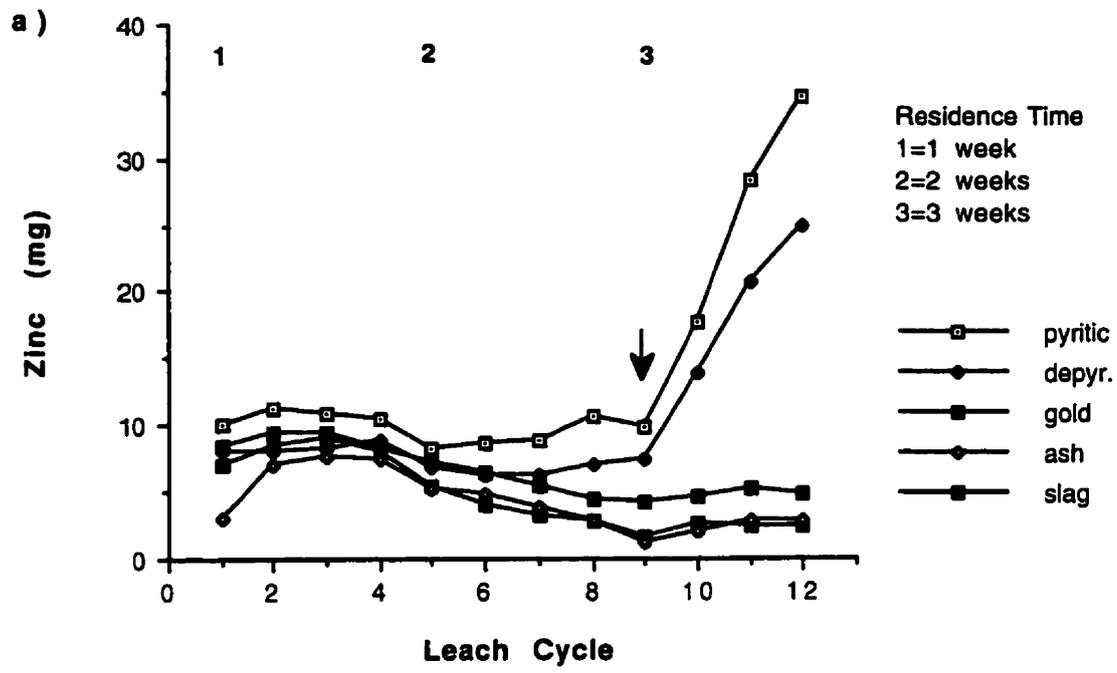


Figure 36: The effect of cover materials on absolute (a) zinc and (b) nickel in leachates generated from a column study (Experiment 6). Arrow indicates start of significant differences.

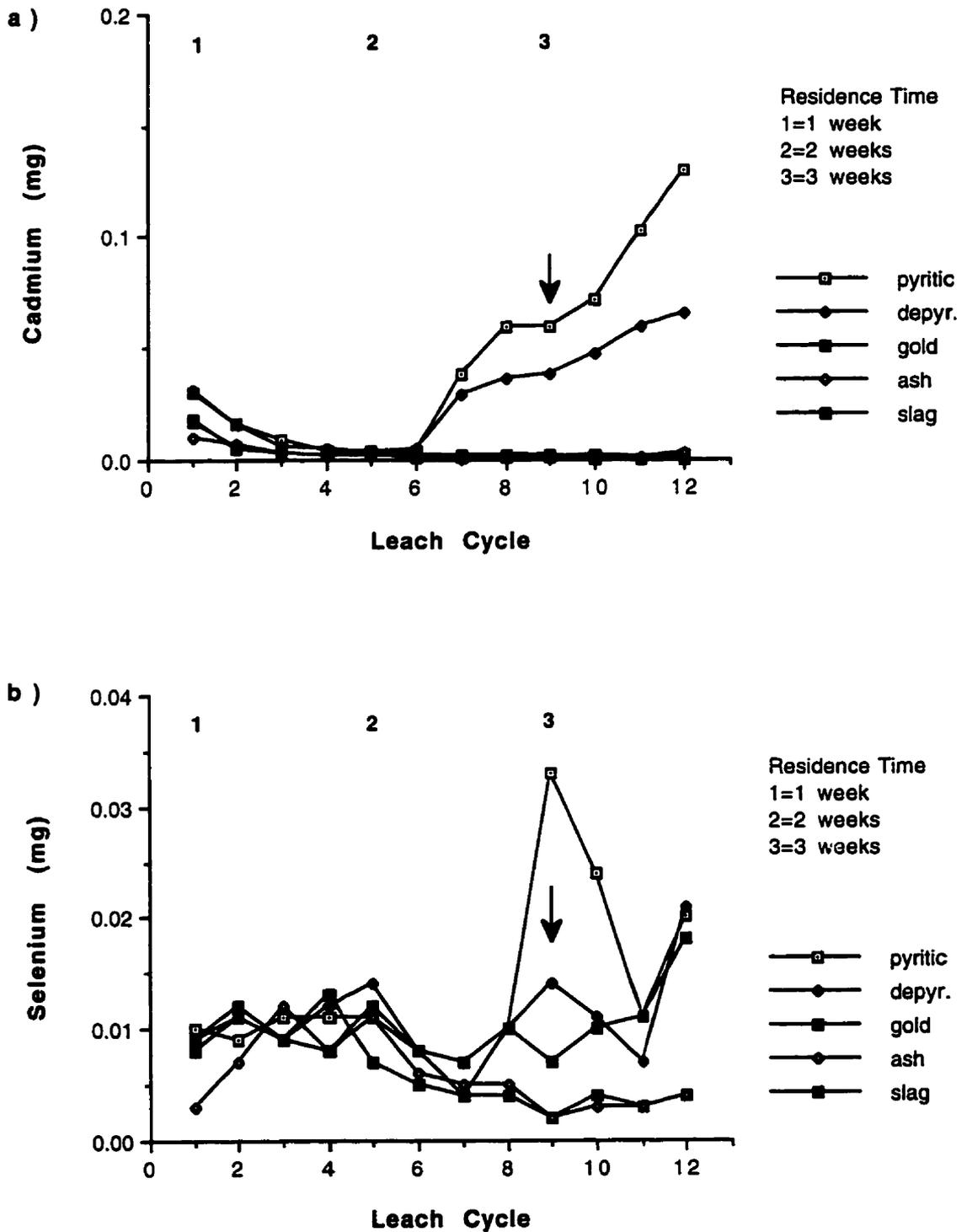


Figure 37: The effect of cover materials on absolute (a) cadmium and (b) selenium in leachate generated from a column study (Experiment 6). Arrow indicates start of significant differences.

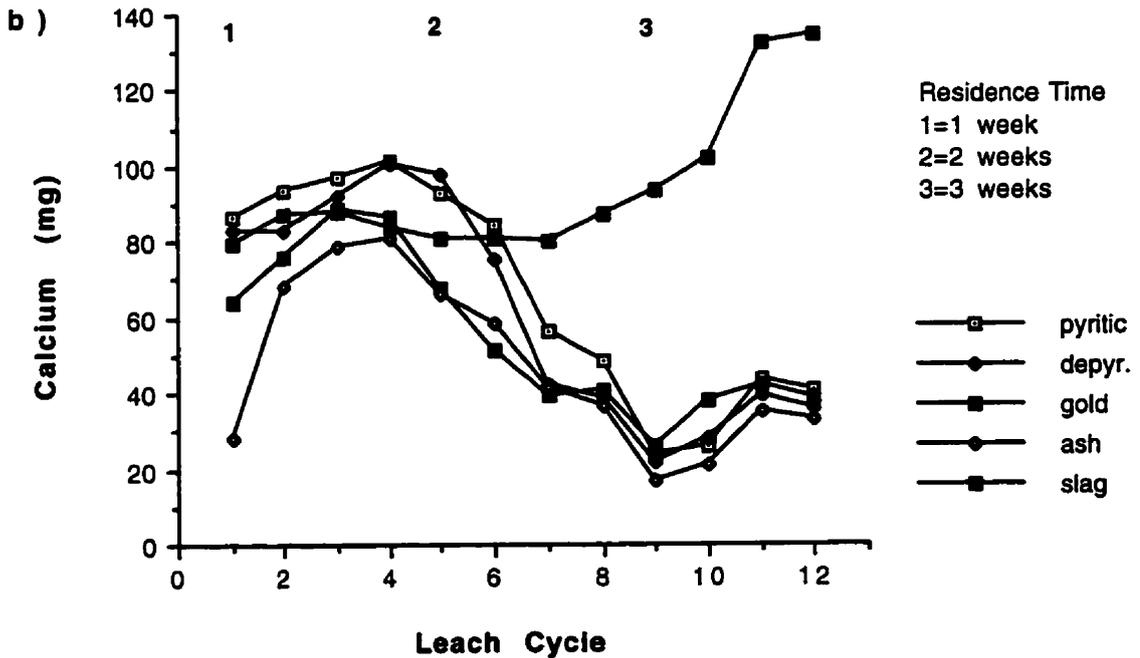
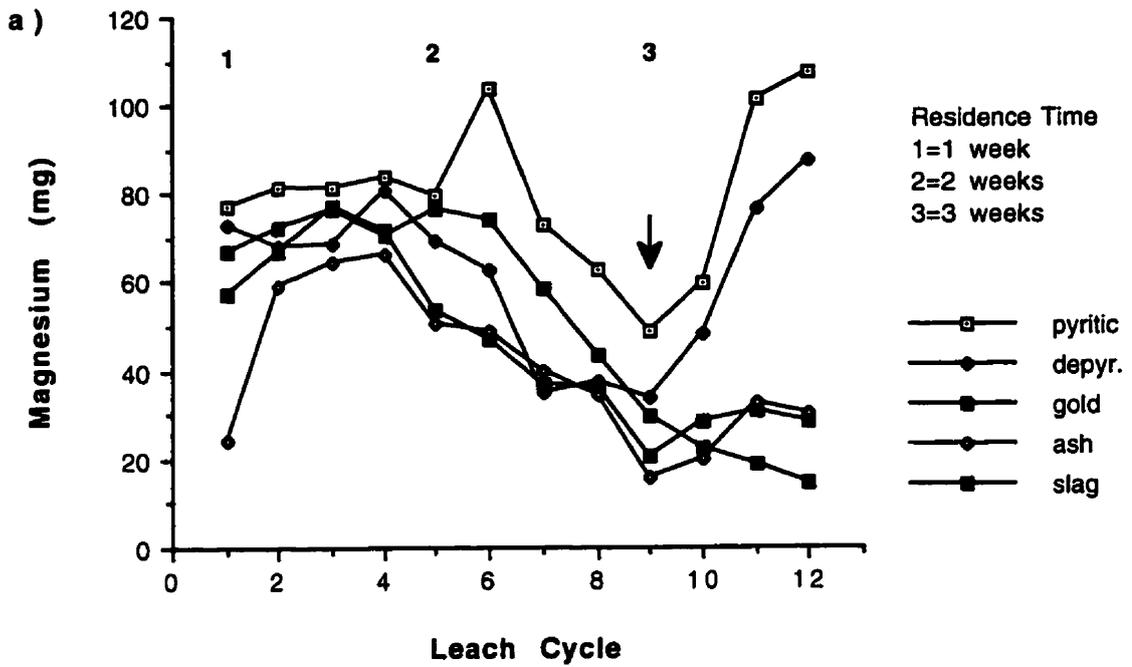


Figure 38: The effect of cover materials on absolute (a) magnesium and (b) calcium in leachate generated from a column study (Experiment 6). Arrow indicates start of significant differences.

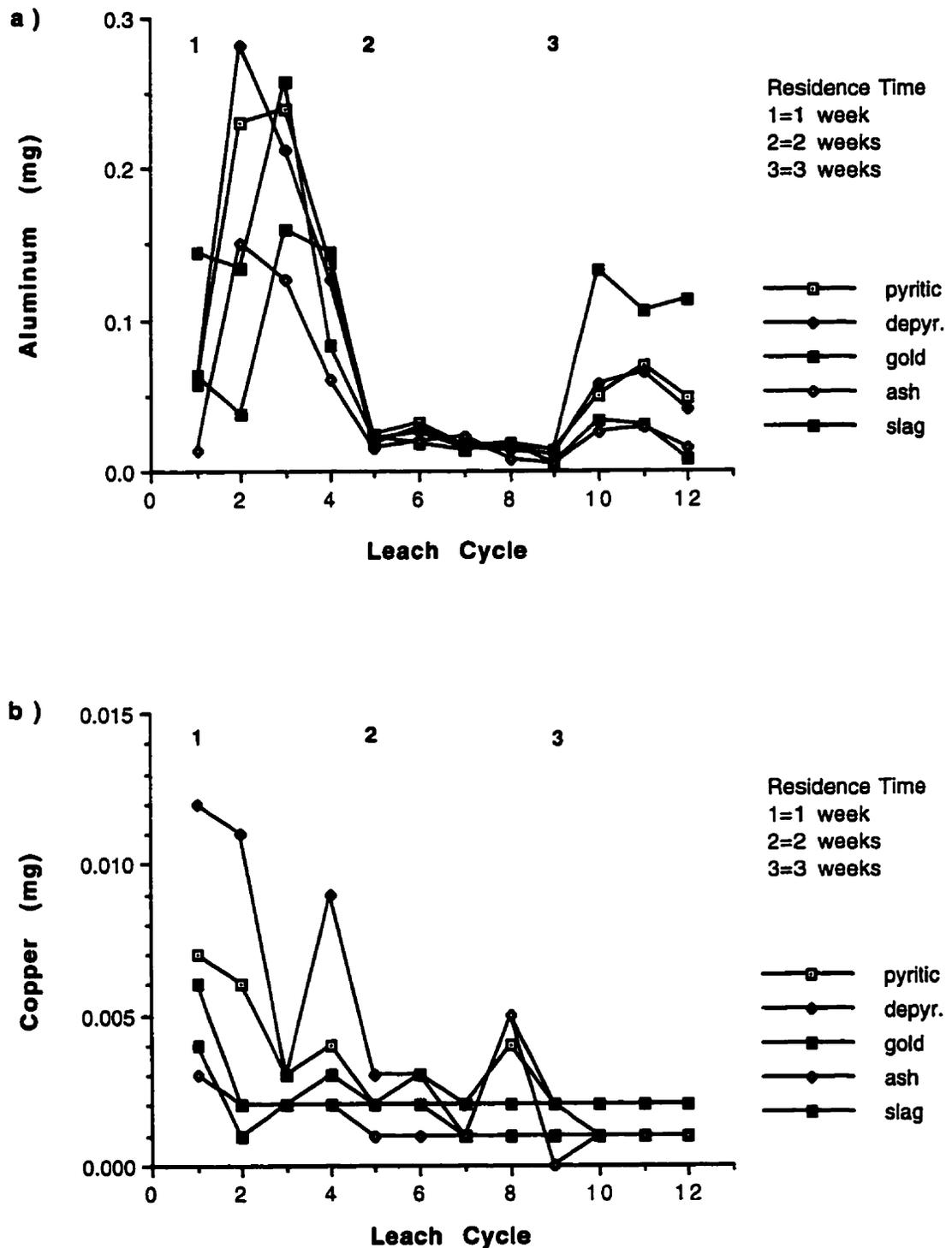


Figure 39: The effect of cover materials on absolute (a) aluminum and (b) copper in leachate generated from a column study (Experiment 6). Arrow indicates start of significant differences.

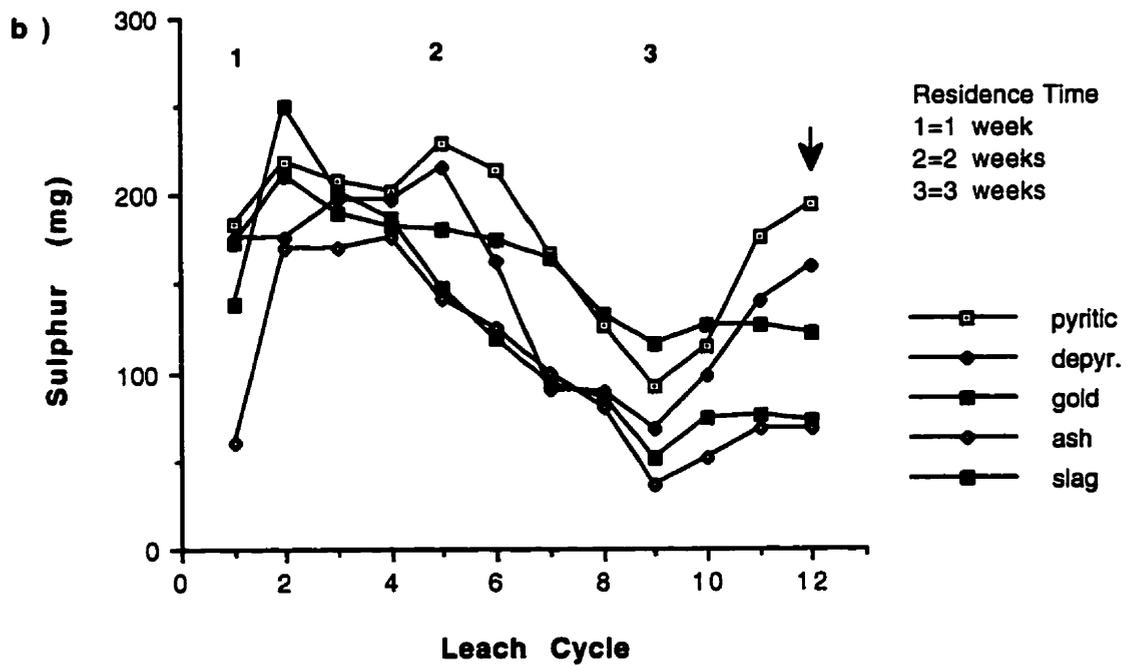
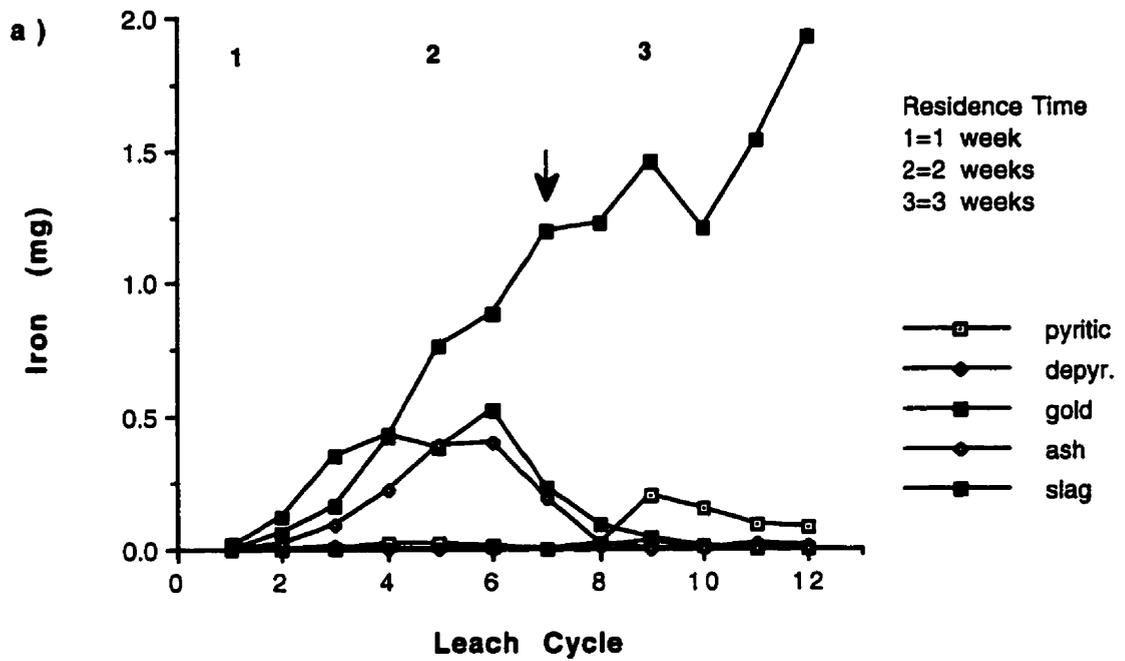


Figure 40: The effect of cover materials on absolute (a) iron and (b) sulphur in leachate generated from a column study (Experiment 6). Arrow indicates start of significant differences.

A 1-way Anova of the computed interactions indicated significant group differences [$F(44,251)=31.3, p<0.0001$]. A Scheffes Multiple Range test ($p=0.05$) revealed that the only significant difference occurred at leach cycle 12, where the absolute sulphur loading was significantly higher from columns containing pyritic (control) and depyritized tailings covers than from columns containing gold tailings or incinerator ash covers (Figure 40b). At no point was the sulphur loading from slag significantly different from any of the other covers. The absolute sulphur loading over time was still similar to that of magnesium, except for the slag-covered columns, where it was slightly elevated.

In general, absolute metal levels exhibited very similar patterns to those of the concentration data. However, leachates from the slag covered columns were slightly elevated with respect to columns covered with gold tailings and incinerator ash for Mn, Zn, Ni, Al (after week 9), and Ca. This was probably a response to the physical nature of the slag cover, which had a poor ability to hold water, and decreased evaporation from the surface, resulting in the generation of an increased volume of leachate. In a field application this effect would likely be much reduced, because the sloped nature of the Kidd Creek tailings would promote runoff at the slag/tailings interface, resulting in less infiltration, and therefore less seepage.

The increase in absolute calcium from slag covered columns was rather striking, and would initially seem to indicate that magnesium depletion was occurring, and that calcium was playing an increasing role in acid neutralization. However, this is more likely to simply be a function of the relative solubilities of Ca and Mg. Calcium carbonate is more soluble in water than magnesium carbonate (Davis *et al.*, 1984), and would be eluted faster in the saturated conditions observed in the pyritic tailings base under a cover of slag (see destructive sampling). This effect was not observed in the remaining columns because of the lower water content in the pyritic tailings base.

4.3.4.3 Cumulative Metal Loadings

Plots of the cumulative metal release are presented in Figures 41 - 46.

It was found that cumulative graphing of the amounts of metal leached, which represented potential metal "loadings" to the surrounding environment, in some cases best discerned the effects of the different covering materials on metal release. In addition, plots of the cumulative data can be used to assess the relative rates at which metal dissolution is occurring.

In general, the pyritic and depyritized tailings-covered columns show a drastic increase in the release of metals associated with factor 1 (Figures 41 - 44a). The steep slope of these lines suggests that the rate of metal release is remaining constant or accelerating. Rates of release from the other columns have generally either declined, or have levelled-off.

The cumulative plots are particularly effective at illustrating the enhanced rate of release of calcium (Figure 44b), aluminum (Figure 45a) and iron (Figure 46a) from the columns containing a cover of granulated slag, and copper (Figure 45b) from columns with depyritized tailings. Columns containing pyritic tailings only (control) released the most sulphur (Figure 46b), which confirms that higher oxidation rates are occurring in these columns than in the columns in which the pyritic tailings are covered.

4.3.4.4 Destructive Sampling of Tailings and Cover Solids

Mean pH values by depth are shown in Figure 47.

A 3-way ANOVA (cover, depth, lime) on the pH data of the pyritic tailings base yielded significant COVER [$F(4,120)=93.3$, $p<0.001$; $\eta^2=0.83$] and DEPTH [$F(2,120)=5.45$, $p=0.005$; $\eta^2=0.14$] main effects, and a COVER x LIME interaction [$F(4,120)=4.84$, $p=0.001$]. The three variables accounted for 71.1% of the variance ($r^2=0.711$).

A oneway ANOVA of the COVER effect showed significant group differences [$F(4,145)=80.57$, $p<0.0001$], and a Scheffé Multiple Range test indicated that the pH of the pyritic base was significantly lower in the columns with a cover of pyritic or depyritized tailings than in the remaining columns (Figure 47). In addition, the pH of the pyritic base from under a cover of incinerator ash was significantly lower than from under a cover of granulated slag. The pH of the

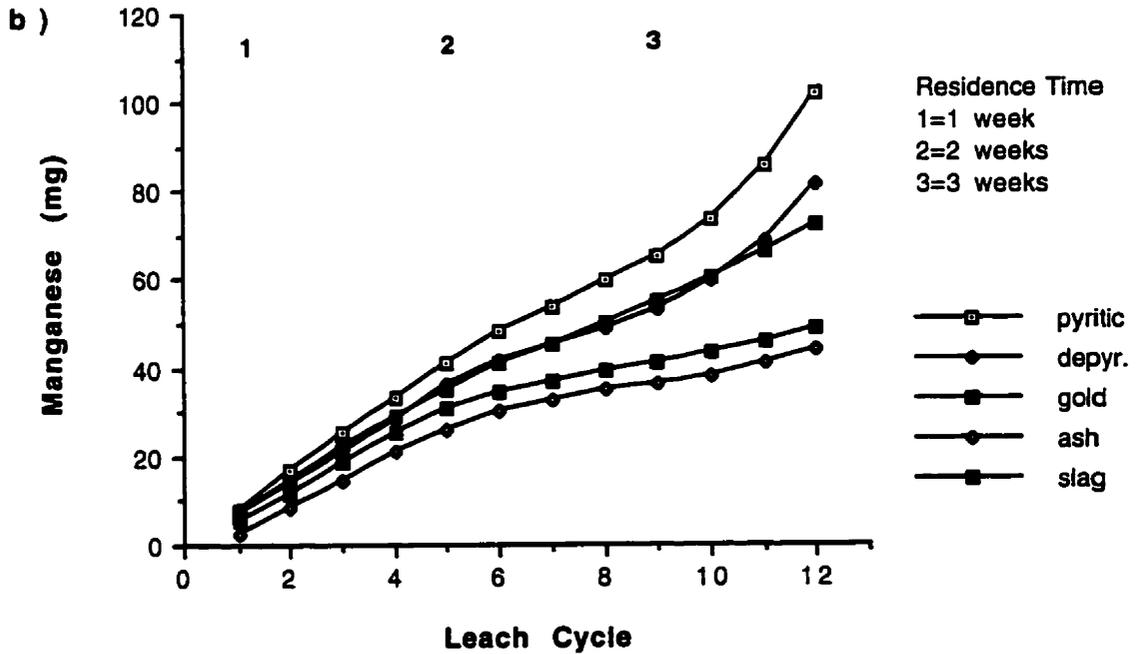
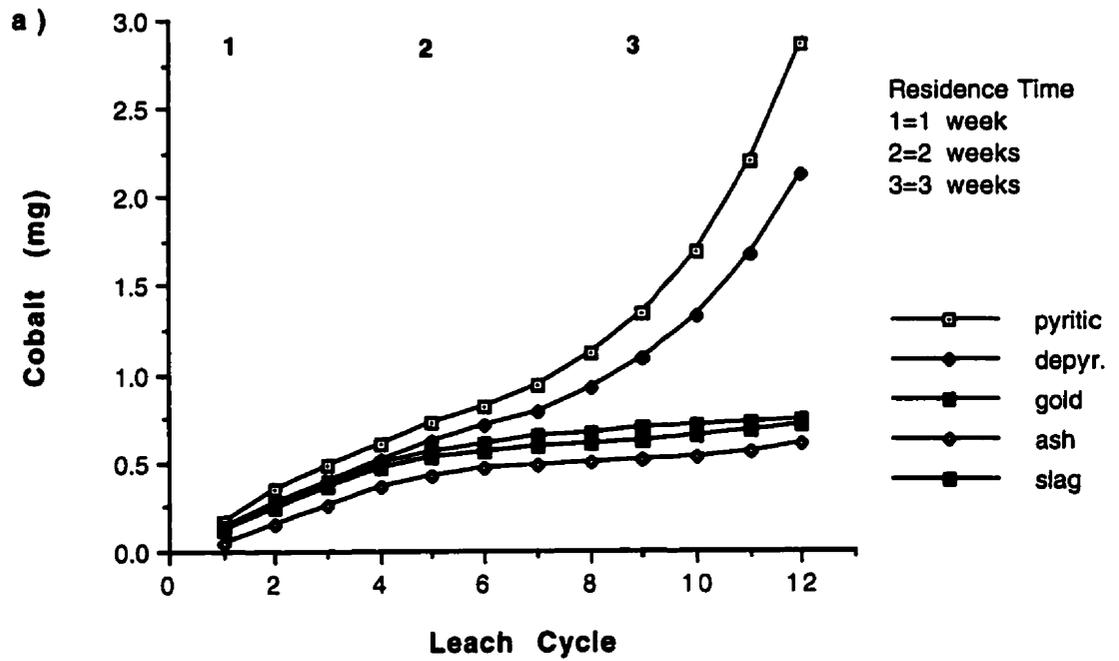


Figure 41: The effect of cover materials on the cumulative amount of (a) cobalt and (b) manganese in leachate generated from a column study (Experiment 6).

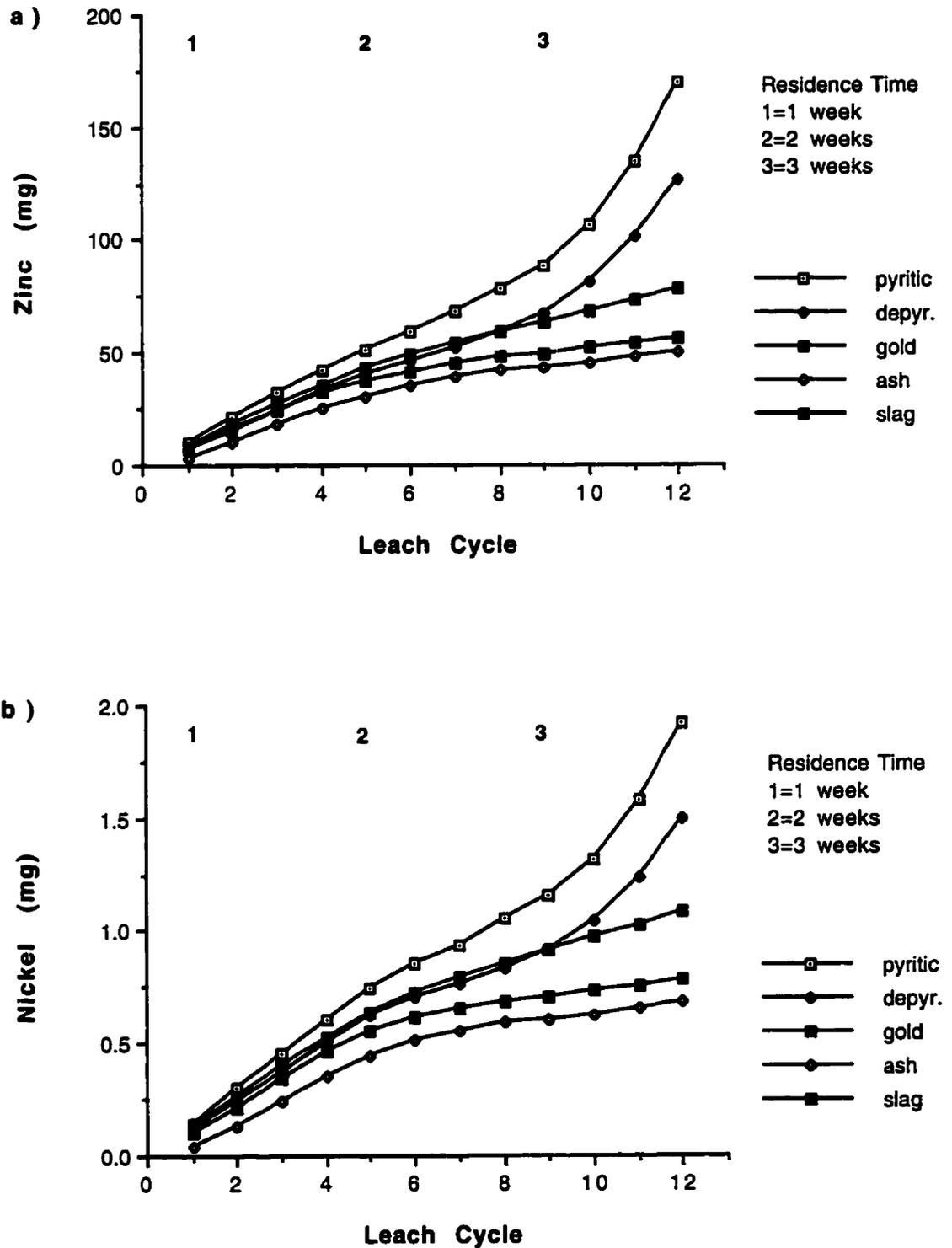


Figure 42: The effect of cover materials on the cumulative amount of (a) zinc and (b) nickel in leachate generated from a column study (Experiment 6).

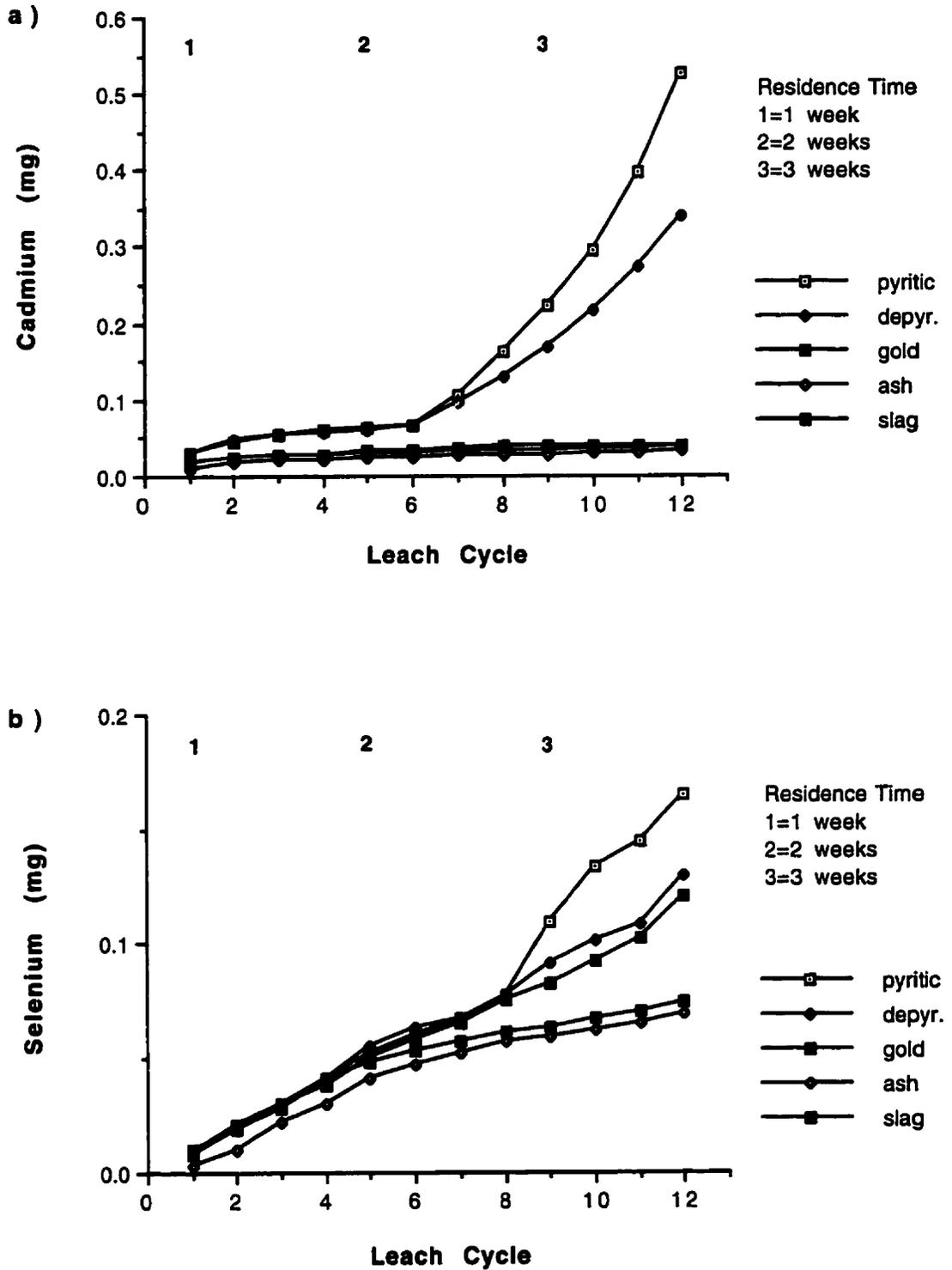


Figure 43: The effect of cover materials on the cumulative amount of (a) cadmium and (b) selenium in leachate generated from a column study (Experiment 6).

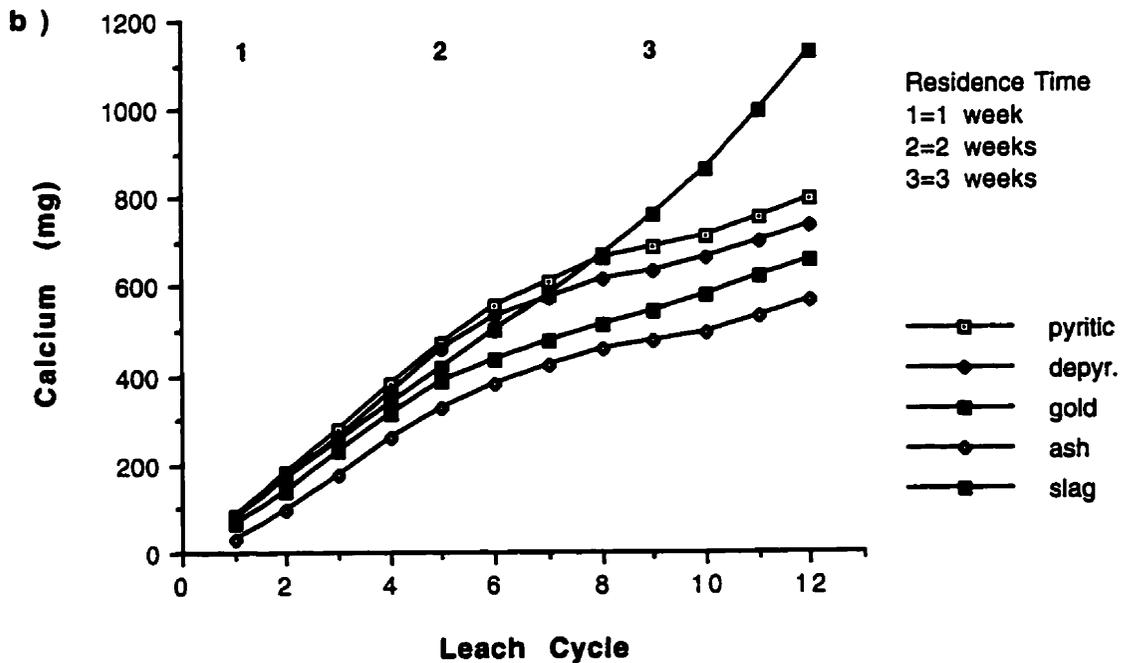
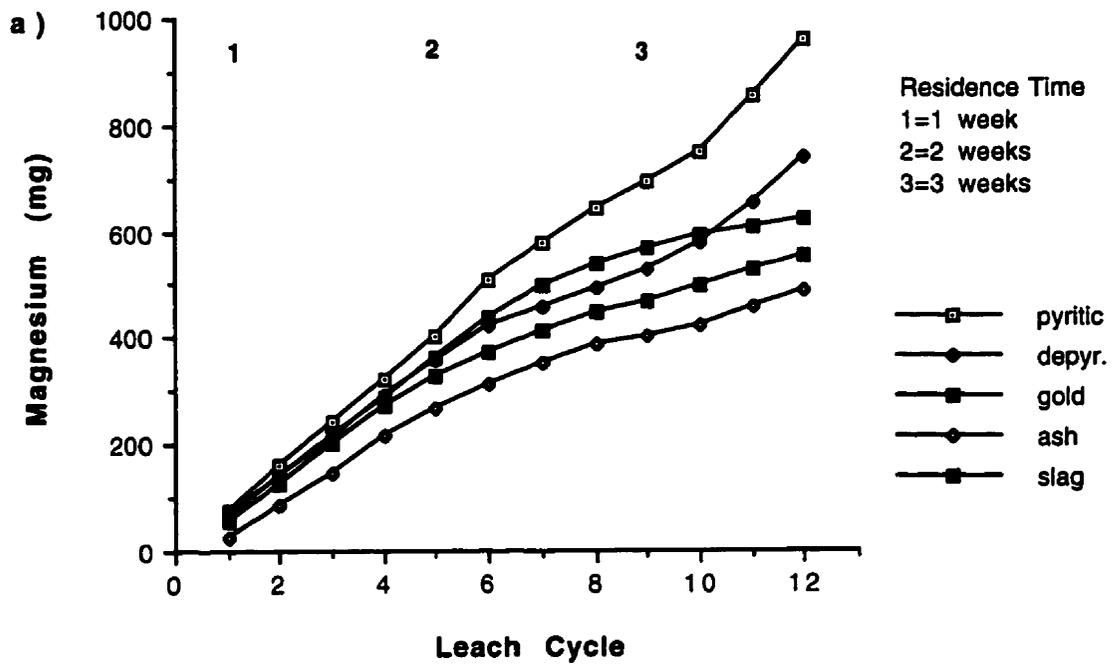


Figure 44: The effect of cover materials on the cumulative amount of (a) magnesium and (b) calcium in leachate generated from a column study (Experiment 6).

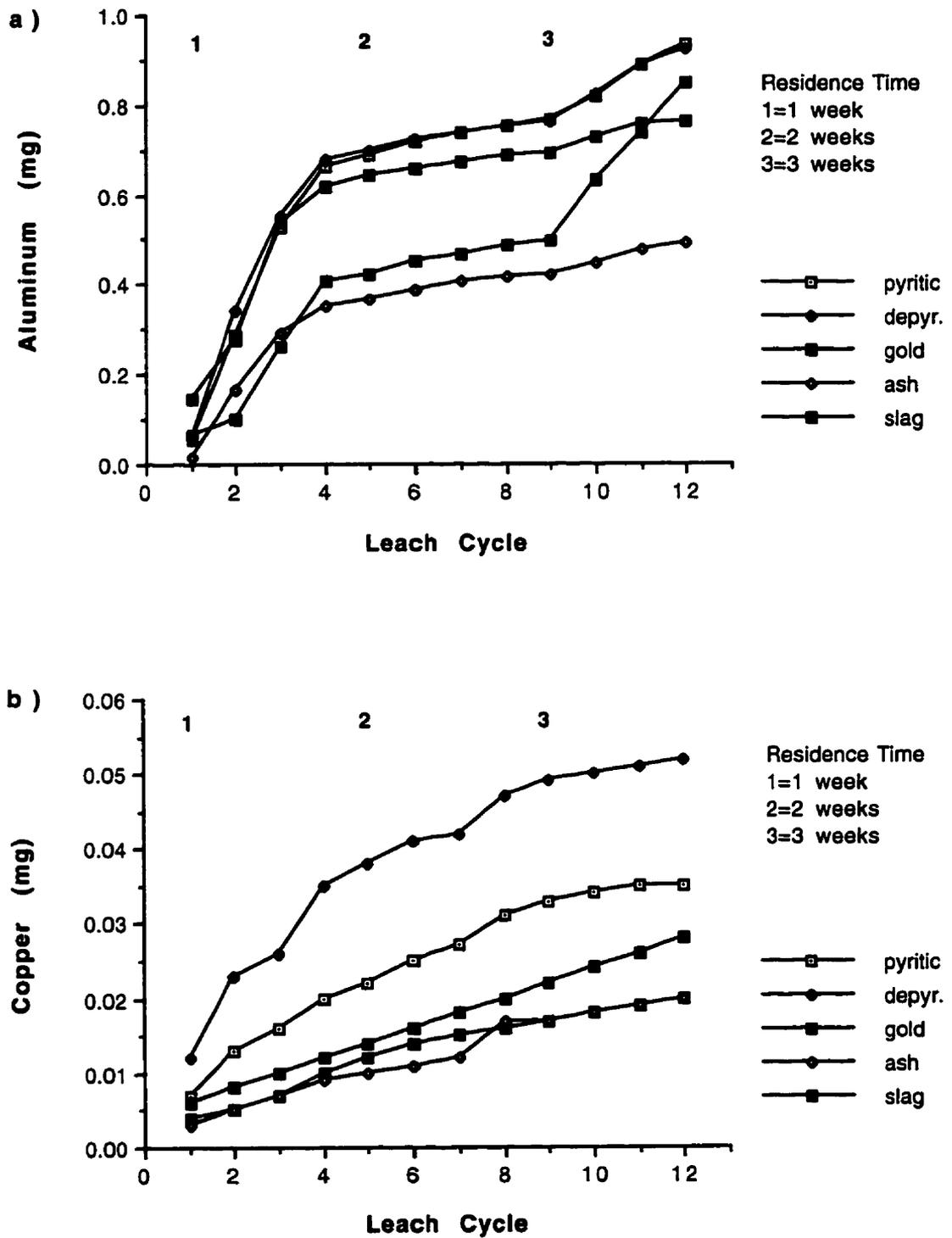


Figure 45: The effect of cover materials on the cumulative amount of (a) aluminum and (b) copper in leachate generated from a column study (Experiment 6).

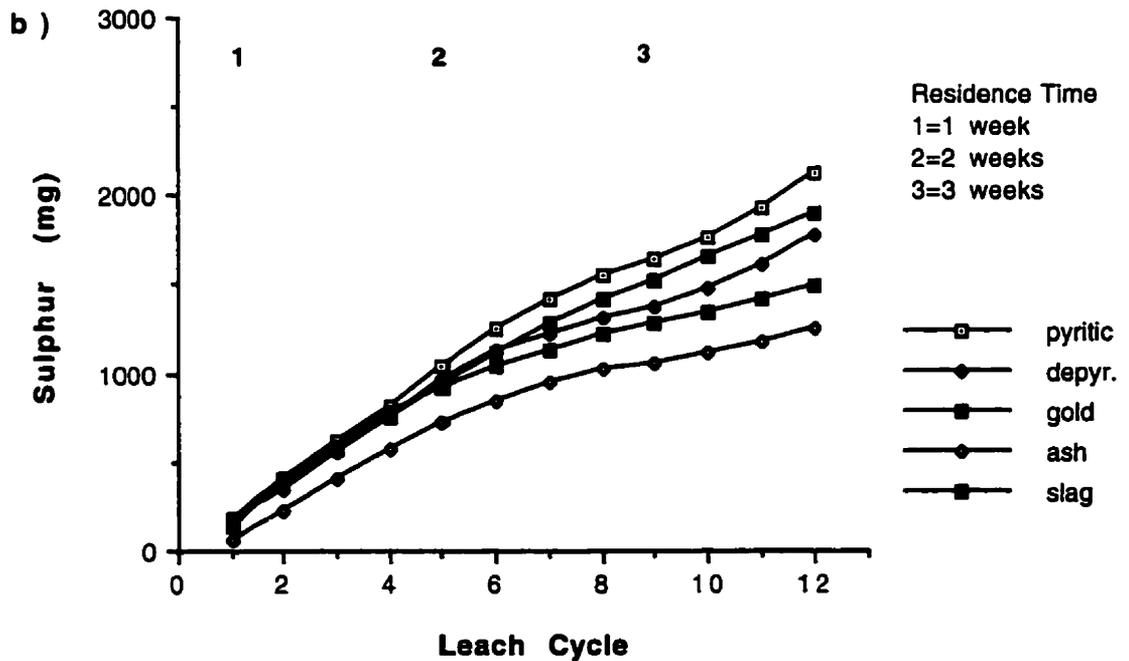
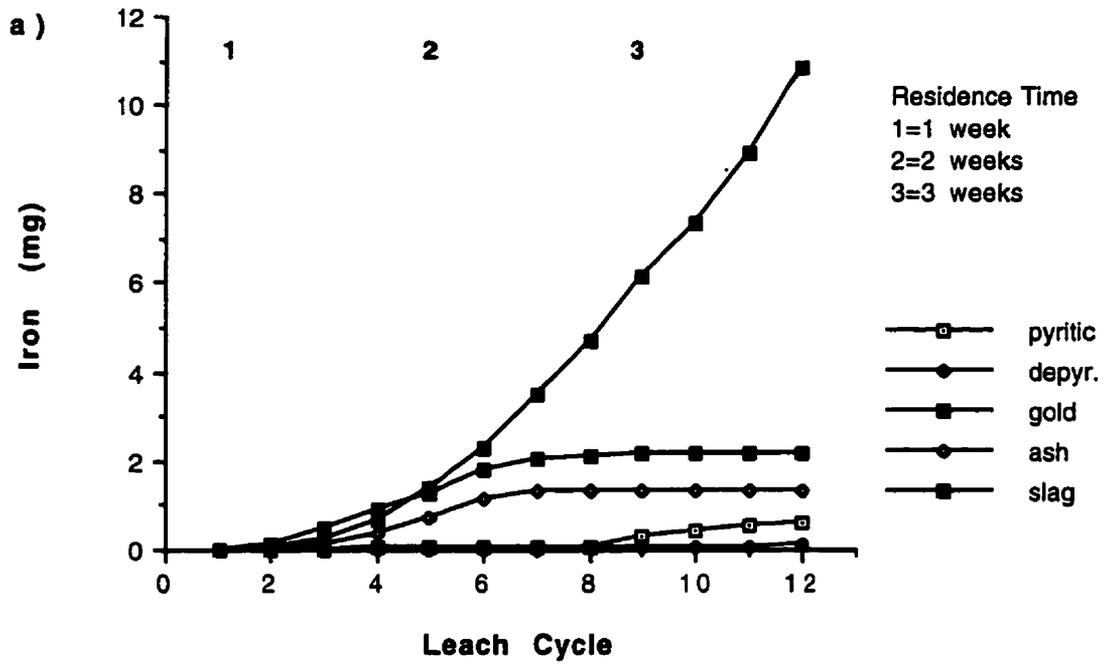


Figure 46: The effect of cover materials on the cumulative amount of (a) iron and (b) sulphur in leachate generated from a column study (Experiment 6).

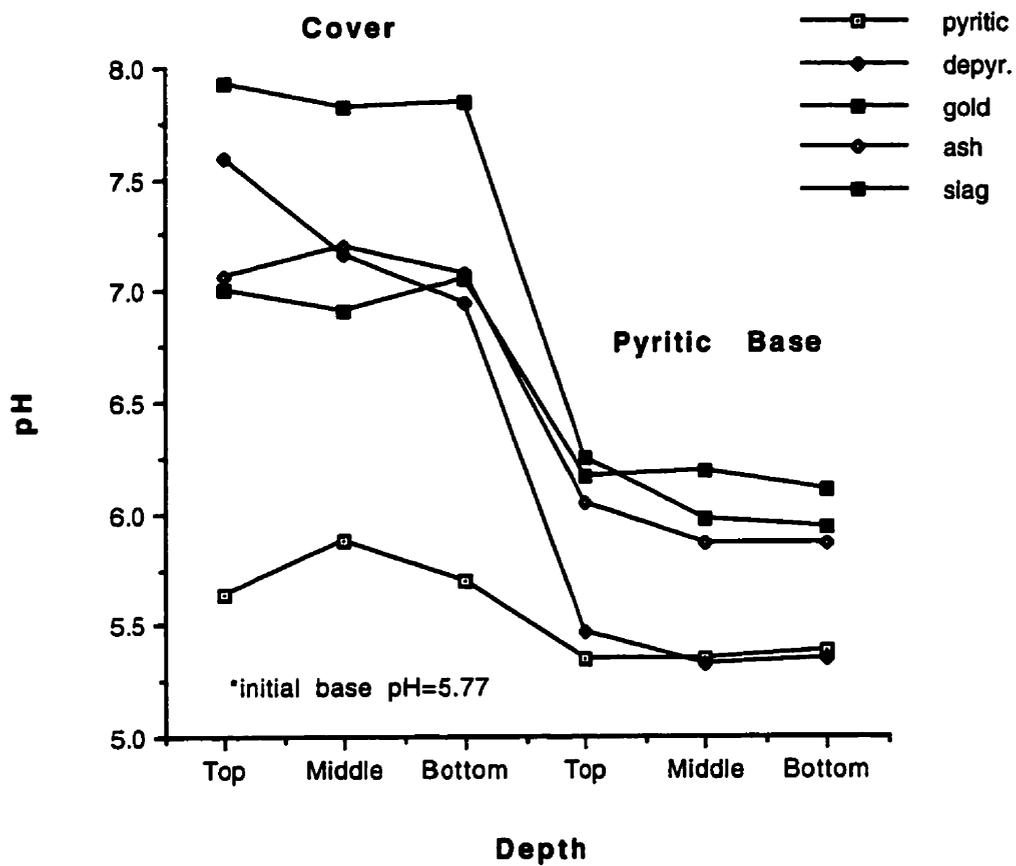


Figure 47: pH profile of the column solids sampled 5 weeks after leaching of the columns ceased.

pyritic base was also slightly higher at the end of the experiment than at the start for columns with a cover of gold tailings, incinerator ash or slag. Identical results were obtained using \log_{10} transformed data, although homogeneity of variance was not present in either.

A oneway ANOVA of the DEPTH effect revealed that there was actually no significant difference in pH of the pyritic base by depth.

A oneway ANOVA of the computed interactions (COVER x LIME) for the original data revealed a significant group difference [$F(9,140)=41.37$, $p<0.0001$], and a Scheffé Multiple Range test indicated that the addition of lime did not result in a significant increase in pH in any of the columns. While the addition of lime did slightly increase the pH of the slag, the pH of the pyritic tailings base was actually lower, although not significantly. This did not occur in any of the other covers, and probably represents the source of the interaction.

A 3-way ANOVA (cover, depth, lime) on the original moisture content data revealed a significant COVER effect [$F(4,120)=422.4$, $p<0.001$; $\eta^2 = 0.96$], with 92.6% of the variance explained ($r^2=0.926$).

A subsequent oneway ANOVA indicated a significant group effect [$F(4,145)=447.7$, $p<0.0001$] and a Scheffé Multiple Range test revealed that the moisture content of the pyritic base was significantly higher under a cover of granulated slag than under all other covers, and that the pyritic base from columns containing pyritic tailings (control) and a cover of depyritized tailings were also significantly lower than from a cover of gold tailings or incinerator ash (Figure 48). Identical results were obtained using log and square root transformed data.

Total metal content of the pyritic base did not show a depth effect; therefore values for the top, middle and bottom were pooled, and are presented in Table 26. The largest difference was an increase of approximately 3% for iron in the pyritic base under a slag cover, and approximately 1.5% under a gold cover. The fact that the iron values reported from the pyritic columns were similar to those of the original material, combined with a lack of evidence from the leachate data that oxidation is occurring faster when under a cover of slag, suggests that the iron is leaching from the slag itself.

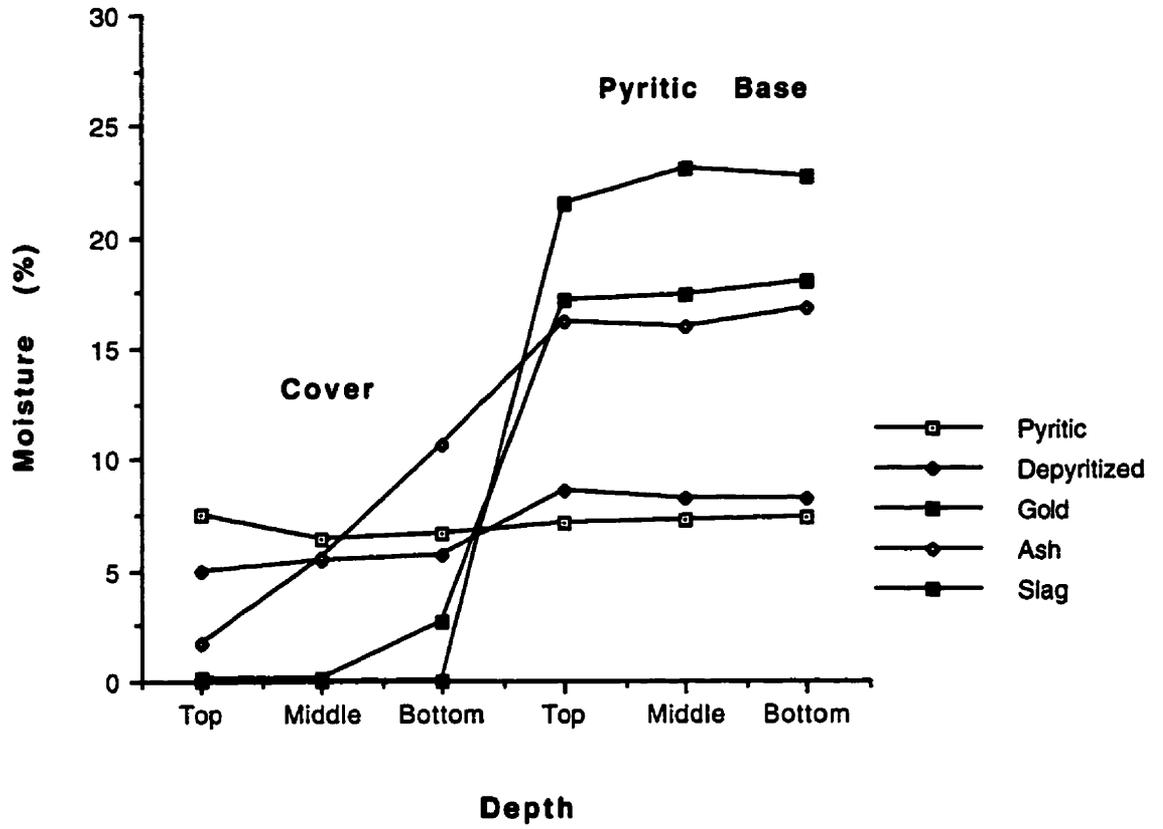


Figure 48: Moisture profiles of the column solids sampled 5 weeks after leaching of the columns ceased.

Table 26: Total Element Content ($\mu\text{g/g}$ unless otherwise indicated) in the Pyritic Base Sampled 5 Weeks After Column Leaching Ceased (Experiment 6).

	Pyritic		Depyritized		Gold		Ash		Slag	
	Total	S.E.	Total	S.E.	Total	S.E.	Total	S.E.	Total	S.E.
*Al	2.00	0.03	1.95	0.02	2.57	0.05	2.93	0.05	2.47	0.06
Ba	33.7	4.3	27.6	0.44	58.4	13.2	56.9	1.80	49.3	2.20
Cd	67.4	0.59	68.8	0.51	71.5	0.22	70.4	0.27	72.0	0.20
Co	162.1	4.07	162.6	1.08	166.8	0.60	165.1	0.67	170.7	0.62
Cr	28.3	1.09	30.1	1.06	18.7	0.74	19.8	0.65	19.3	0.90
Cu	1667	56.3	1574	18.1	1835	8.5	1768	11.6	1742	8.10
*Fe	9.0	0.25	9.1	0.13	10.3	0.07	9.5	0.06	12.6	0.02
Mn	789	24.9	774	10.2	833	6.3	838	29.6	839	8.20
Mo	37.0	1.32	38.7	1.42	19.2	0.39	19.7	0.28	20.0	0.41
Na	837	21.0	842	7.70	960	25.2	1141	20.3	940	28.1
Ni	51.8	1.14	55.0	0.93	46.1	0.32	49.8	0.44	49.7	0.36
P	133.1	2.02	141.3	2.8	120.7	1.3	143.7	3.60	134.3	2.00
Pb	691	8.3	707.0	8.3	680	3.6	684	2.80	713	5.20
*S	6.50	0.10	6.72	0.05	6.38	0.01	6.09	0.04	6.20	0.01
Zn	7790	237	7753	48.0	8347	22.0	8264	29.0	8570	39.0

* indicates measurement in %

Doyle and Mirza (1990) and Håkansson *et al.* (1994) indicate that dissolved iron, acid and high temperatures can accelerate pyrite oxidation, and that dissolved iron also promotes the oxidation of sulphide minerals other than pyrite, which then release metals. Evidence of this from the slag covers was not seen.

In general, and in addition to iron, the pyritic base under a cover of gold, ash or slag contained higher levels of copper, cadmium, aluminum and zinc than the columns containing pyritic and depyritized tailings (Table 26). This is not surprising, due to the high inherent metal content of these materials. However, it is not clear whether the gold, ash and slag have contributed metals to the pyritic base, or whether the enhanced metal dissolution from the pyritic and depyritized columns has somewhat depleted the the reserves of metal. In some cases (eg. Fe and Al), the values from the pyritic columns closely matched the values present in

the tailings originally added to the columns (Tables 2 and 26), while others such as zinc show higher levels in the pyritic base after the experiment. Since there was no clear depth effect, this was unlikely to have been due to leaching or accumulation in the lower layers.

Chromium and phosphorus are two elements that were high in the incinerator ash, although they failed to show any evidence of leaching into the pyritic base. Both of these metals were below detection limits in the leachate, and did not show any accumulation in the pyritic base. In fact, chromium levels were higher in the pyritic base from the columns containing a cover of pyritic (control) and depyritized tailings.

Sewage incinerator ash is formed by the combustion of sewage sludge, which results in the concentration of metals in the ash. Specifically, the ash contains comparatively high levels of Fe, Cr, Ni, and Cu (Table 2), and would be expected to release these metals through leaching processes, especially in the absence of organic matter. The gold tailings, on the other hand, were thought to be relatively inert, even though they have fairly high levels of Al and Cr. Granulated slag was also considered to be relatively inert, despite high levels of Fe, Cr, Cu and Zn (Table 2). In spite of these differences, under leaching conditions all three of these covers basically reacted in similar fashion, with elevated levels of iron in the leachate being the only major contaminant.

However, should the cover materials decline in pH over a longer time period as a result of contact with acid-generating tailings, it is likely that they would contribute significantly more metal to the underlying tailings.

4.3.5 Summary of Findings

1) Compared to a control, the application of a 10 cm cover of gold tailings, incinerator ash or granulated slag were, in the short term, effective at inhibiting the oxidation of the underlying tailings and subsequent metal release, while a cover of depyritized tailings was ineffective.

- 2) The application of gold tailings, incinerator ash and slag covers resulted in an increase in the dissolution of iron, stemming from the cover materials themselves, not from increased oxidation of the underlying tailings.
- 3) The effectiveness of a cover in decreasing tailings oxidation is governed largely by the ability of the material to maintain a higher water content in the underlying tailings, thereby limiting the diffusion of oxygen.
- 4) So long as the pH of the gold tailings, incinerator ash and granulated slag remain circumneutral, contamination of the underlying tailings by elements leached from the covers is unlikely. However, a large sink of heavy metals is potentially available should the pH of the cover decrease as a result of intimate contact with acid-generating tailings over a longer period of time.
- 5) The application of limestone to the covers did not have an effect on the dissolution of metals.
- 6) Magnesium carbonate appeared to be the major neutralizing material associated with the pyritic tailings, although enhanced calcium carbonate dissolution did occur from columns containing a slag cover, apparently in response to increased solubility at higher water contents.

5. GENERAL DISCUSSION AND CONCLUSIONS

Perhaps the most important aspect of the application of a cover material to tailings, from an environmental standpoint, is the ability of the cover to prevent the continued oxidation of the iron sulphides contained in the tailings. This is directly responsible for declining pH's, and the subsequent increase in dissolved metals contained in drainage water.

Covers can be used in various ways and serve several functions, but most are concerned with limiting the transfer of oxygen from the surface to the underlying tailings. This is generally accomplished by either the application of a water cover, or by applying materials with the ability to remain saturated for long periods of time, or which maintain the tailings near saturation. The diffusion coefficient of gaseous oxygen in water is low, at $2 \times 10^{-5} \text{ cm}^2/\text{s}$ compared to $0.178 \text{ cm}^2/\text{s}$ in air (Yanful, 1991). Thus any material or combination of materials that maintains the tailings or the region above the tailings at or near saturation will go a long way toward eliminating tailings oxidation.

More complicated multi-layered, engineered soil covers have received much attention lately, and are currently being designed and evaluated in field applications for their ability to maintain saturated or near saturated conditions in at least one of the layers (Nicholson *et al.*, 1991; Yanful, 1991; Bell *et al.*, 1994; Yanful *et al.*, 1994).

In addition to inhibiting oxidation, covers can also be effective in more readily establishing diverse vegetation communities and in intercepting potential tailings recharge water. In this case, the vegetated cover material holds a large portion of the recharge water and returns it to the atmosphere both through evaporation from the soil and transpiration from plant material before it reaches the underlying tailings. This can result in a drastic decrease in the volume of seepage generated, regardless of whether the tailings continue to oxidize.

This study was designed to test the ability of several waste products to support vegetation, to investigate the effect of a simple, single-layer cover of the indicated waste materials on sulphide oxidation and metal release, and to determine the contribution of metals, if any, from the covers to the underlying tailings.

Chemical analyses indicated that, while each of the materials showed relatively low concentrations of water soluble metals (with a few exceptions) at circumneutral pH, they contain high total levels of such metals as aluminum, iron, copper, manganese, zinc and chromium, which, with the exception of chromium, can become quite soluble as the pH declines.

Germination and early growth experiments indicated that germination was not affected by any of the substrates, but that growth in depyritized and gold tailings and incinerator ash was better than in the pyritic tailings control, and poorer in granulated slag. Growth effects were essentially confined to roots, because of their direct contact with the growth medium. Poor root performance in granulated slag was attributed to higher water soluble copper and low nutrients. Lime was found to have no effect on germination or early growth, which was not surprising, given that the materials were already circumneutral in pH. This section demonstrated that metal levels in the materials do not influence germination, but affect root growth, which may limit the ability of a seedling to become established.

Longer term pot experiments revealed that both root and shoot growth were better in depyritized tailings than in pyritic tailings, and that growth in incinerator ash was better than in gold tailings. Overall, fertilizer was the dominant variable influencing growth. Very limited growth was obtained in granulated slag, regardless of the amendments.

Shoot concentrations of copper, manganese, nickel and zinc were higher than reported background values, but were similar to published values for Redtop grown in metal contaminated substrates. Chromium and iron were the exceptions, with values higher than reported by other authors. Based on these findings, and because of its suspected toxicity, chromium represents a definite potential hazard, especially in vegetation grown on sewage incinerator ash. Manganese showed increased accumulation in shoot tissues with the addition of fertilizer.

A column leaching experiment showed that covers of gold tailings, incinerator ash and granulated slag were effective at limiting oxidation of the underlying tailings. This was measured as a decrease in the concentration of metals normally associated with the oxidation of the pyritic tailings (Al *et al.*, 1994), specifically Co, Mn, Zn, Cd, Ni, Mg, and Se. This was attributed to the ability of these cover

materials to maintain the underlying tailings at a higher water content, through a difference in particle size, i.e. the presence of a capillary break. A cover of depyritized tailings was found to be ineffective, owing to its similar particle size to that of pyritic tailings.

Gold tailings, incinerator ash and slag did not appear to leach metals into the underlying pyritic tailings, with the exception of iron. The relatively high pH of these materials results in low metal solubility. Metal solubility remains a prime concern for long term stability, since decreasing pH as a result of close contact with acid-generating tailings may lead to much increased leaching of metals over time.

Overall, the lower net acid producing potential of depyritized tailings, the net acid-consuming potential of the gold tailings, and the high phosphorus content of the incinerator ash certainly make these materials worthy of further consideration as cover materials, as long as they show no dramatic increases in leaching of potential toxins. SENES (1993) state that depyritized (desulphurized) tailings are industrial wastes with a high potential to be cost effective dry covers for tailings. However, based on the results of the present study, depyritized tailings appear to be of little use as a dry cover, at least when applied as a shallow cover. In addition, depyritized tailings were found to be a poor substrate for the long-term establishment of vegetation. Granulated slag has shown good potential for use as a capillary barrier between pyritic tailings and a cover material, although its physical and chemical characteristics limit its suitability as a revegetation growth medium.

6. LITERATURE CITED

- Aachib, M., M. Aubertin, and R.P. Chapuis. 1994. Column test investigation of milling wastes properties used to build cover systems. In: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, April 24-29, Pittsburgh, PA, 1994, pp. 128-137.
- Adams, F. 1981. Alleviating chemical toxicities: liming acid soils. In: Modifying the Root Environment to Reduce Crop Stress, Arkin and Taylor eds., Amer. Soc. Agric. Eng., pp. 269-301.
- Al, T.A., D.W. Blowes, and J.L. Jambor. 1994. The pore-water geochemistry of the Cu-Zn mine tailings at Kidd Creek, near Timmins, Ontario, Canada. In: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, April 24-29, 1994. Pittsburgh, PA., pp..208-217.
- Ames, S.E. 1981. The reclamation of Sullivan Mine iron tailings. M.Sc Thesis, University of British Columbia, Vancouver, British Columbia, Canada, 236 pp.
- Archambault, D.J.P. 1991. Metal tolerance studies on populations of *Agrostis scabra* Willd. (Tickle Grass) from the Sudbury area. M.Sc Thesis, Laurentian University, Sudbury, Ontario, Canada, 136 pp.
- Bell, A.V., M.D. Riley, and E.K. Yanful. 1994. Evaluation of a composite soil cover to control acid waste rock pile drainage. In: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, April 24-29, 1994. Pittsburgh, PA., pp..113 - 121.
- Black, C.A. 1965. Methods of Soil Analysis, Chemical and Microbiological Properties. American Society of Agronomy Inc., Madison, Wisconsin. 1572 pp.

- Blowes, D.W., C.J. Ptacek, J.G. Bain, K.R. Waybrant, and W.D. Robertson. 1995. Treatment of mine drainage water using in situ permeable reactive walls. In: Proceedings of the Sudbury '95 Mining and the Environment Conference, May 28 - June 1, 1995, Sudbury, Ontario, pp. 979-987.
- Blundon, D.J. 1984. Choosing between metal-tolerant *Deschampsia caespitosa* (L.) Beauv. and agronomic grasses in the revegetation of toxic, metalliferous tailings in the Yukon Territory. M.Sc Thesis, Laurentian University, Sudbury, Ontario, Canada, 147 pp.
- Bohn, H., B. McNeal, and G. O'Connor. 1979. Soil Chemistry. John Wiley & Sons Inc., Toronto, 329 pp.
- Bradbeer, J.W. (1989). Seed Dormancy and Germination. Chapman and Hall, New York, 137 pp.
- Bradham, W.S. and F.T. Caruccio. 1990. A comparative study of tailings analysis using acid/base accounting, cells, columns and soxhlets. In: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, April 23-26, 1990, Charleston, WV., pp. 19-25.
- Bradham, W.S. and F.T. Caruccio. 1991. A comparative study of tailings analysis using acid/base accounting, cells, columns and soxhlets. In: Proceedings of the Second International Conference on the Abatement of Acidic Drainage, Sept. 16-18, 1991, Montreal, Quebec, pp. 157-174.
- Brady, N.C. 1990. The Nature and Properties of Soils 10th ed.. Macmillan Publishing Company, New York, 621 pp.
- Calow, R.W., D. Hevener, and D. Masson-Stogran. 1995. Comparison of the B.C. Research and EPA acid mine drainage predictive static tests. In: Proceedings of the Sudbury '95 Mining and the Environment Conference, May 28 - June 1, 1995, Sudbury, Ontario, pp. 605-612.
- Carter, D.B. and H. Loewenstein. 1978. Factors affecting the revegetation of smelter-contaminated soils. Reclamation Review, vol. 1, pp. 113-119.

- Caruccio, F.T. 1968. An evaluation of factors affecting acid mine drainage production and the ground water interactions in selected areas of Western Pennsylvania. In: Proceedings of the second symposium on coal mine drainage research, Monroeville, Pennsylvania, 1968, pp. 107 - 151.
- Caruccio, F.T., and G. Geidel. 1986. An evaluation of mine waste overburden analytical techniques. In: Proceedings, 1986 National Symposium on Mining, Hydrology, Sedimentology and Reclamation, Dec. 8-11, 1986, University of Kentucky, pp. 147-153.
- Caruccio, F.T., and G. Geidel. 1994. Acid mine drainage: the problem and its solution. Workshop 5, Third International Conference on the Abatement of Acidic Drainage, April 24-29, 1994. Pittsburgh, PA, 58 pp.
- Caruccio, F.T., L.R. Hossner, and G. Geidel. 1988 Pyritic materials: acid drainage, soil acidity, and liming. In: Reclamation of Surface Mined Land, L.R. Hossner ed., CRC Press, Boca Raton, pp. 159 - 189.
- Chaney, W.R., R.C. Strickland, and R.J. Lamoreaux. 1977. Phytotoxicity of cadmium inhibited by lime. *Plant and Soil* 47: 275 - 278.
- Chang, A.C., T.C. Granato, and A.L. Page. 1992. A methodology for establishing phytotoxicity criteria for chromium, copper, nickel, and zinc in agricultural land application of municipal sewage sludges. *J. Env'tl. Qual.*, 21(4): 521 - 536.
- Cochran, W.G. 1947. Some consequences when the assumptions for the analysis of variance are not satisfied. *Biometrics* 3: 22 - 38.
- Cole, D. 1994. Sewage incinerator ash as a potential growth medium and phosphorus source in the revegetation of mine wastes, and the potential role of admixed peat in the release of phosphorus. B.Sc. Thesis, Biology Department, Laurentian University.
- Crovello, T.J. 1970. Analysis of character variation in ecology and systematics. *Ann. Rev. Ecol. Syst.* 1: 55 - 98.

- Curtin, D. and G.W. Smillie. 1986. Effects of liming on soil chemical characteristics and grass growth in laboratory and long-term field-amended soils. *Plant and Soil* **95**: 15 - 22.
- Davis, R.E., K.D. Gailey, and K.W. Whitten. 1984. *Principles of Chemistry*. CBS College Publishing, New York, 884 pp.
- Doepker, R. D. 1988. The interrelation of factors influencing the dissolution of metals in columns of mine tailings. In: *Proceedings, 1988 Mine Drainage and Surface Mine Reclamation Conference*, April 17-22, Pittsburgh. U.S. Bureau of Mines, IC 9184, pp. 210-219.
- Doepker, R.D. 1991a. Column leach study III: Effects of sampling location, sampling methods, and chemical abatement treatments on the dissolution of metals in gold-copper mine tailings. In: *Proceedings, National Meeting of the American Society for Surface Mining and Reclamation*, May 14-17, 1991, Durango, Colorado, pp. 343 - 367.
- Doepker, R.D. 1991b. Column leach study IV: factors affecting the dissolution of metals from sulphitic metal-mine tailings. In: *Proceedings of the Second International Conference on the Abatement of Acidic Drainage*, Sept. 16-18, 1991, Montreal, Quebec, pp. 115 - 138.
- Doepker, R.D., and P.L. Drake. 1991c. Laboratory study of submerged metal-mine tailings III - factors influencing the dissolution of metals. In: *Proceedings of the Second International Conference on the Abatement of Acidic Drainage*, Sept. 16-18, 1991, Montreal, Quebec, pp. 139 - 155.
- Doepker, R. D., and O'Connor, W.K. 1990a. Column leach study I: heavy metal dissolution characteristics from selected copper mine tailings. In: *Proceedings, Fifth Billings Symposium on Disturbed Land Rehabilitation*, March 25-30, 1990, Billings, MT, Vol. 1, pp. 27 - 40.

- Doepker, R.D., and O'Connor, W.K. 1990b. Column leach study II: heavy metal dissolution characteristics from selected lead-zinc mine tailings. In: Proceedings, Mining and Mineral Processing Wastes, Western Regional Symposium, May 30-June 1, 1990, University of California, Berkeley, pp. 69-80.
- Doyle, F.M., and A.B. Mirza. 1990. Understanding the mechanisms and kinetics of acid and heavy metals release from pyritic wastes. In: Proceedings of the Western Regional Symposium on Mining and Mineral Processing Wastes, 1990, Berkely, California, pp.43-51.
- Ebelhar, M.W., R.I. Barnhisel, G.W. Akin, and J.L. Powell. 1982. Effect of lime, N, P and K amendments to surface-mined coal spoils on yield and chemical composition of common bermudagrass. *Reclamation and Revegetation Research* 1 (4): 327 - 336.
- Erickson, P.M. and R.S. Hedin. 1988. Evaluation of overburden analytical methods as means to predict post-mining coal mining drainage quality. In: Proceedings of the Annual Meeting of the American Society for Surface Mining and Reclamation, April 17-22, 1988, Pittsburgh, Pa., pp. 11-19.
- Freedman, B., and T.C. Hutchinson. 1980. Pollutant inputs from the atmosphere and accumulations in soils and vegetation near a nickel-copper smelter at Sudbury, Ontario, Canada. *Can. J. Bot.* 58(1): 108 - 132.
- Garg, R. 1995. Computing via SPSS: a practical approach. Psychology 3256EA notes, Laurentian University, Sudbury, Ontario, Canada, 89 pp.
- Gartside, D.W., and T. McNeilly. 1974. The potential for evolution of heavy metal tolerance in plants II. copper tolerance in normal populations of different plant species. *Heredity* 32 (3), 335 - 348.
- Gentry, C.E., R.B. Willis, and H.G. Halverson. 1992. Chemical and pedogenetic effects of simulated precipitation on strip mine spoil. In: Proceedings, Ninth Annual National Meeting of the American Society for Surface Mining and Reclamation, June 1992, Duluth, Minnesota, pp. 61-67.

- Green , R.H. 1979. Sampling design and statistical methods for environmental biologists. John Wiley & Sons, Toronto, 257 pp.
- Håkansson, K., S. Karlsson, and B. Allard. 1994. Effects of increased iron concentrations on the mobility of cadmium, copper and zinc in leachates after remedial action at an old sulphidic mine waste site. In: Proceedings of the 3rd International Conference on the Abatement of Acidic Drainage, April 24-29, 1994, Pittsburgh, PA., pp. 336 - 345.
- Hammack, R.W., and G.R. Watzlaf. 1990. The effect of oxygen on pyrite oxidation. In: Proceedings, 1990 Mining and Reclamation Conference and Exhibition, April 1990, Charleston, W.V., pp. 257-264.
- Harris, R.J. 1975. A primer of multivariate statistics. Academic Press, New York.
- Hawley, J.R. 1972. The problem of acid mine drainage in the province of Ontario. Mining Industrial Waste Branch. 337 pp.
- Hawley, J.R. 1984. Levels of metals and non metals in vegetation growing on deposits of mineral tailings in the province of Ontario. Water Resources Branch. 261 pp.
- Hazlett, P.W., G.K. Rutherford, and G.W. vanLoon. 1983. Metal contaminants in surface soils and vegetation as a result of nickel/copper smelting at Coniston, Ontario, Canada. Reclamation and Revegetation Research 2: 123 - 137.
- Heath, O.V.S. 1970. Investigation by Experiment. Edward Arnold Ltd., London, 74 pp.
- Henriques, F.S., and J.C. Fernandes. 1991. Metal uptake and distribution in rush (*Juncus conglomeratus* L.) plants growing in pyrites mine tailings at Lousal, Portugal. The Science of the Total Environment 102: 253 - 260.

- Hodgson, J.F. 1970. Chemistry of trace elements in soils with reference to trace element concentrations in plants. In: Trace Substances in Environmental Health III, D.D. Hemphill ed., pp. 45-59.
- Hogan, G.D. 1975. A physiological basis for revegetation: studies on heavy metal tolerance of *Agrostis gigantea* Roth., toxicity and metal contaminated soils from Sudbury, Ontario. M.Sc Thesis, Laurentian University, Sudbury, Ontario, Canada.
- Hogan, G.D., G.M. Courtin, and W.E. Rauser. 1977a. The effects of soil factors on the distribution of *Agrostis gigantea* on a mine waste site. Can. J. Bot. 55: 1038 - 1042.
- Hogan, G.D., G.M. Courtin, and W.E. Rauser. 1977b. Copper tolerance in clones of *Agrostis gigantea* from a mine waste site. Can. J. Bot. 55: 1043 - 1050.
- Hogan, G.D., and W.E. Rauser. 1979. Tolerance and toxicity of cobalt, copper, nickel and zinc in clones of *Agrostis gigantea*. New Phytol. 83, 665-670.
- Holub, Z., V. Banášová, and E. Zeleňáková. 1987. Chronical impact of Pb in the soil on organic matter breakdown and the degree of tolerance of the species. Ekológia 6 (3): 337 - 344.
- Hood, W.C., and A.O. Oertel. 1984. A leaching column method for predicting effluent quality from surface mines. In: Proceedings, Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, Dec. 2-7, Lexington, Kentucky, 1984, pp. 271 - 277.
- Hoving, S.J., and W.C. Hood. 1984. The effects of different thicknesses of limestone and soil over pyritic material on leachate quality. In: Proceedings of the Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, Dec. 1984, Lexington, Kentucky, pp. 251-257.

- Hunter, G., and P.C. Whiteman. 1974. Problems associated with the revegetation of metal-mining wastes. *Journal of the Australian Institute of Agricultural Science*, Dec., 1974, pp. 270 - 278.
- Jackson, M.L., B.R. Stewart, and W.L. Daniels. 1993. Acid mine drainage mitigation using bulk blended fly ash/coal mixtures: Column Study Results. In: *Proceedings of the Pittsburgh Coal Conference*, Pittsburgh PA. 1993.
- Jeffrey, D.W. 1987. *Soil-Plant Relationships: an ecological approach*. Timber Press, Portland, Oregon, 294 pp.
- Jowett, D. 1958. Populations of *Agrostis* spp. tolerant to heavy metals. *Nature* **182**: 816.
- Jurjovec, J., D.W. Blowes, and C. Ptacek. 1995. Acid neutralization in mill tailings and the effect of natrojarosite addition. In: *Proceedings of the Sudbury '95 Mining and the Environment Conference*, May 28 - June 1, 1995, Sudbury, Ontario, pp.29 - 38.
- Kleinmann, R.L.P., D.A. Crerar, and R.R. Pacelli. 1981. Biogeochemistry of acid mine drainage and a method to control acid formation. *Mining Eng.*, **33**: 300 - 305.
- Lakefield Research. 1990. Results of project #3932. Report Prepared for Falconbridge Ltd., Kidd Creek Div., Timmins, Ontario.
- Lane and Associates. 1990. Heavy metal removal from gold mine tailings by indigenous plants (Oldham phase II). Final Report, Prepared for CANMET. P. Lane and Associates Ltd.
- Lapakko, K. 1992. Characterization and static testing of ten gold mine tailings. In: *Proceedings, 9th Annual National Meeting of the American Society for Surface Mining and Reclamation*, June 1992, Duluth, Minnesota, pp. 370-384.

- Lapakko, K. 1994. Evaluation of neutralization potential determinations for metal mine waste and a proposed alternative. In: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, April 24-29, 1994, Pittsburgh, PA, pp. 129-137.
- Lawrence, R.W. 1990. Prediction of the behaviour of mining and processing wastes in the environment. In: Proceedings of the Western Regional Symposium on Mining and Mineral Processing Wastes, 1990, Berkeley, Ca, pp. 115-121.
- Maddox, J.B., J.E. Brown, and G.N. Bartley Jr.. 1977 The effects of fertilizer and acid strip mine spoil on germination of grass seeds. In: Proceedings of the Fifth Symposium on Surface Mining and Reclamation, Oct. 18-22, Louisville, Ky., 1977, pp. 245 - 254.
- McLaughlin, B.E., van Loon, G.W., and A.A. Crowder. 1985. Comparison of selected washing treatments on *Agrostis gigantea* samples from mine tailings near Copper Cliff, Ontario, before analysis for Cu, Ni, Fe and K content. *Plant & Soil*, **85**: 433 - 436.
- McLaughlin, B.E. and A.A. Crowder. 1988. The distribution of *Agrostis gigantea* and *Poa Pratensis* in relation to some environmental factors on a mine-tailings area at Copper Cliff, Ontario. *Can. J. Bot.*, **66**: 2317 - 2322.
- Michalovic, J.G., and L.L. McGee. 1984. Evaluation of coal waste leachate problems. In: Proceedings, Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, Dec. 2-7, Lexington, Kentucky, 1984, pp. 121 - 126.
- Michelutti, B. and M. Wiseman. 1995. Engineered wetlands as a tailings rehabilitation strategy. In: Restoration and Recovery of an Industrial Region. J.M. Gunn Ed., Springer-Verlag, New York, pp. 135 - 141.

- Morin, K.A. and N.M. Hutt. 1994., Observed depletion of neutralization potential over sulphide minerals in kinetic tests: site specific criteria for safe NP/AP ratios. In: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, April 24-29, 1994, Pittsburgh, PA, pp. 148-156.
- Nicholson, R., F.F. Akindunni, R.C. Sydor and R.W. Gillham. 1991. Saturated tailings covers above the water table: the physics and criteria for design. In: Proceedings of the Second International Conference on the Abatement of Acidic Drainage, Sept. 16-18, 1991, Montreal, Quebec, pp.443-460.
- Patterson, W.A. and J.J. Olson. 1983. Effects of heavy metals on radicle growth of selected woody species germinated on filter paper, mineral and organic soil substrates. *Can. J. For. Res.*, 13: 233 - 238.
- Peech, M. 1965. Exchange acidity. In: *Methods of Soil Analysis*, C.A. Black (ed.), American Society of Agronomy, Inc., Madison, Wisconsin, pp. 905 - 913.
- Peters, T.H. 1995. Revegetation of the Copper Cliff Tailings Area. In: *Restoration and Recovery of an Industrial Region*. J.M. Gunn Ed., Springer-Verlag, New York, NY, 1995, 358 pp.
- Peterson, H.B. and R.F. Nielson. 1973. Toxicities and deficiencies in mine tailings. In: *Ecology and Reclamation of Devastated Lands*. Hutnik and Davis Eds., Gordon and Breach, pp. 15-25.
- Pierce, W.G., N. Belzile, M.E. Wiseman and K. Winterhalder. 1994 Composted organic wastes as anaerobic reducing covers for long term abandonment of acid-generating tailing. In: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, April 24-29, 1994, Pittsburgh, PA, pp. 148-157.
- Pirsson, L.V. 1908. *Rocks and Rock Minerals*. John Wiley & Sons, Inc., New York, 426 pp.

- Plass, W.T. 1976. Direct seeding of trees and shrubs on surface mined lands. Green Lands. West Virginia Surface Mining and Reclamation Association, 6(4): 24-32.
- Rauser, W.E., and N.R. Curvetto. 1980. Metallothionein occurs in roots of *Agrostis* tolerant to excess copper. *Nature* 287: 563 - 564.
- Rauser, W.E., and E.K. Winterhalder. 1985. Evaluation of copper, nickel, and zinc tolerances in four grass species. *Can. J. Bot.* 63: 58 - 63.
- Reardon, E.J., and P.M. Moddle. 1985. Gas diffusion coefficient measurements on uranium mill tailings: implications to cover layer design. *Uranium* 2: 111 - 131.
- Renton, J.J., T.E. Rymer, and A.H. Stiller. 1988. A laboratory procedure to evaluate the acid producing potential of coal associated rocks. *Mining Science and Technology*, vol. 7, pp. 227-235.
- Robinsky, E.I. 1978. Tailing disposal by the thickened discharge method for improved economy and environmental control. In: *Proceedings, Second International Tailing Symposium, Tailing Disposal Today*, Miller Freeman Publications, Inc., 1978, Denver, Colorado, pp. 75-92.
- Robinsky, E.I. 1989. Environmental and reclamation advantages of the thickened tailings disposal system. Prepared for Falconbridge Limited, Kidd Creek Division, Timmins, Ontario.
- Robinsky, E.I., S.L. Barbour, G.W. Wilson, D. Borden, and D.G. Fredlund. 1991. Thickened sloped tailings disposal - an evaluation of seepage and abatement of acid drainage. In: *Proceedings of the Second International Conference on the Abatement of Acidic Drainage*, Sept. 16-18, 1991, Montreal, Quebec, pp. 529 - 549.
- Salvas, R.J. 1989. Beneficial characteristics of sloped tailings deposit In: *Proceedings, 28th Annual CIM Conference*, August 1989, Halifax, Nova Scotia, 12 pp.

- SENES, Ltd., 1993. Evaluation of alternative covers for the prevention of acid mine drainage from tailings. Draft Final Report, Prepared for the MEND Program and CANMET. Senes Consultants ltd.
- Sheets, P.J., V.V. Volk, and E.H. Gardner. 1982. Plant and soil reactions to nickel processed tailings. *Journal of Environmental Quality*, **11**(3): 446 - 451.
- Shellhorn, M.A., and V. Rastogi. 1984. Laboratory methods for determining the effects of bactericides on acid mine drainage. In: *Proceedings, Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation*, Dec. 2-7, Lexington, Kentucky, 1984, pp. 77 - 82.
- Shetron, S.G. 1976. Plant nutrient availability changes in tailings as a result of vegetative stabilization. *Mineral Waste Stabilization Liaison Committee Meeting*, Sudbury, Ontario, Canada, 12 pp.
- Skousen, J.G. 1995. Acid Mine Drainage. In: *Acid Mine Drainage - control and treatment. Compiled by J.G. Skousen and P.F. Ziemkiewicz*, West Virginia University and the National Mine Land Reclamation Center, Morgantown, West Virginia, pp. 9 - 12.
- Smith, R.A.H., and A.D. Bradshaw. 1972. Stabilization of toxic mine wastes by the use of tolerant plant populations. *Mining Industry*, **81**: A230-A237.
- Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and laboratory methods applicable to overburdens and minesoils. EPA-600/2-78-054, Industrial Environmental Research Laboratory, Cincinnati, Ohio, 203 pp.
- Spires, A.C. 1975. Studies on the use of overburden soils in facilitating vegetative growth on high sulphide tailings. M.Sc Thesis, Laurentian University, Sudbury, Ontario, Canada, 151 pp.

- Stanley, M.A., G.E. Schuman, F. Rawzi, and L.I. Painter. 1982. Quality and element content of forages grown on three reclaimed mine sites in Wyoming and Montana. *Reclamation and Revegetation Research* 1: 311 - 326.
- Sutcliffe, J.F., and D.A. Baker. 1974. *Plants and Mineral Salts. Studies in Biology* no. 48, Edward Arnold Ltd., London, 60 pp.
- Sydor, R.C. 1992. Engineered mine tailings covers: verification of drainage behaviour and investigation of design parameters. M.Sc. Thesis, Earth Sciences, University of Waterloo.
- Taylor, E.M., and G.E. Schuman. 1988. Fly ash and lime amendment of acidic coal spoil to aid revegetation. *Journal of Environmental Quality*, 17(1): 120 - 124.
- Tisch, B. 1996. The influence of a granulated slag capillary break on the upward movement of acid and metals from oxidized sulphide tailings into a cover material. Report Prepared for Falconbridge Ltd., Kidd Creek Div., Timmins, Ontario, 17 pp.
- Turner, G.D., R.R. Lau, and D.R. Young. 1988. Effect of acidity on germination and seedling growth of *Paulownia tomentosa*. *Journal of Applied Ecology*, 25: 561 - 567.
- Veldhuizen, H., D.W. Blowes, and R.S. Siwik. 1987. The effectiveness of vegetation in controlling acid generation in base metal tailings. In: *Proceedings Acid Mine Drainage Workshop/Seminar, March, 1987, Halifax, Nova Scotia*, pp. 507 - 536.
- Walley, K.A., M.S.I. Khan, and A.D. Bradshaw. 1974. The potential for evolution of heavy metal tolerance in plants I. copper and zinc tolerance in *Agostis tenuis*. *Heredity*, 32 (3), 309 - 319.

- Watkin, E.M. 1988. Factors affecting vegetation establishment on acidic tailings and rock wastes. In: Proceedings of the Mine Drainage and Surface Mine Reclamation Conference, April, 17 - 22, 1988, Pittsburgh, PA.
- Watzlaf, G.R., and P.M. Erickson. 1986. Topical amendments of coal refuse: effect on pore gas composition and water quality. In: Proceedings of the National Symposium on Mining, Hydrology, Sedimentology, and Reclamation. Dec. 8 - 11, 1986, Lexington, Kentucky, pp. 255 - 261.
- Wear, J.I. 1956. Effect of soil pH and calcium uptake on zinc uptake by plants. *Soil Sci.* **81**(4): 311 - 315.
- Webber, M.D. 1975. Metal availability in soils. In: Proceedings of the Workshop on Metals in Agriculture, January 8 - 9, 1975, Guelph, Ontario.
- Whitby, L.M., and T.C. Hutchinson. 1974. Heavy metal pollution in the Sudbury mining and smelting region of Canada. II. soil toxicity tests. *Environ. Conserv.* **1**(3): 191 - 200.
- White, M.C., A.M. Decker, and R.L. Chaney. 1979. Differential cultivar tolerance in soybean to phytotoxic levels of soil Zn. I. Range of cultivar response. *Agron. J.* **71**: 121 - 126.
- Wilkins, D.A. 1957. A technique for the measurement of lead tolerance in plants. *Nature* **180** (4575): 37 - 38.
- Wilson, L.J. 1995. Leach test protocols for slags. In: Proceedings of the Sudbury '95 Mining and the Environment Conference, May 28 - June 1, 1995, Sudbury, Ontario, pp.89 - 97.
- Winterhalder, K., P.J. Beckett, and M.R. Todd. 1984. Metal dynamics in a revegetated ecosystem at Sudbury, Canada. In: Proceedings International Conference on Environmental Contamination, July, 1984, London, England, pp. 499 - 504.

- Winterhalder, K. 1992. The experimental use of various covers and native transplants for the revegetation of the Kam-Kotia tailings site, Timmins, Ontario. In: Proceedings, 9th annual Meeting of the American Association for Surface Mining and Reclamation, June 14 - 18, 1992, Duluth, Minnesota, pp. 385 - 396.
- Winterhalder, K. 1996. Environmental degradation and rehabilitation of the landscape around Sudbury, a major mining and smelting area. *Environmental Reviews*. 4(3): 185 - 224.
- Wong, M.H., and A.D. Bradshaw. 1982. A comparison of the toxicity of heavy metals, using root elongation of rye grass, *Lolium perenne*. *New Phytol.* 91: 255 - 261.
- Wu, L., A.D. Bradshaw, and D.A. Thurman.. 1975a. The potential for evolution of heavy metal tolerance in plants III. the rapid evolution of copper tolerance in *Agrostis stolonifera*. *Heredity*, 34(2): 165 - 187.
- Wu, L., D.A. Thurman., and A.D. Bradshaw. 1975b. The uptake of copper and its effect upon respiratory processes of roots of copper tolerant and non-tolerant clones of *Agrostis stolonifera*. *New Phytol.* 75: 225 - 229.
- Yanful, E. 1991. Engineered soil covers for reactive tailings management: theoretical concepts and laboratory development. In: Proceedings of the Second International Conference on the Abatement of Acidic Drainage, Sept. 16-18, 1991, Montreal, Quebec, pp.461-486.
- Yanful, E.K., B.C. Aubé, M. Woyshner, and L.C. St-Arnaud. 1994. Field and laboratory performance of engineered covers on the Waite Amulet Tailings. In: Proceedings of the Third International Conference on the Abatement of Acidic Drainage, April 24-29, 1994, Pittsburgh, PA, pp. 138 - 147.

Appendices

Methods Used in Substrate Analysis

pH

Subsamples of all homogenized substrate samples were analyzed for pH using the saturated paste method (Peech, 1965).

Silt and Clay Determination by the Hydrometer Method

Duplicate samples of approximately 100 g of each substrate were weighed out and placed in a 500 ml Erlenmeyer flask. Approximately 100 ml of distilled water was added, and the flask was shaken by hand until the substrate was thoroughly wetted. Then 10 ml of calgon (sodium hexametaphosphate) solution was added to the flasks, and more distilled water was added so that the flask were approximately two thirds full. The flasks were then shaken on a Burrell wrist action shaker for 1 hour. After 1 hour, the suspensions were washed thoroughly into sedimentation cylinders, and the cylinders were filled to 1205 ml with the hydrometer in place. The hydrometer was removed and the cylinder was shaken (end over end) 10 times, and the time was noted. After exactly 4 minutes, the hydrometer was placed in the suspension and a reading taken. The hydrometer was then removed, and the suspension was allowed to stand for two hours before being remeasured. The readings were corrected for temperature and used in the calculation of % silt and % clay, with the remaining portion attributed to % sand.

Total Metal/Cation Content

Approximately 0.5 g of air-dried substrate were weighed out in triplicate in 50 ml Erlenmeyer flasks. At the same time approximately 5 g samples of the same substrates were weighed into tared aluminum weighing pans. These were then dried in a drying oven at 100 °C for approximately 48 hours and the moisture content was determined. Approximately 10 mls of concentrated nitric acid was added to each substrate sample, the mixture was swirled gently and allowed to stand overnight. The substrate-acid digest was then gently heated until the digest was almost dry. After cooling the digest, 5 mls of perchloric acid was added and

again the digest was heated until fumes appeared. Heating was continued until fuming had ceased. At this point the flasks were removed from the heat and left to cool. After cooling, 5 mls of concentrated hydrochloric acid was added and the digest was allowed to stand for half an hour. The digest was then diluted to 40 ml and quantitatively transferred with three washings through a small Buchner filter system, using a Whatman #42 filter paper. The filtrate was then quantitatively transferred with thorough washing into a 100 ml volumetric flask and made up to volume. Small samples of these final solutions were placed in vials for analysis.

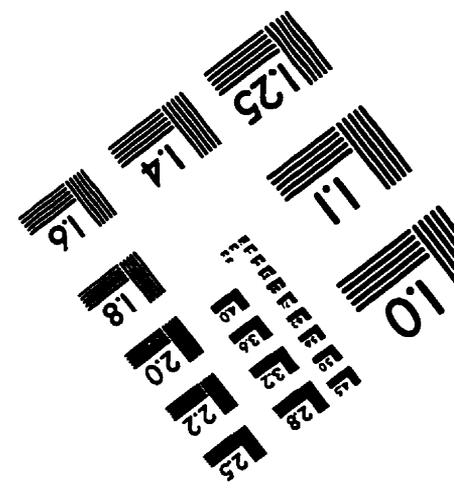
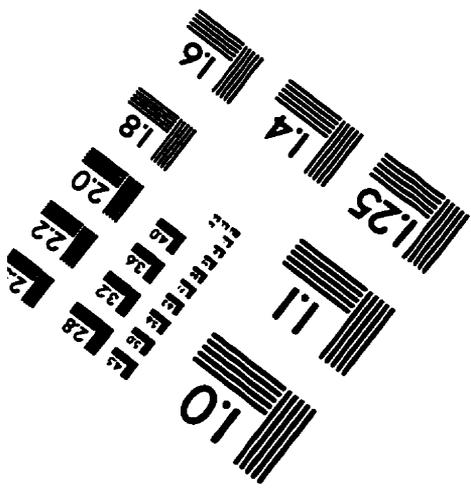
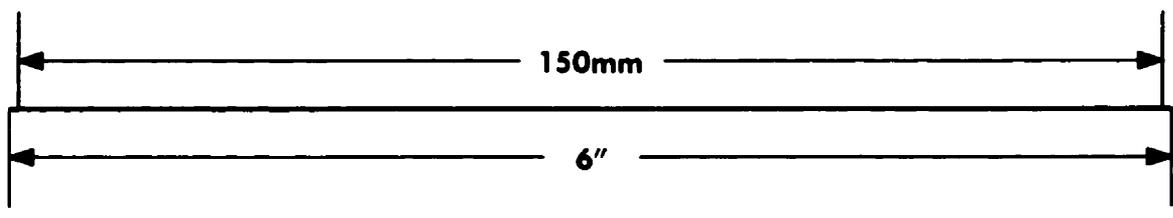
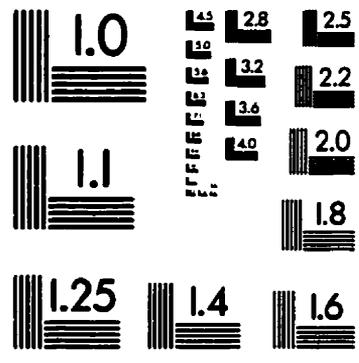
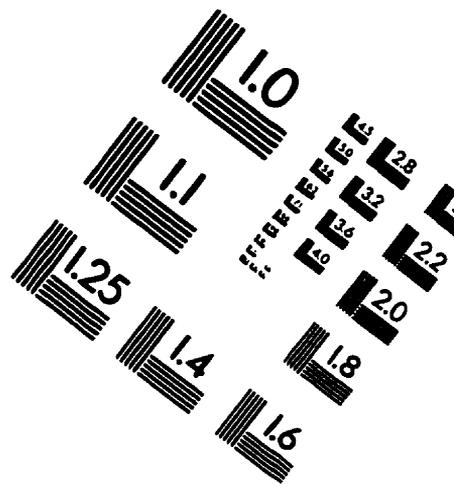
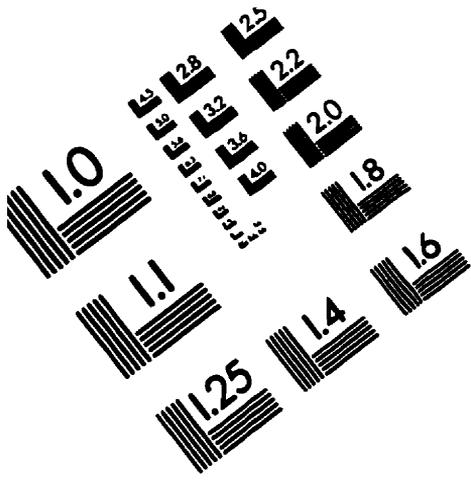
Water-soluble Metal/Cation Content

Triplicate 10 g samples were weighed out and combined with 50 mls of distilled water in 125 ml Erlenmeyer flasks. These were mechanically shaken using a Burrell wrist action shaker for 1 hour. The mixture was then filtered through a Buchner filter system using a Whatman #42 filter paper with thorough washing and diluted to 100 mls in a volumetric flask. Small samples of these solutions were placed in vials for analysis. This technique is a modified version of that of Black (1965).

Extractable Metal/Cation Content

Triplicate 10 g samples were weighed out and combined with 40 mls of extracting solution (0.05N HCl) in 125 ml Erlenmeyer flasks. These were mechanically shaken for 15 minutes using a Burrell wrist action shaker. The mixture was then filtered through a Buchner filter system using a Whatman #42 filter paper with thorough washing and diluted to 100 mls in a volumetric flask. Samples of these solutions were placed in vials for analysis.

IMAGE EVALUATION TEST TARGET (QA-3)



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