

THE USE OF WASTE MATERIALS AS POTENTIAL COVERS ON MILL TAILINGS AT TIMMINS, ONTARIO

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ABSTRACT

In 1973, Falconbridge Ltd. (Kidd Creek Division) of Timmins Ontario implemented the Thickened Tailings Disposal method, which involves the deposition of tailings at 60-65% solids, resulting in a relatively stable and erosion-resistant tailings mass. The TTD method attempts to maintain the tailings at moisture saturation, thereby limiting oxidation and thus metal and acid drainage from the tailings. In conjunction with this disposal method, the company is considering the use of de-pyritized and gold tailings, as well as other waste materials such as sewage incinerator ash and granulated slag, as a cover to aid in the revegetation of the site. Growth experiments have shown that none of the materials has a significant effect on germination. De-pyritized tailings appear to provide a better growth medium than pyritic tailings, especially with respect to root growth. Gold tailings support the best root growth, while sewage incinerator ash gives the best leaf growth. In a column leach test, the amount of iron leached from the column was elevated under a cover of gold tailings, sewage incinerator ash or slag, while the amount of copper leached out was increased under a depyritized tailings cover. Apart from these exceptions, amounts of metals leached remained the same or were reduced under each of the covers.

Introduction

The Kidd Creek metallurgical site is situated twenty-six kilometres east of Timmins, Ontario. It is mainly a copper-zinc milling complex, although indium is a recently added product. Because of the sulphide nature of the ores and the presence of pyrite, the tailings are potentially acid-generating.

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. This is a much more stable and erosion-resistant tailings mass than the traditional version, because the homogeneous nature of the deposit and the sloped surface allow rapid surface runoff and drainage (Robinsky, 1979; Salvas, 1989). The TTD method attempts to maintain the tailings at moisture saturation, limiting oxidation, metal release and acid drainage.

The chemical 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 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. An advantage of the TTD approach is that it allows the progressive reclamation of the tailings during the active life of the operation, so that reclamation activities can ideally proceed on relatively fresh, unoxidized (neutral) tailings. Under these conditions, the application of a suitable cover may prevent or at least delay the oxidation of the tailings 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. According to Hammack and Watzlaf (1990), once bacterially-mediated pyrite oxidation is established, the oxygen partial pressure would have to be maintained below 1% to realize any reduction in oxidation rate. Cover materials that are capable of maintaining these low oxygen values, other than water, are not currently available or economically feasible. However, Hammack and Watzlaf 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.

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, and control the infiltration and runoff of H₂O, thus limiting the oxidative weathering of pyrite and retarding or eliminating the production of acid (Hoving and Hood, 1984). 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 an economically feasible and worthwhile undertaking. Since 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 as the pyritic tailings. Winterhalder & Tisch (1991) found that, although optimal germination, establishment and growth of grass seedlings occurred when the seeds were buried no more than 0.25 cm deep in tailings, germination could occur at a considerably greater depth, and they concluded that the incorporation of seeds into the top centimetre of tailings slurry would be a feasible method of vegetation establishment. Kalin¹ (personal communication) has indicated that the incorporation of seeds into a tailings slurry is not feasible on an operational level because the seeds tend to float to the surface, but the present authors feel that this problem could be circumvented by the use of coated seeds.

It later became evident that the depyritization of the final run of tailings might not be feasible, and attention was turned to other inexpensive but effective covers. Winterhalder (1992) has 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 requires the treatment of 50,000 cubic metres/day of waste water. This extremely large area makes it unfeasible to use conventional and expensive cover materials such as gravel and loam. Thus, attention was turned to other readily available, 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 very economical, but it also eliminates the need for storage of these materials on a site of their own. The problem, however, is that these waste materials often themselves contain potentially toxic substances which may inhibit plant growth or may leach into the surrounding environment, and thus may only serve to worsen the problem.

The objectives of the present study were:

- 1) to determine the influence that each cover exerts on the leaching of heavy metals through a column, and
- 2) to determine the potential of the cover materials to support vegetation.

The material presented in the leaching column portion of this study is based only on data collected thus far, and does not represent a completed experiment.

Materials

Pyritic and depyritized tailings and granulated slag were obtained from Kidd Creek mines in Timmins Ontario. Gold flotation tailings were obtained from Royal Oak mines, an adjacent gold mine. Sewage incinerator ash was obtained from Toronto, through Kidd Creek.

The pyritic and depyritized tailings are extremely fine, with 91.7% and 87.4%, respectively, passing through a 200

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mesh (75µm) sieve. Pyritic tailings showed a net acid-producing potential of 139 kg/tonne, while the depyritized tailings only showed a slight acid producing potential of 3 kg/tonne. The gold tailings were more coarse, with only 27.4% passing through a 75 µm sieve, but showed a net acid consuming potential of 15 kg/tonne.

Among the limited analytical data available on the materials were those for Ontario Ministry of Environment Regulation 309 leachate extractions of pyritic and depyritized tailings. In these materials, only cadmium was at a "registerable" level, but the element was not present in high enough levels to be considered hazardous. Unfortunately, accurate figures for total cadmium content of the materials are not available at this time, but it is known that neither in pyritic nor in depyritized tailings does the cadmium content exceed 1,000 ppm.

The neutralizing material used was agricultural grade dolomitic limestone, and the fertilizer was a 6-24-24 agricultural grade product.

The "Sudbury seed mixture" variant used had the following composition by weight:

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

Methods

All materials were air-dried and thoroughly mixed prior to storage. The pyritic, depyritized and gold tailings were reduced to their original size range after drying by grinding lightly, but they were not sieved. The incinerator ash and granulated slag were passed through a 2 mm sieve in order to obtain a more homogeneous sample.

Total Analysis of Materials

All materials were analyzed for total element content by x-ray fluorescence.

Pot Bioassay

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.

The experiment was based on a randomized block design, with 5 blocks (replicates), i.e.

3 growth materials x 4 treatments x 5 replicates = 60 pots.

Treatments were as follows:

- Treatment 1 - Control
- Treatment 2 - 1 g limestone per pot
- Treatment 3 - 0.25 g fertilizer per pot
- Treatment 4 - 1 g limestone + 0.25 g fertilizer per pot

One 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 diameter 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 consisted of clipping 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 also placed in small paper envelopes.

All samples were then oven-dried at 70-80°C, and the dry weight determined.

Petri Dish Bioassay

This experiment tested the effect of each of the cover materials, with and without the addition of dolomitic limestone, on germination and early root and leaf growth of a grass, using the technique developed by Archambault (1991). It was at this time that the project was expanded to include gold tailings, incinerator ash and granulated slag as alternate covers or revegetation aids.

All treatments were replicated five times in a randomized block design, i.e.:

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

Glass fibre filter paper was placed in the bottom of a small plastic Petri dish, in which ten small holes had been drilled. Twenty grams of pyritic tailings, depyritized tailings, incinerator ash, granulated slag or gold tailings respectively, with or without the addition of 0.2 grams of dolomitic limestone, were then placed on the filter paper and covered with another filter paper. Fifty seeds of *Agrostis gigantea* (Redtop) were placed on the top filter paper.

The lid was replaced on the plastic Petri dish, which was then placed in a larger glass Petri dish, to which water was added. The water moved up through the holes in the bottom of the plastic Petri dish, through the 'soil', moistening the filter paper and seeds (Fig. 1).

The plates were kept mainly under darkened conditions until germination occurred, then were subjected to normal daylight conditions for a period of 8 days. Percent germination was determined, and root and shoot growth were measured to the nearest millimetre.

Leaching Column Construction

Leach columns (Figure 2) were constructed of 47 cm lengths of 10 cm (I.D.) PVC pipe. A 10 cm sewer cap was glued and siliconed to one end of each column. Prior to gluing, each cap had been heated and moulded into a more 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 into 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 siliconed to provide further support and to prevent leakage.

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, which was connected to a 500 ml plastic sample bottle located under the table via a piece of Tygon tubing. This was achieved by drilling a hole through the lid of the sample bottle and inserting the other half of the plastic tubing connector. When the columns had fully drained, the sample bottle was simply unscrewed from the lid and then sealed with a fresh lid. Between leaching cycles, movement of air through the bottom of the column was prevented by a plastic clamp that had been installed on the Tygon tubing.

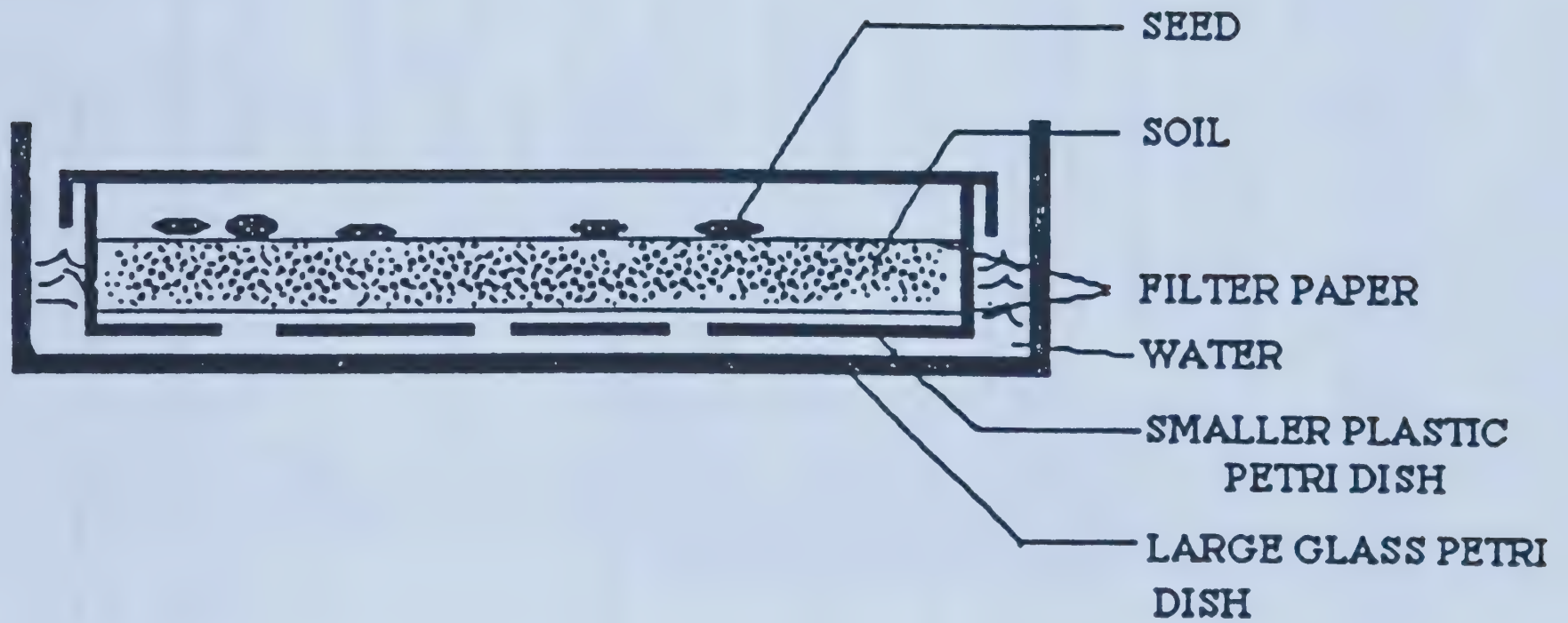


Fig. 1: Petri Dish Design

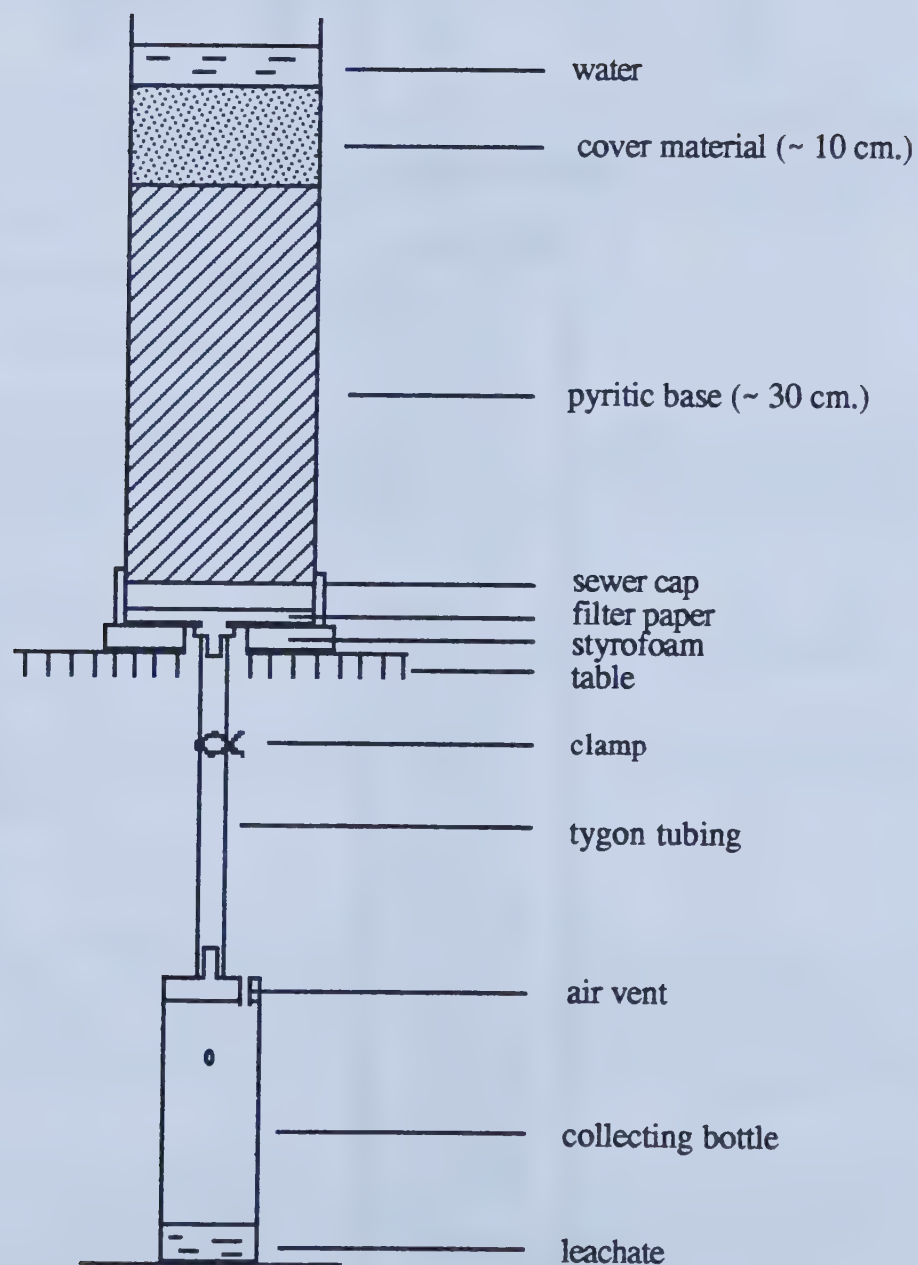


Fig. 2: Leaching Column Design

Leaching Column Experiment

All columns were first loaded with a pyritic tailings base, consisting of 4 kg of dried tails added in 1 kg increments as a slurry (approx. 2.7:1 tails:water by volume ratio), representing a depth of approximately 30 cm. An attempt was made to dislodge air bubbles and promote uniform packing by tapping the columns with a brass bar after each 1 kg addition of tailings.

The experiment was designed to investigate the effect of the use of five covers (depyritized tailings, gold tailings, incinerator ash, granulated slag and, as a control, pyritic tailings) and two treatments (limed and unlimed) on effluent chemistry. The experiment had the following design:

5 covers x 2 treatments x 5 replicates = 50 columns

Cover materials were added by weight so as to obtain 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 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 added in dry form.

The limed treatment was achieved by mixing 12 g of dolomitic limestone into each cover material in a 1000 ml beaker before adding it to the pyritic base.

The columns were thoroughly soaked, and tapped again to try to remove air bubbles. The clamps were opened and the columns allowed to fully drain. Leaching began with the addition of 200 ml of distilled-deionized water. The quantity of leachate and the time were recorded periodically, so as to obtain an estimate of the infiltration rate.

When a constant leachate volume was obtained, 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 time it was deemed that the columns were not drying sufficiently between watering, and the leaching cycle was extended to once every two weeks.

Results and Discussion

Total Analysis of Materials

The results of the analysis are shown in Table 1.

Table 1: Total Content of Select Elements.

| Cover Type | Al (%) | P (%) | Fe (%) | S (ppm) | Cr (ppm) | Ni (ppm) | Cu (ppm) | Zn (ppm) | Pb (ppm) |
|------------|--------|-------|--------|---------|----------|----------|----------|----------|----------|
| Ash | 3.34 | 7.98 | 14.15 | 1849 | 1075.9 | 194.4 | 3551.8 | 6316.7 | 495.1 |
| Gold | 7.18 | 0.07 | 4.17 | 968 | 151.3 | 36.1 | 5.0 | 69.7 | 9.3 |
| Slag | 0.84 | 0.06 | 16.64 | 3684 | 245.6 | 43.5 | 6961.1 | 53364 | 366.5 |
| Depyr. | 5.16 | 0.01 | 8.09 | 4463 | 65.3 | 30.3 | 449.6 | 1711.1 | 100.7 |
| Pyritic | 4.22 | 0.02 | 9.26 | 21880 | 61.3 | 42.0 | 1502.7 | 5957.2 | 537.2 |

It is notable that at least one potentially phytotoxic metal is present at a concentration of greater than 1000 ppm in each of these materials (e.g. chromium in incinerator ash, slag and both forms of tailings). However, these total values give little indication of the amount of metal that is soluble under normal growth conditions, and it is hoped that leaching and growth trials will give some indication of their true phytotoxic (and zootoxic) potential. From the point of view of plant nutrition, the high phosphorus content of the ash is beneficial, but as in the case of the metals, its plant-availability is in question.

Pot Bioassay

The results of the pot bioassay, which was designed to determine the effect of pyrite on the relative growth of vegetation over approximately one field season (appr. 3 months), are summarized in Figures 3, 4 & 5. Although there was no significant difference in % germination between pyritic and depyritized tailings, there was a very pronounced increase in root and shoot weight in depyritized tailings (Figure 3). Surprisingly, this difference in growth does not appear to be due to the oxidation and subsequent acidification of the pyrite in the pyritic tailings, as there was no significant difference in surface pH between pyritic, depyritized and the 50/50 mix (Figure 4). The improved performance in the depyritized tailings was possibly due to a mild inhibitory effect on plant growth by sulphide ions in the pyritic tailings, or to decreased heavy metal content in the depyritized tailings as a result of the depyritization process, as indicated in Table 1. While the main goal of depyritization is the removal of FeS₂ (pyrite), associated sulphides such as CuS, ZnS, and PbS may also be removed.

The results of this experiment also showed that the addition of lime did not significantly affect root or shoot weight (Figure 5). This might be expected, since the initial Ph of both materials was already neutral to alkaline, but the calcium and/or magnesium in limestone can interact with other metals and modify their toxicity. While limestone alone had little effect on growth in either type of tailings, it was beneficial when combined with fertilizer (Figure 5).

Petri Dish Bioassay

The results of the Petri dish experiment, which was designed to determine relative growth during the period immediately following germination (app. 7 days), i.e. during seedling establishment, are shown in Figure 6. Depyritized tailings, gold tailings, and incinerator ash all produced significantly better root growth, while granulated slag produced significantly lower root growth than pyritic tailings. Incinerator ash produced significantly better shoot growth, probably due to a high phosphorus content, while slag produced significantly lower shoot growth. It should be noted that the variation in shoot growth is much lower than that found in root growth. Roots, being in direct contact with the growth medium, usually react in a more sensitive fashion than shoots during early seedling growth, and hence are the most commonly used indicators of toxicity, as pioneered by Wilkins (1957).

Although these experiments have shown that growth directly on the pyritic tailings is possible under greenhouse conditions, field trials have indicated that such an approach is unlikely to be successful under field conditions, even with the use of ameliorants such as lime and fertilizer. This failure is likely to be due to physical problems such as drought and abrasion during seedling establishment, combined with a strong salinity effect. Field trials have shown this to be the case with gold tailings also; although they showed the best growth potential under greenhouse conditions, a vegetative cover failed to establish in the field.

Leaching Column Experiment

The column leach study has shown several trends in the release of metals from the system, as indicated in Figures 7-10. It is important to look not only at the concentration of metals in the leachates, but also at the

total amount of metal leached from each column under a specific leaching regime. Since the volume of leachate obtained in a single leaching event depends on the pore volume of the materials in the column, treatments producing the same **concentration** of metals in the leachate may leach quite different **amounts** of metal due to difference in the **volumes** of leachate obtained. Thus, the release of metals is not only dependent on chemical alterations within the material, but also on the physical characteristic of the material. The effluent from tailings covered with incinerator ash has a similar concentration of cadmium to that from tailings covered by other materials (Figure 7a), but a smaller amount of cadmium has been leached out due to a smaller volume of effluent (Figure 7b).

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, such as is seen in the case of cadmium (Figure 7). These results are similar to those of previous studies, and are thought to be due to the flushing of easily-leached metal forms from the column (Doepker and O'Connor, 1990a & b).

Other metals such as zinc (Figure 8) exhibit a similar pattern of release, although the rapid decrease does not occur until after several leachings. This is likely due to the presence of a sink of these metals, which requires several flushings before all of the easily leached material is released, or simply that it takes longer for these metals to move through the columns.

Once a constant concentration of ions is obtained with successive leachings, it is assumed that the easily-leachable 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).

Treatment of the cover materials with lime had no significant effect on the quality of the leachate. Having and Hood (1984), 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 (1991), who found that abatement treatments such as phosphate, lime and sodium lauryl sulfate were of only marginal value in improving leachate quality.

It was found that cumulative graphing of the amounts of metals leached, which represent potential metal "loadings" to the surrounding environment, best discerned the effects of the different cover materials on metal release. In general, the four cover materials studied resulted in the same or decreased amounts of metals leached out, with the exception of the increased iron from gold tailings, incinerator ash and slag (Figure 9a), and the increased copper from depyritized tailings (Figure 9b). In the case of iron, increased levels would be expected from ash and slag due to their high inherent content (Table 1). Gold tailings, on the other hand, contain half the iron of pyritic tailings, yet showed much higher levels in the leachate (Table 1). This is possible due to a more soluble form of iron in gold tailings. It is thought that these increased iron levels over time for gold tailings, ash and slag are the result of a rather slow rate of movement of iron through the pyritic tailings, and that these values will continually decline over the next few leach cycles.

Depyritized tailings have shown consistently greater leaching of copper over time than pyritic tailings (Figure 9b). This result was not expected, as is not yet understood. Total copper in the depyritized tailings is much lower than in the pyritic tailings (Table 1), yet more is leached from the former. Why the depyritization process should affect copper, but not other metals such as lead and zinc, is not known.

Gold tailings, ash and slag covers all gave decreased total levels of cadmium in the leachate (Figure 10). This appears to be due to a lower volume of leachate produced, as illustrated in Figure 7, rather than the chemical influence of the cover.

Sewage incinerator ash is formed by the combustion of sewage sludge, which results in the concentration of metals in the ash. Specifically, this ash contains comparatively high levels of Fe, Cr, Ni, and Cu (Table 1),

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, are thought to be relatively inert, even though they contain comparatively high levels of Al and Cr. Granulated slag is also considered to be inert, despite high levels of Fe, Cr, Cu and Zn (Table 1). In spite of these differences, all three of these covers behaved in the same fashion, resulting in elevated leachate metal levels for iron alone.

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 ash certainly make these materials worthy of further consideration as cover materials, as long as they continue to show no dramatic increase in leaching of potential toxins.

The physical characteristics of granulated slag do not make it suitable for use as a cover, although the potential does exist for its use as a capillary break between the pyritic tailings and a cover material.

Fig. 3a:

Pot Bioassay
Effect of Pyrite on Root Weight

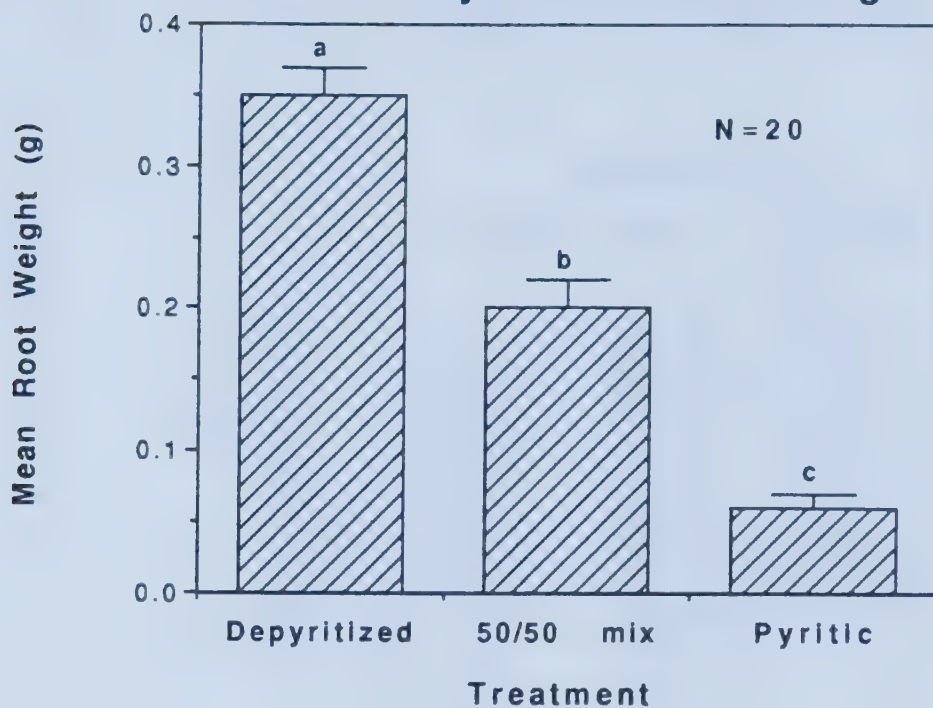
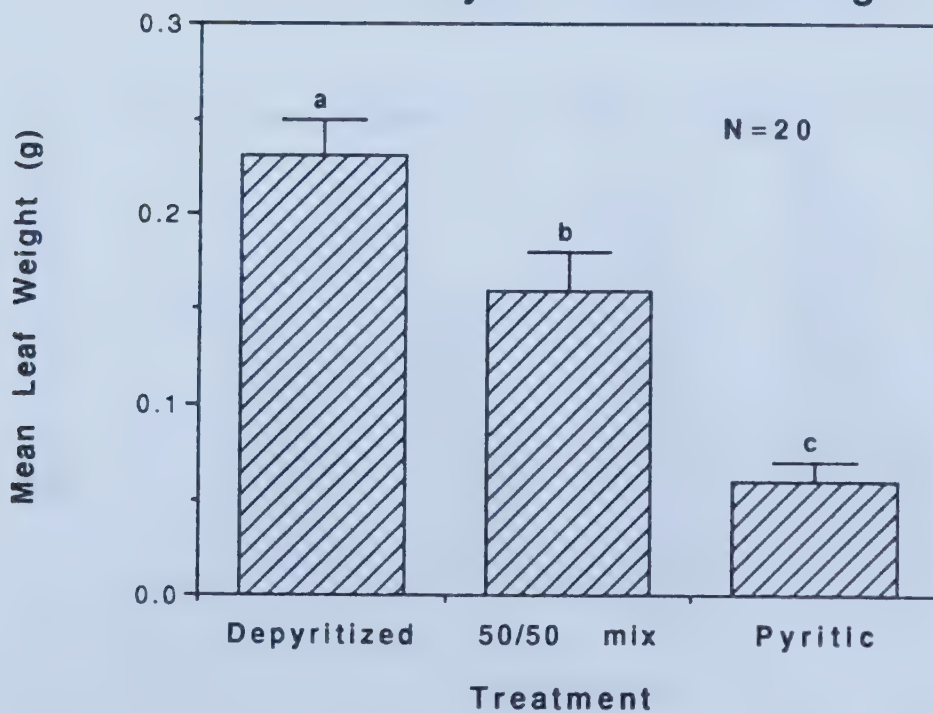


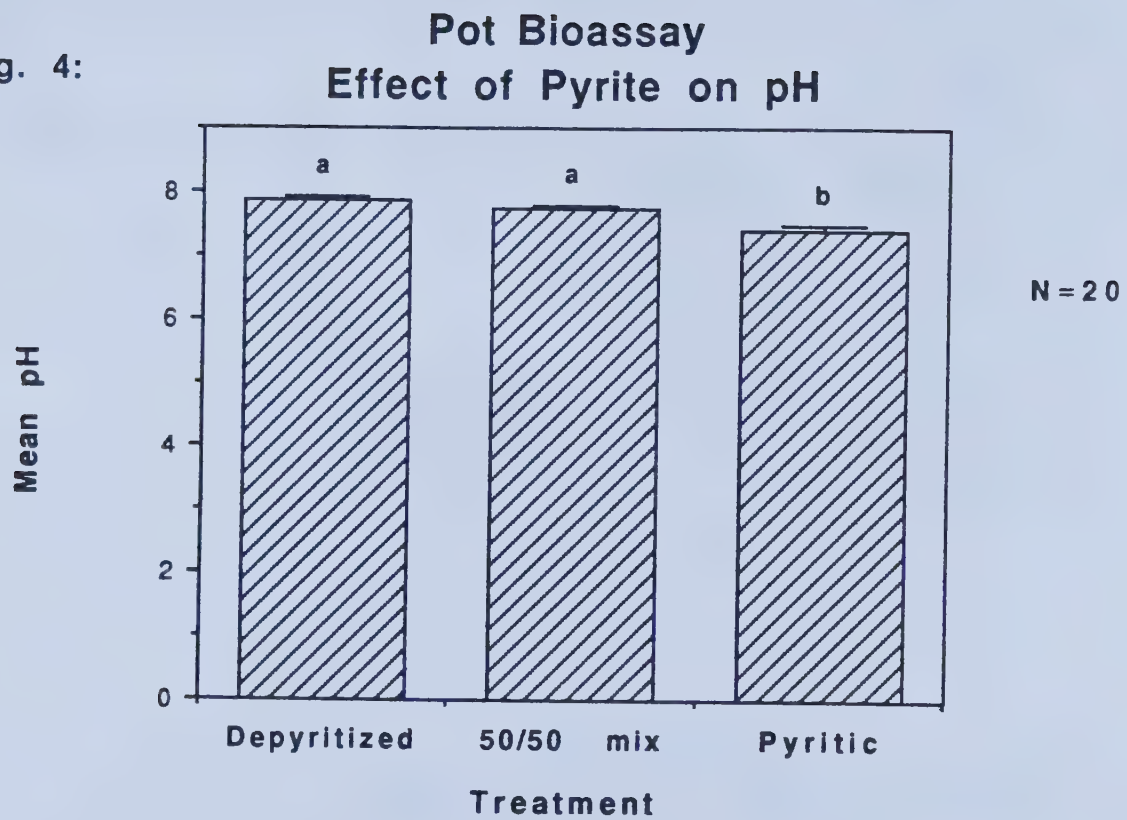
Fig. 3b:

Pot Bioassay
Effect of Pyrite on Leaf Weight



Bars with the same superscript do not differ significantly at the 5% level.

Fig. 4:



Bars with the same superscript do not differ significantly at the 5% level.

Pot Bioassay

Fig. 5a:

Effect of Treatment on Root Weight

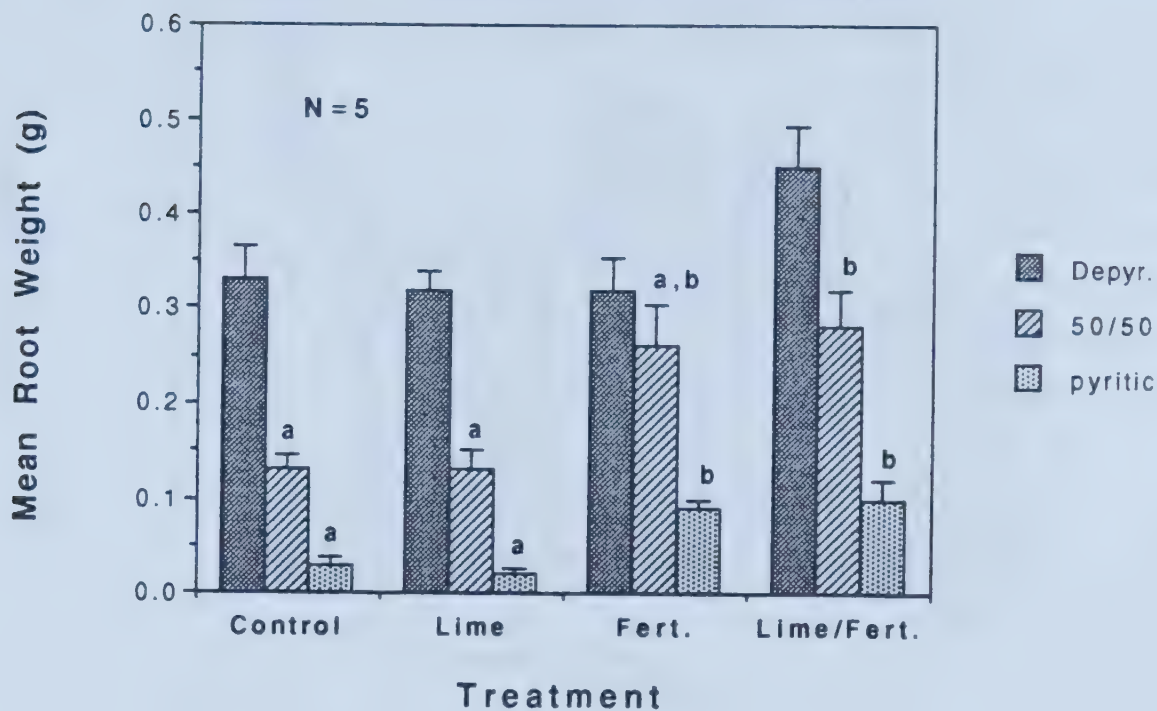
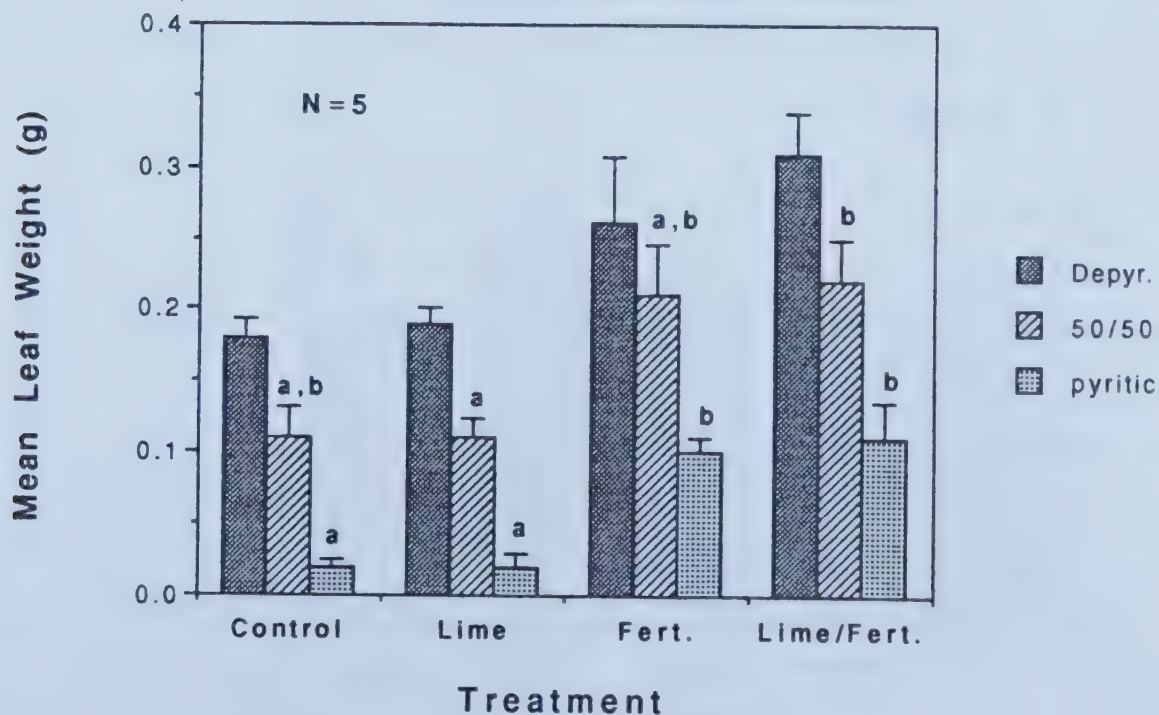


Fig. 5b:

Pot Bioassay

Effect of Treatment on Leaf Weight



Bars with the same superscript do not differ significantly at the 5% level.

Fig. 6a:

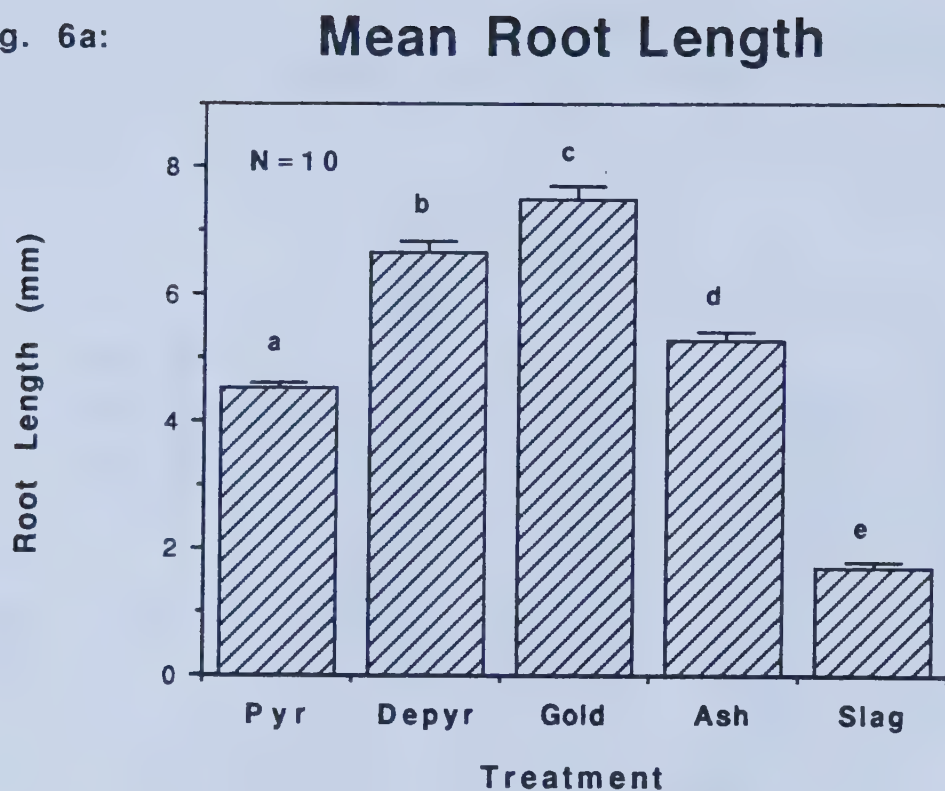
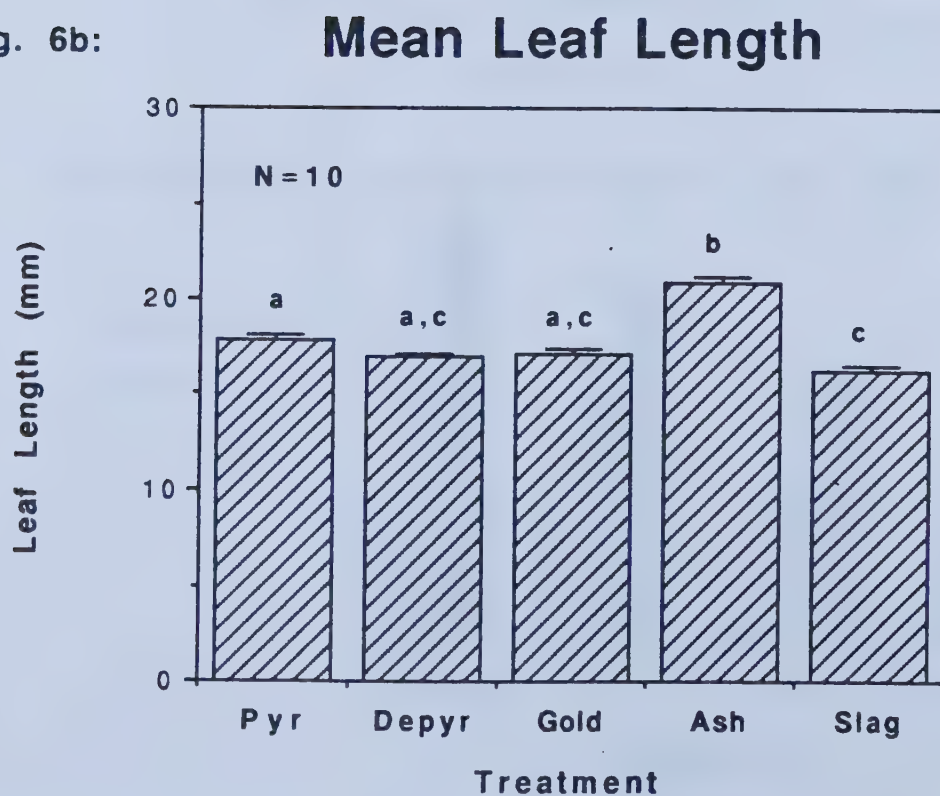


Fig. 6b:



Bars with the same superscript do not differ significantly at the 5% level.

Fig. 7a: **Leachate Cadmium Concentration**

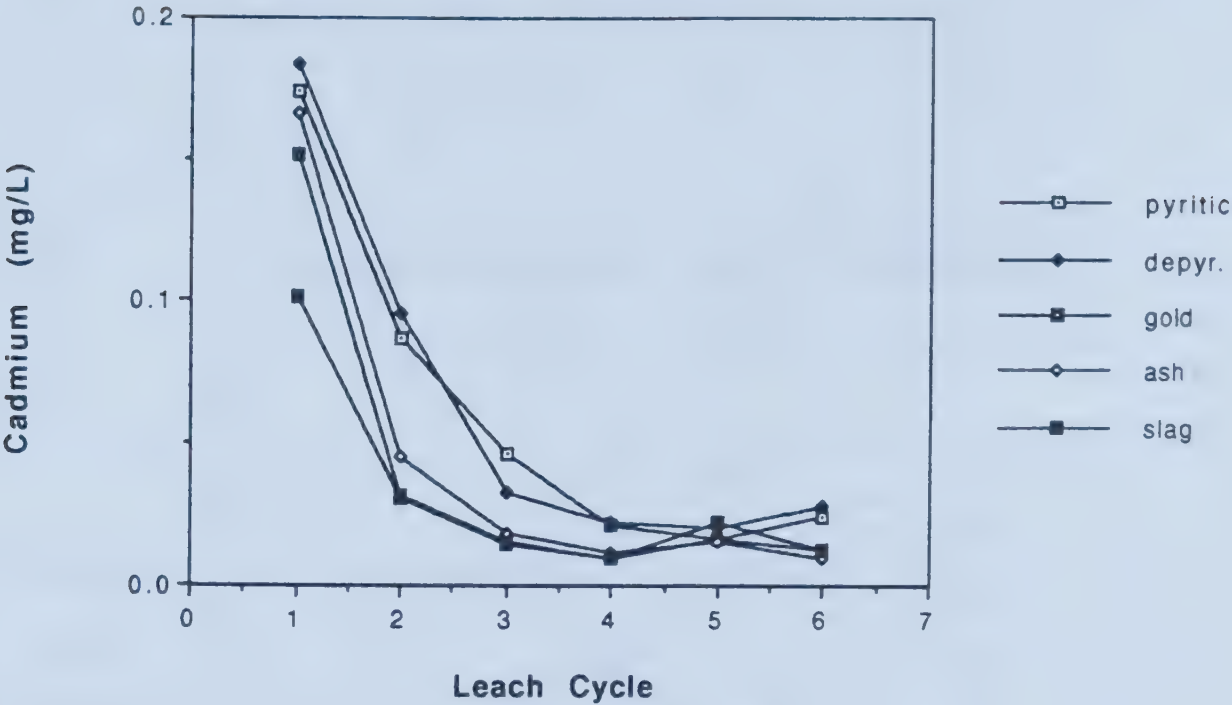


Fig. 7b: **Total Leachate Cadmium**

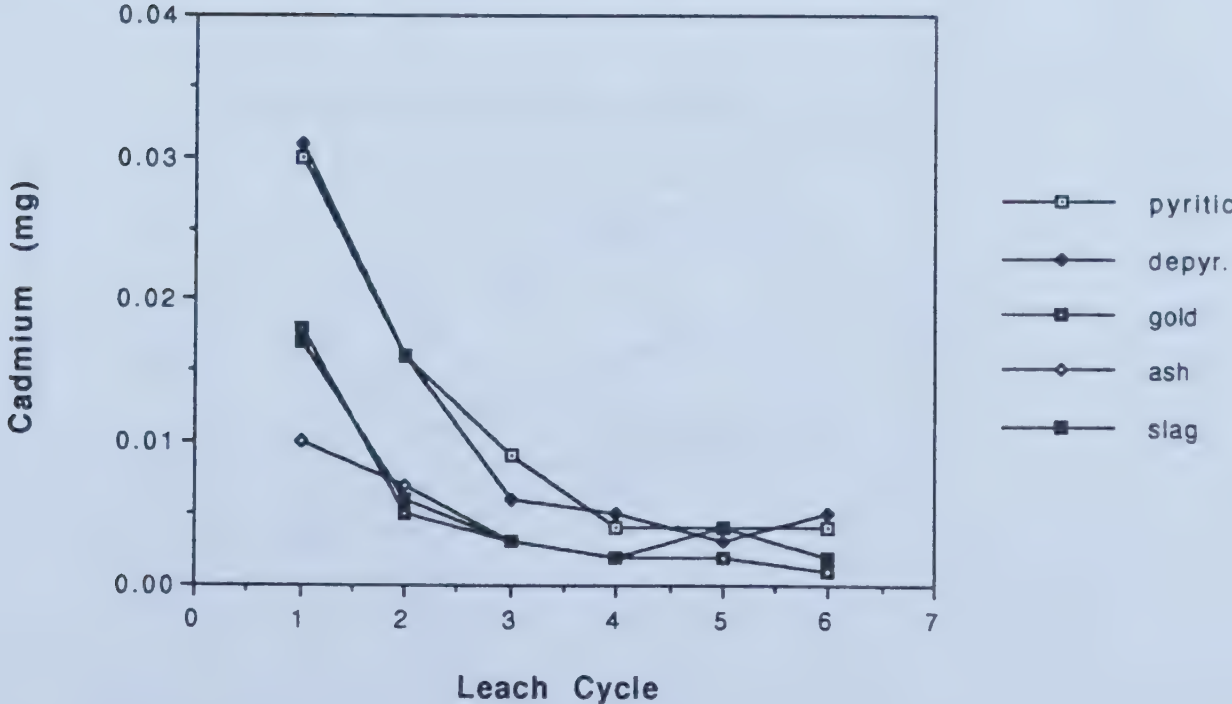


Fig. 8: Leachate Zinc Concentration

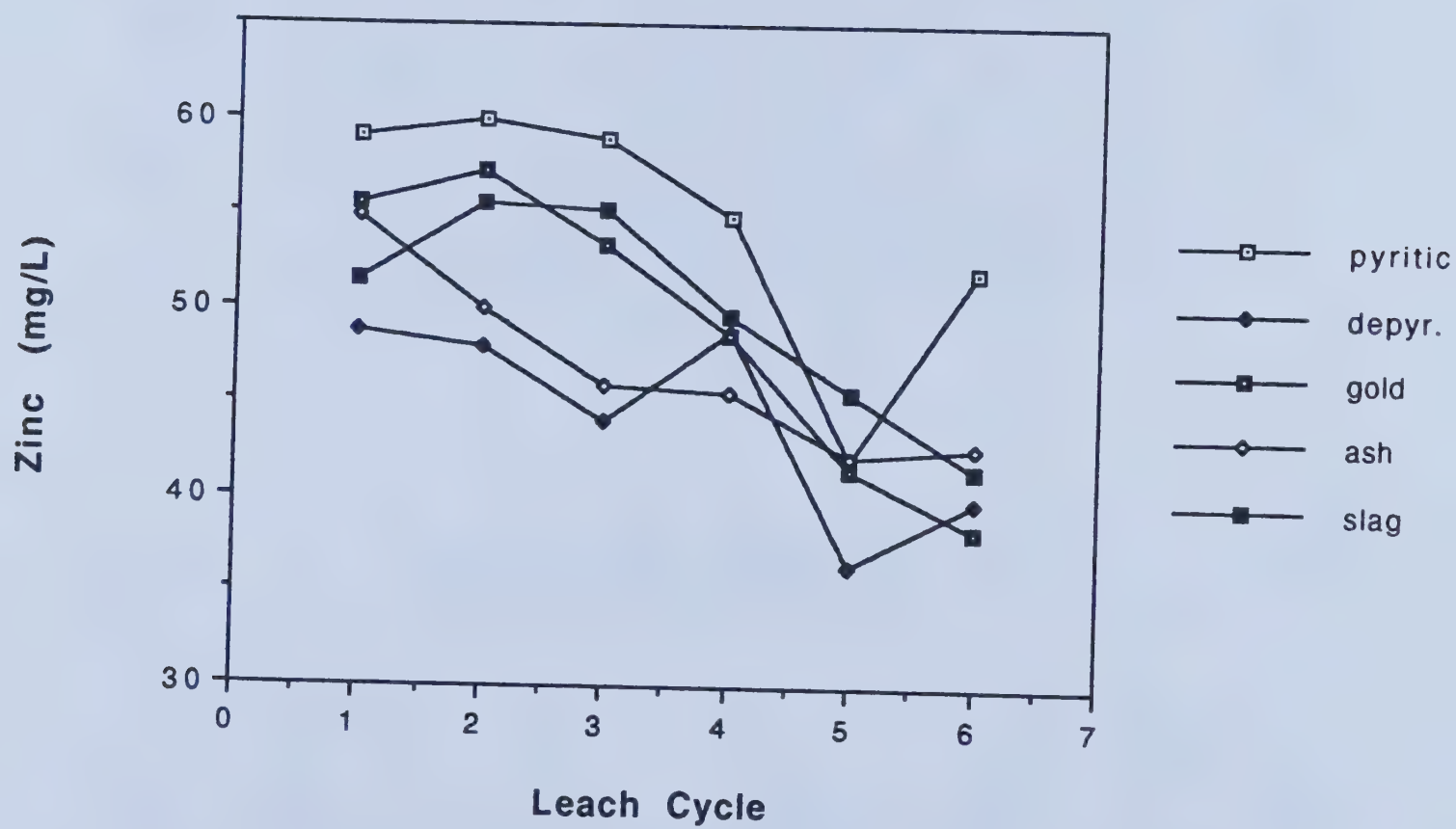


Fig. 9a:

Cumulative Leachate Iron

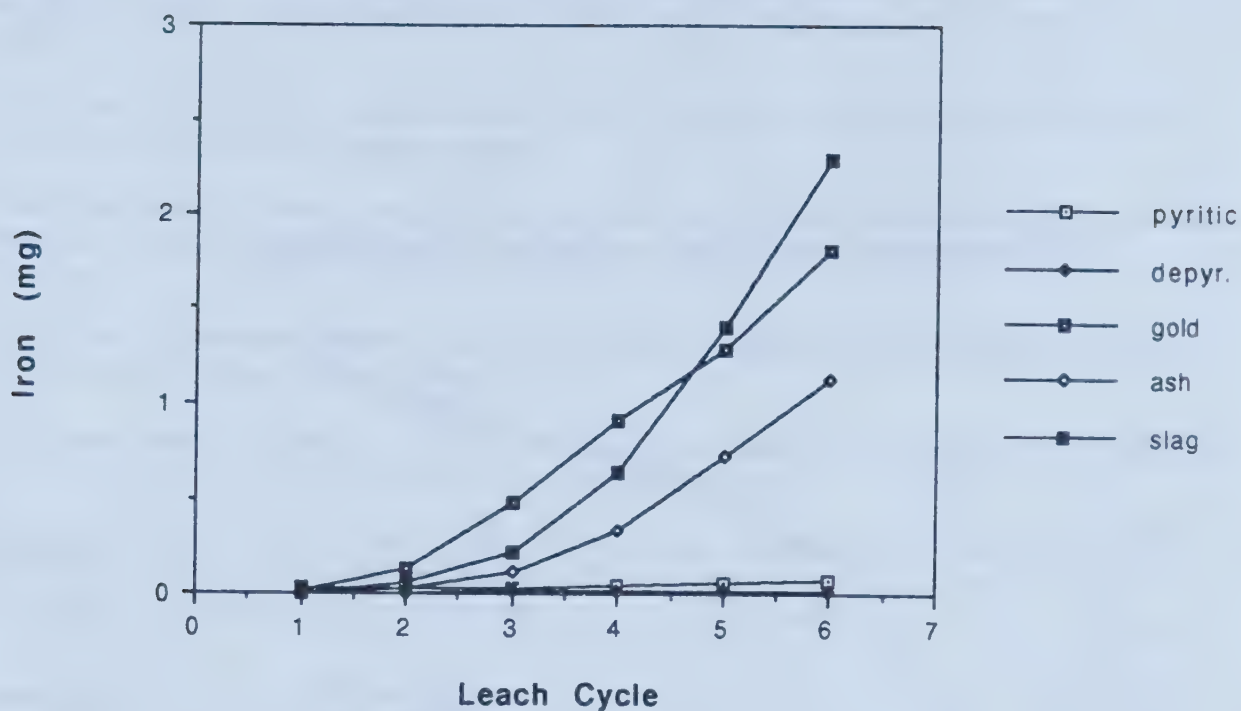


Fig. 9b:

Cumulative Leachate Copper

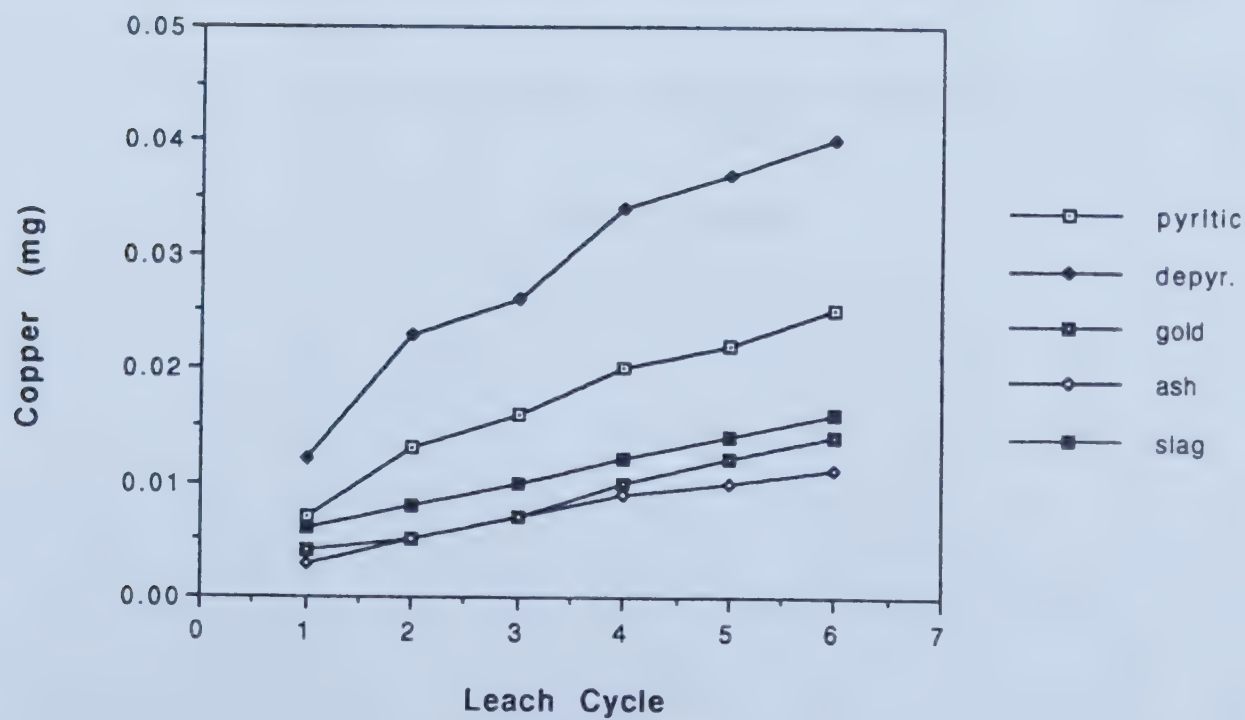
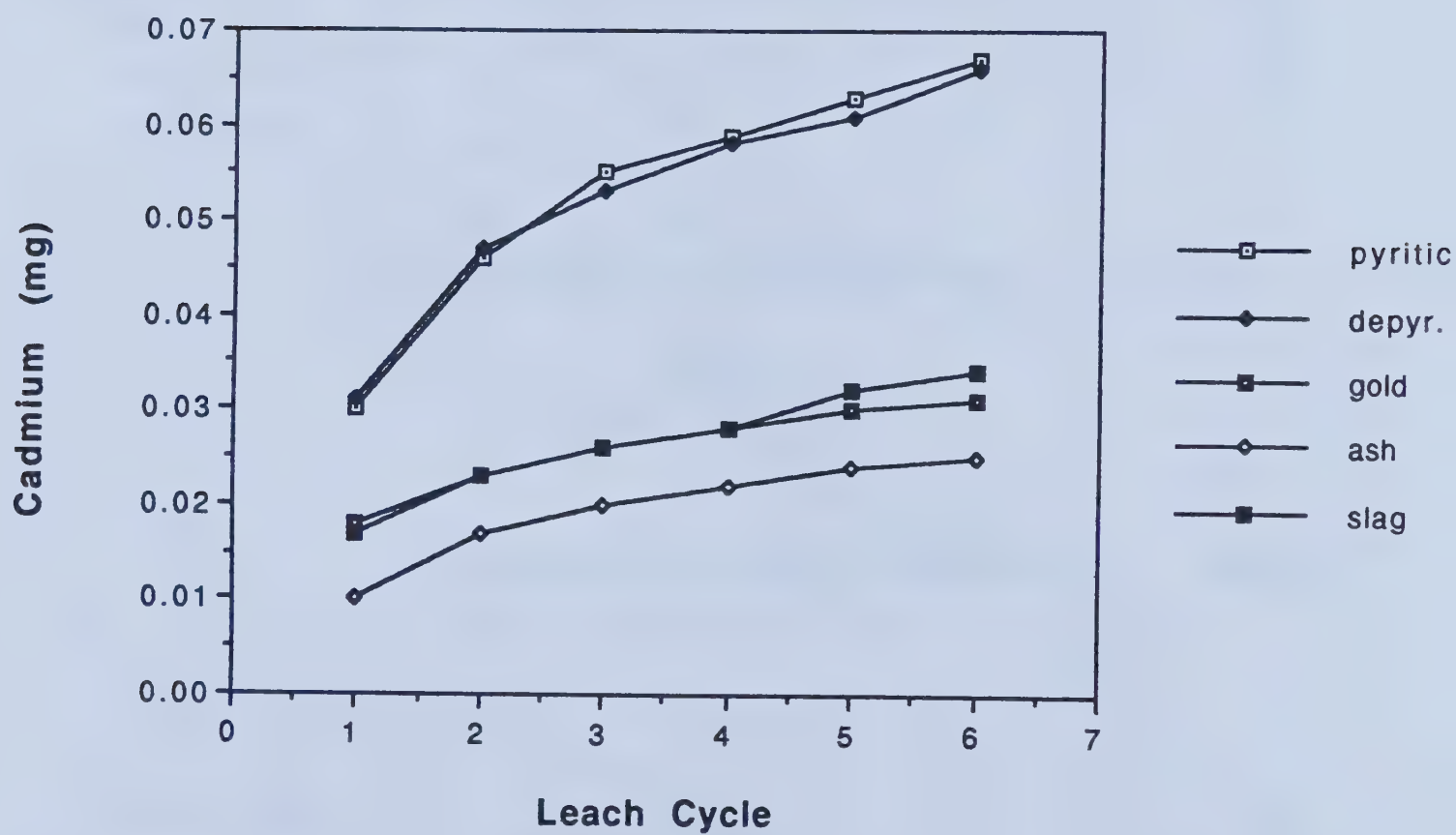


Fig. 10:

Cumulative Leachate Cadmium



Conclusions

1. Depyritized tailings provided a much better plant growth medium than similar tailings prior to depyritization, and exhibited the same or lower levels of metals in the leachate, with the exception of copper.
2. The leachate from depyritized tailings exhibited the same or lower levels of all metals, except copper, than that from similar tailings prior to depyritization.
3. Plant growth on pyritic tailings was significantly improved by the addition of limestone and fertilizer, by the same was not true of depyritized tailings. The response to fertilizer was greater than the response to limestone.
4. When pyritic tailings were covered by a layer of gold tailings, incinerator ash or granulated slag, the levels of all metals were reduced, with the exception of iron.
5. Early plant growth on depyritized tailings, gold tailings, and incinerator ash was significantly better than that on pyritic tailings, while that on granulated slag was significantly poorer.

In general, depyritized copper-zinc tailings, gold tailings and sewage incinerator ash provided a much better growth medium than pyritic tailings, without greatly contributing free heavy metals to the system. Studies are currently under way to attempt to confirm these observations under field conditions.

Acknowledgements

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Annual Meeting, Lindsay, Ontario, August 11th - 13th

TABLE OF CONTENTS

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 John Reynolds

TABLE OF CONTENTS

SESSION I AGGREGATE RECLAMATION

| | | |
|---|---------------|----|
| Rehabilitation of Gravel Pits and Quarries for Biodiversity | Mark Browning | 5 |
| Extraction and Rehabilitation of the Brampton Esker Area | Sherry Yundt | 10 |
| Natural/Aggregate Resources in River Corridors | Don Stewart | 17 |
| Naturalizing Quarry Sites in Southern Ontario | Stephen Monet | 21 |

SESSION II RECLAMATION INITIATIVES

| | | |
|--|--------------------------------------|----|
| Aboriginal Business Development through Reclamation | Karen Etherington and Martin Blair | 29 |
| La Valeur paysagere: Une Plus Value de la Rehabilitation de Site | Marie-Claude Robert et Jean Trottier | 34 |
| The Selection of Native Legume Species for Reclamation | Ann Smreciu | 35 |
| Using Waste Wood Chips to Rehabilitate Landfill Sites | Tom Warner | 38 |

SESSION III WETLAND RESTORATION

| | | |
|--|--------------------------------|----|
| Drainage Design and Water Quality Monitoring for Wooded Swampland Restoration | Chris Hart | 46 |
| Landscape Ecology, Avian Information and the Rehabilitation of Wildland Complexes in the Greater Toronto Area | Paul Harpley and Rob Milne | 48 |
| Vegetative Regeneration with Swampland Hydroperiod Control | Chris Hart and Dr. Jane Bowles | 57 |

SESSION IV MINE RECLAMATION

| | | |
|---|---------------------------------|-----|
| Factors Affecting Vegetation Dynamics on Acid, Metal-Contaminated Soils of the Sudbury Area | Keith Winterhalder | 58 |
| Environmental Initiatives and Landscape Rehabilitation Techniques at the Sudbury Operations of INCO | Ellen Heale | 80 |
| Heterotrophic Bacteria and Grass Covers on Fresh, Base Metal Tailings | A. Fyson, M. Kalin, M. Smith | 81 |
| The Use of Waste Materials as Potential Covers on Mill Tailings at Timmins, Ontario | Bryan Tisch, Keith Winterhalder | 89 |
| Using Populations of <i>Scirpus atrocinctus</i> , a Sedge, for Stabilizing Tailings Beaches and Till Berms | M.P. Smith and Margarete Kalin | 109 |

SESSION V SHORELINE AND AQUATIC REHABILITATION

| | | |
|---|------------------|-----|
| Review of Soil Bioengineering Techniques in Stream Rehabilitation | Glenn Harrington | 116 |
| Case Studies in Shoreline Regeneration | Dr. Chris Wren | 117 |
| Alternatives for Integrated Natural Valley Design | Kevin Trimble | 120 |