The Phytoextraction of Gold and Palladium from Mine Tailings

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P 10. Brownlow (1979) defines humic acids and related compounds (humic substances) as extremely complicated mixtures of high-molecular-weight compounds that form in soil through the breakdown of organic material (e.g. lignin). Humic substances can form coal, kerogen, oil and gas depending on the initial source of organic material.

P 39. Gold will complex with a suitable ligand only in the presence of an oxidizing agent. The extreme case is *aqua regia*. Digestion of gold in this mixture yields a gold chloride complex only after oxidation of the metal by nitric acid. For conventional cyanide dissolution of gold, atmospheric oxygen is a suitable oxidant, while the research in this thesis shows that ferric iron Fe(III) and hydrogen peroxide are good oxidants to promote thiocyanate dissolution. Thiocyanate will also complex with gold in the presence of atmospheric oxygen.
Hydrogen peroxide is known to oxidize thiocyanate to cyanide. Cyanide is recognised as a superior treatment to induce precious metal accumulation in plants (Lamb *et al.*, 2001). The conclusion of this research is that plants may accumulate both cyanide and thiocyanate complexes after treatment with thiocyanate and hydrogen peroxide (oxidised gold and oxidized thiocyanate complexes). This is relative to thiocyanate plus Fe(III) treatment which will only generate thiocyanate complexes for uptake. The proportion of gold thiocyanate and cyanide complexes accumulated after peroxide oxidation remains unknown.

P 61, Tables 4.1 a & b. Three to six replicate plants were treated for all plant-uptake experiments. Reported concentrations are an average of analysed replicates.

P 66 – 67. This research has identified that cyanide can induce a high concentration of gold and palladium uptake in plants. The optimal cyanide treatment level to promote maximum uptake has not been identified. Maximum uptake will be a function of biomass and metal concentration. A higher treatment may lead to low harvested biomass through plant mortality and decay, but a high metal concentration in residual plant tissues. Determination of the relative importance of biomass and metal concentration will be the subject of ongoing study.

P 84. Addition of any concentration of Fe(III) to thiocyanate (for the concentration range used in this research) promoted a significant increase in the solubility of gold relative to thiocyanate alone. There was, however, no significant change in gold solubility as the concentration of Fe(III) was varied. Solution Eh increased and pH decreased through addition of Fe(III). The conclusion drawn from these observation is that the change in Eh and pH promoted by Fe(III) was the same, independent of the concentration of oxidant in the system. Thus, Eh (increased by ferric iron) was more important than the actual concentration of Fe(III) used. In practice this means the optimal concentration of Fe(III) to use is that which promotes an increase in Eh necessary to oxidize gold. The optimal Fe(III) concentration may lie below the range tested in this research. Redox potential (Eh) appears to be a more important factor controlling gold solubility that the Fe(III) concentration, for the experimental range used in this research.

Brownlow, A.H. (1979). Geochemistry (Prentice-Hall, Englewood Cliffs, N.J.) pp 248-250, 270, 271.

Lamb, A.E., Anderson, C.W.N. and Haverkamp, R.G. (2001). The induced hyperaccumulation of gold in the plants *Brassica juncea*, *Berkheya coddii* and chicory. *Chemistry in New Zealand*, 65(2): 34-36.

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Abstract

The extraction of gold and palladium from a South African mine tailing (Klipfontein) and artificial substrate was examined. A variety of solutions were tested and extractants observed to dissolve large quantities of metal were subsequently used in trials investigating plant uptake of gold and palladium.

Extraction by thiocyanate amended with an oxidising agent dissolved large amounts of gold and palladium from the test substrates. Various combinations of thiocyanate/Fe(III) and thiocyanate/H_2O_2 were examined. Metal extraction in the thiocyanate/Fe(III) showed dependence on redox potential and acidity of the solution; this dependence was not observed in the thiocyanate/H_2O_2 system where production of cyanide may be an important factor. The addition of iodide to thiocyanate/Fe(III) did not affect dissolution of metals. Thiourea was also tested. This chemical was shown to be a relatively poor extractant of gold and palladium, with and without an oxidant.

Two plant species, *Berkheya coddii* and *Brassica juncea*, were investigated in plant trials. Initial experiments showed uptake of metals to be independent of plant species. Greatest metal uptake was achieved using cyanide as a chemical amendment, with nearly 500 ppm gold accumulation in *B. juncea* planted in artificial substrate and treated with 1 gL^{-1} KCN every day over 6 days. Nearly 13 ppm palladium had accumulated in these plants - the highest average concentration observed with any treatment. KCN also induced the largest metal uptake from Klipfontein substrate – nearly 1600 ppb gold and 7700 ppb palladium accumulation in *B. coddii*. As an exercise it was shown that the value of gold and palladium that would be recovered from a phytomining operation on Klipfontein substrate would be greater than the cost of cyanide added in such an operation.

Plant uptake of gold and palladium from the mine tailing after treatment with thiocyanate plus an oxidant was poor. Gold and palladium uptake by *B. coddii* from artificial substrate after treatment with thiocyanate + H_2O_2 was improved, with levels of accumulation similar to that of cyanide. Metal uptake by thiocyanate + Fe(III), however, remained poor.

The conclusion of this thesis is that phytomining of gold and palladium offers large potential in both practical and research terms. The relative importance of the species thiocyanate, H_2O_2, and cyanide remain unknown in the thiocyanate/H_2O_2 system and further research is needed to elucidate this behaviour.

Chapter 1 Introduction and Overview of the Current Study

Phytoextraction, the removal of metals from an area of land through the use of plants, is a technology that has received much attention to it's low cost and potential public acceptance. An aspect of phytoextraction is phytomining, where economic benefit is gained through recovery of metals from the plants. Recent studies by Anderson (1998, 2000, 2001a, 2001b) investigating the plant uptake of gold from mine waste have shown that phytomining for this metal offers great promise. However, very little research has investigated plant uptake of other precious metals.

Plants can only take up metals that are present in soil solution. This study can therefore be regarded as having two parts: the dissolution of metals into solution, and the subsequent plant uptake of these metals. The aims of this study were:

1) To maximise dissolution of gold and palladium from a substrate,
2) To maximise plant uptake of gold,
3) To establish if induced plant uptake of palladium is possible and maximise any uptake that does take place.

Chapter 1 serves as an overview of the study. Chapter 2 is a literature review providing background information on phytoextraction and the dissolution of the metals gold, palladium, and platinum. Phytoremediation and phytomining are discussed, and methods of extracting precious metals from mining ores are investigated. This chapter provides evidence of how dissolution of gold and palladium may be maximised.

Chapter 3 – Extraction Trials

A variety of chemicals were tested as solvents for gold. Two substrates were used – tailings from a South African mine and an artificial substrate made up to contain large concentrations of gold and palladium. The effect of an oxidant when added to certain

solutions was also examined. Further trials of solutions observed to dissolve large quantities of metal were conducted with the aim of establishing why and how extraction can be improved.

Chapter 4 – Plant Uptake of Gold and Palladium

Two plant species were chosen to examine plant uptake of gold and palladium: *Berkheya codii* and *Brassica juncea*. Greenhouse trials were conducted, and plants were grown in both the mine tailing and artificial substrate. Solutions used to treat plants were chosen based on effectiveness in extracting gold and palladium as described in Chapter 3. Cyanide, although not used in extraction work, was also tested as a potential plant treatment. Different treatment regimes were investigated, and comparisons made between one-off treatments of high chemical concentration, and daily treatments of lower chemical concentration. The aim of the plant trials was to maximise uptake of gold and palladium.

Chapter 5 – Practical Implications of this Study

Both gold and palladium hold promise for phytomining due to their high value. Phytomining of gold has been discussed by Anderson (2000), and this work has been used as a basis for Chapter 5. However, the potential for phytomining of palladium has never been previously considered. Scenarios are described where the results from this study are applied to a field scenario, and practical and economic aspects of such an operation discussed.