# The Phytoextraction of Gold and Palladium from Mine Tailings

This thesis is presented in fulfilment of the requirements for the degree of Master of Philosophy

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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.

# Chapter 2 The Phytoextraction of Gold, Palladium, and Platinum – A Literature Review

## 2.1 Plant Hyperaccumulation

The ability of some plants to accumulate inordinately high amounts of metal has been known for some time. The first persons to quantify such uptake were Minguzzi and Vergnano (1948), who discovered nickel at a concentration of 0.79% in plants growing in a substrate containing only 0.42% of the metal. It was not until 1977, however, that the term *hyperaccumulation* (Brooks *et al.*,1977) was used to describe the ability of some plants to take up excessive quantities of metals. The metals known to hyperaccumulate in some plants are cadmium, cobalt, copper, manganese, nickel, selenium, thallium and zinc. The modern, accepted criterion for plants to be defined as hyperaccumulating is accumulation at 100 times greater than non-accumulator plants.

## 2.2 Induced Hyperaccumulation

Plants that are not recognised as hyperaccumulators may still be able to concentrate very high levels of metals through the addition of a chemical amendment to the soil. Certain metals may be 'induced' into soil solution by a chemical, and the metal subsequently accumulated in the plant. Huang and Cunningham (1996) were the first to show that induced hyperaccumulation by plants was possible. *Zea mays* (maize) growing on a contaminated soil was observed to accumulate more than 1% lead (dry wieght ) in aerial parts after a solution of ethylenediaminetetraacetic acid (EDTA) was applied. Further studies showed that cadmium, copper, nickel, and zinc could accumulate in *Brassica juncea* after substrate treatment with EDTA (Blaylock *et al.*, 1997; Huang *et al.*, 1997).

Anderson *et al.* (1998, 2000) and Anderson (2001(a)) have studied the effect of treating plants with thiocyanate. Anderson *et al.* (1998) reported findings of up to 57 ppm (μg/g) dry plant weight gold in *Brassica juncea* treated with 0.64 g thiocyanate/kg dry substrate.

They estimated that a gold concentration of 17 μg/g gold in a crop of plants was required for this form of phytomining to be economically feasible.

Induced accumulation of metals by plants is a new technology, and the mechanisms for such uptake are poorly understood. Anderson (2000) stated that "the key variable for successful plant uptake of gold is dissolution of metal within the soil solution". Proper understanding of geochemical pathways and metal solubilities in different solutions is therefore essential when investigating induced hyperaccumulation.

## 2.3 Phytoremediation and Phytomining

Phytoremediation is the term used to describe the *in-situ* remediation of a contaminated soil through the use of plants. Phytomining is a recent advance on this technology, and describes the situation where the costs associated with the recovery of the metal are less then the cost of the metal itself, so that economic benefit is gained. Phytoextraction is a term that describes both phytoremediation and phytomining – the use of plants to remove metals from either a contaminated area or a low grade ore.

Phyomining is based on the principle that plants which can accumulate heavy metals from polluted soils can then be harvested as a "bio-ore". Chaney and Angle (1993), as reported by Brooks *et al.* (1995) suggested that the following steps were involved:

1. Grow a crop of hyperaccumulater plants on polluted land.
2. Harvest the crop and burn it to produce the bio-ore. A typical concentration of metal in this ore is up to 10%.
3. Sell the bio-ore to smelting companies.

The advantages of using metal accumulating plants to remediate contaminated soils are many, including lower cost than the traditional methods of removal of the contaminated land or simple isolation. Phytoremediation can also be applied to a wide range of metals. Other advantages include minimal environmental disturbance, and a large level of public acceptance (Kumar *et al.*, 1995). The use of plants to rid land of pollutants is seen as an environmentally friendly form of remediation.

Precious metals, such as gold, platinum, and palladium, offer good opportunities for the application of phytomining due to their value. The field of phytomining is still very young, and it is only recently that the dicovery of excessive uptake of gold by plants has been made. As mentioned, Anderson *et al.* (1998) were the first to report unusually large amounts of gold uptake by plants, inducing up to 57 ppm of gold in *Brassica juncea* from mine tailings through treatment of the substrate with thiocyanate. There have been no reports of platinum and palladium uptake in phytomining experiments. Fuchs and Rose (1974), however, offered evidence of uptake of these precious metals by plants when 285 ppb (ng/g) palladium was found in the ashed twigs of limber pines (*Pinus flexilis*).

Research by Anderson *et al.* (1998) and Anderson (2000) has centred on the dissolution of a desired metal, as ultimately this will be a limiting factor in the uptake of the metal by a plant. It is also a factor that is relatively easily controlled, unlike plant variables which may be specific to individual plants. The uptake of precious metals can therefore be broken into two parts: the dissolution of gold and the Platinum Group Metals (PGMs) in the soil or substrate, and the subsequent uptake of this solution by plants.

## 2.4 Precious Metal Dissolution in the Mining Industry

One area in which one can look for information about metal dissolution is the mining industry. Cyanidation is widely used to extract gold from ores. Low concentration gold ore is crushed and milled to garner fine particles. Cyanide solution is leached through stockpiles of the ore, undergoing the following reaction (Puddephatt, 1978):

$$4Au + 2H_2O + 8CN^- + O_2 \rightarrow 4Au(CN)_2^- + 4OH^- \qquad (1)$$

The gold is then reprecipitated with zinc:

$$2[Au(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Au \qquad (2)$$

Equation 1 is of particular relevance when considering phytomining. Just as cyanide is used in the mining industry to induce gold solubility, this is perhaps an option in the treatment of plants, along with other cyano-compounds.

Traditionally platinum and palladium have been recovered through a process of flotation and gravity separation. Due to their chemical inertness in the environment, there have been no general or standardised methods for the dissolution of these metals. It is likely, however, that Pd(II) and Pt(II)-cyano complexes are formed, due to their high stability constants (Hartley, 1973). The stability constant (Log$\beta$) is a measure of the association of ligands with metal ions, and can therefore be used as a measure of the tendency of complex ions to form under various conditions. The stability constant can also be viewed as a measure of the ability of complex ions to resist oxidation; the larger the stability constant, the greater the ability of the complex ion to withstand oxidising conditions. Hartley (1973) reports the two major complexes as $M(CN)_2$ and $M(CN)_4^{2-}$, where M is Pd or Pt.

Redox potential (Eh) is used as a measure of the oxidising potential of solutions. As Eh increases, the ability of a solution to oxidise complex ions increases also. The stability of complex ions and Eh are therefore linked – under highly oxidising conditions some complex ions will remain in solution while others will be broken down. Positive redox potential is also required to oxidise metals in order for complex formation to occur. A balance therefore exists between metal oxidation and complex ion destruction.

Platinum and palladium are recovered, along with other noble metals, from the anode slimes (the insoluble residue) produced in the electrolytic recovery of copper and nickel. After treatment with *aqua regia*, ferrous sulphate (or chloride), and ammonium chloride, the precipitate hexachloroplatinate(IV) is formed, which is filtered off from the filtrate, $H_2PdCl_4$, and ignited to give an impure platinum sponge (Hartley, 1973). Chemical treatment can improve the concentration of this sponge to >99.9% pure platinum.

The filtrate from above, $H_2PdCl_4$, is treated with ammonia and then precipitated as $[Pd(NH_3)_2Cl_2]$ by hydrochloric acid. This process is repeated to yield pure $[Pd(NH_3)_2Cl_2]$

which is ignited to give a palladium sponge then cooled in hydrogen. The end product is >99.9 % palladium.

## 2.5 Precious Metal Dissolution in the Environment

An insight into precious metal dissolution can be gained by examining the behaviour of these metals in the environment. During the last century many studies have investigated the mobility (the dissolution, transport, and resettling) of gold and the PGMs under high temperatures and pressures in hydrothermal systems. This is very important, particularly in the mining industry, as the behaviour and location of certain elements can yield clues as to where a desired metal or ore may be concentrated. It is also important to the plant or soil scientist as it provides information about the conditions needed for the dissolution of metals and subsequent uptake by plants.

### 2.5.1 Transport as Chloride Complexes

Traditionally it was thought that, in a groundwater environment, chloride ion was the species most likely to contribute to the transport of gold, platinum, and palladium. This was due mainly to the fact that chloride has a relatively high concentration in many geological fluids (Barnes, 1979), and that platinum and palladium form stable complexes with $Cl^-$ in the form $PtCl_4^{2-}$ and $PdCl_4^{2-}$ (Hartley, 1973). Chloride has also been shown to play an important role in complexing with gold during its transport in hydrothermal fluids (Henley, 1973).

Fuchs and Rose (1974), Westland (1981), and Bowles (1986) provide evidence that the conditions under which platinum and palladium are solubilised are similar to gold. The conditions required for gold solubility therefore offer clues as to how platinum and palladium solubility may be maximised.

Significant though the chloride concentration is in the transport of gold, platinum, and palladium, numerous studies have pointed out the importance of both oxidation state and pH of the fluid. Fuchs and Rose (1974), based on data from Goldberg and Hepler (1968), Pourbaix (1966), and Rossini *et al.* (1969), calculated an Eh-pH diagram which showed that platinum and palladium would only form complexes with $Cl^-$ at a pH of less than 4, and redox potential in the range of 0.7 V to 1.0 V. This mapped closely the range of conditions quantified by Cloke and Kelly (1964) for the dissolution of gold. They found that at pH less than 5.5 and Eh greater than 0.9V, gold was solubilised as the chloride complex $AuCl_4^-$.

The importance of the chloride ion is well established. Under high Eh, low pH, and high chlorinity, gold, platinum and palladium will predominantly be transported as $MCl_4^-$, where M is Au, Pd, or Pt. However, the extreme conditions required for PGM and gold dissolution as chloride complexes are rarely found in the environment. This has led geochemists to suspect that other mechanisms of PGM and gold dissolution were involved in the transport of these metals. It was not until the early 1980's that other possible mechanisms of PGM and gold transport at more moderate pH and Eh were investigated.

### 2.5.2 Transport as Hydroxide Complexes

In the words of Mann (1984), "The actual chemical species for the solution migration of gold has long been a problem for the geochemist. In all probability, different complexing ions are responsible for gold migration in different environmental solutions". This outlook has largely been adopted by geochemists and many studies have subsequently concentrated on establishing the geochemical conditions under which gold will be transported, as well as the complexing species involved. Wood and Mountain (1989) proposed that at neutral or near neutral pH three chemical species other than chloride played a major role: hydroxy complexes, bisulphide complexes, and ammonia complexes.

According to their calculations, Mountain and Wood (1987,1988) found that the hydroxy complexes $Pt(OH)_4^{2-}$ and $Pd(OH)_4^{2-}$ would dominate under neutral pH and oxidising to slightly reducing conditions. This finding was based on a method of estimating stability constants published by Belevantsev *et al.* (1982). Stability constants at 25°C of 50.8 for $Pd(OH)_4^{2-}$ and 62.0 for $Pt(OH)_4^{2-}$ were estimated. Because the hydroxyl ion is always present in a water solvent, and based on the strength of the stability constants calculated, the authors suggested that hydroxide could contribute significantly to platinum and palladium transport in neutral or near neutral solutions. However, in their follow up study, Wood and Mountain (1989), recognising they had made an error in their calculations, re-estimated the stability constants at 25°C of $Pd(OH)_4^{2-}$ and $Pt(OH)_4^{2-}$ as 26.4 and 32.0 respectively. Under a more extreme temperature of 300°C the stability constants were given as 24.0 and 27.0 respectively. They concluded that chloride complexes predominate over hydroxide complexes at a much higher pH than previously thought. While not dismissing hydroxide complexation altogether, they proposed that these complexes would be restricted to a basic pH with relatively oxidising conditions.

### 2.5.3 Transport as Ammonia Complexes

Ammonia complexation in hydrothermal waters was not investigated thoroughly by Mountain and Wood (1988), and it's potential as a transport mechanism was only touched upon by Wood and Mountain (1989). Rasmussen and Jorgensen (1968) gave a stability constant of 35.5 for platinum and 32.8 for palladium at 25°C for the $M(NH_3)_4^{2+}$. Mountain and Wood (1988) estimated these constants to be reduced to 34.0 and 32 respectively at 300°C. The constants at 25°C are comparable to the hydroxide complexes estimated by Wood and Mountain (1989). $NH_3$ is only stable at pH values greater than 9.2, and thus the field for dissolution by ammonia is limited. However, ammonia-chloride complexes are known to occur at low temperatures (Hartley, 1973). While much is still unknown about ammonia complexing, scope for future research certainly exists.

### 2.5.4 Transport as Bisulphide Complexes

While little experimental data on the transport of PGMs as bisulphide complexes has been published, the stability constants for the bisulphide complexes $Pd(HS)_4^{2-}$, $Pd(HS)_3^{1-}$, $Pd(HS)_2^0$, and $Pd(HS)^+$ have been estimated by Elliot (1988) to range from 41 to 68 at 25°C. Platinum concentrations in alkaline bisulphide solutions of 10-100 ppb have been found in solubility experiments by Wood and Mucci (1988). The calculations by Wood and Mountain (1989) have led them to the conclusion that in typical hydrothermal solutions (neutral or near neutral pH) and in low oxidation to reducing conditions, palladium and platinum transport would be primarily through bisulphide complexes. Solubility of palladium and platinum in this form increased up to 300°C while solubility as chloride and hydroxy complexes decreased. Their results showed a strong similarity to gold-bisulphide complexes such as $Au(HS)_2^-$ (Seward, 1973).

### 2.5.5 The Role of Humic Acids

There has been much debate as to the effectiveness and role of humic acids in the weathering process. Despite this, little attention has been paid to the dissolution of gold by humic acids. Freise (1931) studied the dissolution of gold by organic solutions, and his data indicated that humic acids did indeed solubilise gold. By contrast, Ong and Swanson (1969) could not find evidence of significant transportation of gold by humic acids. In view of the reducing properties of humic acid, they questioned the ability of these substances to complex gold as the metal would first have to be oxidised. Investigation of the role of humic substances in dissolving gold and the PGMs is therefore important, not only because of the lack of information, but also because of the abundance of organic materials in some surficial environments which may potentially leach humic acids.

Baker (1973) conducted a leaching experiment to examine the effectiveness of humic acid as a solvent of gold. His results showed that a 0.1% humic acid solution dissolved a wide range of metals, including gold and silver. This conflicted with the results obtained by Ong and Swanson, and suggested that humic acids were far better complexing agents than reductors. In a follow up study Baker (1978) presented further evidence for the dissolution of gold by humic acids. Up to 330 ppb gold was made soluble from an ore by 0.05% humic acid. The redox potential of this solution (300mV) indicated that it was oxidising in character. As humic acid is generally considered to be a reductor, Baker suggested that humic acid may not be as good a reductor as assumed, but that it had very good complexing properties. The positive redox potential suggested that other species, such as dissolved oxygen, were present in humic acid solutions observed to dissolve gold. As these are relatively common in free draining soil profiles, humic acid may therefore be considered to play an important role in the transport of gold.

In a breakdown of some of the constituents of humic acid, Vlassopoulos *et al.* (1990) found that of acetate, benzoate, oxalate, phthalate, salicylate, and thiosalicylate, only the final two ligands were found to complex favourably with Au. Dissolution experiments found that only thiosalicylate dissolved a significant quantity of gold (680 mg/L, compared to less than 25 mg/L for the first five ligands). Nevertheless, these results show that humic acids can complex with gold (in spite of only slightly oxidising conditions), and provide solid evidence for this proposition made by Baker (1978).

## 2.6 The Role of Thioligands in Precious Metal Dissolution

### 2.6.1 Thiosulphate

Reactions

Thiosulphate is one species that has been shown, through laboratory experimentation, to be an important ligand in the dissolution of gold. The oxidation of sulphide leads to the formation of thiosulphate. This species is only stable in slightly acidic to basic pH (6-9), and high Eh (0.5-1.0V) conditions. Goldhaber (1983) showed, during the oxidation of pyrite, that at a temperature of 30°C thiosulphate and sulphite were the predominant species at pH 8-9. Goldhaber postulated that these ions were intermediates in the sulphur-oxidation pathway, and that in this pH range further oxidation was somewhat arrested. At lower pH values of 6-7, tetrathionate and sulphate were the major observed species, while Davis (1958) reported that under strong acidic conditions the intermediate species thiosulphate may disproportionate to sulphite and elemental sulphur. These results were supported by Webster and Mann (1984) who, through a localised study of the Upper Ridges Mine in Australia, concluded that gold migration proceeded through the formation of $Au(S_2O_3)_2^{3-}$ under neutral to basic, moderately oxidising conditions. Bowell *et al.* (1993) recognised, however, that the bacteria *Thiobacillus thiooxidans* will interfere with thiosulphate complexing by oxidising thiosulphate to sulphate. In the field of phytoextraction of precious metals, this is an important factor to consider when using thiosulphate as a complexing agent of gold.

The actual dissolution of gold in thiosulphate proceeds as follows:

$$2Au + 4S_2O_3 + H_2O + 1/2O_2 = 2Au(S_2O_3)_2^{3-} + 2OH^- \qquad (3)$$

*Importance of Thiosulphate in Dissolution of Metals in Hydrothermal Systems*

Thiosulphate has also been suggested as being important in palladium and platinum complexing as $M(S_2O_3)^{2-}$, $M(S_2O_3)^{4-}$, and $M(S_2O_3)^{6-}$, where M is Pt or Pd (Anthony and Williams, 1994). Mountain and Wood (1987) placed thiosulphate complexing with PGMs in a narrow Eh/pH 'window of opportunity', and suggested that transportation of PGMs in hydrothermal environments would be greater during low temperature oxidation of sulphide bearing rocks where carbonate is also present.

Having established the importance of thiosulphate in slightly oxidising, slightly basic hydrothermal conditions, Anthony and Williams (1994) tested the effectiveness of this ligand in complexing with platinum and palladium. Metal blacks (fine-grained powders precipitated by reduction from dissolved chloride salts) were reacted in 500cm$^3$ Ehrlenmeyer flasks with sodium thiosulphate solutions of varying concentration and pH, for durations from 1 to 75 days. These experiments yielded results which have led to a greater understanding of thiosulphate/PGM complexes, and under what conditions these are formed and sustained.

The most significant result of Anthony and Williams' work was the level of palladium and platinum dissolution in thiosulphate. A concentration of 111 ppm was discovered in a 0.1M $S_2O_3^{2-}$ solution after 75 days reaction time. The most platinum discovered in solution was 46 ppm, after reaction with 0.01M $S_2O_3^{2-}$, also for 75 days. By taking aliquots at regular intervals it was discovered that the ability of thiosulphate solutions to dissolve palladium diminished with time, eventually reaching a plateau. The authors attributed this to the destabilisation of the palladium-$S_2O_3^{2-}$ complex over time.

The second important finding was that rates of dissolution, in the absence of other complexing agents for platinum and palladium, were independent of pH in the pH range 6-9. Rates of dissolution were also inversely correlated with thiosulphate concentration; at the lower concentration levels (0.05M) the rate of palladium and platinum dissolution was greater than at the higher levels of 0.1M. The effect of adding chloride to 0.01M $S_2O_3^{2-}$ solutions at a pH of 8.5 was also tested. No additional PGM dissolution was observed, suggesting chloride complex formation was not a factor.

*Potential Applications in Industry*

The research by Anthony and Williams (1994) was important as it gave an insight into how much platinum and palladium could be dissolved by thiosulphate and the preferential conditions for complexing. While they sought to apply their results to metal transport during weathering of mineral deposits, there has been little research into the use of thiosulphate for metal extraction in the mining industry. Murthy and Prasad (1996) viewed thiosulphate as a potential lixiviant[1] for leaching gold in an industrial situation. These authors leached a waste gold ore with 0.5M $Na_2S_2O_3$ at a 1:4 solid/liquid ratio. Over 6 hours only 20.3% of gold was recovered. In contrast, thiourea leached 84% of the present gold, an outcome that has resulted in further testing of thiourea as a lixiviant for gold.

## 2.6.2 Thiourea

The dissolution of gold in acidic solutions of thiourea was first reported by Plaskin and Kozukhova (1941). The practical feasibility of the process was initially investigated by Lodeishchikov *et al.* (1968), who concluded that by comparison with the industry standard leachant, cyanide, the use of acidified thiourea in dissolving gold from ores would be uneconomic due to the high consumption[2] of thiourea. Recent studies, however, have shown that thiourea offers a high rate of gold extraction and in that respect may find some applications in the mining industry.

*Reactions*

The dissolution reaction of gold in thiourea proceeds as shown in equation 2 below:

$$Au + 2CS(NH_2)_2 \rightarrow Au(CS(NH)_2)_2^+ + e^- \qquad (4)$$

---

[1] Solution used to dissolve a desired metal

[2] Consumption refers to the usage of thiourea during reaction with metals or oxidation by other species

As thiourea itself does not act as an oxidant, it is essential that an oxidant is present. In recent studies this has most often been added in the form of either hydrogen peroxide ($H_2O_2$) or ferric ion in the form of $Fe_2(SO_4)_3$.

The overall reaction of $H_2O_2$ with thiourea is as follows:

$$Au + 1/2H_2O_2 + 2SC(NH_2)_2 + H^+ \rightarrow Au(SC(NH_2)_2)_2^+ + H_2O \qquad (5)$$

The addition of Fe(III) to thiourea follows reaction 7:

$$Au + Fe^{3+} + 2SC(NH_2)_2 \rightarrow Au(SC(NH_2)_2 + 2Fe^{2+} + 2H^+ \qquad (6)$$

However, thiourea will react with an oxidant to give formamadine disulphide (FD) as an intermediate species which is also a powerful oxidising agent:

$$2SC(NH_2)_2 + H_2O_2 \rightarrow NH_2(NH)CSSC(NH)NH_2 + 2H_2O \qquad (7)$$

$$2SC(NH_2)_2 + Fe^{3+} \rightarrow NH_2(NH)CSSC(NH)NH_2 + 2Fe^{2+} + 2H^+ \qquad (8)$$

FD, while an oxidation product, can thus be considered a secondary oxidant.

### *Addition of Oxidising Agents*

Numerous studies have investigated the effectiveness of the three oxidants Fe(III), $H_2O_2$, and FD. Groenewald (1976) was the first to make a detailed study of these oxidants, under controlled conditions. Ground ore samples were first "acid-washed" with 0.15M sulphuric acid, as recommended by Lodeischikov *et al.* (1968) as a means of ridding the ore of elements such as iron, copper and zinc, thus reducing thiourea consumption. Acidified solutions of thiourea containing Fe(III), $H_2O_2$, and oxygen were then agitated at a liquid/solid ratio of 2:1 for 60 minutes at room temperature. A solution of 1.0M sulphuric acid, 1.2M thiourea, and 0.1M $H_2O_2$ dissolved 98.5% of the gold after 1 hour. Similarly, acidified solutions of thiourea alone extracted at least 96% of gold within 30 minutes. Groenewald estimated the rate of gold dissolution by a solution containing 0.1M thiourea and 0.01M FD to be 1 x $10^{-8}$ M $cm^{-2}$ $sec^{-1}$. The author contrasted this with a study by Kameda (1949) where it was found that the rate of gold dissolution by cyanide was 2.54 x $10^{-9}$ M $cm^{-2}$ $sec^{-1}$. Groenewald reached the conclusion that although gold could be leached at much greater rates than traditional cyanidation treatment, the consumption of thiourea (1.4 kg thiourea per ton of ore) was much too high to make this method an economic alternative unless very fast rates of extraction were required.

In applications where thiourea is used to leach gold from mining ores, recent studies have concentrated on finding the optimum conditions for gold dissolution. Lacoste-Bouchet *et al.* (1998) utilised a partial factorial experimental design in order to find the best conditions for gold recovery from an ore containing 5.6 g/tonne Au. Amongst the variables controlled were pH, thiourea concentration, and oxidising agent used. Up to 83% of gold was able to be dissolved when a mix of 10 $gL^{-1}$ thiourea and 10 $gL^{-1}$ $Fe_2(SO_4)_3$ was added to the ore. The pH of this solution was 2, monitored by a combination pH probe, pH monitor and variable volume acid pump, and the ore had undergone acid pretreatment. Leaching without pretreatment was much less effective. The authors found that adding excessive amounts of Fe(III) reduced dissolution of gold, due to thiourea being transformed to FD, thereby reducing the quantity of thiourea available for complexation with gold. Total gold extracted using $H_2O_2$ was similar to the use of Fe(III), but operational costs were higher due to an even greater consumption of thiourea. The redox potential of the thiourea/Fe(III) system was noted to be between 410mV and 450 mV. After taking into account cost of reagents, the authors recommended acid pretreatment, followed by leaching with 12 $gL^{-1}$ of thiourea and 5 $gL^{-1}$ ferric sulphate over 72 hours at a pH of 3.

### *Consumption of Thiourea by Oxidants*

A similar study to that carried out by Lacoste-Bouchet *et al.* (1998) was completed by Ubaldini *et al.* (1998) with an ore containing 4 ppm Au. The primary variables studied were temperature, thiourea concentration, and pulp density (weight/volume solids concentration). Ferric sulphate concentration was fixed at 0.5 kg/tonne of ore. Aliquots of samples were taken at various stages to establish thiourea consumption throughout the process. The loss of thiourea through oxidation is a significant factor when considering the economic potential of this chemical as a leachant. The consumption of thiourea when

100 kg/tonne ore was used leaped from 5 kg/tonne of ore at 20°C to 26 kg/tonne of ore at 60°C, a very high rate of usage.

Ubaldini *et al.* (1998) found that gold dissolution was maximised when 100 kg/tonne of thiourea was used. Up to 87% gold was dissolved after 6 hours at a temperature of 20°C. At lower thiourea concentrations of 10 kg/tonne and 50 kg/tonne, recovery did not exceed 25%. The authors recommended a mix of 100 kg/tonne thiourea, 0.5 kg/tonne $Fe_2(SO_4)_3$, temperature of 20°C, and leaching for 6 hours to achieve high gold recovery. However, Ubaldini *et al.* (1998) suggested that minimization of reagent consumption (to around 2 kg/tonne thiourea) could be achieved with 5 kg/tonne thiourea, 0.5 kg/tonne $Fe_2(SO_4)_3$, and 5 kg/tonne sulphuric acid.

The studies by Groenewald (1976), Lodeischikov *et al.* (1968), and Lacoste-Bouchet *et al.*(1998) have all reached similar conclusions regarding the use of thiourea plus an oxidant. At this stage the use of thiourea/Fe(III) or thiourea/$H_2O_2$ is prohibitively expensive due to the consumption of thiourea, unless very high rates of gold extraction are required. It is plainly important that for maximum gold dissolution the right combination of oxidant and complexant must be used.

### 2.6.3 Thiocyanate

Thiocyanate as a solvent for gold was first studied in the early 1900's, but with the success of cyanidation in the mining industry, it was largely overlooked until the mid-1980's when Fleming (1986) again investigated its potential. Since then Barbosa-Filho and Monhemius (1994 a,b,c) have been the main progenitors of the study of thiocyanate, and it is largely through their work that the chemistry of gold dissolution in thiocyanate is understood.

*Oxidation Reactions*

Thiocyanate can participate in three redox systems during its oxidation to sulphate:

$$SCN^- + 4H_2O = SO_4^{2-} + CN^- + 8H^+ + 6e^- \qquad (9)$$

$$SCN^- + 7H_2O = SO_4^{2-} + CNO^- + 10H^+ + 8e^- \quad (10)$$

$$SCN^- + 7H_2O = SO_4^{2-} + CO_3^{2-} + NH_3 + 11H^+ + 8e^- \quad (11)$$

Early experimental data showed that the potentials required for the oxidation of thiocyanate were higher then those predicted through thermodynamic calculations. This led to the suggestion that intermediate species were a part of the oxidation mechanism. The oxidation of thiocyanate therefore proceeds as thus:

$$3(SCN)_2(aq) + 6e^- = 6SCN^- + 4H_2O \quad (12)$$

$$5SCN^- + HCN + SO_4^{2-} + 7H^+ = 3(SCN)_2 + 4H_2O \quad (13)$$

$$SO_4^{2-} + CN^- + 8H^+ + 6e^- = SCN^- + 4H_2O \quad (14)$$

Currently trithiocyanate ($(SCN)_3^-$) is considered to be the intermediate mainly responsible for these overpotentials, while thiocyanogen ($(SCN)_2$) is also widely considered to play a role. Barbosa-Filho and Monhemius (1994a) proposed that trithiocyanate may play a role in gold dissolution, as the dissolution of gold as $Au(SCN)_4^-$ and $Au(SCN)_2^-$ takes place at potentials at which $(SCN)_3^-$ is produced. This is significant as these complexes are the two major thiocyano-auric complexes. Based on thermodynamic considerations, it is thought that gold is complexed as $Au(SCN)_2^-$ at an Eh of around 600mV, while $Au(SCN)_4^-$ is the predominant species at potentials of greater than 680mV.

Barbosa-Filho and Monhemius (1994a) reported that Fe(III) was a suitable oxidant in the Au-SCN-$H_2O$ system. This system will dissolve gold in the pH range 1-2.

The process of oxidation of thiocyanate through the formation of intermediate species is called autoreduction. Barbosa-Filho (1991) described the autoreduction of ferric thiocyanate complexes in the following set of reactions:

$$Fe(NCS)_n^{3-n} \rightarrow Fe^{2+} + (n-1)SCN^- + SCN^{\bullet}\,[3] \quad (15)$$

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[3] Refers to thiocyanate as a free radical ion

$$Fe(NCS)_n^{3-n} \rightarrow FeNCS^+ + (n-2)SCN^- + SCN^\bullet \qquad (16)$$

$$SCN^\bullet + SCN^- = (SCN)_2^- \qquad (17)$$

$$2(SCN)_2^- \rightarrow (SCN)_2 + 2SCN^- \qquad (18)$$

$$2(SCN)_2^- \rightarrow (SCN)_3^- + SCN^- \qquad (19)$$

$$(SCN)_3^- = (SCN)_2 + SCN^- \qquad (20)$$

$$3(SCN)_2 + 4H_2O \rightarrow 5SCN^- + HCN + SO_4^{2-} + 7H^+ \qquad (21)$$

$$4(SCN)_2 + 5H_2O \rightarrow 7SCN^- + HCNO + SO_4^{2-} + 9H^+ \qquad (22)$$

Barbosa-Filho and Monhemius (1994b) calculated that Fe(III) can form six complexes with $SCN^-$: $FeNCS^{2+}$, $Fe(NCS)_2^+$, $Fe(NCS)_3$, $Fe(NCS)_4^-$, $Fe(NCS)_5^{2-}$, and $Fe(NCS)_6^{3-}$. By contrast, the reduction of Fe(III) to Fe(II) as a result of the autoreduction yields only one known Fe(II)-thiocyanate complex: $FeNCS^+$. This complex has a very low stability constant compared to the six Fe(III)-thiocyanate complexes, and is therefore not considered to play a significant role in metal complexation.

Barbosa-Filho and Monhemius (1994c) found that the rate of auto reduction in the Fe(III)-thiocyanate system was initially fast, but slowed with the accumulation of Fe(II) in solution as Fe(III) was reduced. They recognised that the key to maximizing gold leaching was controlling the production of the active intermediate species thiocyanogen and trithiocyanate in the autoreduction process. In this respect, it is the ratio of Fe(II) to Fe(III) in solution which is important and the authors stated that, in order to achieve regulated and continuous production of thiocyanogen and trithiocyanate, 5-10% of iron in solution should be maintained as Fe(II). Barbosa-Filho and Monhemius also suggested that the addition of a secondary oxidising agent could be used to maintain this ratio in industrial applications.

*Hydrogen Peroxide as a Potential Oxidant*

The oxidation of thiocyanate to sulphate and cyanide is shown in equation 14. As cyanide forms very stable complex ions with gold, the addition of an oxidant to thiocyanate would appear to be a promising potential solvent of gold. It has already been shown that this does not happen with the addition of ferric ions to thiocyanate as the intermediate species formed act as complexants and oxidants of gold. Anderson (2001(b), unpublished data) analysed extractant solutions of thiocyanate, thiocyanate/Fe(III), and thiocyanate/$H_2O_2$ for sulphate and cyanide. He found a cyanide concentration of 133 ppm in a solution containing 0.4% ammonium thiocyanate + 2.7% $H_2O_2$. This compared to a cyanide concentration of 1.2 ppm in a 0.4% ammonium thiocyanate/0.2% ferric sulphate solution. The role of this cyanide produced with thiocyanate/$H_2O_2$ in the extraction of gold is poorly understood, and offers further opportunity for study in the field of phytomining.

*Reactions with Gold*

Barbosa-Filho and Monhemius (1994a) likened the behaviour of thiocyanogen and trithiocyanate, which act as both oxidants and complexants of gold, during autoreduction to the homologous halide species $X_2$ and $X_3^-$, where X is Cl, Br, or I. They reported the mechanism of dissolution of gold by thiocyanate solutions at high potentials, outlined by Barbosa-Filho (1991):

$$Au(s) + SCN^- = Au(SCN^-)(ads)^4 \qquad (23)$$

$$Au(SCN^-)(ads) = Au(SCN)(ads) + e^- \qquad (24)$$

$$Au(SCN)(ads) \rightarrow AuSCN(ads) \qquad (25)$$

$$AuSCN(ads) + SCN^- \rightarrow Au(SCN)_2^- \qquad (26)$$

When ferric-thiocyanate solutions are used, $Au(SCN^-)$ in reaction 23 is replaced by Fe(III)-thiocyanate complexes, which go to form Au(SCN)(ads) through autoreduction.

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[4] Refers to the adsorption of the thiocyanate ion onto the gold surface

As well as reaction 25 proceeding, the intermediate species are also formed. At lower potentials these can also react with gold to form complexes through the following set of reactions:

$$\mathrm{Au(s)} + \mathrm{(SCN)_3^-} \rightarrow \mathrm{Au(SCN)_2^-} + \mathrm{SCN^\bullet} \qquad (27)$$

$$\mathrm{Au(s)} + \mathrm{SCN^\bullet(ads)} \rightarrow \mathrm{AuSCN(ads)} \qquad (28)$$

$$\mathrm{Au(s)} + \mathrm{(SCN)_2} \rightarrow \mathrm{2AuSCN(ads)} \qquad (29)$$

$$\mathrm{AuSCN(ads)} + \mathrm{SCN^-} \rightarrow \mathrm{Au(SCN)_2^-} \qquad (30)$$

$$\mathrm{Au(s)} + \mathrm{(SCN)_2^-} \rightarrow \mathrm{Au(SCN)_2^-} \qquad (31)$$

Through leaching experiments Barbosa-Filho and Monhemius (1994c) postulated that three sequential stages occur during the dissolution of gold in solutions of Fe(III)-thiocyanate. The first is where the formation of $Au(SCN)_4^-$ results in most of the gold being dissolved. Following the autoreduction of Fe(III) and the subsequent decrease in mixed potentials, gold is dissolved as $Au(SCN)_2^-$. Finally, gold is dissolved at lower mixed potentials as the complex $Au(SCN)_2^-$.

*Effectiveness of the Thiocyanate/Fe(III) system*

In a direct comparison of the effectiveness of thiocyanate/Fe(III), thiourea/Fe(III), and cyanide, Munoz and Miller (2000) found that, both before and after acid washing, the thiocyanate combination was a more effective solvent of gold. A solution containing 8.1 $gL^{-1}$ (24.3 kg/tonne of ore) thiocyanate and 4.5 $gL^{-1}$ (13.5 kg/tonne of ore) ferric ion was able to dissolve 49.5% of gold from an ore containing 7.8 g/tonne gold at pH 2 before acid pretreatment. After acid washing this rose to 84.3%. Up to 97.6% of gold was leached by 0.04M (5.9 kg/tonne of ore) cyanide solution without chemical washing. By contrast, thiourea was found to be a very ineffective solution for dissolving gold. With a thiourea concentration of 0.15M (34.2 kg/tonne of ore), Fe(III) concentration of 0.02M (3.36 kg/tonne), and pH of 2, thiourea consumption was very high at 38.3 kg/t of ore, with

27.6% of gold dissolved from an ore containing 70.5 ppm gold. Without chemical pretreatment, thiocyanate/Fe(III) dissolved slightly more gold at 49.5% of gold present in the ore, compared with 84.6% after acid washing.

Munoz and Miller explained the poor thiourea and thiocyanate results through the presence of a sulphur-reaction product. Their results suggested that elemental sulphur is formed when leaching with thiourea/Fe(III) or thiocyanate/Fe(III). It was thought this elemental sulphur coats the gold surface, which inhibits gold dissolution.

The decomposition of thiocyanogen and trithiocyanate through hydrolysis[5] in the Fe(III)-thiocyanate system to stable oxidation products is a major drawback when attempting to release gold into solution. Monhemius and Ball (1995) conducted leaching tests using a two level factorial design to study the effectiveness of a Fe(III)-iodide-thiocyanate mix, where the variables were thiocyanate concentration, iodide concentration, ferric ion concentration, and pH. Each variable was tested at a high and low value while the other variables remained constant. Up to 93.7% of gold was extracted from a Dominican ore containing 68.2 g/tonne gold by a solution of 0.1M thiocyanate, 0.055M Fe(III), and 0.002M iodide at a pH of 1. The results were as good as with cyanidation and better than thiourea. This result was attributed to the formation of relatively stable iodide-thiocyanate species which play a role in the dissolution of gold (Barbosa-Filho and Monhemius, 1994d). While $(SCN)_3^-$ and $(SCN)_2$ are unstable in water, this is not the case with the iodide equivalents $I_3^-$ and $I_2$. Iodine is poorly soluble in water, but the addition of iodine to thiocyanate leads to the formation HCN and $SO_4^{2-}$ through the following reaction:

$$SCN^- + 3I_2 + 4H_2O = SO_4^{2-} + 6I^- + HCN + 7H^+ \qquad (32)$$

This reaction proceeds through the formation of the intermediate species $I_2SCN^-$ and $I(SCN)_2^-$. Barbosa-Filho and Monhemius (1994d) suggested that these species play a similar role to that of trithiocyanate in the dissolution of gold and that, furthermore, upon reduction to $SCN^-$ and $I^-$ these mixed intermediate species would also offer oxidising and complexing ability. Monhemius and Ball (1995) proposed that it was these iodide-

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[5] Reaction with water

thiocyanate species, in combination with the intermediate species trithiocyanate and thiocyanogen, which led to such good gold extraction.

# Chapter 3 Extraction of Gold and Palladium From Substrates

## 3.1 Introduction

In any study of phytoextraction, two factors are very important: the amount of metal present in soil solution, and the ability of plants to take up this metal. This chapter investigates the effectiveness of various extractants in solubilising gold and palladium. While the potential for the extraction of gold from mine tailings has been investigated by Anderson (2000), no such precedent exists for palladium.

Two substrates were used during the course of this study. An actual mine tailing from Klipfontein near Rustenburg in South Africa was used initially for the extractions. This contained 61.4 ppb gold and 315 ppb palladium. For comparative purposes an artificial substrate was made up to contain 5 ppm gold and 5 ppm palladium (digestions showed these concentrations to be 4.75 ppm gold and 148 ppb palladium).

Extractant solutions were chosen based on reported ability to dissolve gold and the PGMs. Literature in the fields of both geochemistry and mining gave clues as to what treatments may be effective. Initial trials eliminated some treatments as potential solvents for gold and palladium. Solutions that were found to extract large quantities of the desired metals were researched further in additional trials. In the course of these experiments the effect of oxidant concentration in solution was investigated as it was thought that this factor may play an important role in the dissolution of metals. The effect of varying complexant concentration was also examined.

The aim of this section was therefore to investigate what solutions are most effective at dissolving the metals concerned and how any extraction of gold, palladium, and platinum from substrates can be maximized. It was also hoped to gain better understanding of the geochemical relationship between substrate and solution. Ultimately, the intent of the extractions was to treat plants with solutions observed to dissolve large amounts of gold and the palladium.

## 3.2 Methods and Materials - Extractions

### 3.2.1 Trial Design

Design of trials in this chapter was based on 'sets' of extractions involving different extractant solutions. Solutions that demonstrated good extraction potential were investigated further in subsequent tests. Initial sets of extractions investigated the extraction capabilities of the groundwater and hydrothermal species commonly known to form complex ions with gold: bisulphide ion, ammonia, hydride ion, humic acid, as well as the thioligands thiourea, thiocyanate, and thiosulphate. Combination solutions of thiourea or thiocyanate and an oxidant were also trialed.

Having established which solutions promised best dissolution of gold and palladium (section 3.3.1), further detailed groups of extractions were carried out. These are described in section 3.3.2.

### 3.2.2 Extraction Methodologies

A set volume of solution (30 mL) was used to extract metal from 3 g of substrate. Where treatment consisted of only one chemical additive, as in 2 $gL^{-1}$ $NH_4SCN$, 1 g of chemical was weighed, dissolved in reverse osmosis water, and made to volume in a 500mL volumetric flask. Where treatments consisted of two chemical additives (e.g. 2 $gL^{-1}$ $NH_4SCN$ + 1$gL^{-1}$ $Fe_2(SO_4)_3$), separate solutions were made. In the given example, separate solutions of 4 $gL^{-1}$ $NH_4SCN$ and 2 $gL^{-1}$ $Fe_2(SO_4)_3$ were made, and 15 mL of each added to substrate, for a total volume of 30 mL. For treatments involving three chemicals, such as 2 $gL^{-1}$ $NH_4SCN$ + 0.5 $gL^{-1}$ $Fe_2(SO_4)_3$ + 0.25 $gL^{-1}$ KI, each chemical specified was added to a single volume of reverse osmosis water, and this made to volume in a 1 L volumetric flask. A set volume of this solution (30 mL) was then taken for each extraction.

Hydrogen Peroxide ($H_2O_2$) and ammonia solution ($NH_3$) were available only as aqueous solutions. Ammonia solution (100 mL of 30% w/w) was diluted with reverse osmosis water to volume in a 1 L volumetric flask to make 3% ammonia solution. $H_2O_2$ was available as 27% w/w solution (300 $gL^{-1}$). A solution made to contain 2 $gL^{-1}$ $H_2O_2$ can therefore be regarded as 0.18% $H_2O_2$ w/w.

Chemicals used in this study are listed in appendix 3.

### 3.2.3 Replication

Treatments were made in triplicate. A blank sample and a control sample of homogenous substrate were also tested for each reagent.

### 3.2.4 Preparation of Plant Growth Substrates

#### *3.2.4.1 Klipfontein Growth Substrate*

A 1:1 w/w growth substrate was made by combining 5kg Klipfontein tailings, 5 kg sieved pumice (to improve the drainage properties of the substrate), and 50 g osmocote slow release fertiliser. This was then transferred to 200 mL plant pots in preparation for planting, or stored for later use.

#### *3.2.4.2 Artificial Growth Substrate*

50 mL of 1000 ppm (1g/kg) gold solution was dripped into 5 kg of quartz sand. This was placed in a 100°C oven for 24 hours. 0.5 g of 10 % palladinised carbonate was mixed in with the quartz sand, and this subsequently made up to 10 kg with 4.95 kg of sieved pumice and 50 g osmocote slow release fertiliser. This was then transferred to 200 mL pots, or stored for later use. Target metal concentration of this substrate was 5 mg/kg (ppm) for both gold and palladium.

### 3.2.5 Experimental and Analytical Methods

Gold and the PGMs are generally present in geological samples at low concentration and hence graphite furnace atomic absorption spectroscopy must be employed (GFAAS). Clarity of the signal is enhanced through selective extraction of a gold chloride complex into an organic phase. The most suitable organic solvent is methylisobutylketone (MIBK), after Brooks and Naidu (1985).

#### *3.2.5.1 Extractable Gold, Palladium, and Platinum*

The method used below largely follows that described by Anderson (2000).

*Thiocyanate Extractions*

**1** 3g of sieved auriferous substrate (<1mm[*]) was weighed into a 50 mL polypropylene centrifuge tube. Extractant solution (30 mL) was added, and the tubes placed in an end-over-end shaker for approximately 20 hours.

**2** The solutions were filtered through Whatman No 41 filter paper into 30 mL plastic tubes.

**3** A 5 mL aliquot of the extractant filtrate was placed in a 10 mL tube and 5 mL of 2M HCl added.

**4** For gold analysis, 1mL of MIBK was added, and the tube sealed and shaken.

**5** For platinum and palladium analysis, 0.1 mL of 100% KI solution was added prior to MIBK. The tube was then sealed and shaken.

**6** The MIBK fraction was subsequently removed from the tube and analysed by GFAAS.

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[*] Substrate used in section 3.3.2a was not sieved

The 10 mL aliquots were sometimes divided into two 5mL aliquots if gold and PGM analyses were to be completed on different days. When very high gold and palladium results were expected, aliquots were diluted.

### *Non thiocyanate Extractions*

A problem with the use of thiosulphate is that elemental sulphur will precipitate following acidification of the solution, occluding any gold in solution, and thus leading to low recovery in MIBK. Subsequently a different system was employed. This method was used for all non thiocyanate extractions as it was uncertain how well the standard procedure of Anderson (2000) would work.

1. 3g of sieved auriferous substrate (<1mm) was weighed into a 50 mL polypropylene centrifuge tube. Extractant solution (30 mL) was added, and the tubes placed in an end-over-end shaker for approximately 20 hours.

2. The solutions were filtered through Whatman No 41 filter paper into 30 mL plastic tubes.

3. A 5 mL aliquot of the extractant filtrate was transferred to a 50 mL conical flask. 5 mL *aqua regia* as well as several boiling chips were added to the flask. Any sulphur will quickly precipitate, but this is destroyed through strong acid digestion.

4. The acid/extractant mixture was digested on a hotplate until approximately 3 mL remains.

5. Concentrated HCl (5 mL) was added and the digestion continued until 3 mL volume was again reached.

6. The residual liquid was transferred to a 10 mL tube and made to 10 mL with reverse osmosis water.

7. For gold analysis, 1mL of MIBK was added, and the tube sealed and shaken.

**8** For platinum and palladium analysis, 0.1 mL of 100% KI solution was added prior to MIBK. The tube was then sealed and shaken.

**9** The MIBK fraction was subsequently removed from the tube and analysed by GFAAS.

### *3.2.5.2 Analysis of Substrates*

**1** 2 g of substrate less than 1 mm in diameter is weighed into a 50 mL conical flask.

**2** *Aqua regia* (10 mL) was added, and the mixture boiled on a hotplate until approximately 3 mL remained.

**3** Concentrated HCl (10 mL) was added and the solution again boiled until approximately 3 mL remained.

**4** The digestion solution was then transferred to a 50 mL volumetric flask and made up to volume.

**5** The solution was filtered. 5 mL of the filtrate was added to 10 mL tubes and made to 10 mL. Dilutions were made as necessary.

**6** For gold analysis, 1mL of MIBK was added, and the tube sealed and shaken.

**7** For platinum and palladium analysis, 0.1 mL of 100% KI solution was added prior to MIBK. The tube was then sealed and shaken.

**8** The MIBK fraction was subsequently removed from the tube and analysed by GFAAS.

#### *Hydrofluoric Acid Digestions*

Digestion efficiency of the standard methodology was checked using a hydrofluoric acid (HF) digestion procedure. Substrate (2 g) was weighed into plastic beakers and 5 mL HF and 5 mL $HNO_3$ added. This was placed in a 100°C water bath and left till dry. *Aqua* *regia* (10 mL) was then added, and the solution digested to dryness. Concentrated HCl (5 mL) was then added, and this digested until approximately 3 mL remained. This was transferred to 50 mL volumetric flasks, made up to volume, and the procedure continued as per standard substrate digest method above.

### 3.2.6 Statistical Analysis

Analyses of variance (ANOVAs) were used to test for significant difference between means of data. In all cases the 5% level of significance has been used. Error bars in all graphs represent standard error of the means. Means with the same letter on graphs are not significantly different (ANOVA $p>0.05$).

## 3.3 Results and Discussion

### 3.3.1 Klipfontein Extractions:

*Initial Extractions*

A number of extractions were carried out initially on Klipfontein substrate to establish which extractants offered greatest potential for extraction of gold and the PGM's. Digestion of the substrate revealed a palladium concentration of 315 ppb and a gold concentration of 61.4 ppb. Tables 3.1, 3.2, and 3.3 display the results of extractions of this substrate by various solutions.

Perhaps the most noticeable result from the first set of extraction results (Table 1) is the fact that gold and palladium solubility was promoted through extraction with thiocyanate/Fe(III) and thiocyanate/HCl. A relatively high redox potential was reached with these two solutions.

Although thiosulphate is known to dissolve gold and, to an extent, platinum and palladium, extracted gold was not of the same order as thiocyanate/Fe(III), and no alladium was dissolved. This is perhaps due to the pH of 5.6 (Webster and Mann (1984) concluded that neutral to basic pH and moderately oxidising conditions were required for gold complexing with thiosulphate). The chloride ion was also added to thiosulphate in the form of dissolved KCl to determine if it enhanced solubility. No gold or palladium dissolution was observed. Although chloride complexing is only effective at low pH and high Eh (Mountain and Wood, 1988), the absence of any metal extraction cannot be explained.

**Table 3.1** Extraction of gold and palladium from Klipfontein substrate by a variety of extractants

| | | | ng of metal extracted per g of substrate (ppb) | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L $Na_2(S_2O_3)$ | 250 | 5.6 | 28.0 | 0.00 | 48.57 | 0.00 |
| 30 mL 2g/L $Na_2(S_2O_3)$ + 1g/L KCl | 209 | 5.5 | 0.00 | 0.00 | 0.00 | 0.00 |
| 30 mL 2g/L $NH_4SCN$ | 285 | 4.5 | 125 | 0.00 | - | 0.00 |
| 30 mL 2g/L $NH_4SCN$ + 0.05 mol/L HCl | 435 | 1.9 | 49.9 | 10.9 | 6.41 | 6.80 |
| 30 mL 2g/L thiourea | 156 | 4.7 | 16.2 | 0.00 | 2.01 | 0.00 |
| 30 mL 2g/L thiourea + 1g/L $Fe_2(SO_4)_3$ | 200 | 3.1 | 69.1 | 0.00 | 14.2 | 0.00 |
| 30 mL 2g/L $NH_4SCN$ + 1g/L $Fe_2(SO_4)_3$ | 448 | 2.9 | 117 | 11.7 | 20.0 | 1.08 |

Note: Figures reported are mean values. s.d. = standard deviation. All values reported are to 3 significant Figures. Standard deviation is not given for thiocyanate treatments as only one result was obtained from this solution.

The addition of Fe(III) to thiourea served to raise the Eh, lower pH and increase the level of gold dissolution. No palladium or platinum was extracted using thiourea, and the levels of gold dissolution were lower than for thiocyanate/Fe(III).

One could read into the comparison of thiocyanate with thiocyanate/HCl that it is better to use straight thiocyanate with no additive. According to these results, treating the substrate with thiocyanate alone gives the best return of gold dissolution out of all the lixiviants. This high gold concentration (125 ppb) could be due to the fact that it is highly unlikely that samples taken from the Klipfontein substrate are perfectly homogenous. However, raw data (refer to appendix 1) shows that variability between individual extractions within a solvent set is, on the whole, not marked.

Table 3.2 reports gold and palladium extractions for several other naturally occurring solutes. The addition of the bisulphide ion in the form of hydrated sodium hydrosulphide extracted very little gold, but extracted a relatively large amount of palladium. Likewise, 3% ammonia solution achieved good gold and palladium dissolution.

Both hydroxide and humic acid dissolved little gold or palladium. The pH of the hydroxide solution was very high, and Eh low. Both of these factors will have played an important role in the low metal dissolution. Wood and Mountain (1989) proposed that hydroxide complexation of palladium and platinum is most favourable at a basic pH with relatively oxidising conditions. Plainly these conditions have not been met. A low concentration of humic acid (0.5 $gL^{-1}$) was used because of the very viscous nature of more concentrated solutions, which hindered separation of aqueous and solid phases during preparation for analysis. Gold dissolution was good, but lower than thiocyanate. Thiocyanate was repeated in this set of extractions as a comparison with the previous set. Both Eh and pH were very different. However, the amount of gold and palladium extracted was similar. Preliminary trials showed that 24.4 ppb palladium was extracted using thiocyanate/Fe(III), indicating that further investigation of thiocyanate plus an oxidant is needed in further trials.

**Table 3.2** Extraction of gold and palladium from Klipfontein substrate by chemical species typically found in groundwater systems.

| | | | **ng of metal extracted per g of substrate (ppb)** | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L NaHS | 471 | 10.8 | 4.07 | 12.1 | 10.4 | 7.12 |
| 30 mL 3% ammonia | 150 | 11.8 | 10.7 | 12.3 | 8.83 | 5.68 |
| 30 mL 2g/L KOH | 90 | 12.3 | 1.79 | 1.79 | 2.14 | 0.972 |
| 30 mL 0.5g/L humic acid | 105 | 8.0 | 10.1 | 3.52 | 15.5 | 2.26 |
| 30 mL 2g/L $NH_4SCN$ | 136 | 6.9 | 200 | 2.82 | 143 | 2.55 |

Table 3.3 shows the results from the third set of extractions. The significant result here is the level of gold extracted by the thiocyanate/Fe(III)/KI combination. Mixing these species produces a stable thiocyanate-iodide complex, which assists in the dissolution of gold (Barbosa-Filho and Monhemius, 1994d). Although some of the variability may be inherent in the substrate samples, it is felt that the formation of this complex is the more important factor in explaining the high level of gold in solution.

Hydrogen peroxide was also tested as an oxidising agent, primarily with thiourea in mind, as $H_2O_2$ oxidises thiourea to formamadine disulphide (FD), itself a good oxidising agent. The addition of 2 $gL^{-1}$ $H_2O_2$ resulted in 41.8 ppb gold extraction. However, the greater amount of gold was dissolved when adding $H_2O_2$ to thiocyanate, with 87.1 ppb gold extracted on addition of 2 g/L $H_2O_2$ to thiocyanate. This effectively doubled the amount of gold extracted over the addition of 0.05 $gL^{-1}$ $H_2O_2$ to thiocyanate. It is possible that the increased Eh with this mixture has played a role. However, hydrogen peroxide oxidises thiocyanate to form cyanide, according to equation 33 (section 3.3.2a). If cyanide is present in the solution, it seems likely that this would have improved gold dissolution.

**Table 3.3** Extraction of gold and palladium from Klipfontein substrate by thiocyanate and thiourea with varying oxidants

| | | | ng of metal extracted per g of substrate (ppb) | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L thiourea + 0.05g/L $H_2O_2$ | 123 | 6.2 | 0.00 | 0.00 | 0.00 | 0.00 |
| 30 mL 2g/L thiourea + 1g/L $H_2O_2$ | 137 | 5.5 | 41.8 | 0.00 | 21.8 | 0.00 |
| 30 mL 2g/L $NH_4SCN$ + 0.05g/L $H_2O_2$ | 180 | 6.6 | 50.7 | 0.00 | 44.0 | 0.00 |
| 30 mL 2g/L $NH_4SCN$ + 1g/L $H_2O_2$ | 225 | 6.4 | 87.1 | 1.13 | 8.25 | 0.85 |
| 30 mL 2g/L $H_2O_2$ | 330 | 6.6 | 4.33 | 0.00 | 4.77 | 0.00 |
| 30 mL 2g/L $NH_4SCN$ + 0.5g/L $Fe_2(SO_4)_3$ + 0.25g/L KI | 243 | 4.8 | 171 | 0.00 | 21.7 | 0.00 |

There was little or no palladium dissolution in any of the solvents. This may be due to the low Eh values. However, Tables 3.1, 3.2, and 3.3 show that the addition of an oxidant to thiourea or thiocyanate significantly improves extraction of gold, and possibly palladium. The addition of hydrogen peroxide to thiocyanate improves gold dissolution without dramatically changing Eh or pH. These issues are discussed in further detail in section 3.3.2.

## 3.3.2 Artificial Substrate Extractions

### *3.3.2a Extractions where concentration of oxidant is varied*

Due to the limited availability of Klipfontein substrate, and for comparative purposes, an artificial substrate was made up to contain 5 ppm gold and 5 ppm palladium. Upon digestion and analysis , this substrate was found to contain 4.75 ppm gold and 148 ppb palladium. The reason for the discrepancy between the target palladium concentration and actual palladium concentration is unknown. Based on the high levels of gold and palladium dissolved in the initial extractions when an oxidant was added to a thioligand, it was decided to investigate the role of the oxidant further.

*Varying the Level of Fe(III) with Thiocyanate*

The Eh, pH, and metal concentrations are shown in Table 3.4, with Eh increasing and pH decreasing as the concentration of Fe(III) increased. This is to be expected as Fe(III) has high acidity and high redox potential. These results match closely previous Eh and pH results for 2 $gL^{-1}$ thiocyanate and 1 $gL^{-1}$ Fe(III) (refer to section 3.3.1). The addition of ferric ions to thiocyanate has clearly improved the solubility of gold, and this increased dissolution occurs across the full concentration range of Fe(III). At the low concentration of Fe(III) (and therefore lower Eh and higher pH) there is a reduced dissolution of gold, although it does not appear to be significantly lower. This issue will be discussed further.

The maximum dissolution of gold (8520 ppb) was attained using a mixture of 2 $gL^{-1}$ SCN and 3 $gL^{-1}$ $Fe_2(SO_4)_3$. The large amount of gold extracted is repeated in the other extractions in this trial and this is a concern as the substrate contained only 4750 ppb (4.75

ppm) gold. It seems likely that all the gold has been extracted, and it is possible that thiocyanate/Fe(III) is simply better at extracting gold from the artificial substrate than *aqua regia*. However, the exact reason for this discrepancy is unknown. The extraction results are valid for comparison as they show the relative effects of various oxidants.

The difference between means for the extractable gold concentration results is not large in solutions where Fe(III) was added to thiocyanate (Figure 3.1). It can be seen that gold dissolution with combinations of thiocyanate/Fe(III) are much larger than when thiocyanate or Fe(III) alone were used as extractants. The standard deviations for all of the extractions are very high and an ANOVA reveals that there is no significant difference across the means of the thiocyanate/Fe(III) solutions. In the range of 0.25 $gL^{-1}$ to 3 $gL^{-1}$ $Fe_2(SO_4)_3$, the level of oxidant does not affect the amount of complexing with gold that takes place.

**Table 3.4** Extraction of gold and palladium from artificial substrate with constant thiocyanate + varying ferric sulphate

| | | | ng of metal extracted per g of substrate (ppb) | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L $Fe_2(SO_4)_3$ | 512 | 2.5 | 722 | 1.91 | 1033 | 0.65 |
| 30 mL 2g/L $NH_4SCN$ | 270 | 4.7 | 825 | 40.6 | 234 | 16.7 |
| 30 mL 2g/L $NH_4SCN$ + 0.25g/L $Fe_2(SO_4)_3$ | 283 | 4.3 | 4490 | 63.9 | 1030 | 39.4 |
| 30 mL 2g/L $NH_4SCN$ + 0.5g/L $Fe_2(SO_4)_3$ | 301 | 3.2 | 7320 | 57.7 | 780 | 34.7 |
| 30 mL 2g/L $NH_4SCN$ + 1.0g/L $Fe_2(SO_4)_3$ | 429 | 2.6 | 5700 | 112 | 642 | 20.2 |
| 30 mL 2g/L $NH_4SCN$ + 2.0g/L $Fe_2(SO_4)_3$ | 453 | 2.4 | 5320 | 76.3 | 1220 | 11.7 |
| 30 mL 2g/L $NH_4SCN$ + 3.0g/L $Fe_2(SO_4)_3$ | 462 | 2.4 | 8520 | 34.8 | 5540 | 11.4 |

With regard to palladium, addition of the oxidant increased the amount of palladium extracted from the substrate, and this increase is nearly 3 fold (Table 3.4). Figure 3.2 shows these results graphically. No clear pattern emerges from the means of these extractions. The 1 $gL^{-1}$ ferric sulphate / 2 $gL^{-1}$ thiocyanate mixture extracted most

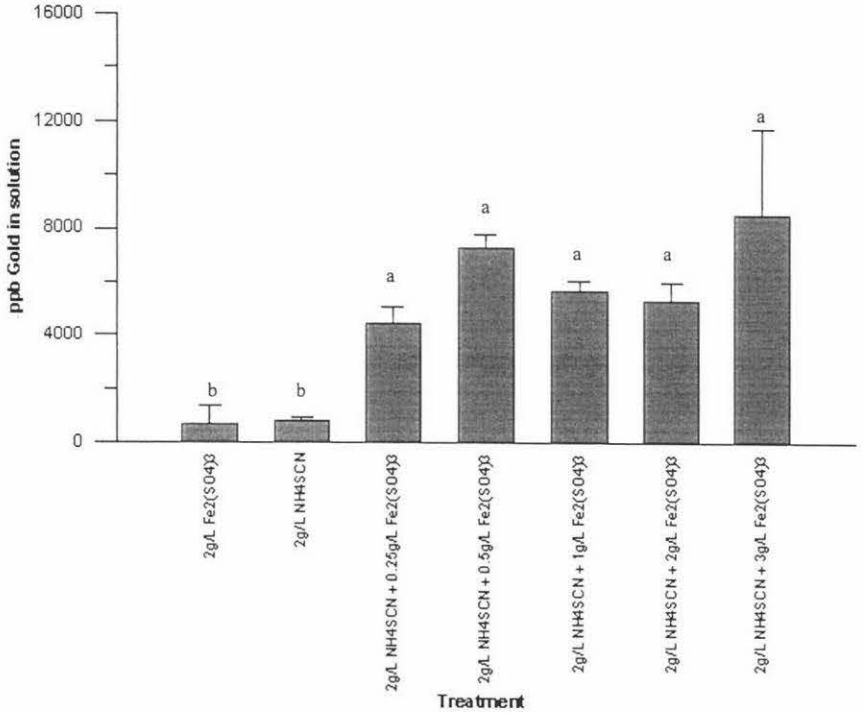

**Figure 3.1** Gold extraction from artificial substrate when thiocyanate concentration is constant and Fe(III) concentration is varied. Means with the same letter are not significantly different. Error bars show standard error.

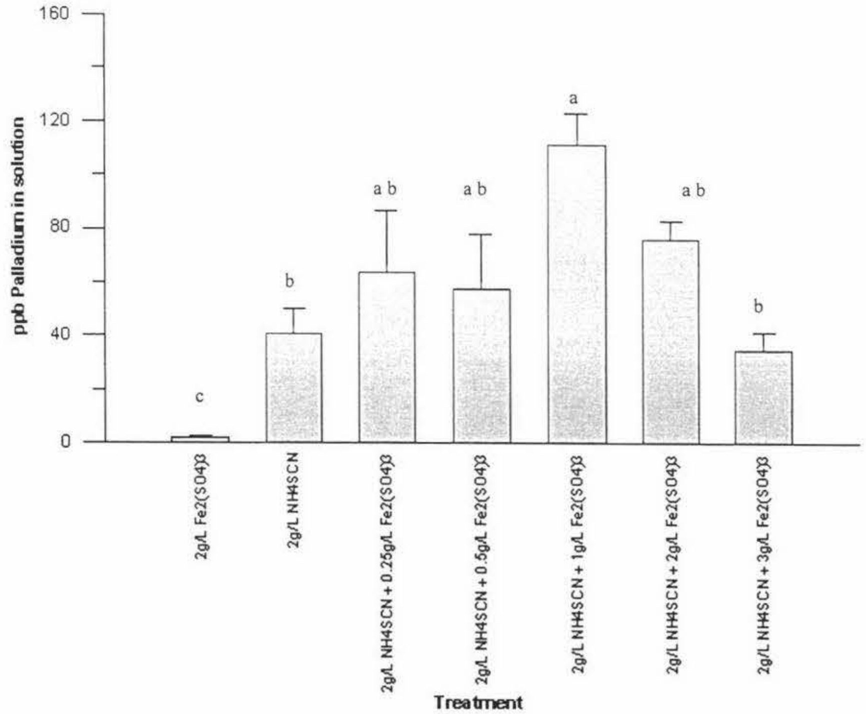

**Figure 3.2** Palladium extraction from artificial substrate when thiocyanate concentration is constant and Fe(III) concentration is varied.

palladium, and this also had a relatively low standard deviation. The lower results emerged when Fe(III) concentration was either very low or very high. The difficulty associated with extracting palladium from a substrate may also have played a role in the nature of these results. In the range of concentrations examined, palladium extraction was independent of the amount of Fe(III) present.

**Summary:** A strong relationship appears to exist between pH and the quantity of metal dissolved. The addition of Fe(III) to thiocyanate substantially reduced the pH and increased the Eh of all the extractants and this corresponded to a dramatic increase in gold extraction. The amount of gold extracted when using Fe(III) as an oxidant in the presence of thiocyanate, therefore, appears to be dependant on pH and, in the Fe(III) range tested, independent of ferric ion concentration. Addition of 1 $gL^{-1}$ $Fe_2(SO_4)_3$ to thiocyanate significantly increased palladium extraction.

*Varying the level of $H_2O_2$ with thiocyanate*

Table 3.5 shows the Eh, pH, and metal extraction results for solutions of thiocyanate and $H_2O_2$. As the concentration of $H_2O_2$ increased, Eh rose, while pH decreased. This was expected, as $H_2O_2$ itself has a low pH and high Eh.

Very high levels of palladium and gold were extracted with the oxidant alone (Figures 3.3 and 3.4, Table 3.5). This is particularly noticeable when compared with the results for thiocyanate. A reason for this, yet one which has not been qualified, is that the gold and palladium present in the artificial substrate may be in a form which is easily extracted by aqueous solutions. Hydrogen peroxide is a very powerful oxidising agent and it is possible that gold is being oxidised and subsequently forming complex ions with species present in the synthetic substrate, such as chloride. Gold-hydroxide complexes may also be forming. Statistically there is no significant difference in gold extraction across all the treatments (Figure 3.3). However, eliminating the thiocyanate/3$gL^{-1}$ treatment from the ANOVA reveals that significant difference does exist between all other thiocyanate/$H_2O_2$ combinations and the thiocyanate and $H_2O_2$ treatments alone ($p=0.005$).

Extraction of palladium by thiocyanate/$H_2O_2$ was greater than thiocyanate/Fe(III). Assuming a total substrate palladium concentration of 148ppb, it appears that 100% of the palladium has been dissolved. An ANOVA completed on the palladium results (as well as for gold) where the $H_2O_2$ concentration was varied, allows us to conclude that the means of the palladium extracted by solutions of varying $H_2O_2$ content are not significantly different. The same can be said for gold.

Although they are not as high as with thiocyanate/Fe(III), the gold results, as with palladium, are consistently even across the full range of $H_2O_2$ concentrations. Again this shows that very little hydrogen peroxide is required to improve the dissolution of gold from this substrate.

**Table 3.5** Extraction of gold and palladium from artificial substrate with constant thiocyanate + varying hydrogen peroxide

| | | | ng of metal extracted per g of substrate (ppb) | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L $H_2O_2$ | 364 | 5.6 | 1630 | 31.8 | 328 | 14.9 |
| 30 mL 2g/L $NH_4SCN$ | 235 | 6.0 | 734 | 17.8 | 178 | 11.4 |
| 30 mL 2g/L $NH_4SCN$ + 0.25g/L $H_2O_2$ | 265 | 5.9 | 3060 | 170 | 413 | 39.6 |
| 30 mL 2g/L $NH_4SCN$ + 0.5g/L $H_2O_2$ | 313 | 5.7 | 3440 | 168 | 592 | 49.9 |
| 30 mL 2g/L $NH_4SCN$ + 1.0g/L $H_2O_2$ | 327 | 5.5 | 3030 | 131 | 1070 | 29.0 |
| 30 mL 2g/L $NH_4SCN$ + 2.0g/L $H_2O_2$ | 344 | 5.3 | 3870 | 164 | 1560 | 65.1 |
| 30 mL 2g/L $NH_4SCN$ + 3.0g/L $H_2O_2$ | 383 | 4.7 | 2880 | 149 | 2110 | 91.2 |

Both $H_2O_2$/thiocyanate and Fe(III)/thiocyanate appear to extract similar amounts of gold. However, Tables 3.4 and 3.5 show that the pH of the thiocyanate/$H_2O_2$ solutions are not as low as the thiocyanate/Fe(III) solutions. While dissolution of gold by thiocyanate/Fe(III) may simply be a function of acidity, the small change in pH and Eh when $H_2O_2$ is added to thiocyanate indicates that some other variable may be involved.

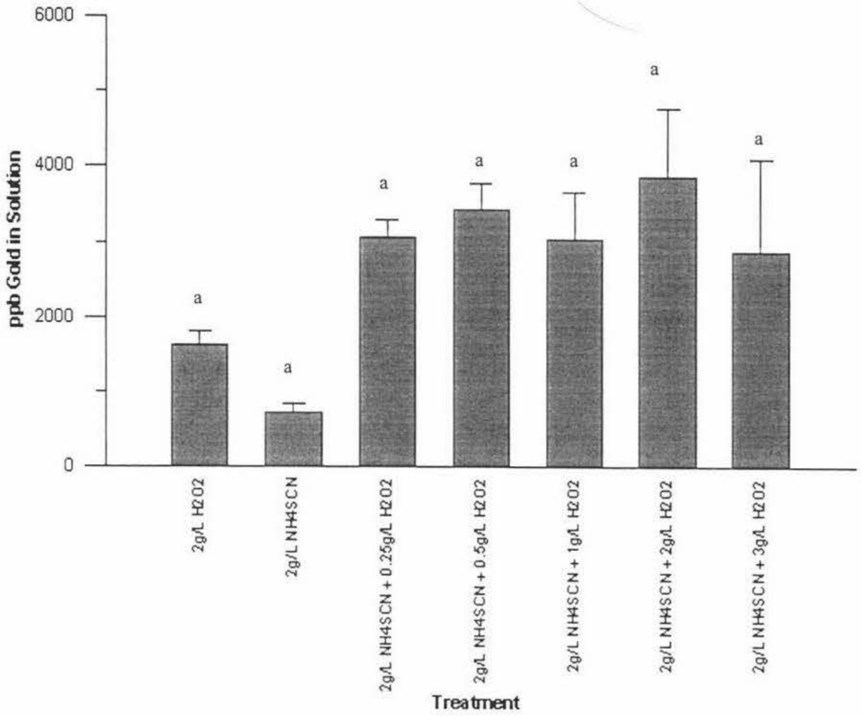

**Figure 3.3** Gold extraction from artificial substrate when thiocyanate concentration is constant and $H_2O_2$ concentration is varied.

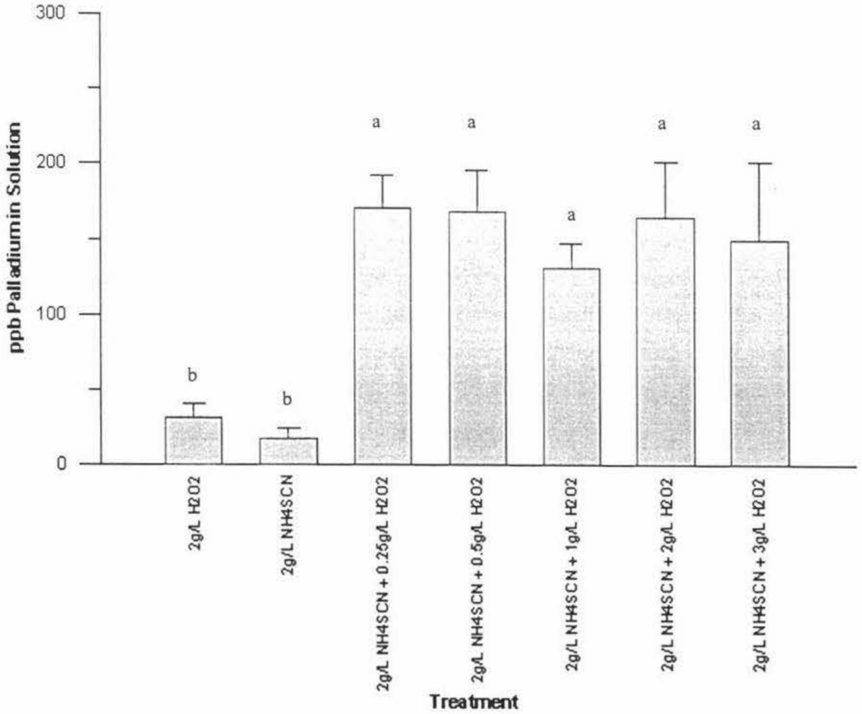

**Figure 3.4** Palladium extraction from artificial substrate when thiocyanate concentration is constant and $H_2O_2$ concentration is varied.

### *Thiocyanate/$H_2O_2$ Oxidative System*

It is already well established that the oxidation of thiocyanate leads to the formation of cyanide. In an aqueous thiocyanate/$H_2O_2$ system, $H_2O_2$ may be reacting to form small quantities of cyanide, according to equation 33 below (molar and mass equivalents are also written):

$$\underset{\substack{\text{3mol*34.01g/mol} \\ \text{= 102.03g}}}{3H_2O_2} + \underset{\substack{\text{1mol*76.116g/mol} \\ \text{=76.116 g}}}{NH_4SCN} \rightarrow SO_4^{2-} + 2H_2O + \underset{\substack{\text{1mol*27.0256g/mol} \\ \text{= 27.0256 g}}}{HCN} + H^+ + NH_4^+ \qquad (33)$$

The mass ratio required for this reaction to go to completion is 1.34 g of $H_2O_2$ per gram of ammonium thiocyanate. This ratio was not reached until 3 $gL^{-1}$ $H_2O_2$ was added to thiocyanate. The quantity of cyanide produced would be limited by the amount of oxidant added at $H_2O_2$ levels less than 3 $gL^{-1}$, leading to an excess of thiocyanate. Assuming that the reaction goes to completion (all $H_2O_2$ is used up in the reaction), a gradual increase in cyanide production with $H_2O_2$ concentration, and subsequent gold extraction, could be expected. Yet extracted gold was the same for all extractants. Table 3.6 shows how much cyanide will be produced by each solution assuming the reaction goes to completion. As the levels of gold extracted were very similar across all thiocyanate/$H_2O_2$ solutions, it is possible that not all $H_2O_2$ is being used up in reaction, and $H_2O_2$ and thiocyanate may be acting independently to oxidise and complex gold.

The explanation described in this discussion could also justify the large levels of palladium extracted relative to thiocyanate/Fe(III). Though the intermediate species in the autoreduction of thiocyanate act as powerful oxidants and complexants, they are not as effective as cyanide (Munoz and Miller, 2000). It is possible that the small amount of cyanide produced in the thiocyanate/$H_2O_2$ system is enough to induce greater palladium dissolution than the intermediate species in the thiocyanate/Fe(III) system. It is also possible that any unreacted $H_2O_2$ and thiocyanate may be acting independently to dissolve palladium. $H_2O_2$ is a more powerful oxidant than Fe(III), and would thus be able to oxidise palladium more effectively.

**Table 3.6** Concentration of cyanide in solution when $H_2O_2$ is added to thiocyanate, varying hydrogen peroxide concentration

| Solution | Concentration of cyanide produced in solution (g/L) |
|---|---|
| 30 mL 2g/L $NH_4SCN$ + 0.25g/L $H_2O_2$ | 0.064 |
| 30 mL 2g/L $NH_4SCN$ + 0.5g/L $H_2O_2$ | 0.128 |
| 30 mL 2g/L $NH_4SCN$ + 1.0g/L $H_2O_2$ | 0.256 |
| 30 mL 2g/L $NH_4SCN$ + 2.0g/L $H_2O_2$ | 0.512 |
| 30 mL 2g/L $NH_4SCN$ + 3.0g/L $H_2O_2$ | 0.684 |

Note: The above table assumes completion of the reaction, according to equation 33.

<u>Summary</u>: Very good gold and palladium extraction was observed by thiocyanate/$H_2O_2$. Two possible situations exist in the thiocyanate/$H_2O_2$ system.

1. $H_2O_2$ is oxidising thiocyanate to cyanide, and this species may be dissolving gold and palladium.

2. As it seems unlikely that all $H_2O_2$ is being used in the production of cyanide, the possibility remains that $H_2O_2$ and thiocyanate are acting independently to oxidise and complex gold and palladium.

It is unknown to what extent each of these mechanisms is acting.

*Varying the Level of Fe(III) and Potassium Iodide with Thiocyanate*

The addition of Fe(III) to thiocyanate increased Eh and decreased pH (Table 3.7). This was predicted, due to the high acidity and redox potential characteristics of Fe(III) and iodide.

The amount of palladium extracted by thiocyanate alone is quite low compared to the previous thiocyanate extractions. An ANOVA testing for difference between palladium concentrations extracted by thiocyanate solutions (without amendment) in Table 3.4, Table 3.5, and Table 3.7 shows a significant difference between these means (p=0.036). The level of gold extracted by thiocyanate in the three extraction experiments was not significantly different.

**Table 3.7** Extraction of gold and palladium from artificial substrate with constant thiocyanate + varying ferric sulphate + varying potassium iodide.

| | | | ng of metal extracted per g of substrate (ppb) | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L $NH_4SCN$ | 180 | 6.0 | 1110 | 8.35 | 464 | 0.43 |
| 30 mL 2g/L $NH_4SCN$ + 1g/L $Fe_2(SO_4)_3$ + 0.5g/L KI | 309 | 2.9 | 5280 | 64.2 | 4180 | 23.2 |
| 30 mL 2g/L $NH_4SCN$ + 0.5g/L $Fe_2(SO_4)_3$ + 0.25g/L KI | 307 | 3.2 | 6930 | 63.0 | 4330 | 24.8 |
| 30 mL 2g/L $NH_4SCN$ + 1g/L $Fe_2(SO_4)_3$ + 0.25g/L KI | 275 | 3.1 | 3150 | 77.8 | 1030 | 32.4 |
| 30 mL 2g/L $NH_4SCN$ + 1g/L $Fe_2(SO_4)_3$ + 1g/L KI | 360 | 2.9 | 3500 | 71.1 | 1920 | 13.7 |
| 30 mL 2g/L $NH_4SCN$ + 0.25g/L $Fe_2(SO_4)_3$ + 1g/L KI | 299 | 3.8 | 3810 | 111 | 792 | 33.8 |
| 30 mL 2g/L $NH_4SCN$ + 0.25g/L $Fe_2(SO_4)_3$ + 0.25g/L KI | 296 | 3.8 | 8100 | 78.8 | 4840 | 10.1 |

The idea to perform this experiment was based largely on work completed by Barbosa-Filho and Monhemius (1994d) and Monhemius and Ball (1995), where up to 93.7% of gold was extracted from an ore using a mixture of thiocyanate, Fe(III), and iodide. Previous experiments (refer to Table 3.3) have shown that this combination of oxidants and complexant works well. Varying the relative concentrations of Fe(III) and iodide have no effect on the amount of gold or palladium extracted from the artificial ore, as there was no significant difference between the means for both gold and palladium.

The results from the thiocyanate/Fe(III)/iodide experiment for both gold and palladium are very similar to the results from the thiocyanate/Fe(III) extractions. There is nothing in these results to suggest that there is any benefit in adding iodide to the thiocyanate/Fe(III) system. The contrast of this data with that of Barbosa-Filho and Monhemius (1994d) and Monhemius and Ball (1995) suggests that the effect of iodine could be substrate specific. This was not investigated further in the current study.

Summary: Good gold and palladium extraction was observed with all combinations of Fe(III), potassium iodide, and thiocyanate. However, there seems little benefit in introducing iodide to thiocyanate/Fe(III) as gold and palladium extraction was not improved.

*Varying the level of Fe(III) with Thiourea*

Table 3.8 outlines the Eh, pH , and metal dissolution results for this set of extractions. Eh increased with the increase in concentration of oxidant. Likewise, pH decreased as Fe(III) concentration increased.

**Table 3.8** Extraction of gold and palladium from artificial substrate with constant thiourea + varying ferric sulphate

| | | | **ng of metal extracted per g of substrate (ppb)** | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L $Fe_2(SO_4)_3$ | 488 | 2.5 | 73.7 | 13.8 | 128 | 1.04 |
| 30 mL 2g/L thiourea | 89 | 6.6 | 1750 | 0.00 | 322 | 0.00 |
| 30 mL 2g/L thiourea + 0.25g/L $Fe_2(SO_4)_3$ | 144 | 4.3 | 2380 | 0.00 | 28.4 | 0.00 |
| 30 mL 2g/L thiourea + 0.5g/L $Fe_2(SO_4)_3$ | 165 | 3.4 | 2530 | 0.00 | 252 | 0.00 |
| 30 mL 2g/L thiourea + 1.0g/L $Fe_2(SO_4)_3$ | 180 | 3.1 | 2610 | 11.6 | 132 | 3.18 |
| 30 mL 2g/L thiourea + 2.0g/L $Fe_2(SO_4)_3$ | 212 | 2.6 | 2170 | 31.8 | 945 | 22.9 |
| 30 mL 2g/L thiourea + 3.0g/L $Fe_2(SO_4)_3$ | 232 | 2.4 | 3360 | 47.0 | 1430 | 5.25 |

Note: The straight thiourea result of 1750 ppb seems very high, and it is likely that contamination has played a part in this result.

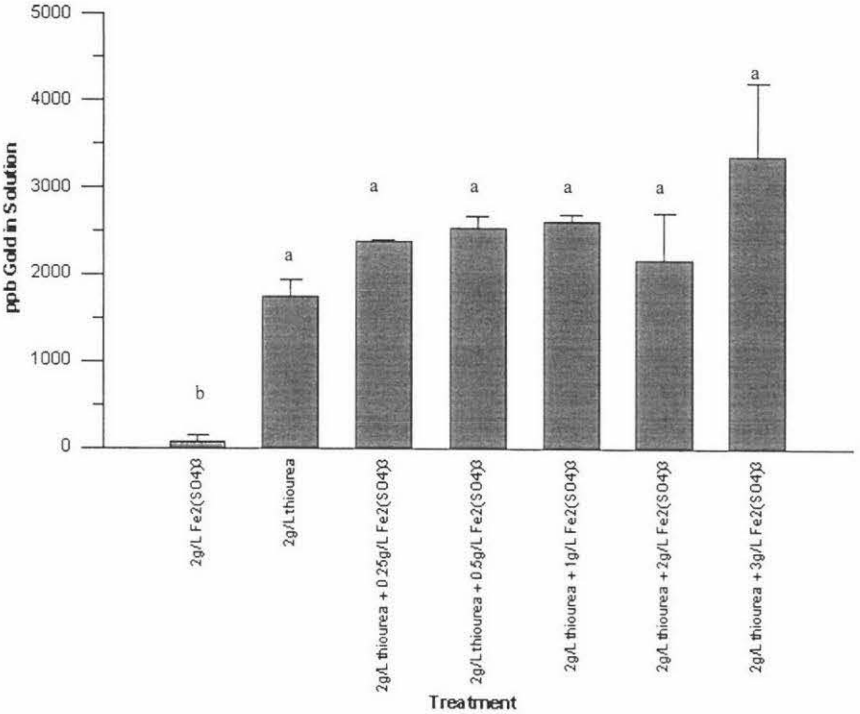

**Figure 3.5** Gold extraction from artificial substrate when thiourea concentration is constant and Fe(III) concentration is varied

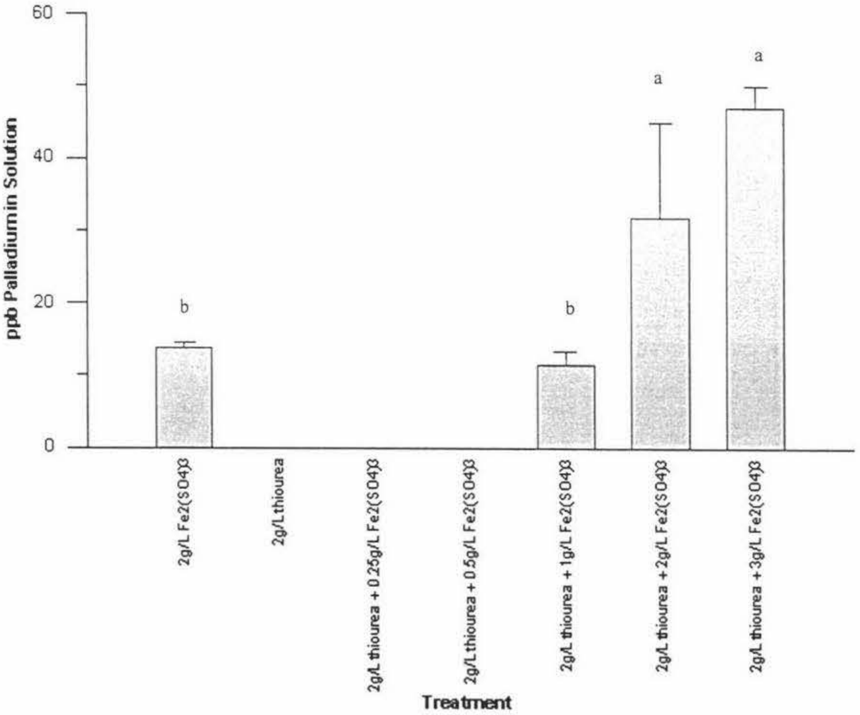

**Figure 3.6** Palladium extraction from artificial substrate when thiourea concentration is constant and Fe(III) concentration is varied

Good gold extraction was observed throughout the range of Fe(III) concentrations (Figure 3.5, Table 3.8). Very high extraction was also observed with thiourea alone. An ANOVA shows that, again, the concentration of Fe(III) in the range tested does not appear to have an effect on the total amount of gold extracted. While the amount of gold extracted is reasonably high, it is not near the amounts extracted when thiocyanate is mixed with ferric sulphate. The thiocyanate/$H_2O_2$ combination also outperforms thiourea/Fe(III) in this regard. An ANOVA completed on these two sets of results confirmed that there is a significant difference between the means ($p=0.044$).

Palladium extraction was not observed until 1 $gL^{-1}$ $Fe_2(SO_4)_3$ was added to thiourea (Figure 3.6, Table 3.8). The level of palladium extraction increased with an increase in concentration of the oxidant. However, even the highest result (47.0 ppb, achieved when 3 $gL^{-1}$ $Fe_2(SO_4)_3$ was added to the thiourea) is much lower than results we have already seen with thiocyanate plus an oxidant.

Thiourea can be oxidised to formamadine disulphide (FD), an intermediate species in the overall oxidation of thiourea, and that this in itself is a powerful oxidizing agent. This may be playing a role in the thiourea/Fe(III) system; the intermediate species formed when Fe(III) is added to thiocyanate may simply be better oxidants and complexants than FD and thiourea. A comparison between the Eh and pH values (Tables 3.4 and 3.8) certainly shows that the redox potential and acidity in the thiocyanate/Fe(III) are far more conducive to the extraction of gold. The fact that no palladium was extracted at the low concentrations of Fe(III) supports this theory.

It also appears likely that as more ferric ions are added to thiourea more FD is produced, thus enabling gold to be oxidised in sufficient amounts such that complexing with any remaining thiourea is noticeable. Equation 34 shows the reaction of hydrated ferric sulphate with thiourea.

$$\underset{\substack{2\text{mol}*27.116\text{g/mol}\\=152.232\text{ g}}}{2SC(NH_2)_2} + \underset{\substack{1\text{mol}*562.004\text{g/mol}\\=562.004\text{g}}}{Fe_2(SO_4)_3.9H_2O} \rightarrow \underset{\textbf{FD}}{NH_2(NH)CSSC(NH)NH_2} + 2H^+ + SO_4^{2-} + 9H_2O \qquad (34)$$

A mass ratio of 3.69 g $Fe_2(SO_4)_3.9H_2O$ to 1 g thiourea is required for this reaction to go to completion and produce the maximum amount of FD. As this ratio was never reached in this experiment, most FD would have been produced when the most concentrated Fe(III) solution was added to thiourea. A situation would therefore exist where, as more Fe(III) is added, more FD is produced, but thiourea would still have been present to complex with gold. This mechanism could also explain the increase in solution palladium concentration with increasing ferric ion concentration. At low levels of Fe(III) not enough FD exists to oxidise palladium, whereas at the higher concentrations of Fe(III) the concentration of FD may be large enough to induce palladium into solution and subsequently complex with thiourea.

Summary: Extraction of gold was good, though addition of Fe(III) to thiourea is not as effective as the addition of Fe(III) to thiocyanate. Palladium extraction was poor, and was non existent at lower levels of Fe(III). It is likely that FD is being produced, and this species appears to be playing a role in the oxidation of gold and palladium from the artificial substrate.

### *Varying the Level of $H_2O_2$ with Thiourea*

The Eh, pH, and metal extraction results are presented in Table 3.9. The trend of decreasing pH and increasing pH with increasing concentration of oxidant was again observed.

Gold extraction was poor at all levels of $H_2O_2$ (Figure 3.9) although there was noticeably more gold at the higher concentrations of oxidant. The trend appears to be increasing gold concentration in solution with increasing $H_2O_2$ concentration. Aside from straight oxidant, there was no noticeable palladium extraction at all concentrations of hydrogen peroxide (Table 3.9 and Figure 3.10).

Close analysis of both the thiourea/Fe(III) and thiourea/$H_2O_2$ results leads to an interesting discussion. The pattern of increasing palladium extraction with increasing Fe(III) concentration emerges for gold when thiourea/$H_2O_2$ is used as the extractant. Figures 3.7 and 3.8 demonstrate this graphically, with regression analysis returning almost identical

**Table 3.9** Extraction of gold and palladium from artificial substrate with constant thiourea + varying hydrogen peroxide

| | | | ng of metal extracted per g of substrate (ppb) | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 2g/L $H_2O_2$ | 350 | 4.1 | 376 | 14.8 | 165 | 5.38 |
| 30 mL 2g/L thiourea | 90 | 6.3 | 333 | 5.33 | 191 | 1.48 |
| 30 mL 2g/L thiourea + 0.25g/L $H_2O_2$ | 70 | 5.3 | 576 | 4.93 | 142 | 1.02 |
| 30 mL 2g/L thiourea + 0.5g/L $H_2O_2$ | 86 | 4.3 | 576 | 1.79 | 59.7 | 1.59 |
| 30 mL 2g/L thiourea + 1.0g/L $H_2O_2$ | 82 | 4.5 | 849 | 3.60 | 95.4 | 2.62 |
| 30 mL 2g/L thiourea + 2.0g/L $H_2O_2$ | 100 | 4.0 | 1310 | 0.00 | 180 | 0.00 |
| 30 mL 2g/L thiourea + 3.0g/L $H_2O_2$ | 150 | 3.5 | 1540 | 2.18 | 490 | 3.78 |

Note: Discrepancies between different data sets with regard to Eh and pH have been observed. The pH of $H_2O_2$ of 4.1 in this data set compared to 5.6 in Table 3.5 is an example of this. However, the general trend of increasing Eh and decreasing pH with increasing oxidant concentration has remained across all extraction experiments.

$R^2$ values. This implies that the change in gold uptake when varying $H_2O_2$ with thiourea is the same as the change in palladium uptake when Fe(III) is altered with constant thiourea. In both cases, metal extraction is small or negligible up to a concentration of 2

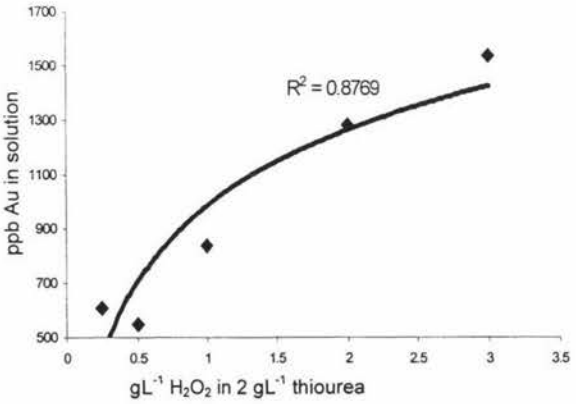

**Figure 3.7** Pattern of gold extraction from artificial substrate for thiourea + $H_2O_2$

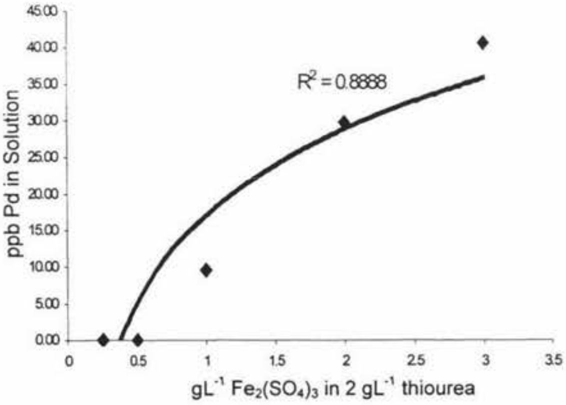

**Figure 3.8** Pattern of palladium extraction from artificial substrate for thiourea + Fe(III)

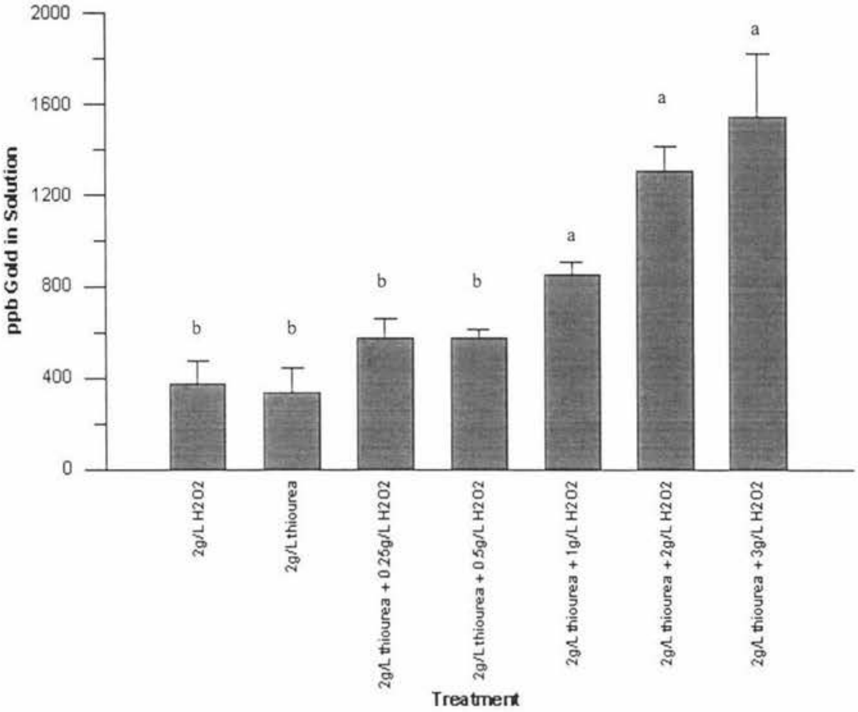

**Figure 3.9** Gold extraction from artificial substrate when thiourea concentration is constant and $H_2O_2$ concentration is varied

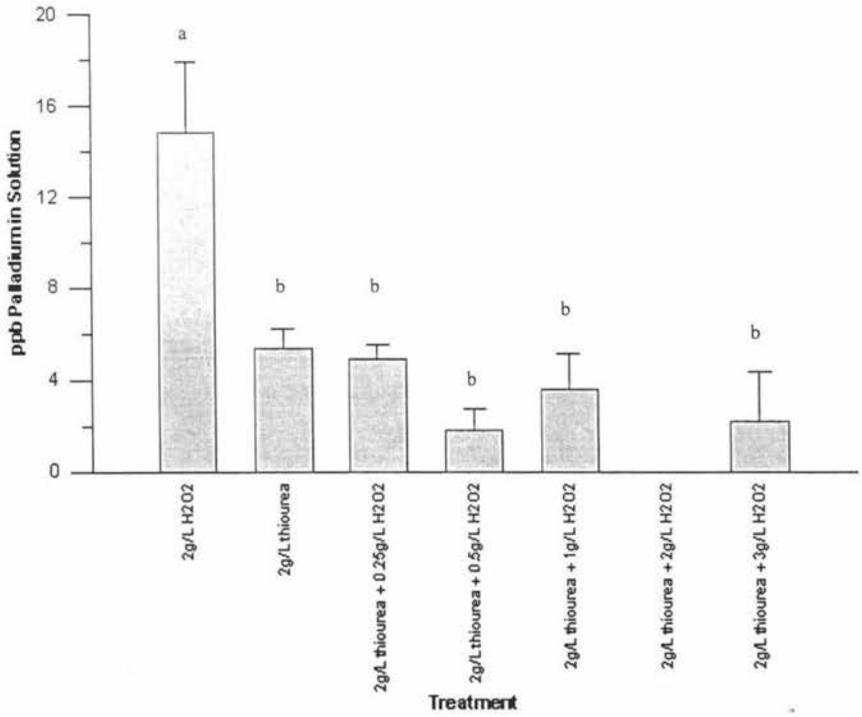

**Figure 3.10** Palladium extraction from artificial substrate when thiourea concentration is constant and $H_2O_2$ concentration is varied

$gL^{-1}$ oxidant, at which point a pattern of increasing gold/palladium extraction emerges.

The mass ratio of oxidant to complexant for the complete formation of FD in the thiourea/ $H_2O_2$ system is 4.48 g thiourea to 1g $H_2O_2$. Equation 35 shows this reaction.

$$2(SC(NH_2)_2) + H_2O_2 \rightarrow FD + 2H_2O \qquad (35)$$

2mol*76.116g/mol    1mol*34.015g/mol

= 152.232 g    = 34.015 g

This ratio of 4.48 is reached in this trial with a low $H_2O_2$ concentration of between 0.25 $gL^{-1}$ and 0.5 $gL^{-1}$. This means that for $H_2O_2$ concentrations 0.5 $gL^{-1}$ and above in this experiment, there would be an excess of $H_2O_2$ present in solution. With the gradual increase in gold dissolution as $H_2O_2$ concentration increases it is likely that excess $H_2O_2$ is playing a role. The problem remains, however, that if the reaction is going to completion there would be no thiourea for gold to complex with. While $H_2O_2$ is a strong oxidant, it reacts slowly (Hampel and Hawley, 1973). It is possible that the reaction is not going to completion and $H_2O_2$, and not FD, is the species predominantly responsible for oxidising gold present in the substrate.

This principle would also explain the palladium results for thiourea/Fe(III). With Fe(III) being a poorer oxidant than $H_2O_2$ (Stark and Wallace, 1991), less thiourea would be oxidised to FD, leaving more Fe(III), especially at the higher concentrations, to assist in the extraction of palladium. It may also be that Fe(III) is not powerful enough an oxidant to oxidise thiourea. This contradicts arguments in the previous section where it was proposed that the increase in Fe(III) concentration led to increased palladium extraction due to more FD being produced.

There is simply not enough evidence here to suggest that one argument is correct and the other wrong. An in depth analysis of the composition of the extractants, as well as the oxidation potential of FD, would help establish exactly what is happening in these geochemical systems.

Summary: Gold extraction with thiourea/$H_2O_2$ was low, while palladium extraction was negligible. The production of the intermediate species FD again seems to be playing a role. The presence of any excess $H_2O_2$ appears to be an important variable in the extraction of gold from artificial substrate using thiourea/$H_2O_2$ solution.

### *3.3.2b Extractions Where Concentration of Thiocyanate is Varied*

*Varying the Level of Thiocyanate with Fe(III)*

The Eh, pH, and metal extraction results are reported in Table 3.10. The pH of solutions increased with an increase in thiocyanate concentration, while the Eh decreased. The change in these two variables is only very slight relative to experiments where oxidising agent was varied. For example, Eh decreases from 463 mV to 434 mV across the range of concentrations tested, while pH increased only 0.2 units, from 3.1 to 3.3. Table 3.4 shows the results for pH and Eh when the concentration of Fe(III) is varied. Comparison of these two sets of results indicates that Eh and pH are more dependent on the concentration of Fe(III) than thiocyanate.

**Table 3.10** Extraction of gold and palladium from artificial substrate with constant ferric sulphate + varying thiocyanate

| | | | **ng of metal extracted per g of substrate (ppb)** | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 0.5g/L $Fe_2(SO_4)_3$ | 504 | 2.8 | 104 | 0.00 | 20.3 | 0.00 |
| 30 mL 2g/L $NH_4SCN$ | 276 | 6.5 | 1530 | 58.3 | 113 | 20.2 |
| 30 mL 0.5g/L $Fe_2(SO_4)_3$ + 0.25g/L $NH_4SCN$ | 463 | 3.1 | 13200 | 139 | 1840 | 9.11 |
| 30 mL 0.5g/L $Fe_2(SO_4)_3$ + 0.5g/L $NH_4SCN$ | 461 | 3.1 | 14800 | 196 | 1790 | 52.4 |
| 30 mL 0.5g/L $Fe_2(SO_4)_3$ + 1.0g/L $NH_4SCN$ | 453 | 3.2 | 14400 | 171 | 2480 | 37.4 |
| 30 mL 0.5g/L $Fe_2(SO_4)_3$ + 2.0g/L $NH_4SCN$ | 444 | 3.2 | 16200 | 282 | 3740 | 70.3 |
| 30 mL 0.5g/L $Fe_2(SO_4)_3$ + 3.0g/L $NH_4SCN$ | 434 | 3.3 | 16000 | 231 | 1330 | 215 |

Figure 3.11 compares the amount of gold extracted between the various thiocyanate concentrations. Addition of Fe(III) to thiocyanate solution significantly increased the

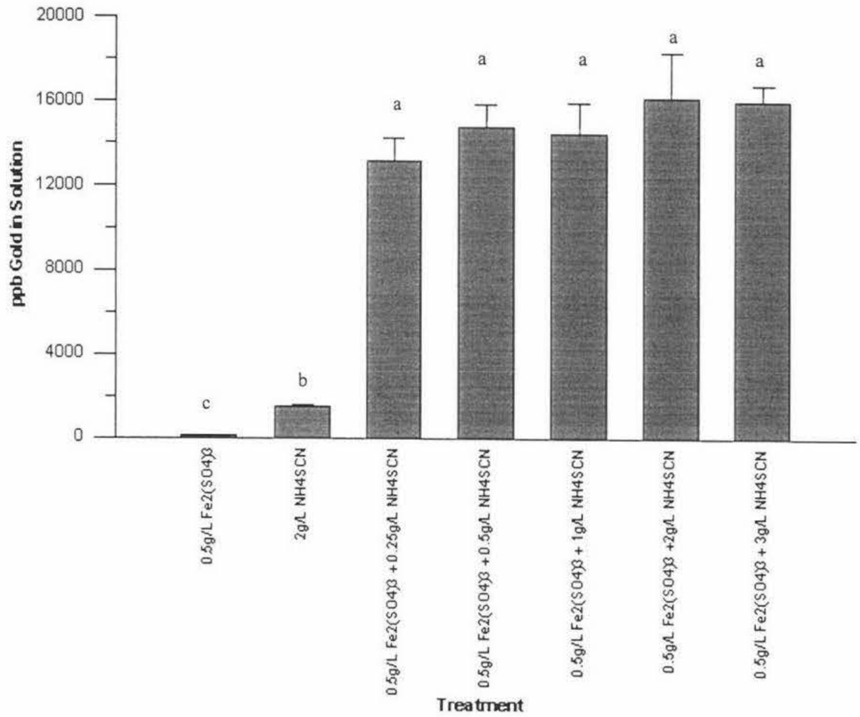

**Figure 3.11** Gold extraction from artificial substrate when thiocyanate concentration is varied and Fe(III) concentration is constant

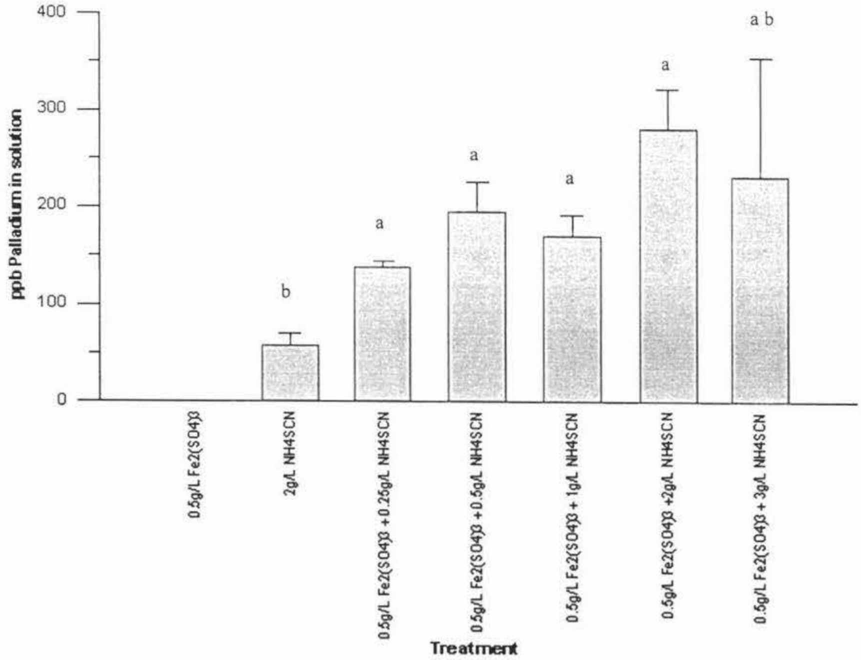

**Figure 3.12** Palladium extraction from artificial substrate when thiocyanate concentration is varied and Fe(III) concentration is constant

amount of gold extracted, although there was no significant difference between varying amounts of Fe(III). Extraction by thiocyanate and Fe(III) alone was low. The fact that there is no significant difference between the means could be explained by the low concentration of Fe(III). It is possible that at 0.5 $gL^{-1}$, all the ferric ions are being used up in the production of the intermediate species thiocyanate and thiocyanogen, with any remaining thiocyanate after this process playing an insignificant role in the dissolution of gold, as shown by the relatively poor extraction of gold by thiocyanate alone. It is also possible that all gold is already extracted at a $Fe_2(SO_4)_3$ concentration of 0.5 $gL^{-1}$.

As in the previous thiocyanate/Fe(III) extractions, the reason for the observed extraction trend could be that, in the thiocyanate/Fe(III) system, gold dissolution is simply a function of Eh and pH. As pH decreases and Eh increases, the amount of gold extracted from the substrate is seen to increase. Gold-thiocyanate complexes have a high geochemical stability in high Eh, low pH solutions, and it is therefore expected that greater gold dissolution will be observed under these conditions.

The results of the palladium extractions are also shown in Table 3.10 and Figure 3.12. Addition of Fe(III) significantly increased palladium dissolution although there was no significant difference between thiocyanate + 3 $gL^{-1}$ $Fe_2(SO_4)_3$ and thiocyanate alone due to large variability in extractions by the former solution. Levels of extraction by Fe(III) were negligible. Levels of palladium extracted by thiocyanate/Fe(III) in this experiment are greater than those observed in section 3.3.2a. This perhaps indicates that palladium dissolution is more dependent on thiocyanate than Fe(III) concentration. Another reason for the consistency of these results is that it appears all extractable palladium has been dissolved. This will be discussed further below.

Summary: Very large levels of gold extraction were observed, with possibly all gold being dissolved. Dissolution of gold in the thiocyanate/Fe(III) system appears to be a function of Eh and pH. Palladium dissolution was also very high. Thiocyanate concentration appears to be more dependent on thiocyanate concentration than Fe(III) concentration.

### *Varying the Level of Thiocyanate with $H_2O_2$*

Eh, pH, and metal dissolution results are presented in Table 3.11. Very little change in Eh and pH of solutions was observed. As the concentration of thiocyanate was increased the pH decreased while Eh increased, though these changes were very small.

Table 3.11 shows that Eh and pH varied little with various thiocyanate concentrations, yet Figure 3.13 shows that gold solubility increased with increasing thiocyanate concentration. This is further evidence that gold solubility in the thiocyanate/$H_2O_2$ system is independent of Eh and pH.

**Table 3.11** Extraction of gold and palladium from artificial substrate with constant hydrogen peroxide + varying thiocyanate

| | | | **ng of metal extracted per g of substrate (ppb)** | | | |
|---|---|---|---|---|---|---|
| **Extractant** | **Eh** | **pH** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 30 mL 0.5g/L $H_2O_2$ | 276 | 6.4 | 2480 | 0.00 | 249 | 9.32 |
| 30 mL 2g/L $NH_4SCN$ | 228 | 6.3 | 1120 | 20.5 | 439 | 12.9 |
| 30 mL 0.5g/L $H_2O_2$ + 0.25g/L $NH_4SCN$ | 312 | 6.2 | 3720 | 154 | 550 | 30.0 |
| 30 mL 0.5g/L $H_2O_2$ + 0.5g/L $NH_4SCN$ | 330 | 6.0 | 4210 | 83.3 | 568 | 17.7 |
| 30 mL 0.5g/L $H_2O_2$ + 1.0g/L $NH_4SCN$ | 328 | 5.9 | 7860 | 126 | 868 | 43.1 |
| 30 mL 0.5g/L $H_2O_2$ + 2.0g/L $NH_4SCN$ | 337 | 5.8 | 14200 | 146 | 337 | 76.4 |
| 30 mL 0.5g/L $H_2O_2$ + 3.0g/L $NH_4SCN$ | 336 | 5.7 | 15000 | 174 | 693 | 48.2 |

When hydrogen peroxide is added to thiocyanate, cyanide is produced (equation 33). One of the reasons for the increase in gold dissolution with thiocyanate could be that, at low thiocyanate concentrations, all the thiocyanate is being oxidised to cyanide, thereby limiting the amount of gold that can be dissolved. As previously discussed, in a thiocyanate/$H_2O_2$ solution maximum cyanide is produced when the ratio of oxidant to complexant is 1.34. This ratio is reached early in this set of extractions, which infers that should the reaction be going to completion, the level of cyanide in all of the solutions will be the same. Table 3.12 shows how much cyanide will be produced for each solution assuming the reaction goes to completion. If cyanide alone is inducing gold extraction then one would expect the amount of gold extracted to be similar across the range of solutions tested. This is not the case, and an ANOVA shows that the means across the various combinations of thiocyanate/$H_2O_2$ are significantly different. As in the experiments where the concentration of oxidant was altered it appears that it is not just the production of cyanide that is having an effect. $H_2O_2$ and thiocyanate may be acting independently to oxidise and complex with gold respectively.

**Table 3.12** Concentration of cyanide in solution with varying concentrations of thiocyanate are added to 0.5 $gL^{-1}$ $H_2O_2$

| Solution | Concentration of cyanide produced in solution (g/L) |
|---|---|
| 30 mL 0.5g/L $H_2O_2$ + 0.25g/L $NH_4SCN$ | 0.0866 |
| 30 mL 0.5g/L $H_2O_2$ + 0.5g/L $NH_4SCN$ | 0.127 |
| 30 mL 0.5g/L $H_2O_2$ + 1.0g/L $NH_4SCN$ | 0.127 |
| 30 mL 0.5g/L $H_2O_2$ + 2.0g/L $NH_4SCN$ | 0.127 |
| 30 mL 0.5g/L $H_2O_2$ + 3.0g/L $NH_4SCN$ | 0.127 |

Note: The above table assumes completion of the reaction according to equation 33.

Levels of palladium dissolved are even across the full range of thiocyanate + $H_2O_2$ concentrations used (Figure 3.14). An ANOVA across these results shows no significant difference in palladium extracted. One explanation is that, as the level of $H_2O_2$ is constant, this is the limiting factor in the production of cyanide (refer to section 3.3.2a), and the level of cyanide produced will be constant across all of the thiocyanate/$H_2O_2$ solutions. Any excess thiocyanate present in these solutions will therefore have minimal effect, especially as this species extracts relatively little palladium alone. It appears, therefore, that palladium is complexing primarily with cyanide in the solutions tested. An ANOVA comparing the palladium results for thiocyanate + oxidant from Tables 3.10 and 3.11 showed that there was no significant difference between these sets of results (p=0.063).

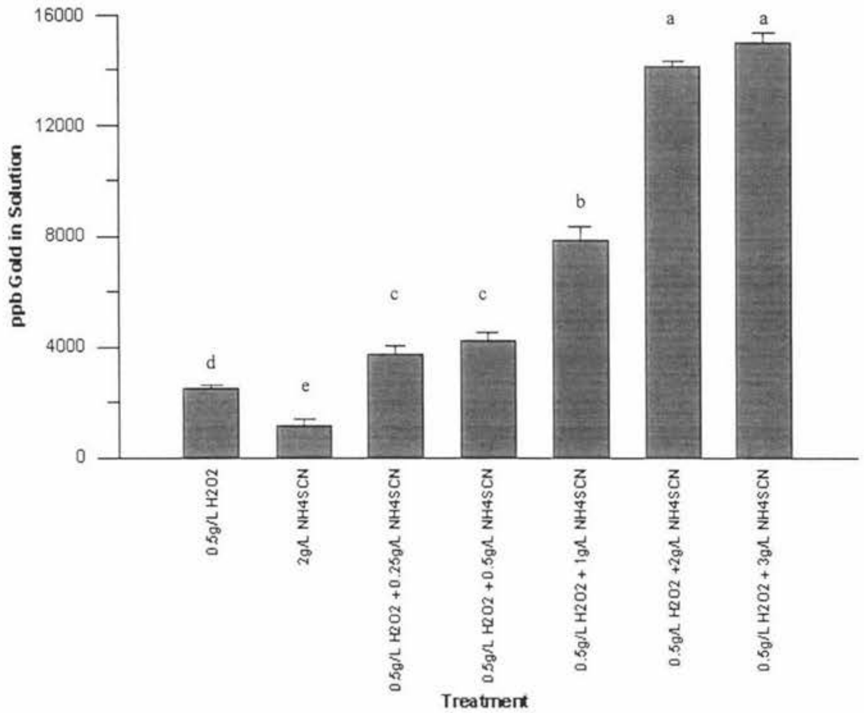

**Figure 3.13** Gold extraction from artificial substrate when $H_2O_2$ concentration is constant and thiocyanate concentration is varied.

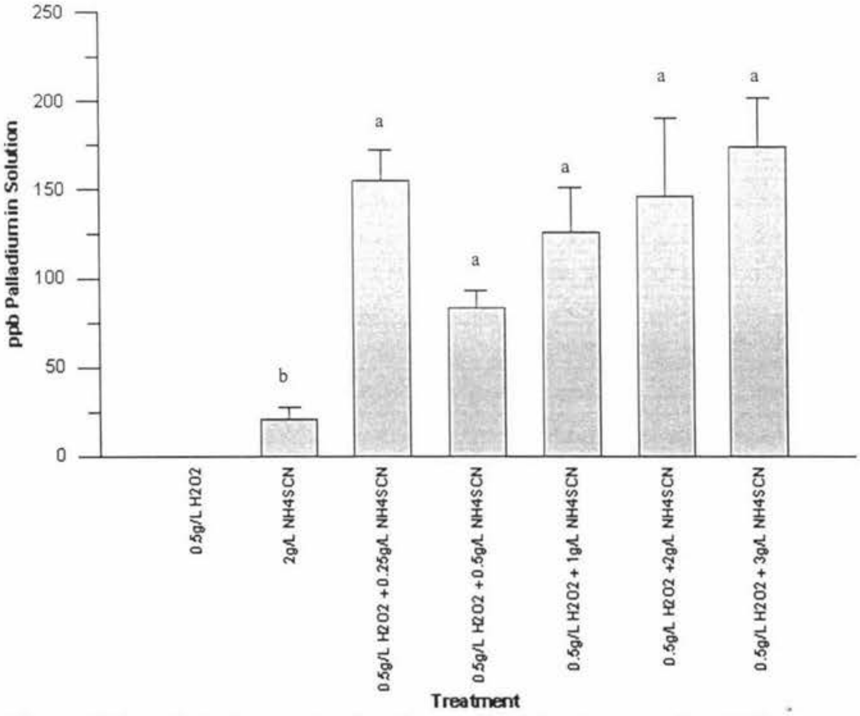

**Figure 3.14** Palladium extraction from artificial substrate when $H_2O_2$ concentration is constant and thiocyanate concentration is varied.

One reason for this could be that all extractable palladium has been dissolved by both sets of solutions. This certainly seems feasible as digestion analysis of the artificial substrate showed it to contain only 148 ppb Pd. Indeed, with both sets of extractions yielding an average of around 156ppb, it is likely that any cyanide produced has dissolved all palladium present. It appears that this is also the case with the thiocyanate/Fe(III) extractions (refer to Table 3.10).

Summary: Thiocyanate/$H_2O_2$ extraction of gold appears to be independent of Eh and pH. Gold dissolution does not appear to be a function solely of cyanide present in solution, and may be a result of $H_2O_2$ and thiocyanate acting independently to oxidise and complex with gold respectively. Cyanide appears to be the major species with which palladium is forming complex ions.

## 3.4 Conclusions

- **Initial extractions of gold and palladium from Klipfontein substrate revealed the thioligands to be better extractants of gold and palladium than other species commonly found in groundwater systems.** This was especially true when the oxidants ferric sulphate and hydrogen peroxide were added to thiocyanate and thiourea. This information was used to carry out further investigation of these oxidants using the artificial substrate.

- **Thiocyanate + ferric sulphate was found to be a very good lixiviant of gold.** Previous studies have shown that the intermediate species in this system played a significant role in gold solubility.

- **Gold extraction by thiocyanate/Fe(III) may be a function of pH and Eh.** Very large gold extraction in this system was observed under high Eh, low pH conditions.

- **The addition of hydrogen peroxide to thiocyanate dramatically increased gold and palladium uptake.** As hydrogen peroxide is a very strong oxidant it is postulated that cyanide is being produced and it is this species that is dissolving gold and palladium. Gold and palladium solubility in this system does not appear to be dependent on Eh and pH. It is unknown whether the reaction of thiocyanate + hydrogen peroxide is going to completion. The exact magnitude of the effect of the individual species thiocyanate, hydrogen peroxide, and cyanide is unknown and it is possible that all three play a major role in the dissolution of gold and palladium, with $H_2O_2$ and thiocyanate acting independently to oxidise and complex with gold respectively.

- **The addition of iodide to thiocyanate and ferric sulphate did not increase either gold or palladium dissolution.**

- **The addition of Fe(III) to thiourea provided better extraction of gold and palladium than the addition of hydrogen peroxide.** This is possibly due to the production of the intermediate species FD when thiourea is oxidised. The magnitude of the role of FD is unknown and will be dependent on the respective abilities of Fe(III) and $H_2O_2$ to oxidise thiourea, and the rate of this oxidation.

- **Thiocyanate + oxidant offers better extraction of gold and palladium than thiourea + oxidant.**

- **The combination of thiocyanate/Fe(III) resulted in most dissolution of gold.** While this combination also dissolved large quantities of palladium (in some cases all palladium present in substrate), palladium extraction at least as high was observed with thiocyanate/$H_2O_2$.

- **Thiocyanate/Fe(III) and thiocyanate/$H_2O_2$ systems dissolved equal concentrations of palladium.**

# Chapter 4 Plant Uptake of Gold and Palladium

## 4.1 Introduction

Although the induced plant uptake of gold from aqueous solutions was first investigated in 1970 (Shacklette *et al.*), phytomining of this metal was not proposed until the late 1990's (Anderson, 2000). The induced plant uptake of palladium is without precedent.

Metals must be in an aqueous form in order for plant uptake. Plant uptake of a metal will therefore be limited by the concentration of metal in solution. Typically in the environment, gold and PGMs are oxidised from a solid ore, and then form complex ions with species such as chloride, thiosulphate, hydroxide, and thiocyanate that are available for complexing. It is these complex ions that the plants are able to accumulate.

*Berkheya coddii* and *Brassica juncea* were the two species of plants investigated. These species had been shown by Anderson (2000) to grow well in substrates containing high concentrations of metals.

Solutions used to treat plants were based on results from extraction trials. Treatments that had been observed to extract large quantities of gold and palladium were used subsequently in plant trials. Extraction experiments and plant trials were undertaken concurrently.

KCN was amongst the solutions used to treat plants. While a dangerous solution to handle, the very good extraction of gold by cyanide, as evidenced by it's widespread use in the mining industry, meant that this chemical could not be ignored as a treatment.

As induced plant uptake of gold is already well documented (Anderson, 2000), the aims of this section of study were to maximise plant uptake of gold. It was also hoped to induce plant uptake of palladium and maximise any uptake that did take place.

## 4.2 Methods and Materials – Plant Trials

### 4.2.1 Trial Design and Experimental Method

#### *4.2.1.1 Seeding and Growth of Plants*

*Brassica juncea* and *Berkheya coddii* were initially seeded in potting mix, and watered daily inside. Once the first pair of leaves were visible, seedlings were transplanted to 200 mL pots containing substrate. The plants were watered every day until roots could just be seen growing through the bottom of the pots (approximately 6 weeks). At this stage treatment of the plants took place. All plant trials took place in a greenhouse.

#### *4.2.1.2 Plant Treatments*

All plant treatments were based on 0.5g thiochemical[•]/kg of substrate. This application rate was chosen based on previous work of Anderson (2000). All treatments involved either thiocyanate, thiourea, or cyanide, and included control plants. A mass of approximately 200g substrate was present in every pot, and 10 mL chemical solution volume was used for every treatment, using 10 g/L thiocyanate, thiourea, or cyanide solutions. Replicates (3-6) were used for every treatment

#### *4.2.1.3 Harvesting and Analysis of Plants*

Plants were harvested when necrosis set in , or after 10 days. Only aerial parts of plants were harvested. These were then dried for 24 hours in a 70°C oven. Samples were homogenized by breaking down with scissors.

### 4.2.2 Preparation of Plant Growth Substrates

Growth substrates used were Klipfontein and artificial substrate. These were prepared as per Methods and Materials, section 3.2.

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[•] Refers to cyanide as well as thiocyanate and thiourea

### 4.2.3 Analytical Methods

*Ashing and Digestion*

**1** Approximately 0.1 g of the homogenized plant sample is weighed into borosilicate ashing tubes

**2** Tubes are packed into a beaker and then placed in the muffle furnace at 530°C overnight.

**3** The ash is transferred to 50 mL conical flasks and 10 mL *aqua regia* added. The mixture is boiled until approximately 3 mL remains.

**4** A further 5 mL of concentrated HCl is then added to each flask and the digestion continued until approximately 3 mL remains.

**5** The digestion solution is transferred to 10 mL tubes and made to volume with RO water.

**6** For gold analysis, 1mL of MIBK is added, and the tube sealed and shaken.

**7** For platinum and palladium analysis, 0.1 mL of 100% KI solution is added prior to MIBK. The tube is then sealed and shaken.

**8** The MIBK fraction is subsequently removed from the tube and analysed by GFAAS.

A sample blank is included in all digestions at a rate of at least 1 per 20 samples.

### 4.2.4 Statistical Analysis

Analyses of variance (ANOVAs) were used to test for significant difference between means of data. In all cases the 5% level of significance has been used. Error bars on graphs represent standard error of the means. In all cases the 5% level of significance has been used. Error bars in all graphs represent standard error of the means. Means with the same letter on graphs are not significantly different (ANOVA $p>0.05$).

## 4.3 Results and Discussion

### 4.3.1 Plant Uptake from Klipfontein Substrate – Initial Trials

For the first set of plant uptake results, both *Berkheya coddii* and *Brassica juncea* were investigated. Tables 4.1a and 4.1b show the results from this trial. Plant uptake of gold and palladium was similar for both *B. coddii* and *B. juncea. Berkheya coddii* seeds were readily available and grew well in the mixed Klipfontein/pumice substrate, while *B. Juncea* growth in this substrate was poor. For these reasons, *B. coddii* was the only plant examined for the set of results shown in Table 4.2.

The importance of oxidising agents in promoting metal uptake can be seen in Tables 4.1a,b. A nearly 5-fold increase in gold uptake by *B. coddii* was observed when Fe(III) was added to thiocyanate. This confirms results from previous studies showing increased uptake by plants in this situation (Anderson 2001(a) and 2001(b), unpublished data). *Brassica juncea* also showed an increase in gold uptake, though this was not as pronounced as for the other species. Statistical comparison of gold concentration in plants after thiocyanate/Fe(III) treatment showed that there was no significant difference in gold uptake between *B. coddii* and *B. juncea* ($p=0.58$).

Plant uptake of palladium was observed. Statistical comparison of palladium concentration in plants after thiocyanate/Fe(III) treatment showed that there was no significant difference in palladium uptake between *B. coddii* and *B. juncea* ($p=0.89$). It appears that the induced uptake of gold and palladium is dependent mainly on the treatment used, not plant species. Although the concentrations of accumulated palladium were small, the presence of this metal in the aerial parts of both *B. coddii* and *B. juncea*

**Table 4.1a** Gold and palladium concentrations in *B. coddii* growing in Klipfontein substrate after various chemical amendments

| Treatment | Concentration of metal in dried plant (ppb) Au | Pd | s.d. Au | s.d. Pd |
|---|---|---|---|---|
| 10 mL 10g/L thiourea | 241 | 0.00 | 98.3 | 0.00 |
| 10 mL 10g/L thiourea + 10g/L $Fe_2(SO_4)_3$ | 187 | 0.00 | 19.9 | 0.00 |
| 10 mL 10g/L $NH_4SCN$ | 73.6 | 31.8 | 31.2 | 15.6 |
| 10 mL 10g/L $NH_4SCN$ + 10g/L $Fe_2(SO_4)_3$ | 312 | 7.41 | 209 | 12.8 |
| Control | 0.00 | 0.00 | 0.00 | 0.00 |

**Table 4.1b** Gold and palladium concentrations in *B. juncea* growing in Klipfontein substrate after various chemical amendments

| Treatment | Concentration of metal in dried plant (ppb) Au | Pd | s.d. Au | s.d. Pd |
|---|---|---|---|---|
| 10 mL 10g/L thiourea | 219 | 0.00 | 82.0 | 0.00 |
| 10 mL 10g/L thiourea + 10g/L $Fe_2(SO_4)_3$ | 73.6 | 0.00 | 77.1 | 0.00 |
| 10 mL 10g/L $NH_4SCN$ | 120 | 24.6 | 153 | 13.2 |
| 10 mL 10g/L $NH_4SCN$ + 10g/L $Fe_2(SO_4)_3$ | 237 | 8.44 | 175 | 9.33 |
| Control | 0.00 | 0.00 | 0.00 | 0.00 |

shows that these species can indeed be induced to take up PGMs. The greatest uptake of palladium was induced using thiocyanate alone. This result was unexpected based upon experience gained from the geochemical component of the study. It is possible that the level of toxicity related to Fe(III) concentration is greater than for thiocyanate. It was observed that nearly all of the plants had died within 5 days of treatment.

Good gold uptake was observed in both plant species after treatment with thiourea. However, no palladium uptake was observed.

**Table 4.2** *Berkheya coddii* uptake of gold, platinum, and palladium from Klipfontein substrate after various chemical amendments – further treatments

| | **Concentration of metal in dried plant (ppb)** | | | | | |
|---|---|---|---|---|---|---|
| **Treatment** | **Au** | **Pd** | **Pt** | **s.d. Au** | **s.d. Pd** | **s.d. Pt** |
| 10 mL 10g/L $NH_4SCN$ | 36.4 | 27.7 | 0.00 | 54.2 | 23.5 | 0.00 |
| 10 mL 10g/L $NH_4SCN$ + 5g/L $H_2O_2$ | 183 | 389 | 0.00 | 158 | 182 | 0.00 |
| 10 mL 10g/L $NH_4SCN$ + 0.5mol/L HCl | 112 | 231 | 0.00 | 53.9 | 134 | 0.00 |
| 10 mL 10g/L $NH_4SCN$ + 2.5g/L $Fe_2(SO_4)_3$ + 0.0625g/L KI | 237 | 156 | 0.00 | 183 | 69.8 | 0.00 |
| 10 mL 10g/L KCN | 1580 | 7677 | 183 | 578 | 2720 | 139 |
| Control | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

Note: Due to the very low sensitivity of the GFAAS when analysing for platinum, the uptake of this metal was not investigated during this study. However, after the very high palladium result was observed, platinum was also investigated for this particular experiment.

Table 4.2 and Figures 4.1 and 4.2 show the results of further *B. coddii* treatments. These graphs also show the results for *B. coddii* from Table 4.1a for comparison. All plants

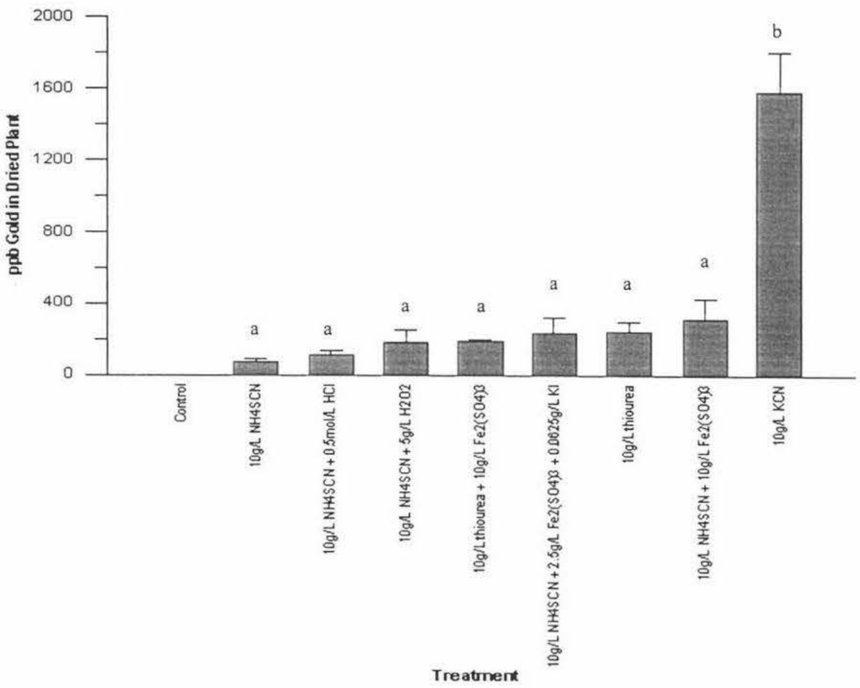

**Figure 4.1** Uptake of gold by *Berkheya coddii* from Klipfontein substrate – initial trials. Means with the same letter are not significantly different. Error bars show standard error.

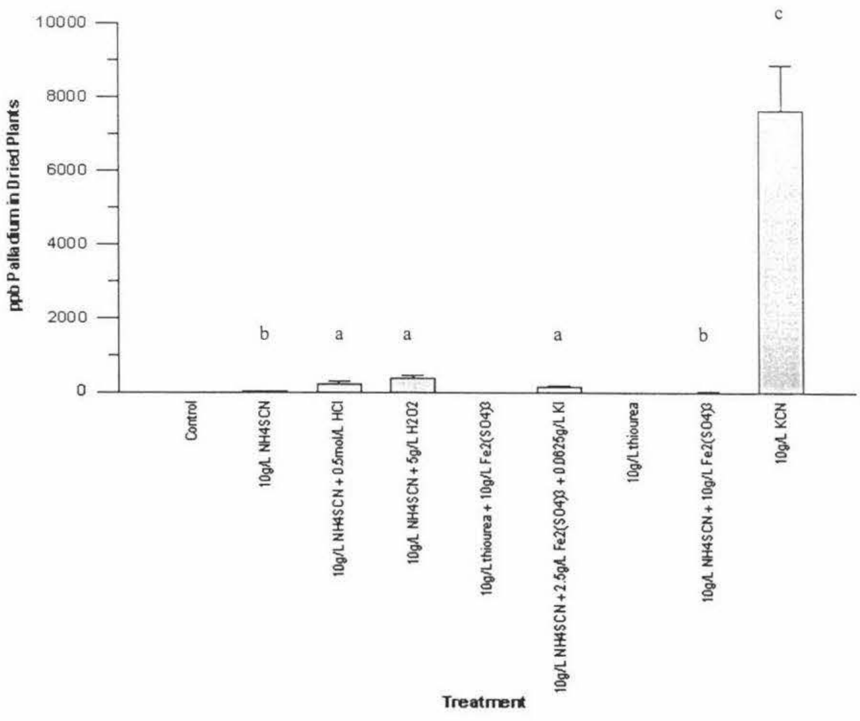

**Figure 4.2** Uptake of palladium by *Berkheya coddii* from Klipfontein substrate – initial trials

(except controls) showed signs of death within 3 days of treatment. *B. juncea* was not retrialled because of poor growth in the Klipfontein substrate.

Cyanide induced very high gold uptake. This is consistent with the use of this chemical for gold extraction in the mining industry.

The thiocyanate/Fe(III)/KI combination yielded a comparable result for gold to the thiocyanate/Fe(III) reported in Table 4.1a. The addition of both $H_2O_2$ and HCl to thiocyanate increased uptake of gold by *B. coddii*.

Palladium uptake was induced in all treatments. Cyanide induced most uptake. Cyanide was also the only solution able to induce platinum uptake.

Thiocyanate induced palladium uptake, which increased after addition of oxidants. Addition of $H_2O_2$ resulted in the greatest uptake of palladium. This was surprising as $H_2O_2$/thiocyanate did not extract as much gold as Fe(III)/thiocyanate from the Klipfontein substrate (refer to Tables 3.1 and 3.3). This appears to support the idea that the production of cyanide in the thiocyanate/$H_2O_2$ system may be playing a role in the plant uptake of palladium and gold. Another reason for this result, however, could simply be that the plants are killed more quickly with thiocyanate/Fe(III), thereby allowing less time for uptake than with thiocyanate/$H_2O_2$.

The thiocyanate/Fe(III)/KI combination also induced very good uptake, especially when compared with the thiocyanate/Fe(III) results from Table 4.1a. Gold uptake is similar in both cases, but addition of KI increased palladium uptake 20-fold over thiocyanate/Fe(III). The exact reason for this large increase is unknown, although the intermediate mixed thiocyanate/iodide species may be stabilising palladium in solution, thereby promoting greater uptake.

The standard deviation of all the plant results was very high as the geochemical and biochemical environment within each plant pot will not be identical. Large variation between samples is therefore to be expected.

The level of palladium uptake by all the solutions is encouraging. The use of cyanide in particular seems to offer most promise, and these results prove that palladium can be induced into a bio-ore in a greater concentration than the original ore. The addition of Fe(III) and $H_2O_2$ to thiocyanate in the treatment of plants induced very good levels of plant uptake, and the use of these solutions is discussed further in section 4.3.2.

## 4.3.2 Plant Uptake from Artificial Substrate – Initial Trials

The averaged plant uptake results from the first artificial substrate plant trials are shown in Table 4.3, while Figures 4.5 and 4.6 present these results graphically.

**Table 4.3** *Berkheya coddii* uptake of gold from artificial substrate after various chemical amendments

| | **Concentration of metal in dried plant (ppb)** | | | |
|---|---|---|---|---|
| **Treatment** | **Au** | **Pd** | **s.d. Au** | **s.d. Pd** |
| 10 mL 10g/L $NH_4SCN$ | 2730 | 90.3 | 585 | 37.8 |
| 10 mL 10g/L $NH_4SCN$ + 20g/L $Fe_2(SO_4)_3$ | 13100 | 266 | 7120 | 243 |
| 10 mL 10g/L $NH_4SCN$ + 5g/L $Fe_2(SO_4)_3$ | 5330 | 566 | 1650 | 306 |
| 10 mL 10g/L $NH_4SCN$ + 20g/L $H_2O_2$ | 29600 | 2240 | 5910 | 1020 |
| 10 mL 10g/L $NH_4SCN$ + 5g/L $H_2O_2$ | 23400 | 2340 | 6470 | 811 |
| 10 mL 10g/L KCN | 66700 | 11000 | 8130 | 10000 |
| 10 mL 1g/L KCN | 52500 | 6560 | 31300 | 2650 |
| 10 mL 10g/L KCN + 5g/L $H_2O_2$ | 30500 | 3760 | 14900 | 2330 |
| Control | 74.9 | 17.9 | 38.7 | 21.6 |

The most noticeable feature of these the results is the high level of plant uptake observed by treating the plants with 10 $gL^{-1}$ KCN. A maximum of 75.9 ppm gold was taken up by one of the plants, while for palladium up to 28.0 ppm uptake was observed (refer to appendix 1, data set section 4.3.2). According to Anderson (Pers. Commn., 2001), these levels of metal are very close to the levels required (100 ppm Au and 40 ppm palladium in dried plant matter (DPM)) for phytomining to be considered financially viable. All of the plants treated with 10 $gL^{-1}$ KCN were dead within three days of treatment (refer to Figure 4.3). These results are consistent with results from the previous plant trials where plants treated with KCN died very quickly but took up large amounts of the desired metal.

**Figure 4.3** ***Berkheya coddii*** plants treated with $10gL^{-1}$ cyanide 3 days after treatment (boxed).

High concentrations of gold and palladium were discovered in the plants treated with 1 $gL^{-1}$ KCN. The level of uptake was second only to the 10 $gL^{-1}$ KCN treatments. However, Figure 4.5 shows that there is no significant difference between these means. The highest concentration of gold discovered in this DPM was in fact higher than the 10 $gL^{-1}$ treatments at 84.2 ppm, and another plant was discovered to have a level of 79.7 ppm gold in the DPM. Standard deviation amongst plants of this treatment was high. This may be in part due to the fact that plants treated with 1 $gL^{-1}$ were still alive and appeared to be healthy (refer to Figure 4.4) after 8 days when harvesting took place. More time would therefore be available in which natural variations in plant uptake could have occurred. While the level of palladium in these plants is similar to that found in the plants treated with 10 $gL^{-1}$ KCN (an ANOVA showed no significant difference between the means), no very large Pd concentrations were observed in the DPM (the largest observed concentration was 9.8 ppm). The exact relationship between cyanide concentration and plant uptake of precious metals therefore remains unknown. It does appear, however, that there is no difference between 10 $gL^{-1}$ and 1 $gL^{-1}$ treatments when *B. coddii* is used, and that adding 1$gL^{-1}$ KCN has the dual advantages of reduced cost and longer plant survival periods after treatment.

**Figure 4.4** *Berkheya coddii* plants treated with 1 $gL^{-1}$ cyanide 8 days after treatment (boxed)

Negligible uptake was observed in the control plants, and these survived the full 8 days from treatment to harvesting. Because water is a poor solvent of gold and palladium, this was expected. Aside from the controls, plants treated with thiocyanate alone recorded the lowest levels of palladium and gold uptake. The difference in gold and palladium levels between these plants and those treated with thiocyanate plus an oxidant is significant. In the case of gold, adding $H_2O_2$ to thiocyanate resulted in a level of uptake of over 10 times the level with thiocyanate alone. For palladium, adding $H_2O_2$ to thiocyanate resulted in nearly 25 times the uptake over thiocyanate alone. The difference when ferric sulphate is added to thiocyanate is much less but, as already reported in chapter 3, the extraction results for Fe(III) where gold is concerned are similar to those for $H_2O_2$. This shows that, while extractions can be used as a guideline for further experimentation, solutions that initially appear to offer promising treatment cannot be guaranteed to give excellent plant

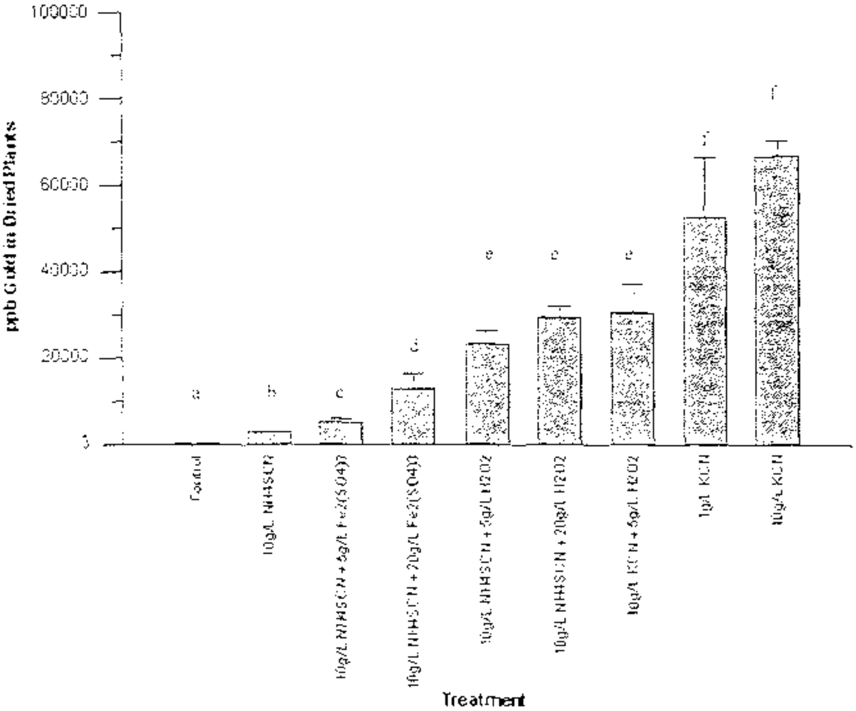

**Figure 4.5** Uptake of gold by *Berkheya coddii* from an artificial substrate.

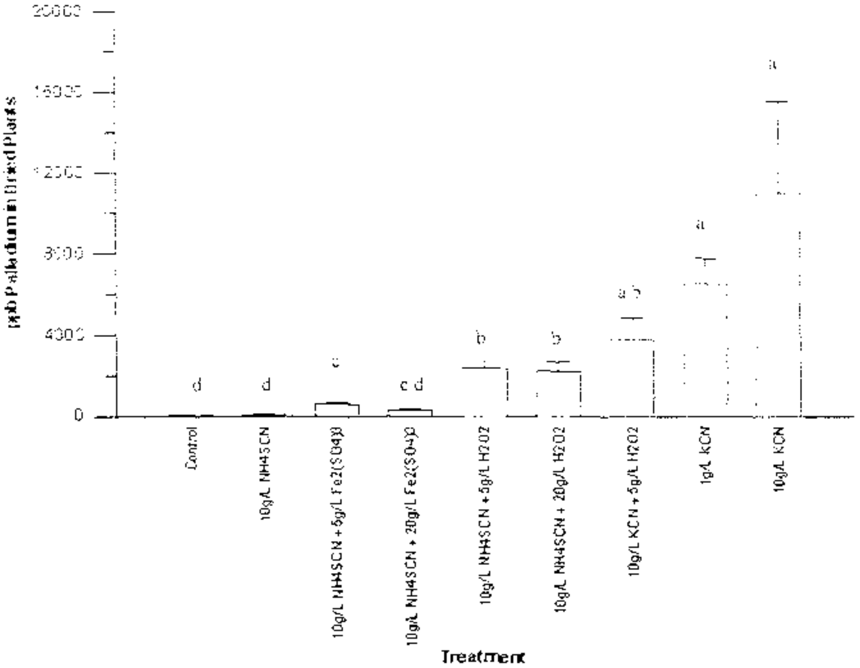

**Figure 4.6** Uptake of palladium by *Berkheya coddii* from artificial substrate.

uptake. The ferric ion may kill plants faster than $H_2O_2$. Another reason is that root/substrate interactions are variable between individual plants. In a practical sense this shows that it is unwise to dismiss a treatment based on extractions alone.

The greater efficacy of thiocyanate/$H_2O_2$ to induce metal uptake relative to thiocyanate/Fe(III) lends further support to the notion that cyanide is being formed as a result of the addition of $H_2O_2$ to thiocyanate. However, it is also possible that $H_2O_2$ is oxidising gold, which is then being recomplexed with thiocyanate in solution. Equation 33 showed that the amount of cyanide produced (should the reaction go to completion) is the same for both 5 $gL^{-1}$ and 20 $gL^{-1}$ $H_2O_2$ when added to 10 $gL^{-1}$ ammonium thiocyanate (refer to appendix 2). The total amount of cyanide produced (3.42 $gL^{-1}$) is similar to the amount added in the form of 10 $gL^{-1}$ KCN (4.0 $gL^{-1}$ $CN^-$, appendix 2). Levels of gold and palladium extracted would therefore be expected to be similar. However, significantly more metal dissolution was observed with 10 $gL^{-1}$ cyanide. It seems likely, therefore, that most gold is not being dissolved and taken up by plants as gold-cyanide complexes, but as gold-thiocyanate complexes.

Metal uptake with thiocyanate/$H_2O_2$ was significantly greater than with thiocyanate/Fe(III). However, the artificial substrate extraction results (section 3.3.2a) showed that gold extraction was greater with thiocyanate/Fe(III). While the ratios of oxidant to complexant are equivalent in both the plant trials and extractions, the actual concentrations of these chemicals vary. It is likely that these chemicals have different plant toxicities and this may be affecting total plant uptake.

The addition of $H_2O_2$ to KCN does not appear to have improved plant uptake concentration of gold and palladium over straight KCN; gold concentration in the plants is only marginally larger than for 10 g/L thiocyanate/20g/L $H_2O_2$ (Figure 4.5). This cannot be easily explained, although $H_2O_2$ may be reacting with cyanide before it can complex with gold and palladium, thereby reducing the dissolution and uptake.

## 4.3.3 Follow-up Artificial Substrate and Klipfontein Substrate Plant Uptake Results

It is appropriate to discuss the following results in one section as plants were treated with identical amendments in an identical environmental situation.

### *4.3.3a Trials Performed on* Berkheya Coddii *Grown in Klipfontein Substrate*

Gold and palladium uptake results from Klipfontein substrate by *Berkheya Coddii* are shown in Table 4.4 and Figures 4.7 and 4.8.

Palladium and gold uptake by control plants was negligible. This is consistent with previous results. Gold and palladium uptake when thiocyanate was used was also very low, and an ANOVA comparing these results with those from Table 4.1a shows that there is no significant difference between these means ($p=0.13$ for gold, $p= 0.31$ for palladium).

Treatment with 0.1 $gL^{-1}$ KCN yielded very poor plant uptake of gold and palladium. The concentration of cyanide in solution was very low and this would appear to be the reason why metal uptake was negligible. Treatment with this level of cyanide every day over the nine days appears to have improved the uptake of gold. The plants were still alive and appeared to be growing well when harvested. The use of 0.1 $gL^{-1}$ cyanide treatments every day can not, therefore, be immediately discounted. It would be interesting to assess the effect of this level of treatment on uptake over a period of months rather than days.

Very low concentration of metals in the plants treated with 10 $gL^{-1}$ KCN were found. Based on results in sections 4.3.1 and 4.3.2, these plants were predicted to contain the highest levels of gold and palladium. The very poor results are most likely due to the plants being killed very quickly without having a chance to extract the metals from the soil solution. These plants were harvested only three days after being treated and appeared dead after only one day.

**Table 4.4** Plant uptake of gold and palladium by *Berkheya coddii* from Klipfontein substrate containing 315 ppb palladium and 61.4 ppb gold – further results

| Treatment | Concentration of metal in dried plant (ppb) Au | Pd | s.d. Au | s.d. Pd |
|---|---|---|---|---|
| 10 mL 10g/L $NH_4SCN$ | 181 | 115 | 93.8 | 28.5 |
| 10 mL 10g/L $NH_4SCN$ +<br>2.5g/L $Fe_2(SO_4)_3$ | 121 | 39.2 | 145 | 30.8 |
| 10 mL 10g/L $NH_4SCN$ + 2.5g/L $H_2O_2$ | 1030 | 122 | 1810 | 85.3 |
| 10 mL 10g/L KCN | 187 | 377 | 229 | 480 |
| 10 mL 1g/L KCN<br>(0.05 g KCN/kg substrate) | 1525 | 461 | 1270 | 240 |
| 10 mL 1g/L KCN (t.e.d.) | 2680 | 791 | 2430 | 96.5 |
| 10 mL 0.1g/L KCN<br>(0.005 g KCN/kg substrate) | 11.3 | 55.6 | 11.4 | 90.5 |
| 10 mL 0.1g/L KCN (t.e.d.) | 157 | 74.8 | 159 | 52.2 |
| Control | 19.5 | 42.82 | 11.4 | 14.0 |

Note: t.e.d. = treated every day with this amendment

Greatest uptake of metals was observed in the treatments involving 1 $gL^{-1}$ KCN. Previous trials (refer to section 4.3.1) had shown that a one off treatment of 1$gL^{-1}$ KCN induced gold uptake almost to the level of 10 $gL^{-1}$ KCN, yet did not kill the plants. While there appears to be greater gold uptake after treatment every day, statistical analysis shows there is no significant difference between these means. Statistical analysis showed significant difference across all the treatments ($p=0.050$). However, there was no significant difference across the means when control results were excluded ($p=0.063$). This clearly shows that more replicates are required to improve precision of statistical analysis. It can be seen that while treatments with 1 $gL^{-1}$ appears to improve overall uptake of gold and palladium, plant variability is large.

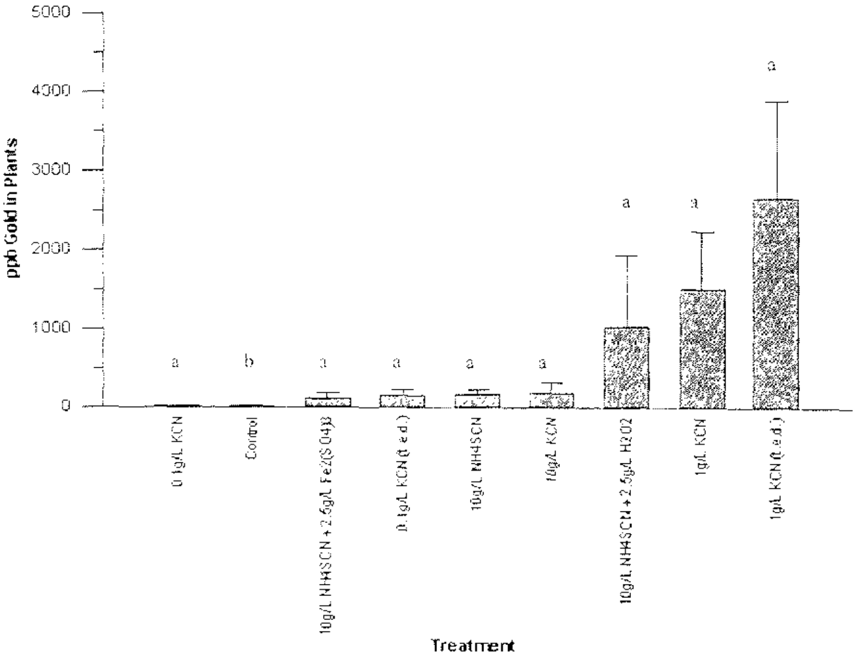

**Figure 4.7** Uptake of gold by *Berkheya coddii* from Klipfontein substrate – final trials

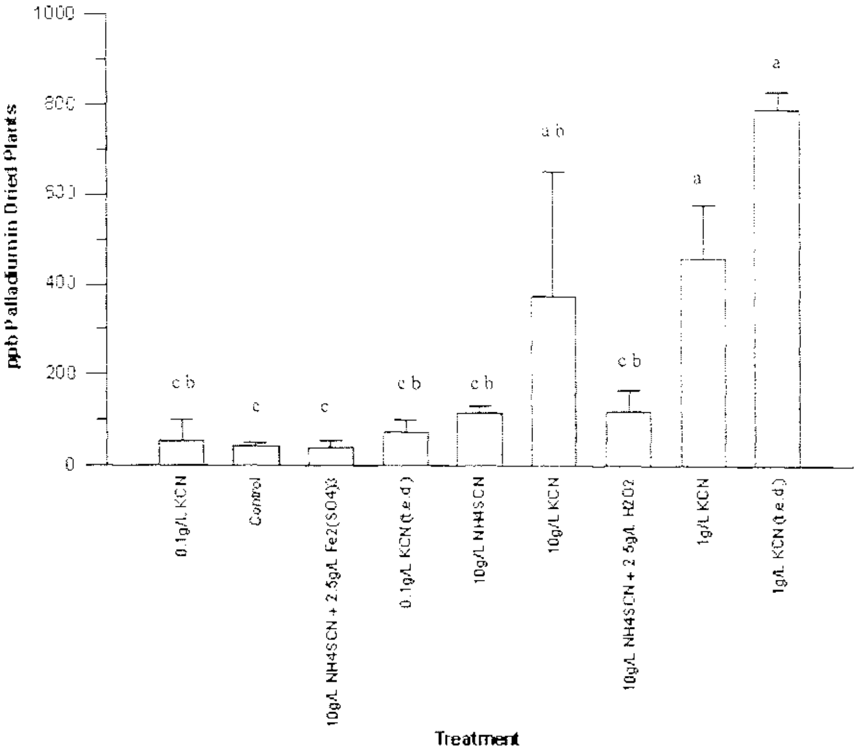

**Figure 4.8** Uptake of palladium by *Berkheya coddii* from Klipfontein substrate – final trials

Although treatment every day with 1 $gL^{-1}$ KCN appears to induce almost double the uptake of palladium than the single treatment with 1 $gL^{-1}$ KCN, there is no significant difference between these means ($p=0.078$). However, treatment every day would ensure the permanent presence of a high concentration of cyanide, and subsequent formation of palladium-cyanide complex, in the soil solution. The treatment of plants every day offers opportunities for more detailed research.

Two other sets of treatments killed the plants very quickly and forced an early harvest only three days after treatment. Thiocyanate/$H_2O_2$ and thiocyanate/Fe(III) have both been found in the previous trials (refer to sections 4.3.1 and 4.3.2) to induce good plant uptake. It is likely these plants died early once again due to the high concentration of thiocyanate. Analysis of the dried plant material showed that, while the means were not significantly different, palladium uptake by *B. coddii* when treated with thiocyanate/$H_2O_2$ was generally higher than with thiocyanate/Fe(III). Although gold uptake by plants treated with thiocyanate/$H_2O_2$ was larger, this was due to the very high concentration of gold found in one plant. This fact emerges in the very large standard deviation of gold found in these plants. If this result is eliminated as an outlier, the mean gold concentration falls to 119 ppb, which is very similar to the thiocyanate/Fe(III) result of 121 ppb. However, the large size of some of the thiocyanate/$H_2O_2$ results (appendix 1, data sets section 4.3.3) supports previous assertions that this is a better combination to use due to the production of cyanide. The amount of cyanide produced does not appear to be enough to induce death, due to the fact that we would expect much higher metal uptake after three days if a significant concentration of cyanide was produced. Future plant trials should reduce the amount of thiocyanate used so that plant life is extended.

### *4.3.3b Trials Performed on* Brassica Juncea *Grown in Artificial Substrate*

*Brassica juncea* was chosen to be used in these artificial substrate trials due to its superior rate of growth over *B. coddii*, and a lack of *B. coddii* plants. Table 4.5 and Figures 4.9 and 4.10 show these results.

The concentration of both palladium and gold in plants treated only with thiocyanate was low, and duplicated similar results when *B. coddii* was used in artificial substrate trials (refer to Table 4.3). Plants treated with 0.1 $gL^{-1}$ KCN also recorded very low concentrations of gold and palladium, demonstrating again that a single treatment of cyanide at such a low concentration is ineffective. However, like the *B. coddii* trial, treatment every day for 9 days resulted in a four fold increase in palladium uptake, and nearly a forty fold increase in gold uptake. The plants survived through the nine days of treatment and looked well when harvested.

**Table 4.5** Plant uptake of gold and palladium by *Brassica juncea* from artificial substrate containing 148 ppb palladium and 4.75 ppm gold

| | **Concentration of metal in dried plant** | | | |
|---|---|---|---|---|
| **Treatment** | **Au (ppm)** | **Pd (ppb)** | **s.d. Au** | **s.d. Pd** |
| 10 mL 10g/L $NH_4SCN$ | 4.18 | 126 | 4.54 | 42.1 |
| 10 mL 10g/L KCN | 130 | 9900 | 46.6 | 3340 |
| 10 mL 1g/L KCN | 168 | 925 | 150 | 582 |
| 10 mL 1g/L KCN (t.e.d.) | 484 | 12800 | 389 | 17500 |
| 10 mL 0.1g/L KCN | 1.12 | 109 | 1.37 | 103 |
| 10 mL 0.1g/L KCN (t.e.d.) | 40.1 | 455 | 20.2 | 225 |
| Control | - | 6.35 | - | 12.7 |

Note: t.e.d. = treated every day with this amendment. Gold control samples were destroyed during analysis.

Plants treated with 10 $gL^{-1}$ KCN died quickly and were harvested after three days. They did not appear as unwell as the *Berkheya coddii* treated with the same solution, perhaps due to their larger size and the better drainage of the artificial substrate. The large palladium and gold concentrations of nearly 10000 ppb and over 130 ppm respectively were not unexpected, based on previous trials (refer to Table 4.3). The main disadvantage of a cyanide concentration of this level is that it acts promptly to kill the plants, but in the interests of this study it is an effective benchmark. The average level of gold in the plants exceeds the level required for phytomining to become financially viable (Pers Commn. Anderson, 2001) and shows that it is possible to exceed 100 ppm in the plants.

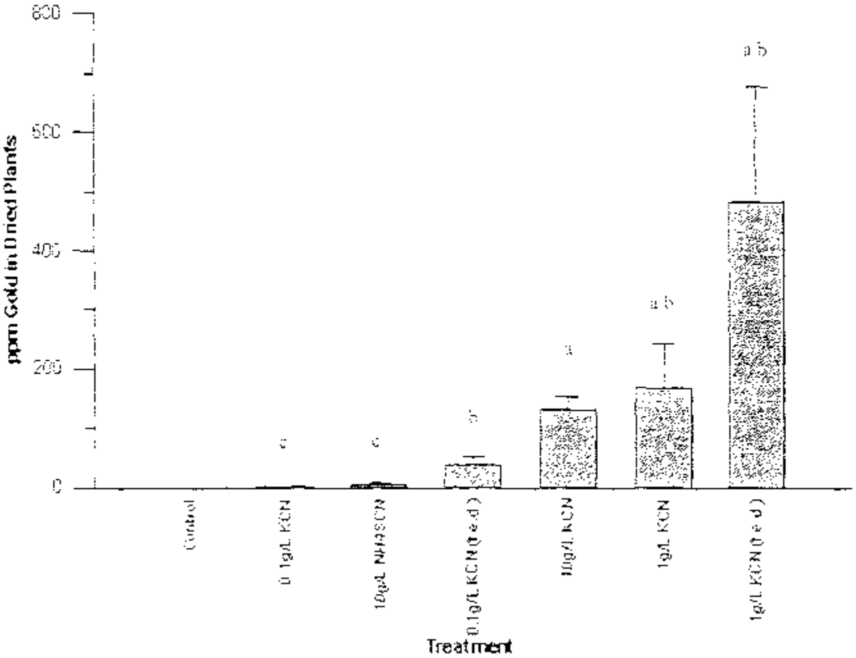

**Figure 4.9** Uptake of gold from artificial substrate by *Brassica juncea* - final trials

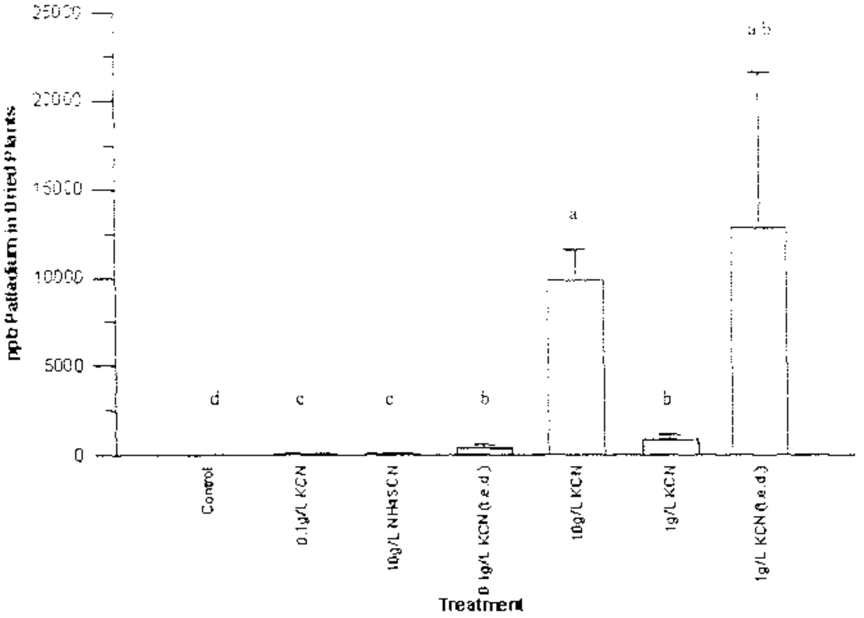

**Figure 4.10** Uptake of palladium from artificial substrate by *Brassica juncea* – final trials

The one-off treatment with 1 $gL^{-1}$ KCN induced very good gold uptake. The plants survived through to harvest after nine days, and there was no significant difference between this mean gold concentration and that of the 10 $gL^{-1}$ treatments. Palladium uptake, however, was low compared to treatment with 10 $gL^{-1}$ KCN.

Very high gold and palladium uptake by *B. juncea* was observed after treatment with 1 $gL^{-1}$ KCN every day for six days, at which stage the plants had died. There was no significant difference between the means of palladium concentration of this treatment and 10 $gL^{-1}$ KCN. This perhaps demonstrates a benefit in treating the plants regularly at a lower concentration, rather than a single shock treatment. It also shows that the longer cyanide remains in soil solution, the better plant uptake will be. This is also demonstrated with the everyday treatment of plants with 0.1 $gL^{-1}$ KCN, where for both *B. juncea* and *B. coddii* plant uptake was improved. The daily treatments with 1 $gL^{-1}$ KCN produced very high concentrations of gold, with uptake of nearly 1000 ppm in individual plants (refer to appendix 1, data sets section 4.3.3).

It appears that the ideal concentration of KCN when treating plants daily lies below 1$gL^{-1}$ to ensure plant survival, but above 0.1$gL^{-1}$ to ensure a sufficient rate of uptake by the plants. This is the equivalent of treatment with between 0.04 $gL^{-1}$ and 0.4 $gL^{-1}$ pure cyanide ($CN^-$), a level reached when 5 $gL^{-1}$ $H_2O_2$ is added to 10 $gL^{-1}$ thiocyanate (refer to appendix 2) if the reaction goes to completion. This scenario of cyanide production and its relative importance has been discussed in chapter 3. It would be interesting to analyse thiocyanate/$H_2O_2$ solutions of varying concentrations to assess exactly how much cyanide is being produced in this reaction.

## 4.4 Conclusions

- The chemicals used to induce uptake in this chapter were chosen due to their effectiveness as extractants, based on results from chapter 3. **While extractions offer a guide as to what might work as a plant treatment, it is unwise to dismiss a possible treatment solution unless it offers poor extraction of gold and palladium.**

This is because the substrate itself may affect rates of plant uptake, depending on solutions used.

- **Treatment of plants with KCN resulted in highest gold and palladium uptake.** One-off treatments of 10 $gL^{-1}$ KCN killed the plants very quickly, but resulted in gold concentrations in the plants that exceeded the levels required to make phytomining economically viable, although this was with an artificial substrate. Palladium levels in the plants never reached 40 ppm.

- **Treatment every day with 1 $gL^{-1}$ cyanide improves plant uptake of gold and palladium in artificial substrate to the point that concentrations of these metals in plants is at least as good as that with 10 g/L cyanide.** The dual benefit of longer plant life and continuous cyanide presence in the soil solution makes this method of plant treatment the most promising for future research. As plant uptake of gold and palladium with 0.1 $gL^{-1}$ KCN treatments is poor, it is suggested that daily plant treatments of around 0.5 $gL^{-1}$ KCN will maximise concentration of these metals in plants.

- **Thiocyanate + $H_2O_2$ and thiocyanate + $Fe_2(SO_4)_3$ offer the most promising future when treating plants with a solution of complexant + oxidant.** Gold uptake by plants is similar for both treatments, while thiocyanate + $H_2O_2$ offers better palladium uptake. This could be due to either the production of cyanide in this solution, but is more likely a result of the independent oxidising and complexing activity of $H_2O_2$ and thiocyanate respectively.

- **Plant survival rates for thiocyanate + oxidant treatments were poor.** It is unknown whether this is due to complexant, oxidant, production of intermediate species (in the case of thiocyanate + ferric sulphate), or the production of cyanide. This factor should be investigated further as it is likely that early plant death is an inhibitor of metal uptake.

- **Gold and palladium uptake do not appear to be dependant on plant species**. Very similar metal uptake was observed for both *B. coddii* and *B. juncea*. *Brassica juncea* did not grow well in Klipfontein substrate but flourished in artificial substrate, while *B. coddii* grew equally well in both substrates. The choice of which plant to use in future trials may depend on substrate.

# Chapter 5 Practical Aspects of Phytomining

Anderson (Pers. Commn., 2001) proposed that, in order for the phytomining of gold to return a profit, 100 ppm needed to be accumulated in the plants. At this time the cost of palladium was roughly 2.5 times more than gold; a concentration of 40 ppm palladium in plants was therefore the present target. Levels of gold found in *Brassica juncea* planted in artificial substrate and treated with cyanide and thiocyanate/$H_2O_2$ exceeded 100 ppm, proving that some plants can accumulate gold above the required level. The problem remains that this was attained with an artificial substrate containing 4.75 ppm gold, a high concentration that is unlikely to be found in mine tailings. Up to 25.5 ppm gold was found in *Berkheya coddii*, planted in Klipfontein substrate and treated with cyanide (refer to appendix 1, data set section 4.2.3). As the gold concentration in Klipfontein was around 50 ppb, this is an increase in concentration of around 500 times. While 40 ppm palladium was not reached in any of the plants analysed, this value was approached, with 28 ppm being found in one *Berkheya coddii* plant in artificial substrate, treated with cyanide (refer to appendix 1, data set section 4.3.2). As the level of palladium in artificial substrate was 148 ppb, gold was thus able to be concentrated to over 150 times the concentration in substrate. As a means of accumulating metals in a more concentrated form, the phytoextraction of gold and palladium with chemical amendments is therefore very efficient.

## 5.1 Inhibiting factors in the Plant Uptake of Gold and Palladium

A large quantity of metal may be lost to direct leaching through the soil profile after the plants have been treated. With 200 g of Klipfontein growth substrate, at 30 ppb gold and 158 ppb palladium, a total of 6 μg gold and 31.6 μg palladium was present in each pot. Assuming concentrations in dried plant matter of 2700 ppb gold and 7600 ppb palladium after treatment with cyanide (figures 4.7 and 4.2 respectively) and a typical dried plant mass of 0.1 g, up to 4.5% total gold and 2.4% total palladium was taken up by plants. This could be due to not all metal being made soluble. However, leaching of dissolved metals may also have been a problem here. In future plant trials, and in the field, it will be important to ensure leaching is minimal by striking a balance between plant uptake of solution and actual solution added.

Chapter 4 discussed chemical toxicity and plant mortality rates. High concentrations of thiocyanate, Fe(III), $H_2O_2$, and cyanide will quickly kill plants. Section 4.3.2b showed that by reducing the concentration of cyanide, and treating plants daily, mortality was improved and, in some cases, metal uptake increased. However, the exact relationship between plant mortality and treatment concentration is unclear. Further work investigating the relative toxicity of the mentioned chemicals is encouraged. Hydroponic trials with cyanide, Fe(III), thiocyanate, and $H_2O_2$ of varying concentrations would confirm fatal doses.

Another inhibiting factor may be that treatments are substrate specific. Anderson *et al.* (1999) reported that plants treated with thiocyanate were unable to take up gold from a tailings containing a high concentration of gold. In contrast, 100% of gold was able to be dissolved from a tailing containing a lower concentration of this metal. In practical terms, this may mean that a standard method detailing exact types and concentrations of chemicals to be used may never eventuate. Rather, extraction and plant trials may need to be applied to each potential phytomining site.

## 5.2 Cyanide as a Potential Treatment

In practice, the use of cyanide offers most potential at this stage. Anderson (2000) investigated the feasibility of a gold phytomining operation with thiocyanate being applied; this model has been used in this discussion with Klipfontein, a genuine mine tailing, the substrate used to illustrate the feasibility of phytomining. *Berkheya coddii* is able to accumulate 7600 ppb palladium, as observed in plant trials (refer to table 4.2). Assuming a crop with a biomass of 20 t/ha, 5.4oz of palladium could be concentrated in the plants. At a present cost of around US$400/oz, palladium to the value of US$2160/ha could be concentrated in plants. Chapter 4 discussed treatment application rates. A standard application of 0.5g KCN/kg substrate (10 $gL^{-1}$ KCN) was used initially. However, trials showed that palladium uptake did not decrease when plants were treated with 10% of this cyanide concentration over 6 days (figure 4.8). Thus the cost of applying potassium cyanide at 0.05 g/kg substrate over 6 days to a depth of 15 cm is \$945/ha, at an approximate unit cost for KCN of US\$2.10/kg and assuming a substrate density of 1 ton/m$^3$.

Where gold is the target metal, cyanide usage can be decreased further. Chapter 4 showed that there was no significant difference in gold uptake between plants treated with 0.5 g/kg substrate and 0.05 g/kg substrate. At a current gold price of US\$300/oz, a possible plant concentration of 7500 ppb (refer to figure 4.7), and total biomass of 20 t/ha, 1.7 oz of gold could be concentrated in plants at a value of US\$510. Total cost of KCN used would be US\$158.

The basic calculations above show that the total amount of gold recovered from a phytomining operation may be enough to meet the costs of treatment. The scenario discussed does not appreciate costs associated with running such an operation, which might include employment of workers, amenities and services, and extraction of the metals from the bio-ore. The target of consistently inducing 100 ppm gold and 40 ppm Pd must therefore remain. However, this study has shown that plants can accumulate gold to nearly 1000 ppm (0.1%), albeit from an artificial ore (section 4.3.3). Continuing research into improving plant uptake of precious metals, including field trials, will ensure that the cost/benefit ratio associated with phytomining can only improve. Phytomining of palladium and gold (in particular) does seem feasible.

## 5.3 Risks Associated with the use of Cyanide in the Field

As it is envisaged that many future phytomining operations will take place on used mine tailings, the treatment of plants with cyanide is likely to pose the same risks as the process of heap leaching. Figure 5.1 shows current field trial plots on used mine tailings at the Klipfontein site near Rustenburg in South Africa:

**Figure 5.1** Plants growing on used mine tailings

The possibility exists that cyanide solution entering the subsurface may be volatilized to hydrogen cyanide, and this form of cyanide inhaled (Kjeldsen, 1998). However, this risk has not been quantified. The presence of constructed lining underneath leach pads would prevent escape of contaminated fluid to outside water systems. The degradation of free cyanide ($CN^-$) by various microbes is well documented. Free cyanide will degrade to ammonia which will nitrify to nitrate in groundwater. Escape of groundwater off site would therefore seem to pose risk in the form of nitrate, which can lead to eutrophication of waterways, as well as the risk of exposure to free cyanide in groundwater.

While cyanide induces exceptional plant uptake of gold and palladium, public acceptance of the use of simple cyanides such as potassium cyanide or sodium cyanide is likely to be low. Cyanide is regarded by the general public as a fast acting, very dangerous poison – Kjeldsen (1998) reports fatal dosage to be 0.5 – 3.5 mg/kg body weight. The addition of an oxidant to thiocyanate to produce cyanide offers potential in this area. Thiocyanate is much less toxic than cyanide – lethal doses range from 50 – 80 mg/kg body weight, as reported by reported by Kjeldsen (1998). However, metal uptake by plants after treatment with these solutions remains low compared to cyanide.

# Chapter 6 General Conclusions

- **Addition of an oxidant to thiocyanate is vital to increasing extraction of gold and palladium.** Extraction of these metals was significantly improved through the addition of both Fe(III) ions (in the form of ferric sulphate) and hydrogen peroxide to thiocyanate.

- **Extraction of gold and palladium in the thiocyanate/Fe(III) system may be dependent on Eh and pH.** Chapter 3 shows that the addition of even small quantities of Fe(III) to thiocyanate resulted in significant increases in metal extraction, while changes in Eh and pH were large. The difference in values for Eh and pH, however, between solutions of varying Fe(III) and thiocyanate concentrations were small, lending strong support to the notion that Fe(III) concentration is not as important as Eh and pH in the thiocyanate/Fe(III) system.

- **Extraction of gold and palladium in the thiocyanate/$H_2O_2$ system may be dependent on either: a) the production of cyanide, b) the oxidising and complexing properties of $H_2O_2$ and thiocyanate respectively, or c) both.** The addition of $H_2O_2$ to thiocyanate resulted in only a small change of Eh and pH, yet change in metal extraction was large. Gold and palladium extraction is therefore likely to be less dependent on Eh and pH then the proposed formation of cyanide in the thiocyanate/$H_2O_2$ system. It seems likely that, if cyanide is being produced, it is not the only species responsible for extraction of gold and palladium. $H_2O_2$ and thiocyanate may be acting separately and independently to oxidise and complex with gold respectively. The magnitude of the roles of cyanide, thiocyanate, and $H_2O_2$ are unknown.

- **Cyanide offers most potential for induced uptake of gold and palladium by plants.** In all trials, plants treated with cyanide took up the largest quantity of metals. Daily treatments of plants with between 0.5 $gL^{-1}$ and 1.0 $gL^{-1}$ potassium cyanide solution will ensure very good gold and palladium uptake and will ensure plant mortality is good. Very good plant uptake of gold and palladium by thiocyanate/$H_2O_2$ may also be explained to some extent by the production of cyanide in this system.

- **The potential for phytomining of gold and palladium is large.** The model used in this study sets a concentration of 100 ppm in dried plant material in order for phytomining to be profitable. Gold concentrations in plants of up to 950 ppm from artificial substrate proves that very large amounts of this metal can be concentrated in aerial parts of plants. The phytomining of gold, therefore, looks very promising. Induced palladium uptake by plants before this study was unprecedented. Plants were shown to be induced to take up large quantities of palladium, though not at the levels previously regarded to ensure economic viability of phytomining. However, recovery of both this metal and gold from a hypothetical phytomining operation was shown to have greater value than the cost of treatment applied. Further research into plant species, treatment rates, treatment toxicity, environmental factors, and production of cyanide in the thiocyanate/$H_2O_2$ system will improve concentrations of gold and palladium in plants.

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# Appendix 1 Data Set

Raw data is supplied on the disk provided. Alternately, data sets can be obtained from the Soil and Earth Sciences Department, Institute of Natural Resources, Massey University.

# Appendix 2

### Calculation of $CN^-$ present in different solutions

For $5gL^{-1}$ $H_2O_2$ + $10\ gL^{-1}$ $NH_4SCN$:

$3H_2O_2 + NH_4SCN \rightarrow SO_4^{2-} + 2H_2O + HCN + H^+ + NH_4^+$

$5\ gL^{-1}$ $10\ gL^{-1}$

number moles $NH_4SCN = 10gL^{-1} / 76.116gmol^{-1}$ $0.1314molL^{-1}$
number moles $H_2O_2 = 5gL^{-1} / 34.0146gmol^{-1} = 0.1470molL^{-1}$

therefore number moles $NH_4SCN$ is limiting factor. Ratio of $NH_4SCN : HCN$ is 1:1, therefore have $0.1314\ molL^{-1}$ HCN.

$gL^{-1}$ HCN = $0.1314molL^{-1} \times 27.0256gmol^{-1} = 3.55\ gL^{-1}$ HCN
But want $gL^{-1}$ $CN^-$. Mr ($CN^-$) = $26.0177\ gmol^{-1.}$
26.0177 / 27.0256 = **3.42 $gL^{-1}$ $CN^-$**

For $20gL^{-1}$ $H_2O_2$ + $10gL^{-1}$ $NH_4SCN$:

Number moles $H_2O_2 = 0.5880 > 0.1314$ moles $NH_4SCN$
Therefore Limiting component is $NH_4SCN$, and total number of moles of $CN^-$ produced remains at **3.42 $gL^{-1}$**.

Number moles $CN^-$ in 10 $gL^{-}$ KCN solution:

Mr (KCN) = $65.116\ gmol^{-1}$, Mr ($CN^-$) = $26.0177\ gmol^{-1}$. Proportion of $CN^-$ in KCN is 26.0177 / 65.116 = 0.3996.
Have 10 $gL^{-1}$ KCN. $0.3996 \times 10\ gL^{-1}$ = **0.4 $gL^{-1}$ $CN^-$**.

# Appendix 3 Chemicals used in Extractions and Plant Treatments

| Chemical used | Added in form | Chemical formula |
|---|---|---|
| thiosulphate | sodium thiosulphate | $Na_2(S_2O_3)$ |
| thiocyanate | ammonium thiocyanate | $NH_4SCN$ |
| thiourea | thiourea | $SC(NH_2)_2$ |
| ferric ion | hydrated ferric sulphate | $Fe_2(SO_4)_3.9H_2O$ |
| bisulphide | hydrated sodium hydrosulphide | $NaHS$ |
| ammonia | ammonia solution | 30% $NH_3$ solution |
| hydroxide | potassium hydroxide | $KOH$ |
| humic acid | humic acid | various |
| hydrogen peroxide | hydrogen peroxide solution | 27% hydrogen peroxide solution |
| iodide | potassium iodide | $KI$ |
| cyanide | potassium cyanide | $KCN$ |
| hydrochloric acid | hydrochloric acid | 69% $HCl$ solution |
| chloride | potassium chloride | $KCl$ |

# Appendix 4 Characteristics of Substrates

Concentrations of metals are as measured using standard *aqua regia* digest described in Chapter 3.

| Substrate | ppb gold | ppb palladium | ppb platinum | pH |
|---|---|---|---|---|
| Klipfontein | 61.40 | 315.45 | 344.77 | 5.7 |
| Artificial | 4752.64 | 147.80 | - | 6.5 |