The Recovery of Nickel from Hyperaccumulator Plant Ash

A thesis presented in partial fulfilment of the requirements
for the Degree of Master of Science in Chemistry
at Massey University, Palmerston North,
New Zealand

Anthony Hans Peter Kirk
2000

Errata

Throughout this thesis the data received from X-ray powder diffraction analysis was referred to as a spectrum or spectra. The correct terminology for such diagrams is in fact X-ray diffraction patterns or X-ray diffraction diagrams.

2.2.10.1 paragraph 2, page 24.

A UV/visible spectrum of the ash extract **solution**, ranging 190-820 nm, was obtained using a Hewlett Packard spectrophotometer (model 8452A).

3.3.2 paragraph 4, page 62.

Aluminium and iron especially are known to precipitate as hydroxides, even in mildly acidic solutions **(pH~2)**, while their phosphates may co-precipitate.

4.2.3.3 paragraph 5, page 77.

The solution was tested again for electrowinning at 100 mA, 60°C and a period of 25 minutes, with a **visually** identical green deposit observed.

4.2.3.6 paragraph 3, page 79.

A green Ni hydroxide deposit was observed as predicted **(see p. 75)**, indicative of the nitrate content of the solution.

4.3.1.4 paragraph 5, page 86.

The introduction of formaldehyde into the electrolysis solution, offering an alternative oxidation reaction to the **electrolysis** of water, should have had its greatest and possibly only effect on E_{pos}, the counter electrode potential.

5.2.1.3 paragraph 1, page 111.

A 200 ml solution, with Ni, Mg and K concentrations similar to those of the *A. corsicum* extract (pH 4.75) was **prepared** using the sulfate salts of each element: 0.250 M Ni^{2+} (introduced as $NiSO_4.6H_2O$), 0.368 M Mg^{2+} and 0.440 M K^+ (introduced as anhydrous sulfates).

5.2.1.4 paragraph 2, page 112.

A small quantity of insoluble material was filtered off using filter paper and the remaining 195 ml ash extract solution was refrigerated **(4°C)** for 24 hours, after which time a 0.5 ml sample was taken and made up to 100 ml.

Abstract

Nickel hyperaccumulator plants have the unusual ability to absorb nickel from the soil they grow in and incorporate it into their structure, to concentrations greater than 1% dry weight. This selective accumulation process occurs with the relevant exclusion of most other metals from the plant material. Combustion of this material then results in a nickel-rich ash (10-15%) of relatively high purity when compared to commercially mined ore (1-4% Ni). Much work has focused on the plants themselves, with suggestions of them being applied to the commercial extraction of nickel from soil, with yields up to 200 kg per hectare. However, little work has been undertaken on the recovery of nickel from the plant material. Given the refined nature of nickel hyperaccumulator ash and that any commercial enterprise is governed by economics, it was thought that a more specific nickel recovery process could be determined for the ash than simply smelting with nickel ore. Such a process should produce an end product of greater worth than smelted nickel. To this end nickel electrowinning and nickel salt crystallisation were investigated.

Ashing of the plant material by open flame combustion was found to produce a *bio-ore* suitable for nickel solubilisation, with the energy produced by the process possibly being of economic benefit if applied to the generation of electricity.

Leaching of the nickel from the ash was investigated using a variety of acids with sulfuric acid primarily used, owing to the common usage of a sulfate medium in both nickel electrowinning and crystallisation. A 96% solubilisation of the nickel from the ash was achieved using 4M H_2SO_4, with resulting extracts containing nickel at approximately 0.35 mol/l concentrations. The addition of nitric acid to aid in nickel leaching while successful, also solubilised greater quantities of impurities and caused complications in later processing.

Electrowinning of nickel from an ash extract solution, once neutralised to pH values of 4-6, required the balancing of sulfate and nitrate concentrations. Excesses or indeed the absence of either, proved to inhibit metallic nickel electrodeposition, instead two· different hydroxide products were observed. However, once balanced a metallic nickel deposit was produced with a current efficiency for the electrowinning period of 94%.

From solutions containing a range of potassium and nickel sulfate concentrations it is found that the double salt $K_2Ni(SO_4)_2.6H_2O$ will crystallise. The ash extract, being of hyperaccumulator origin, contains both Ni and K in high concentrations, with SO_4^{2-} being added during the leaching process. It was found that double salt crystals formed without chemical aid even in a highly acidic solution, but with the addition of KOH and/or K_2SO_4 could be crystallised to the extent where as little as 1.5 g/l Ni remained in solution. The blue/green cubic crystals are easily recovered in good yield, corresponding to a 98% recovery of nickel from the ash extract. While no large market exits for the material at present, there are possibilities for its use and given a theoretical yield of 690 kg $K_2Ni(SO_4)_2.6H_2O$ per hectare, there is potential for substantial monetary return.

Acknowledgements

I'd like to thank Associate Professor Roger Reeves for his support and encouragement, also for allowing me the freedom to investigate my own crazy ideas. This work would have been impossible without Roger's amazing depth of knowledge for all things science.

Secondly, I'd like to thank Dr Simon Hall for taking the time to answer the multitude of trivial and often irrelevant questions I had. The frequently denied role of secondary supervisor was always greatly appreciated.

Thank you Bec for being the best! For putting up with the little spiels about nickel and stuff. I greatly appreciate all your input on your "second thesis".

Really big thanks to Ma and Pa for giving me support (and food!) when I needed it and for listening to all my little problems with a sympathetic ear.

Cheers to Justin and G for the good times and entertainment.

Thank you to Massey University for the research money and scholarships, allowing me to undertake this work.

Finally thank you to the monkey and the wookie in the organic lab.

Table of Contents

List of Figures

List of Tables

Chapter One

Introduction

1.1 Overview

The ability of plants to extract valuable resources from the earth has always been exploited by mankind. In recent years this has extended from essential nutrients to include heavy metals. The term phytoextraction has been coined to describe the method by which metals may be extracted from soil by plants. This relies on a plant's ability to extract and concentrate heavy metals into its structure.

Two types of metal extracting operation are described using the term phytoextraction, these being phytoremediation and phytomining. Both utilise the same basic procedure

1) Growing and harvesting of plants on soils containing some heavy metal(s).
2) Combustion of raw plant material to produce metal rich ash.
3) Extraction or storage of metals in some form.

The two methods basically differ only in their intent. Phytomining is the profit-based application of phytoextraction, the overall goal being commercial gain from the value of the metals extracted. Phytoremediation is the utilisation of phytoextraction for the decontamination of polluted soils. This may be organic or inorganic contamination such as pesticides and heavy metals. Given the topic of study focus will be placed on heavy metal phytoremediation.

Phytoextraction has its basis in the plants used. Given that the aim is to remove metals from soil, one particular group of plants, known as hyperaccumulators, stands out due to their exceptional metal extracting properties (Chaney et al., 1983). While some forms of heavy metal phytoremediation employ non-hyperaccumulator plants such as willow trees, most of the advances in the field of phytoextraction have been inspired by hyperaccumulators.

1.2 Hyperaccumulators

The term hyperaccumulator was first used by Jaffre' et al. (1976) to describe plants with nickel concentrations of greater than 1000 μg/g or 0.1% of their dry leaf weight. This definition, now in common use was redefined by Reeves (1992) to include only those species that could attain such concentrations in their natural environment. Other elements were also covered; zinc hyperaccumulation was defined as greater than 10000 μg/g or 1.0% in the dried leaf material due to its higher natural abundance in plants and soils (Baker et al., 1989). The Ni value was chosen from histograms showing that no overlap in plant metal concentrations occurred between two populations of *Alyssum*, one of hyperaccumulators the other non-accumulators (Brooks, 1998). Other elements were also defined in more arbitrary ways, with varying thresholds for hyperaccumulation set (Baker et al., 1997).

Both physical and philosophical knowledge of these metal tolerant plants has been growing since as early as the 16th century when Caesalpino (1583) noted a plant species (probably *Alyssum*) confined to serpentine. Minguzzi and Vergnano (1948) were the first to report a hyperaccumulator species. They found up to 0.79% nickel in the dried leaves of *Alyssum bertolonii*, this from a plant growing in soils containing only 0.42% nickel.

Since this relatively recent identification, more than 400 species of hyperaccumulators have been identified, largely through the analysis of herbarium specimens (Brooks, 1998). The element/s of accumulation are predominantly nickel, zinc, copper and lead.

Hyperaccumulator plants belong to a much larger group known as metallophytes. These species have a high tolerance to heavy metals and are endemic to soils containing elevated concentrations of the metal(s) accumulated by the plant. The majority of hyperaccumulators accumulate nickel and it is usual for these to occur on serpentine (ultramafic) soils. This apparent majority is most likely the result of larger areas of Ni mineralisation compared to other metals. With larger areas comes the opportunity for greater genetic variation through the process of evolution. Such soils are generally infertile, characterised by low Ca:Mg ratio, and potentially phytotoxic concentrations of nickel. Indeed the success of some plant species in overcoming these edaphic conditions is such that they can exist relatively free of competition (Baler, et al., 1997). It is unclear as to whether hyperaccumulators have been confined to metalliferous areas from once widespread populations by competition from other plants (paleo-endemism), or whether they have developed from non-tolerant or non-accumulating precursors, which have colonised metalliferous areas by the process of natural selection and undergone a morphological divergence (neo-endemism).

The geographical distribution of hyperaccumulators is mainly limited to certain tropical to warm temperate areas of the world. It has been noted by Reeves et al. (1983), that both nickel hyperaccumulation and serpentine endemism are associated with sites that have not undergone glaciation during the last ice age. As sites of such metalliferous soils occur in small disjunct locations, there is little possibility of revegetation from far distant surviving populations. Brooks (1987) proposed that this observed hyperaccumulator distribution was the result of insufficient time since the last ice age for the evolution of new hyperaccumulator species.

The metalliferous environment of growth for many metallophytes proves detrimental to most non-tolerant species. Large metal concentrations are known to retard the growth of a plant and can result in death. Baker (1981) proposed two strategies by which metallophytes could sustain life in soils with phytotoxic metal concentrations.

(1) Exclusion of the metals from the plant tissue. Only a low transport of metals occurs to the shoots of the plant allowing concentrations to remain low.

(2) Accumulation of metals, by which heavy metals are absorbed into the plant tissue, with some changes in physiology providing tolerance to concentrations that would otherwise be toxic.

In the case of exclusion, high metal concentrations can be observed in the roots of the plant, but due to the limiting transportation of metals, the stem and leaf material contain only low concentrations. In some species the roots actually exude a complex that causes the metals to precipitate in the soil, thus inhibiting its transport even into the roots. This is not the case with hyperaccumulators, as transport of metals is not limited and metal concentrations are often higher in the above surface parts of the plant where it is stored.

There is a third metal tolerant strategy that falls between exclusion and hyperaccumulation. Indicator plants are capable of transporting and concentrating metal(s) to a degree that correlates well with metal concentrations in the soil. These plant species have been used for mineral exploration, as high metal concentrations in these plants are indicative of metal mineralisation, a process called biogeochemical prospecting. Another form of mineral exploration, geobotanical prospecting, utilises the endemic nature of many metallophyte species to distinguish areas of minerallisation simply by their presence (Brooks, 1998).

It is common for a given hyperaccumulator species to employ differing metal tolerant strategies depending on the metal in question. Baker et al. (1994) demonstrated that

Thlaspi caerulescens, a known hyperaccumulator of nickel and zinc, also exhibited exclusion characteristics with respect to Pb, Cr, Cu, Al and Fe. This differing approach to metal tolerance is also evident in certain *Alyssum* species.

The root/shoot transfer of metals can be thought of as passing a single membrane. Root metal concentrations are representative of the soil and the shoots/leaves can be thought of as the product. The accumulated metals pass the membrane and are concentrated in the product, while the excluded metals are inhibited from entering into the product. The effect is a refinement of the accumulated metals from soil to plant material. Such selectivity toward metal accumulation is a key characteristic of hyperaccumulators and indeed is advantageous for phytomining and metal recycling (through phytoremediation).

Many of the hyperaccumulator plants are herbaceous perennials and biennials with the roots surviving for two or more years. It has been suggested by Vergnano Gambi et al. (1982), and Schlegel et al. (1991) that the leaves act as a metal sink for the plant. Metals are transported out of the perennial root organ, thus protecting it from the toxic effects of high metal concentrations. It also allows for the easy removal of much of the accumulated metal at leaf fall. Investigations into elemental distribution show that accumulated metals are predominantly localised in the superficial regions. The xylem acts as a medium for transport only, in most hyperaccumulators, with 30% of the shoot nickel being found in the xylem of *A. bertolonii* (Gabbrielli et al., 1997). Leaf material, being the target for metal transport, has its highest metal concentrations in the vacuoles of the epidermis (Ernst et al., 1992).

Metal tolerance comes with an ecological cost. In the case of hyperaccumulators this is often evident in their slow growth rates and can result in selection against metal tolerant species on unpolluted soils, as reported by Ernst (1992). The costs of tolerance can be partly explained by an increased need for the metals in question. Often hyperaccumulators exhibit maximum growth at elevated, normally toxic levels of metals where the activity of their metal-stimulated enzymes are increased. This explains the endemism characteristic of almost all hyperaccumulator plant species, to regions of high soil-metal concentrations where non-metal tolerant species do not compete as successfully.

1.3 Hyperaccumulation Process

Accumulation of heavy metals is initiated by the solubilisation of the metals outside the roots. As suggested by Raskin et al. (1994), this solubilisation may involve:

(1) Excretion of metal chelating molecules (e.g. phytosiderophores) into the rhizosphere.

(2) Acidification of the rhizosphere to dissolve metal precipitates.

(3) Reduction of metals ions in the soil by enzymes to a more easily transportable form.

Once solubilised the metal may enter the roots through the root cell plasma membrane and from there be transported to the appropriate areas.

The actual metal content of the soil available to the plant, either directly or through solubilisation is not the same as the soil's total metal concentration. The available portion depends on the form the metals are present in and is termed the bio-available metal content.

Hyperaccumulators demonstrate a strong ability to transport their respective accumulated metals away from the root organs and store them in stem and leaf material. The very nature of hyperaccumulators, with otherwise toxic metal levels, implies that the plants have developed detoxifying biomechanisms. Although others have been proposed, the most likely means of transport and storage involves the complexation of metals by chelating ligands and/or sequestration of metals away from sites of metabolism (Baker et al., 1997). This avoids possible enzyme inhibition and free radical production (Robinson, 1997). Three groups of chelates distinguished by their oxygen, sulfur and nitrogen donor atoms have been hypothesised as contributing to the metal detoxification evident in the hyperaccumulator phenotype.

Increased concentrations of organic acids such as citrate, malate, malonic and oxalic acids containing oxygen donor atoms are observed in some hyperaccumulator species, with amounts produced often correlating with accumulated nickel (Lee et al., 1977, 1978). Carboxylates are important ligands for the complexation of metals in the vacuole (Ernst et al., 1992). However evidence suggests that in most cases this a-general metabolic response that serves to maintain charge balance during metal storage (Osmond, 1976) rather than a specific one that accounts for tolerance and hyperaccumulation toward a particular metal (Thurman and Rankin, 1982).

Two classes of sulfur-containing ligands, metallothioneins and phytochelatins, have been identified in plants and are thought to be potentially involved in metal tolerance. Metallothioneins are involved in cellular homeostasis of metal ions in mammals and fungi. Phytochelatins are thought to be a functional analogue of this regulator and be directly involved in plant metal tolerance. Although these compounds have the ability to bind to a wide variety of metals, there is contradictory evidence that suggests metal tolerance does not decrease with sulfur deficiency, as summarised by Baker et al. (1997).

Amino acids were thought to be significant for metal chelation in the xylem, aiding especially the root to shoot transfer of potentially toxic metals. Krämer et al. (1996) reported that the exposure of hyperaccumulator *Alyssum lesbiacum* to nickel, causes a correspondingly linear increase in histidine concentration within the xylem. Histidine was also supplied to *A. montanum* a non-hyperaccumulator species of *Alyssum*. The results showed both increased nickel tolerance and capacity for nickel transportation to the shoot. This indicates that histidine is involved both in the mechanism for metal tolerance and in the high rates of nickel transport in the xylem required for hyperaccumulation in the shoot of *Alyssum* species.

It is apparent that the bio-mechanisms for metal detoxification vary between hyperaccumulator families and often species. In general carboxylic acids seem predominantly utilised as storage ligands within the vacuole of the stem and leaf, while amino acids are responsible for transportation of nickel from the roots, at least in *Alyssum*.

The addition of complexing agents such as EDTA has been shown by Blaylock et al. (1997) to induce hyperaccumulation of Pb in plant species that do not usually hyperaccumulate this element. The Pb is solubilised in the soil and crosses root cell membranes into the xylem. Transportation to the stem and leaf portion of the plants occurs before the phytotoxicity of the element results in the plants death. Robinson (1997) showed that when EDTA was added to the nickel hyperaccumulator *Berkheya coddii* the nickel concentration in the dry matter actually decreased even though the bioavailability increased. This was concluded to be the result of competition with the. plant's own nickel-binding agents causing nickel to diffuse out down its concentration gradient.

With greater understanding of the mechanisms of hyperaccumulation, it may be possible to enhance phytoextraction by existing hyperaccumulators or safely induce it in non-hyperaccumulators.

1.4 Nickel

First isolated in the 18th century, nickel is of primary importance in the production of steel alloys and has had a major role in the development of the chemical and aerospace industries. The addition of nickel to other metals, forming alloys, currently accounts for the use of more than 80% of the world's nickel production, with 60% being used in the production of stainless steel. Its use imparts strength, resistance to corrosion and various other electrical, magnetic and heat resistance properties.

There are two main types of nickel ore exploited by the mining industry. The first is the primary sulfide mineral pentlandite $(Fe, Ni)_9S_8$, found in lodes in mafic and ultramafic igneous rocks and occurring naturally with pyrrhotite (Fe_nS_n+1), pyrite (FeS_2) and chalcopyrite ($CuFeS_2$). Such ores generally form parts of ancient volcanic lava flows and are often found in regions where glacial action has removed much of the overlying weathered rock surface such as Canada, Russia and Finland. However, such primary nickel deposits also make up 60% of the known nickel ores of Australia, where they occur with a nickel content ranging 1-4% (Tunderman et al., 1992).

The second major nickel ore is associated with some laterites, where nickel is found in the minerals garnierite ($(Ni, Mg)SiO_3.nH_2O$) and nickeliferous limonite (a mixture of nickel and iron oxides). These are the products of weathering of nickel-bearing mafic and ultramafic rocks, commonly associated with tropical and subtropical climates. The high rainfall of these localities allows for leaching of the surface layer with nickel solutions being re-deposited and concentrated in a zone between laterite (above) and primary rock (below) as oxides and silicates. Nickel-bearing laterites such as those found in New Caledonia, often referred to as oxide ores, make up the majority of the world's nickel ore resources with nickel content commonly from 1-2%.

Mining of nickel ores is achieved primarily using conventional open-cut and underground methods. The treatment of the extracted ores varies depending on their composition and the desired product, with processes used to recover nickel from sulfide and lateritic ores differing considerably because of their differing physical characteristics. The sulfide ores contain nickel, iron and copper in a mixture of distinct minerals, allowing for initial concentration by mechanical methods (Tunderman et al., 1992), while nickel oxide ores are generally treated chemically for beneficiation.

Sulfide ores are commonly ground and crushed, liberating the nickel minerals from the surrounding rock or gangue (Keynes, 1976). After crushing the ore is mixed with various organic reagents (commonly of the members of the xanthate group) and oils, rendering the minerals hydrophobic. After transfer to a flotation cell containing water, the ore is stirred and air is blown through the mixture with the result that a froth of oil-coated bubbles is created. The minerals, now hydrophobic, adhere to the bubbles and are carried to the surface, where the froth can be scraped off and collected. The addition of differing reagents to the crushed ore produces varying results and indeed can be manipulated to separate a series of different minerals from the same ore. The overall effect is to concentrate the nickel bearing minerals into a refined ore with a content ranging from 11-20% Ni (Tunderman et al., 1992).

Minerals once concentrated are transported to a smelter for further processing. They undergo a series of pyrometallurgical processes that consist of roasting, smelting and converting. Roasting oxidises the iron and liberates sulfur dioxide, while the smelting process removes a siliceous slag containing the iron oxide and other oxide compounds. Further amounts of sulfur dioxide are released and the end product is an impure nickel matte. The converter or Bessemerizing process removes virtually all the remaining iron and more sulfur (as sulfur dioxide) by adding silica and blowing air through the molten matte. The end product contains 71-72% Ni and 5-6% Cu, commonly being produced in a granulated form.

Further treatment of this matte is determined primarily by the copper content. If this is low enough the matte may be cast directly into anodes for electrolytic refining. More common it is necessary to separate the nickel and copper sulfides. This is achieved by cooling the matte to allow crystal growth, crushing, and then separation by flotation. Any nickel-copper alloy is separated magnetically. The nickel sulfide once collected can either be cast into anodes for electrolysis or roasted to produce a nickel oxide sinter, with 76% Ni content.

Nickel is extracted from lateritic ores by either pyrometallurgical (heating the ore to perform mineral separation) or hydrometallurgical (involving a liquid extraction) methods. In the first of these a sulfiding material such as gypsum is added during smelting to produce an iron-nickel matte akin to that encountered with nickel sulfide ore smelting. Treatment from here would include those procedures applied to the sulfide ore matte, or the nickel matte may be roasted to an oxide, ground, compacted and reduced to metal using charcoal in a muffle furnace. This produces a different nickel product, with a metal content of 99.3% Ni. An alternative to the addition of sulfides is to smelt the nickel oxide ore in an electric furnace using coke to reduce the metal, producing a ferronickel alloy which contains 20-30% Ni.

Hydrometallurgical extraction of nickel from lateritic ores involves a leaching process with sulfuric acid. During acid leaching the nickel, but not iron is solubilised, using increased pressure and temperature to aid the extraction. The nickel rich solution once purified is treated with hydrogen sulfide to precipitate nickel and cobalt sulfides.

There are a number of techniques commonly used for the refining of crude nickel, as produced by leaching and smelting of either lateritic or sulfide nickel ore. Electrolytic refining is carried out with a high purity cathode and an anode cast from either nickel matte or nickel sulfide. The electrolyte is pumped continuously through the electrolysing tank and through filters to remove soluble impurities. The anode decays as nickel is oxidised, subsequently the freed nickel ions are reduced to nickel metal at the cathode. The final product has purity greater than 99.9% Ni (Tunderman et al., 1992).

Another refining option is nickel carbonyl production. Crude nickel is reacted with carbon monoxide at 100°C to form toxic nickel carbonyl. Upon further heating to 300°C the nickel carbonyl decomposes to a fine nickel metal. The presence of nickel powder also encourages nickel carbonyl decomposition, with nickel metal being deposited on the powder to form pellets. Metal produced by this procedure is of high purity with greater than 99.9% Ni.

Leaching crude nickel with ammonia in a hydrometallurgical process is employed at the Kwinana refinery in Australia. The resulting nickel-bearing solution is treated with hydrogen sulfide gas to remove copper as a copper sulfide, then treated with hydrogen gas under pressure to precipitate metallic nickel. Any remaining nickel is precipitated by hydrogen sulfide addition, as a mixed sulfide product with cobalt. Nickel is sold as a powder with approximately 99% purity or heated, to be sold as sintered nickel. The remaining solution, being rich in ammonium sulfate, is crystallised for use as a fertiliser. An alternative hydrometallurgical refining method, as used in the Yabulu plant that processes ores from New Caledonia and Indonesia, includes precipitating the nickel as a carbonate. This is further treated to give sintered nickel and nickel oxide containing 85, 88, 98 or 99.5% Ni.

For the year 1992, the use of nickel worldwide was estimated at 814000 tonnes, corresponding to a monetary value of 6 billion dollars for the nickel mining and refining industries. The economic nickel reserves as of 1992 were estimated to be 47 million tonnes. With an average increase in nickel consumption of 2% annually the existing reserves would be depleted by 2030. This figure defines economic nickel as coming from ores containing greater than 1% nickel, with some as low as 0.8%. There are substantial nickel resources with grades currently considered less than economic, but in the future may be amenable to mining and refining.

There are two main factors driving the development of new mining and metal refining techniques: economics and environmental concern.

Nickel reserves are finite and the majority of high-grade ores with greater than 1% Ni are being depleted. Mining low-grade ores at present is uneconomical using conventional techniques of open cut or underground mining. Until this is offset by a large increase in the price of nickel, the only option is to look for new mining techniques that can efficiently extract nickel from low-grade ores.

In recent times, with increased environmental and pollution awareness, the mining industry is being held accountable for any damage caused to the environment during its operations. Pressure is being applied from governments and the general public to find alternatives to the older destructive and wasteful mining techniques.

The two governing factors of economics and environment coincide when restrictions are imposed on pollution and environmental damage. This has resulted in a large additional outlay of money being required to both get permission for and establish a mining or metal refining venture. Existing industry too has needed to invest substantially in upgrading and modernising their sites.

1.5 Phytomining

Phytoextraction, in the form of phytomining, offers a metal extracting method that is capable of exploiting ores with metal concentrations too low for economic recovery by conventional techniques. More importantly for mining operations, it has the potential to do so with relatively low cost.

First suggested by Baker and Brooks (1989), phytomining can be applied to naturally metal rich soils either as a stand-alone mining method or to supplement existing mining techniques. As economics dominates the parameters of phytomining (Brooks, 1998) there are restrictions on the type of metal amenable to the procedure. Possible yields of metal (function of biomass and plant metal concentration) and their relevant prices limited their selection. Brooks has suggested that only cobalt, nickel, copper and manganese may be considered for phytomining. Of these metals nickel must be considered the most likely candidate for a profitable phytomining operation, owing to the availability of both low-grade ores and suitable plants. Nickel accumulation accounts for 318 of the more than 400 species of hyperaccumulators. Recent work by Anderson (1998) using sequestering agents such as thiocyanate to induce gold phytoextraction suggests phytomining other metals may be possible. Reagents such as EDTA have been employed for a similar purpose on various metals (both for phytomining and phytoremediation). It is not known what effect adding such sequestering reagents has on soil ecology and much research is still required to determine whether their addition is beneficial for long-term results.

Once harvested, the plant material can be combusted resulting in a reduction in mass to approximately 10% of the original and hence concentration of metals. Masses reduced to as low as 4% were reported Nicks and Chambers (1995). With some hyperaccumulator plants extracting in excess of 10000 μg/g Ni into their dry weight, upon ashing, a nickel rich inorganic medium or *bio-ore*, is created with >10% Ni. Estimates that depend on plant Ni concentration and the degree of mass reduction put the possible content as high as 20% Ni. This is considerably more enriched than laterite or sulfide ores commercially mined, with nickel content normally less than 3% Ni. The use of non-hyperaccumulators is excluded from phytomining as combustion of such plant material results in an ash of comparatively low metal concentration.

Hyperaccumulators such as *A. bertolonii* show strong selectivity towards nickel. Other metals such as Fe that make up a large portion of the soil are relatively excluded in elemental uptake. Thus phytomining nickel is not only a means of recovering the metal from soil, but also a refining process. The plant ash is a more pure product than the original soil.

Nicks and Chambers (1995) carried out the first practical study using *Streptanthus polygaloides* to produce a nickel-rich crop. They showed that the energy recovered from combustion of the plant material aided in making the process cost effective. During the combustion of cellulose 17.5 GJ/tonne of heat is produced. On a large scale, recovery of a portion of this energy is justified. Such an energy recovery may be in the form of electricity produced from plant material combustion, either at a large commercial power station, or a smaller local (perhaps onsite) incinerator and power generator. Alternatively, the energy could be recovered in the form of heat, to either aid drying further plant material or for use in the processing of previous batches of bio-ore.

Phytomining can be viewed as not just an economical mining technique, but also as a "green" alternative to open cast mining. The process, utilising living organisms to achieve mining goals, is more aesthetically pleasing and leaves the remaining soil intact, as opposed to complete removal and consumption. Tailings are non-existent, and no acidic mine runoff is produced, two of the key polluting aspects of open cut mining. However as the phytoextraction only occurs in the top layer of soil the plants are grown in, there is a need to excavate this layer, once an adequate nickel extraction has been achieved, allowing access to further ore. This may be done initially, with the top layer being placed with an acceptable thickness at another locality, effectively increasing the surface area amenable to phytoextraction. This need for soil removal, is a limitation when considering processing an entire ore body. The "hole" may be refilled with the mined soil, thus limiting environmental damage and allowing for revegetation with native species. However costs incurred with the removal of soil would be equivalent to conventional ore removal techniques, potentially making the operation uneconomical.

There is the possibility for nickel farming, in the sense that very low-grade ore or serpentine soils may be farmed for nickel. Such an operation would not require the extraction of nickel from an entire ore body; thus excavation of the soil would be unnecessary, with plowing being adequate for regeneration of Ni in the phytoextraction soil layer. If this proved to be economically comparative or better than other forms of crops farming, previously un-farmable soils may be utilised.

In the case where open cut mining operations are already in operation, it is often found that low-grade ores and tailings are removed and discarded into heaps in order to allow access to higher grades of ore. Phytomining may find a niche on the treatment of such low-grade refuse, supplementing the nickel yield from the open-cut mining operation.

1.6 Phytoremediation

Much emphasis has been put on phytoremediation as this process lacks the restrictions of profit-making, through the value of the extracted metal associated with phytomining. First mentioned in the 1970's, phytoremediation was examined in greater detail in 1983 by Chaney. Unlike phytomining this application of phytoextraction is emerging as a proven technology, starting to be used in industry (Robinson, 1997). Any metal known to be accumulated in significant proportions is capable of being the subject for phytoremediation. However, given the choice of hyperaccumulators, nickel is still favoured for industrial removal, owing to the availability of suitable plants.

Pollution associated with many past and present industries is widespread. In 1993 the United States had identified 1235 sites that required remediation (USEPA, 1993), with costs expected to exceed 300 billion dollars. A large portion of these sites are contaminated with heavy metals. Existing remediation techniques frequently involve the removal of contaminated soil and either disposal or chemical treatment. This proves to be expensive, environmentally destructive and in some cases not possible. Phytoremediation offers an environmentally safe alternative with the advantage of *in situ* treatment and relatively low cost.

The use of non-hyperaccumulators in phytoremediation is more common for organic contaminants, for example the suggestion the recent research into the use of tobacco plants for remediating TNT contaminated soil. When employed for heavy metal removal their low metal concentrations are offset by the much larger biomass capable of being produced. Thus adequate proportions of the contaminant can be removed but are contained in much larger biomass. Their use for nickel removal has not received as much attention owing to the availability of hyperaccumulators such as *A. bertolonii* and *Berkheya coddii* that have great potential with this metal.

Cost recovery from phytoremediation is an important aspect of the process, as it must be realised that soil remediation only occurs when someone agrees to pay for the process (Chaney et al., 1997). The chief form of economic return is from increased land value. Industry can buy relatively worthless heavy-metal polluted land and through phytoremediation greatly inflate its value. Another obvious form of economic return is the extraction of metals from the contaminated soil for resale as a commodity. Nickel-rich plants produced by a phytoremediation operation should be treated in the same manner as those related to phytomining, in order to maximise return and thus cost of remediation.

The overall goals of remediation and mining by phytoextraction become blurred, when considering the recovery of nickel as a commodity. If the sale of reclaimed nickel from the remediation of contaminated sites produced a profit, then such contaminated soils could be considered as a form of low-grade nickel ore. With both goals of remediation and mining for profit achieved the distinction between phytomining and phytoremediation is removed. The implications of such a development for soil decontamination would be vast; however, it should be noted that this is simply an end goal, with numerous factors to be addressed and much further research required before such lofty ideals may be reached.

1.7 Phytoextraction Approaches

No matter whether for environmental or mining purposes, the basic goal of phytoextraction is to maximise the yield of heavy metals extracted from the soil. This is limited both by the plants utilised in phytoextraction and the nature of the soils involved.

The initial step in ascertaining phytoextraction feasibility is to determine the bioavailability of the metal in question. Robinson (1997) determined that the concentration of Ni in the hyperaccumulator *B. coddii* was logarithmically related to the nickel extracted by a 1M ammonium acetate solution. Bioavailability analysis by this method enables theoretical nickel yields to be calculated and an economic assessment of metal recovery made.

The overall yield of metal from a phytoextraction operation is a function of the concentration, biomass and rate of uptake by the plant. It is important that a balance be reached between these variables. Plants with high concentrations often have a small biomass, while large biomass plants have low metal concentration and/or slow growth rates. An example such as *Thlaspi caerulescens*, which accumulates nickel to high concentrations (>2% dry weight) over an acceptable period (6-9 months), has a resulting biomass so small as to inhibit its use in commercial Ni phytoextraction. On the other hand, *Sebertia acuminata*, a tree with a mean nickel content of 0.25% and large biomass, could potentially remove hundreds of kilograms of nickel per hectare, but its growth is too slow, requiring decades (Robinson, 1997).

Remediation is possible over long periods of time, but to make an operation economic the soil nickel concentration should be reduced to acceptable levels within about 10 years. Yearly harvesting would be advantageous to ensure continuous cost recovery, while the use of plants that do not require either complexing reagent addition or reseeding after each harvest would also be beneficial.

Fast-growing shrubby or herbaceous plants have been suggested for most situations, providing adequate biomass and metal concentration. Plants such as *A. bertolonii, B. coddii* and *S. polygaloides* have been identified as being suitable for nickel phytoextraction. In studies of phytomining serpentine soil, *B. coddii* crops, with a maximum content of 0.7% Ni, were estimated to produce 22 tonne/ha dry plant material. *A. bertolonii* achieved 9 tonne/ha at a maximum concentration of 1.5% Ni (Robinson, 1997).

The use of fertilisers with hyperaccumulator plants, specifically *A. bertolonii*, has been shown by Robinson *et al.* (1997) to dramatically increase the biomass. The addition of a mixture of nitrogen, phosphorus and potassium had the effect of increasing the biomass by as much as 300% in one study. Nitrogen-based fertiliser used alone achieved 130% increase in biomass, higher than the other single fertiliser additions. Such a large increase was observed in *T. caerulescens* also which achieved a 195% biomass increase (Brooks, 1998). Gabbrielli et al. (1990), showed that the addition of Ca to the growth medium of *A. bertolonii* actually reduced biomass and metal uptake, due to the plants edaphic adaptation to low serpentine Ca concentrations. However, Chaney et al. (1999) contradicted this by reporting that Ca addition did not inhibit hyperaccumulator plant growth and actually increased Ni tolerance in the plants.

Hyperaccumulators are often characterised by their rich variety of genotypes found in their wild populations (Brooks, 1998). This is evident in the differing biomass of plants for a given species, which may only grow 20 cm apart. This is an advantage when considering selective breeding of a plant species to produce a high-yielding strain. Metal uptake can also vary markedly from plant to plant, another possibility for selective breeding. There may be some difficulty however, in establishing a high degree of metal accumulation and high biomass in one plant, as with good hyperaccumulation it is usually found that plant growth suffers.

Kumer *et al.* (1994) discussed the possibility of incorporating the genes responsible for hyperaccumulation from a low biomass plant into a fast-growing high biomass species such as *Brassica juncea*. Such an achievement would dramatically increase metal yields and turnover of phytoextraction crops, opening up this field of metal recovery, and making for an exciting technology. However, research into hyperaccumulator gene splicing is still in its infancy (Brooks, 1998).

In terms of economics, the treatment of the nickel rich bio-ore is of equal importance to maximising the nickel yield from a phytoextraction crop. Overall income from the nickel extracted depends on the processing costs and efficiencies, saleability and price of the final commodity, as much as it does on the availability of the nickel itself.

1.8 Plant Treatment

Suggestions for the treatment of the nickel bio-ore have primarily been for its use as a supplementary feedstock in existing nickel smelting operations. This is seen as the easiest way of recovering Ni from the ash and thus recovering costs from the phytoextraction.

The use of existing smelting operations saves costs on establishing newer, more specialised techniques, and requires no additional variations on the procedure used for ore in order to account for the ash content. While convenient, smelting has a number of drawbacks with respect to hyperaccumulator plant ash.

(1) Inefficiency of process. The smelting of nickel is an energy intensive process. Large amounts of electricity are required to separate nickel, with a melting point of 1450°C, from the surrounding material to produce a marketable nickel matte.

(2) Low sale cost of product, therefore a reduced return. The price of nickel metal fluctuates dramatically. The beginning of 1999 saw prices drop as low as $1 US/kg, while a year later (2000) nickel returned $10.09 US/kg. The matte product from smelting contains approximately 75% Ni, limiting the sale price to below that of more pure products. If other constituents such as copper are in low abundance, the matte may be sold for alloying. To achieve higher returns, the nickel needs further processing to either improve purity or create a marketable nickel salt e.g. $NiSO_4.6H_2O$.

(3) Poor use of relatively refined starting material. The process of hyperaccumulation has the secondary characteristic of selectivity of nickel over other metals. Such is the selectivity, that Fe, Al, Cu and Zn are all largely excluded, with the resulting bio-ore even more refined than ore that has undergone a beneficiation process. It

would be economically advantageous to utilise this refinement to create a high purity, high-value product.

Hydrometallurgical processing of the hyperaccumulator plant ash has been suggested as an alternative to smelting. This eliminates the expensive middle step between ore and refined product. Nicks and Chambers (1995) proposed leaching the ash with sulfuric acid to create a nickel rich solution. From such a solution, numerous techniques may be employed to extract a pure nickel product, whether metal or compound. Such processes have been described in the refining of nickel matte and nickel sulfide, electrowinning, nickel carbonate precipitation, reduction by hydrogen sulfide addition, nickel carbonyl production and reduction to metal.

Given the sulfate medium that leaching the ash with sulfuric acid creates, and the relative absence of other electroactive metals, electrowinning of Ni from plant ash was considered possible and indeed of interest. Alternatively, the high abundance of nickel in a sulfate environment suggests that crystallisation of a nickel sulfate salt should possible.

This project was aimed at verifying the feasibility of these two techniques as a direct means of extracting nickel from hyperaccumulator plant ash, to produce a marketable product.

Chapter Two

Ashing and Acid Extraction

2.1 INTRODUCTION

The treatment of the hyperaccumulator plant material, once harvested, has a significant effect on later processes and any possible product. Initially there are two choices:

(1) Extraction of nickel from the fresh plant matter, where organic compounds and water still make up a large portion of the material.

(2) Recovery of nickel from the ash of the harvested hyperaccumulator plants. This involves a drying and combustion process to produce the bio-ore.

Bowen's extraction series (Bowen et al., 1961) determines the portion of nickel, present in the plant, that is amenable to various extractive solutions. This series and the proportions of extractable metal, also correlate with the way in which the nickel is stored within the plant. With respect to nickel hyperaccumulators, one such investigation concluded that the majority of nickel could be removed by macerating the plant material in the presence of a dilute acid (Shaw, 1980). Although this type of extraction removes an adequate portion of the nickel from the plant material, it has a number of disadvantages that inhibit its use as a large-scale technique. Owing to the larger volume and comparatively low nickel concentration of fresh material compared to the plant ash, the resulting extract solutions would have a much smaller nickel concentration than that obtainable from an ash extract. Also, the presence of large quantities of organic compounds within the solution would cause processing problems in the majority of nickel recovery techniques.

On combustion, water and the majority of carbon is removed from the hyperaccumulator material, while the metallic elements form oxide and carbonate products. The effect is to concentrate the non-volatile inorganic elements, as their organic complexes are removed. Once in this reduced form, the nickel is readily acid-soluble, enabling an acid extraction to be performed. To date it is unclear whether the product of open-flame combustion is adequate for such an acid extraction, or whether controlled ashing, as used in laboratory destruction of organic matter, is necessary to enable an adequate nickel recovery. Open-flame combustion generates a large amount of heat; this energy may be recovered and either converted to electricity to be sold or utilised elsewhere. Controlled ashing would require large amounts of energy, increasing the costs and limiting the application of the phytoextraction technique. For this reason it was important to ascertain whether the uncontrolled combustion would result in an ash product suitable for nickel recovery and any possible limitations such a product may place on an acid extraction.

Acids are used for the separation of metals from many media types both for analysis on a laboratory scale and large-scale commercial extractions. Although there are accepted methods for the separation and purification of metals directly from the solid phase, these are predominantly energy intensive. Acid extraction offers not only separation of the metals from unwanted material, but also gives a change of phase, from solid to liquid. Extraction of metals from the liquid phase is predominantly more energy efficient and results in a purer product, whether this is as a metal or metal compound.

Hyperaccumulator plant ash is an ideal material for acid extraction, with its high nickel content and ease of extraction enabling extracts with high nickel concentrations to be produced. Equally important is the relative lack of metal impurities such as iron, copper and zinc. The absence of such electro-active metals in high concentrations broadens the possibilities for recovery of the nickel from the ash extract. Techniques such as electrowinning and crystallisation may be employed to produce a high purity product, potentially of greater worth than conventional nickel smelting product.

All initial work was done with electrowinning as the extractive goal. For this reason when choosing the type of acid to be used for ash leaching, thought was given to the possible effects their respective anions could have during electrolysis. Sulfuric acid was chosen as the basis for nickel extraction, as a sulfate medium is ideal for electroplating Ni. HCl was avoided as Cl_2 gas is produced during electrolysis, causing both health risks and environmental damage.

2.2 MATERIALS AND METHODS

2.2.1 Hyperaccumulator Plant Material

Nickel-rich plant material made up predominantly of *Alyssum corsicum* and smaller portions of other Turkish hyperaccumulators (*A. floribundum, A. masmenaeum, A. callichroum)*, was collected from various sites in Turkey by Associate Professor

Roger Reeves. The material was dried, broken to no larger than 2 cm in length pieces and mixed to make *ca.* 200 g composite of nickel-rich hyperaccumulator plant material.

Once in New Zealand, a 0.5 g representative sample consisting of leaves and shoots was taken from the *A. corsicum* material and ashed in a muffle furnace for 4 hours at 500°C. The ash was then digested in hot 2M HCl, diluted and analysed for Ni concentration using flame AAS (model GBC 905AA). The Ni content of the dry matter was found to be 1.12%.

2.2.2 X-ray Powder Diffraction Analysis and Comparison of Ashing Techniques

Samples of 2 g taken from the *A. corsicum* material were ashed. One sample was ashed in a muffle furnace for 6 hours at 500°C, while the second sample was ashed by open flame combustion in a clean fireplace, with temperatures in excess of 800°C. In the second case, ashless filter paper was used to aid the combustion without leaving excessive residue. This allowed a sample to be collected that was comparable to ash that might be produced by industrial open flame combustion.

Both ash samples were ground by mortar and pestle, then set to glass slides with acetone. Analysis by X-ray powder diffraction was carried out and the spectra collected.

2.2.3 Simulated Nickel-rich Plant Material

Owing to the limited quantity and availability of authentic nickel-rich plant material, there was a need to produce a synthetic counterpart, on which ashing and Ni extraction could be investigated.

Assorted plant material was collected from local plants, with overall leaf to stem proportions similar to those found in high-biomass nickel hyperaccumulators. This material was dried at 45°C until a constant weight of *ca.* 1 kg was achieved. A nickel solution consisting of 89.56 g $NiSO_4.6H_2O$ in 200 ml water was poured over the dry plant material and mixed, adding a total of 20 g Ni to the plant material. This gives a comparable dry weight concentration to that of high Ni-yielding hyperaccumulators with 2% Ni.

After drying to remove excess water, the material was ashed by open flame combustion in a clean fireplace. The total collectable ash was 176 g. Assuming complete conservation of the 20 g nickel this gives an inorganic medium of 11.4% Ni.

2.2.4 HF Extraction

A 0.15 g sample of the synthetic ash was placed in a 50 ml Teflon beaker, to which 10 ml 1:1 HF/HNO_3 was added. The solution was heated on a steam bath and taken to dryness, before a further 10 ml concentrated HCl was added with stirring. This too was taken to dryness, followed by the addition of 10 ml warm 2M HCl. The solution was stirred and heated to ensure dissolution of sample residue, then made up to 10 ml with water. Dilution and analysis by ICP – AES was then undertaken to determine the major inorganic element concentrations of the ash.

2.2.5 Small-Scale (0.25 g) Sample Investigations

Initial experiments to determine the best-suited acid or acid mixture for the extraction of Ni from plant ash were done using 0.25 g ash samples.

Samples were weighed using a four-figure balance, recorded and placed in 30 ml glass beakers for acid dissolution. A standard volume of 10 ml acid was used to ensure consistency, with all samples being stirred at regular intervals.

When required, refluxing on a hot plate was carried out, with a watch glass covering the beaker, ensuring no loss of volume and maintaining boiling point temperatures.

Solutions were filtered using vacuum filtration and a porous sinter funnel to remove the remaining insoluble material, which was washed with deionised water. Sample solutions were then diluted and analysed using flame AAS. The results were compared to the known Ni concentrations in the synthetic ash and the % Ni extracted from the ash samples by the acid determined. These percentages were used for the comparison of acids and extraction conditions.

2.2.5.1 Effects of Refluxing

Samples of 0.25 g were treated with acid for 30 minutes. In some cases periods of refluxing were undertaken in the later part of the allotted time.

Extraction conditions included: cold water, cold 4M H_2SO_4, 4M H_2SO_4 with 15 min refluxing, and 4M H_2SO_4 with 30 min refluxing.

2.2.5.2 HCl Ash Extraction

A short study was undertaken on the potential of HCl to extract nickel from plant ash. Extraction conditions used were: cold 2M HCl, 2M HCl with 15min refluxing and 1:2 2M HCl/HNO_3 with 15min refluxing. All 0.25 g samples were treated for a total of 15 min. with 10 ml acid and stirred regularly.

2.2.5.3 HNO_3 Addition to Leaching Solutions

The advantage of adding HNO_3 to H_2SO_4 was investigated by adding conc. HNO_3 in varying proportions: 9:1 4M H_2SO_4/HNO_3, 4:1 4M H_2SO_4/HNO_3 and 1:1 4M H_2SO_4/HNO_3. Samples of 0.25 g were refluxed for 15 min in 10 ml acid. A 10 ml 4M H_2SO_4 extraction was used as the control.

2.2.5.4 Effects of Varying Acidity

Samples of 0.25 g were treated with 10 ml acid mixture: 9:1 4M H_2SO_4/HNO_3, 2M H_2SO_4/HNO_3, 4M H_2SO_4/8M HNO_3, 2M H_2SO_4/8M HNO_3, with 4M H_2SO_4 as a control. Solutions were refluxed at boiling point for 15 min.

2.2.6 Extract Residue and Comparison with Primary Ash Composition

To determine what portion of the ash was insoluble in the acid mixture 9:1 4M H_2SO_4/HNO_3 a sample of 0.5 g was weighed, using a four-figure balance, into a 30 ml glass beaker. Ten ml of acid mixture was added and the solution refluxed for 15 min. After cooling, the solution was filtered using vacuum filtration and ashless filter paper. The filter paper and insoluble material were heated in a muffle furnace for 4 hours at 500°, leaving only ash residue, which was weighed to determine its proportion of the whole ash sample.

A 0.25 g synthetic ash sample was treated in the same manner as previous 1:1 HF/HNO_3 digests for the investigation of primary ash composition.

For the production of an adequate mass of residue a 2 g synthetic ash sample was treated with 80 ml acid mixture 9:1 4M H_2SO_4/HNO_3 (maintaining the acid/sample ratio used in the 0.25 g acid extractions). This was refluxed for 15 min after which it was allowed to cool and centrifuged for 10 minutes at 4000 rpm. The supernatant was drained off and the remaining solid washed twice with 80 ml aliquots of deionised water, each being centrifuged and discarded. The insoluble material was then washed

into a beaker and dried at 60°C until all water was removed. A 0.25 g sample was taken and a 1:1 HF/HNO_3 extraction performed using the previous procedure.
Solutions from both primary ash and residue were diluted before elemental analysis by both ICP-AES and flame AAS, allowing a comparison between ash and residue.

2.2.7 Larger-Scale (1 g) Sample Investigations

The elemental concentrations of Ni, Ca, Mg, Fe and K from two different acid extractions, 9:1 4M H_2SO_4/HNO_3 and 19:1 4M H_2SO_4/HNO_3, were investigated using flame AAS. A sample of 1 g synthetic ash was treated with 10 ml acid, refluxed for 15 min and allowed to cool. Solutions were then filtered and diluted for analysis.

2.2.8 Lower Concentration Acids

Acid mixtures with overall [H^+] less than 9:1 4M H_2SO_4/HNO_3 were used to treat 1 g synthetic ash samples. Ten ml 9:1 2M H_2SO_4/HNO_3, 9:1 1.5M H_2SO_4/HNO_3 and 9:1 2M H_2SO_4/8M HNO_3 were used, with 9:1 4M H_2SO_4/HNO_3 as a control. Each was refluxed for 15 min before being filtered and diluted for Ni analysis using flame AAS.

2.2.9 Effect of Ash on Extract Acidity

To investigate the neutralisation of an acid solution with varying quantities of ash, 10 ml of 9:1 4M H_2SO_4/HNO_3 were used to dissolve 0.5, 1.0, 1.5, 2.0 and 2.5 g synthetic ash samples. Each was refluxed for 15 min, allowed to cool and centrifuged for 5 min at 4000 rpm, enabling a 1 ml sample to be taken. This was diluted 100 fold and the pH measured (Denver Instrument model 50 pH meter). From each recording the [H^+] of the ash extract was determined.

2.2.10 Large Volume (20 g Ash per 100 ml Acid) Extractions

2.2.10.1 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extraction

A synthetic ash sample of 20 g was weighed into a 200 ml round-bottomed flask to which 100 ml 9:1 2M H_2SO_4/8M HNO_3 was added. The solution was refluxed with a Bunsen burner for 1 hour to ensure thorough mixing and heating.
After cooling the mixture was centrifuged for 10 min at 7000 rpm to separate residue material. The clear green ash extract was decanted, yielding 85 ml, with the remaining 15 ml contained within the packed insoluble material.

A UV/visible spectrum of the ash extract ranging 190-820 nm was obtained using a Hewlett Packard spectrophotometer (model 8452A). The Ni concentration was determined using the same instrument since high Ni concentrations can be determined conveniently at 720nm without the need for dilution.

Two 0.5 ml samples were taken for ICP analysis, while another 0.5 ml sample was diluted and the pH tested, to determine the remaining [H^+] of the ash extract.

2.2.10.2 4M H_2SO_4 Synthetic Ash Extraction

An identical extraction, following the same procedure as above, but with 4M H_2SO_4 was carried out for comparison, with UV/Vis analysis to obtain the Ni concentration and the spectra 190-820 nm.

2.2.10.3 *Alyssum corsicum* Material Treatment and 9:1 2M H_2SO_4/8M HNO_3 Extraction.

In a clean fireplace, the bulk sample of 200 g *A. corsicum* was interspersed between layers of ashless filter paper to aid in combustion. The material was ignited and consumed by flames, with estimated temperatures in excess of 800°C being reached. The ash was collected (19.44 g), and stored in a glass screw-top jar.

Following the procedure outlined above for 20 g synthetic ash sample treatment, a 100 ml 9:1 2M H_2SO_4/8M HNO_3 acid mixture was added to 19.44 g of *A. corsicum* ash in a round-bottomed flask with reflux apparatus attached. The solution was refluxed for 2 hours, ensuring mixing.

Centrifuging the cooled mixture for 15 min at 7000 rpm separated the residue material, leaving 85 ml of clear green solution from which two 0.5 ml samples were diluted to 5 ml and 250 ml for analysis by ICP. A UV/Vis spectrum, from 190-820 nm, of the extract was obtained using a Hewlett Packard spectrophotometer. This instrument was also used for a quantitative determination of Ni concentration using the peak at 720nm.

The remaining insoluble material was shaken with 15 ml deionised water and centrifuged for 5 min at 7000 rpm to remove the portion of the nickel in solution trapped between insoluble particles. This washing resulted in a further 15 ml of nickel-bearing solution, which was added to the initial extract, increasing the total nickel yield for the extraction. Another 0.5 ml sample of the extract was taken at this point, diluted and analysed by AAS to determine the Ni concentration.

A 1:1 HF/HNO_3 extract was performed on 0.1754g of the insoluble material, using the previously specified method for such extractions. The sample was made to 10ml with 2M HCl and an elemental analysis performed using ICP-AES.

2.2.11 Composite Hyperaccumulator Plant Material

Assorted dried and finely ground hyperaccumulator plant material was combined and mixed thoroughly to produce a composite of nickel-rich plant material. Portions added were taken from larger samples of plants from Turkey (*Alyssum virgatum*) and the Philippines (*Brackenridgea palustris* ssp. *foxworthyi*, *Phyllanthus 'palawanensis'*, *Walsura monophylla*) (Baker et al., 1992). Ni content for this plant material ranged from 3983 μg Ni/g to 10500 μg Ni/g, giving an estimated 6000 μg Ni/g for the composite. A 0.2618 g sample was taken and ashed in a muffle furnace at 500°C for 4 hours, then dissolved in hot 2M HCl. This was subsequently diluted to 25 ml and analysed for elemental content by ICP-AES.

A further collection of dried whole plant material consisting predominantly of shoots and leaves of *Alyssum corsicum*, *A. floribundum* and *A. callichroum*, with a weight of 34.45 g, was added to the finely ground composite, giving a total of 179.45 g hyperaccumulator material. Addition of this larger material was to both increase the mass and aid in the combustion of the finely ground material.

All material once combined was ashed in a coal skip, using ashless filter paper and a Bunsen burner to assist combustion. The ash was then heated in a muffle furnace for 6 hours to remove the remainder of the carbon still present. This combustion process gave a total of 8.4025 g ash, from which a 0.0492 g sample was taken and dissolved in hot 2M HCl, diluted to 25 ml then analysed using ICP-AES.

2.2.12 4M H_2SO_4 Extraction of Composite Hyperaccumulator Ash

An extraction using 4M H_2SO_4 was chosen for the treatment of the above hyperaccumulator composite. Most of the ash (8.30 g) was placed in a round-bottomed flask with reflux attachments. To this, 41.5 ml of 4M H_2SO_4 was added, maintaining the proportion of ash : acid at 200 g ash per litre of acid. The solution was refluxed for 1 hour and allowed to cool before being centrifuged for 15 min at 7000 rpm, separating 33 ml clear green nickel-rich solution from the insoluble material. Two 0.5 ml samples were taken from the solution and diluted to 250 ml and 25 ml for ICP-AES elemental analysis and determination of H^+ concentration of the solution.

The UV/Vis spectrum of the extract was also obtained from 190-820nm, with the 720 nm peak used to determine the Ni concentration, which was compared to the ICP results.

The insoluble ash residue, after centrifugation, was washed with an excess of double-deionised water to remove any nickel-bearing solution. A 0.1705 g sample was taken from this material and a 1:1 HF/HNO_3 extraction performed upon it using the previously specified method. The sample, now with a volume of 10 ml, was analysed by ICP-AES for elemental concentrations.

2.3 RESULTS AND DISCUSSION

2.3.1 X-ray Powder Diffraction Analysis and Comparison of Ashing Techniques

The X-ray spectra of both samples produced from controlled and uncontrolled combustion showed a high degree of crystallinity, with sharp identifiable peaks. Major peaks corresponded to NiO, MgO and $CaCO_3$. The chemical form of the potassium present could not be identified because of their absence from the mineral powder diffraction database that was being searched. Given later ICP results it is assumed that either K_2O or K_2CO_3 is present.

In terms of size and position of the peaks there appeared to be little difference in products between the two methods of ashing (Fig. 2.1), suggesting the open flame method should be adequate for treating the plant material. Along with the cheaper cost and convenience of this method, comes the possibility for energy recovery (refer 2.1) and its resulting economic return.

2.3.2 HF Extraction

The ICP results, shown in Table 2.1, compares the theoretical *A. corsicum* ash composition with the known simulated ash elemental composition. The theoretical *A. corsicum* ash composition was calculated from average *A. corsicum* plants' elemental concentrations (unpublished *A. corsicum* data, Köyçeğiz, Turkey) and multiplied by a factor of ten (the approximate decrease in mass upon combustion). The comparison of selected elements is shown graphically in Figure 2.2.

Figure 2.1: X-ray diffraction spectra of *A. corsicum* ash. Representative of both open-flame and controlled ashing techniques.

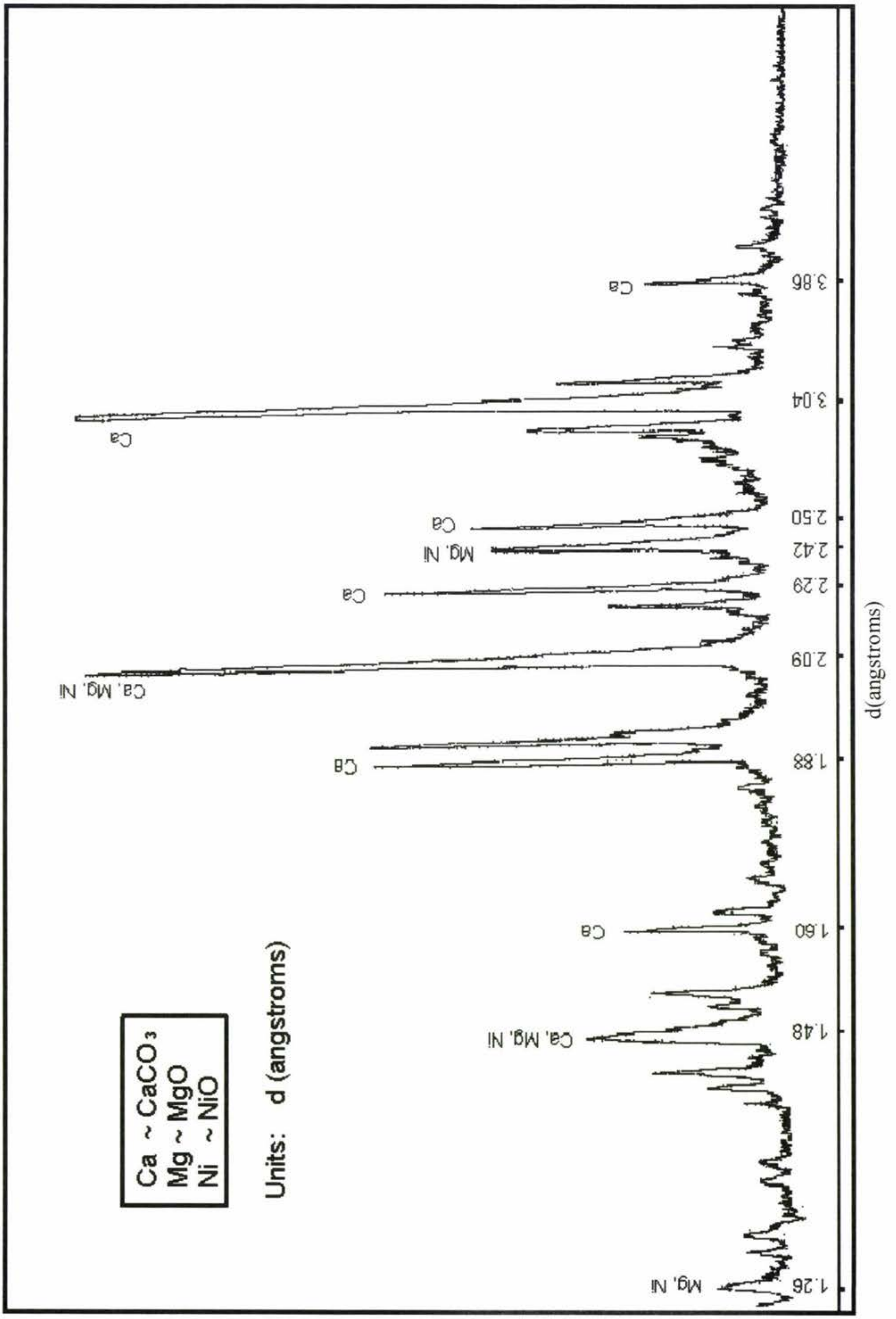
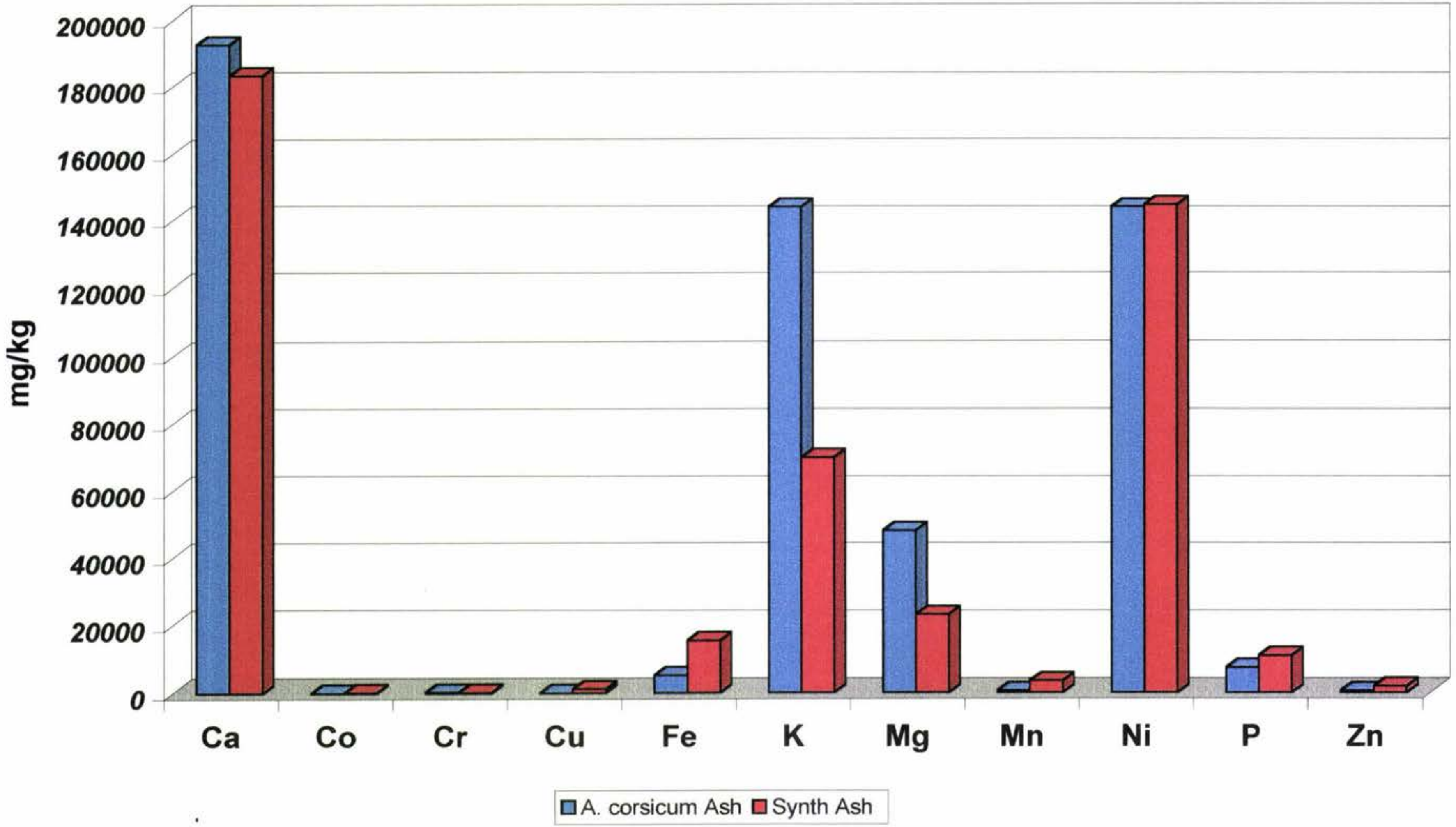

Ca ~ CaCO$_3$
Mg ~ MgO
Ni ~ NiO
Units: d (angstroms)
Ca
Ca
Ca
Mg, Ni
Ca
Ca, Mg, Ni
Ca
Ca
Ca, Mg, Ni
Mg, Ni
3.86
3.04
2.50
2.42
2.29
2.09
1.88
1.60
1.48
1.26
d(angstroms)

Figure 2.2: Elemental Concentrations of Typical *A. corsicum* Ash and Synthetic Ash



The concentration of Ni in the synthetic ash was elevated from the expected value of 11.4% Ni. This figure was calculated with the assumption of complete conservation of nickel during ashing and collection. A more realistic concentration would be 10-11%, given some loss of material. Not surprisingly, bearing in mind the method of its preparation, the synthetic ash is rather inhomogeneous in nature, with NiO concentrating in specific particles, thus allowing unusually high Ni concentration and variation in results, especially from small samples. The concentrating of NiO particles may be the result of incomplete ashing during open flame combustion, such as fixation to carbon, or possibly the effect of high temperatures in excess of 800°C.

Compared to the product of Ni-accumulating *Alyssum* species, the synthetic ash had lower K and Mg concentrations, and a rather higher Fe concentration.

The synthetic ash was still considered adequate for the purpose of assessing acid extractions. The nature of the synthetic ash with high Ni and Ca concentrations as well as other representative elements still closely resembles what would be found in nickel hyperaccumulator plant ash.

Table 2.1: ICP results for 1:1 HF/HNO$_3$ Extraction

Elements	Typical wt% *A. corsicum* Ash	wt% Synthetic Ni-Rich Ash
Al		3.50
Ca	19.28	18.35
Cd		<0.01
Co	<0.01	<0.01
Cr	<0.02	<0.01
Cu	<0.01	0.12
Fe	0.52	1.55
K	14.42	7.00
Mg	4.81	2.33
Mn	0.07	0.37
Ni	14.43	14.50
P	0.75	1.10
Pb		<0.15
Si		14.50
Sn		<0.03
Zn	0.06	0.20

2.3.3 Small-Scale (0.25 g) Sample Investigations

The initial experiments to determine the best-suited acid or acid mixture for the extraction of Ni from plant ash were done using 0.25 g samples. This amount was considered reasonably representative of the bulk ash while being small enough not to deplete the ash too quickly.

2.3.3.1 Effects of Refluxing

Using H_2SO_4 as the standard acid for the extraction of Ni from plant ash, the increased extractive potential of acids when heated was investigated.

Table 2.2: % Ni extracted for refluxing experiments

Extraction Solution	% Ni Extracted
H_2O	0.3
4M H_2SO_4 (cold)	20.4
4M H_2SO_4 (15 min reflux)	77.9
4M H_2SO_4 (30 min reflux)	63.1

It was observed that the activity of the acid greatly increased with heating, however once all soluble material is dissolved, further heating is irrelevant. The findings of this investigation were employed in most of the remaining studies, with 15 min of refluxing being standard to optimise Ni extraction. It should be noted that refluxing also involves the continuous mixing of sample within the acid, an effect separate to that of temperature that could also aid in extraction. The period required to maximise extraction will vary with differing sample sizes and indeed even when the sample size is constant, due to the inhomogeneous nature of the ash. An accurate determination of efficient heating times will require a larger more representative sample.

2.3.3.2 HCl Ash Extraction

HCl solutions are frequently used in the preparation of material of organic origin for elemental analysis. For this reason, although not practical in terms of electrowinning nickel, a short investigation was performed.

The results (Table 2.3) clearly demonstrate the need for heating, as was concluded previously using H_2SO_4. The complete extraction of Ni from ash by heated 2M HCl confirms that HCl has greater extractive properties for the removal of metals from ash than H_2SO_4 as found by Gilliam and Canon (1980), reaffirming its use for plant analysis in laboratories worldwide.

Table 2.3: % Ni extracted by HCl Treatment

Extraction Solution	% Ni Extracted
2M HCl (cold)	14.1
2M HCl (15 min refluxing)	100
1:2 2M HCl/HNO_3	100

2.3.3.3 HNO_3 Addition to Leaching Solutions

The dissolution properties of acids on both inorganic and organic samples can often be enhanced by the addition of a second acid. Examples such as 1:1 HF/HNO_3 and aqua regia (1:3 HNO_3/HCl) are commonly used for sample analysis on a laboratory scale.

Table 2.4: % Ni extracted with H_2SO_4 and with HNO_3 Addition

Extraction Solution	% Ni Extracted	H^+ molar % From H_2SO_4	$[H^+]$ mol/l (see below)
4M H_2SO_4	88.0	100	4.0
9:1 4M H_2SO_4/$HNO_{3\,\text{conc.}}$	98.8	69	5.2
4:1 4M H_2SO_4/$HNO_{3\,\text{conc.}}$	98.1	50	6.4
1:1 4M H_2SO_4/$HNO_{3\,\text{conc.}}$	94.0	20	10.0

For simplicity in estimating the $[H^+]$ or overall acidity of these solutions, H_2SO_4 is treated as a monoprotic acid, since HSO_4^- is not extensively dissociated in solutions of very high H^+ concentration.

The increased extractive property of acid mixtures over non-mixtures is evident from the percentage Ni extraction results in Table 2.4. The addition of HNO_3 to a molar proportion of 31% is sufficient to increase Ni extraction to almost 99%. A decreasing trend in percentage extraction with increasing HNO_3 concentration, above 50% HNO_3 was observed. This trend is explained by the reduced metal extractive ability from ash of HNO_3 compared to H_2SO_4, as concluded by T. Gilliam and R. Canon (1980) from their investigation of coal ash.

2.3.3.4 Effects of Varying Acidity

By varying the concentration of the H_2SO_4 and HNO_3 individually, the effect of acidity on Ni extraction can be assessed. This allows for a comparison of overall acidity versus percentage Ni extraction and also aids in identifying the more active component of the acid mixtures.

Table 2.5: % Ni extracted and corresponding [H⁺] for varying Acid extracts.

Extraction Solution	% Ni Extracted	$[H^+]$ mol/l
4M H_2SO_4	93.7	4.0
9:1 4M $H_2SO_4/HNO_{3\,conc.}$	99.1	5.2
9:1 4M H_2SO_4/8M HNO_3	100	4.4
9:1 2M $H_2SO_4/HNO_{3\,conc.}$	98.1	3.4
9:1 2M H_2SO_4/8M HNO_3	92.3	2.6

The results (Table 2.5) clearly show an increase in percentage Ni extraction for acid solutions containing both H_2SO_4 and HNO_3, as observed in previous experiments. This is the case even when the overall acidity is less than the single acid solution. The effect of individual acid concentration on nickel extractions was not easily determined when comparing mixtures of two acids. Taking the HNO_3 as constant, a comparison of 9:1 4M H_2SO_4/HNO_3 and 9:1 2M H_2SO_4/HNO_3 showed little difference in percentage extractions, while a difference is observed between 9:1 4M H_2SO_4/8M HNO_3 and 9:1 2M H_2SO_4/8M HNO_3. Each has the same change in overall acidity of 1.8 mol/l H^+. The same can be observed by comparing acid mixtures holding the H_2SO_4 constant. From this analysis it can be determined that the percentage Ni extracted remains high until the overall acidity drops below a certain point (between 3.4 and 2.6 mol H^+/l), where the percentage extraction drops.

2.3.4 Extract Residue and Comparison with Primary Ash Composition

The acid mixtures used, with H_2SO_4 as the basis, are not sufficiently reactive to dissolve all the inorganic components of the synthetic ash. The remaining insoluble material causes separation and disposal problems that would need to be addressed in a larger scale operation. Whether to be treated, recycled or disposed of, an investigation into this material was necessary to determine quantities produced and composition.

Residue from a 9:1 4M H_2SO_4/HNO_3 extraction corresponded to 19-20% of the weight of original ash. However, this can not be taken to mean that 20% of the original ash remained un-reacted, as the insoluble residue includes reaction products such as $CaSO_4$ from the reaction of Ca initially present as carbonate.

A compositional analysis of major elements was performed on the insoluble material using HF/HNO_3 extraction and analysis by ICP-AES, with the results shown in Table 2.6. This was compared to the undigested ash as shown in Figure. 2.3.

Table 2.6: Comparison of ICP results for % elemental composition of synthetic ash and residue.

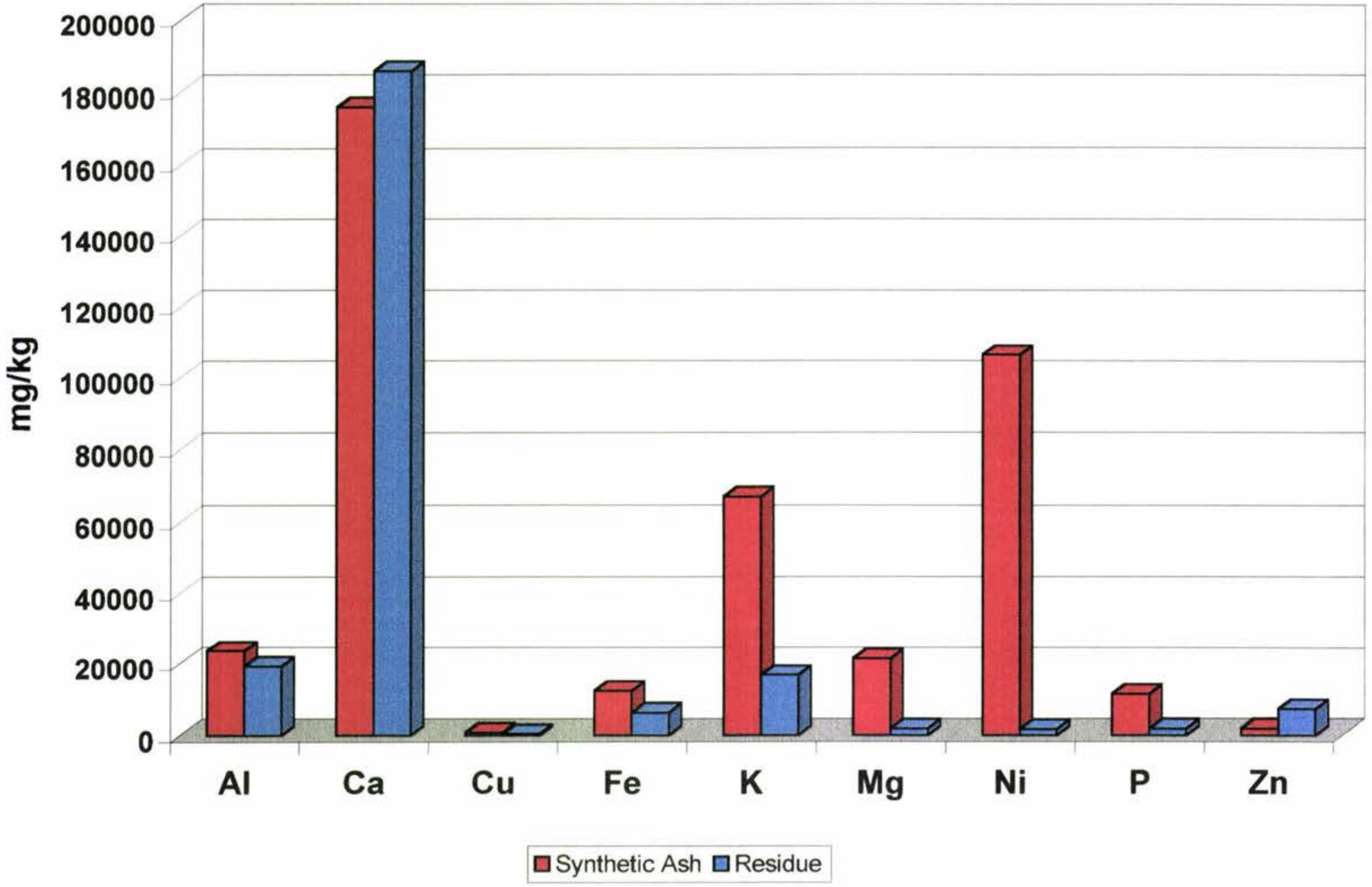
Elements	wt% of Ash	wt% of Residue
Al	2.37	1.93
Ca	17.58	18.57
Cu	0.08	0.04
Fe	1.24	0.63
K	6.72	1.69
Mg	2.17	<0.19
Ni	12.44	0.17
P	1.16	<0.19
Zn	0.73	0.19

Analysis of the ash extract by flame AAS was also undertaken to determine Ni concentration and act as a comparison to the ICP result. This analysis determined the nickel content of the ash to be 10.65%, a little different from the ICP determination. This is probably due to differing standards, and as the AAS standards were of high quality, the figure of 10.65% was used for all further investigations as the standard Ni content of the synthetic ash.

Ni removal, corresponding to a 98.5% extraction, appears to be preferential to that of the other metals. Al, Cu and Fe show no more than 50% extraction, while Zn even shows comparative enrichment (more probably the result of non-homogeneous ash sample than enrichment). Such an efficient extraction with little nickel remaining in the residue implies there is no economic benefit in further treatment.

Upon adding acid, $CaCO_3$ reacts to free Ca^{2+}, H_2O and CO_2. In this predominantly sulfate medium the rather insoluble $CaSO_4$ quickly forms. This contributes to an increase in Ca from 17.6% of the ash to 18.6% of the residue.

Figure 2.3: Comparison of Elemental Composition for Synthetic Ash and Residue



2.3.5 Larger-Scale (1 g) Sample Investigations

Larger synthetic-ash sample sizes were used to more closely simulate an industrial acid extraction, yielding solutions with Ni concentrations high enough for Ni electrowinning. The use of 1 g samples allows for an analysis with elemental compositions more representative of the bulk ash material to be performed.

Table 2.7: % Extractions of major elements for 1 g ash/ 10 ml acid

Extract Solutions	Ni	Ca	Mg	Fe	K
9:1 4M H_2SO_4/HNO_3	96.2	20.4	90.8	87.6	88.4
19:1 4M H_2SO_4/HNO_3	94.5	11.1	89.0	93.5	86.6

Acids used previously were capable of extracting an adequate portion of the Ni present in these larger ash samples, with percentage extractions comparable to the small sample size experiments.

The reduction in HNO_3 concentration causes only a slight decrease in extracted Ni, an amount that could easily be the result of the inhomogeneous nature of the ash. The decrease in extracted Ca is of more interest. As concluded previously, free Ca^{2+} ions react in the sulfate medium to form $CaSO_4$. With increased nitrate concentration in the form of HNO_3, a proportional increase in the amount of Ca in the extract is observed. From the results in Table 2.7 and comparison in Figure 2.4 it is apparent that higher concentrations of HNO_3 are responsible not so much for better Ni extraction but the inclusion of greater quantities of impurities in the extract.

2.3.6 Lower Concentration Acids

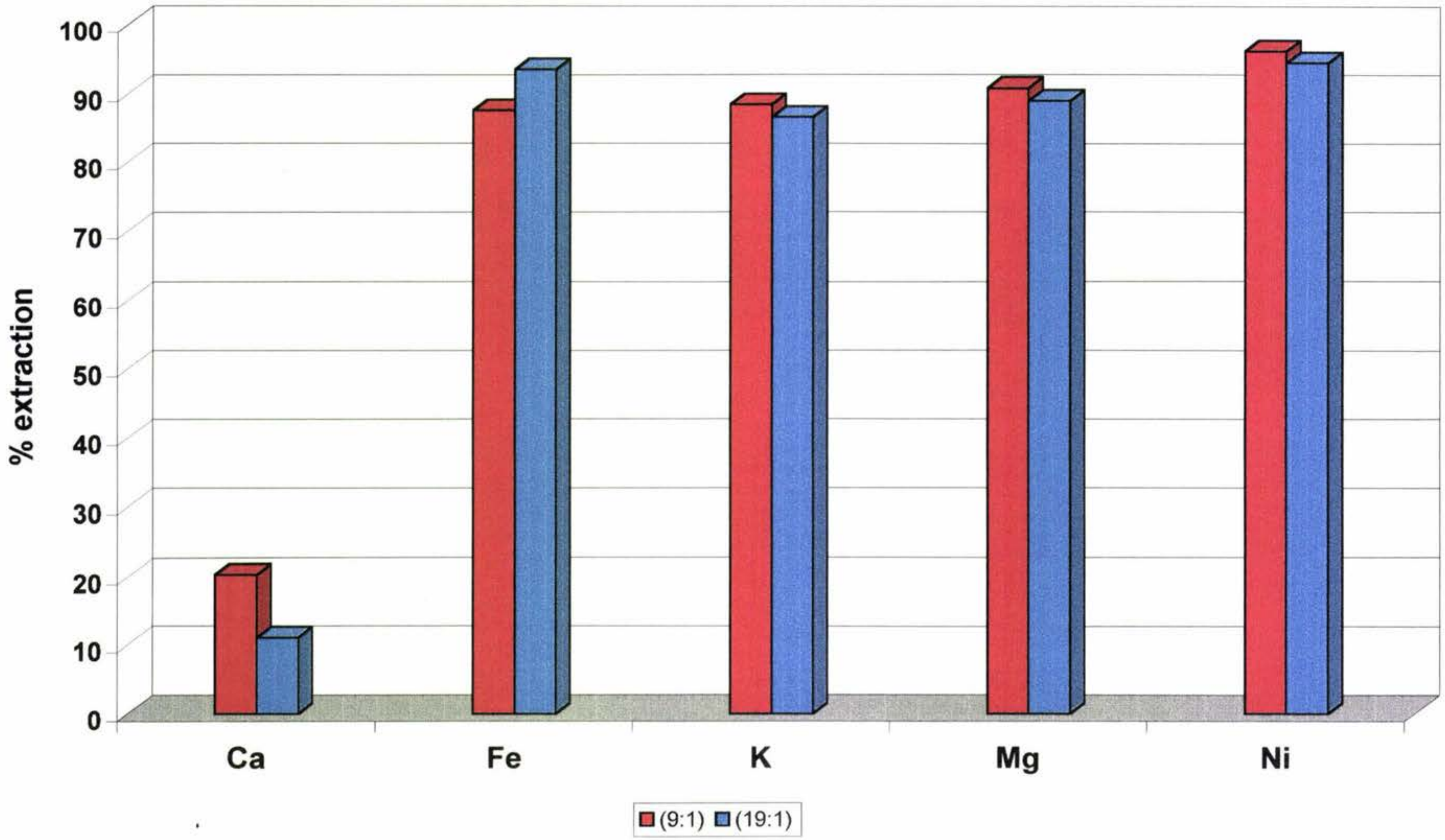
The results from the comparison of acid mixtures showed that lower concentration acids may be used effectively on 0.25 g samples. Using theoretical calculations that assume: (1) ash consists only of NiO and $CaCO_3$,

(2) ash consists of 10.65% Ni,

(3) H_2SO_4 is treated as a monoprotic acid,

it can be calculated that for every 100 g of ash there is 1.04 mol of (Ni + Ca) to be reacted. Each of these reacts with 2 H^+ ions, giving a total of only 2.08 mol/l H^+ theoretically required for dissolution of 100 g ash per litre of acid.

Figure 2.4: Comparison of % Elemental Extractions for 9:1 4M H_2SO_4/HNO_3 vs. 19:1 4M H_2SO_4/HNO_3



Acid mixture acidity was lowered and the 2.08 mol/l H^+ ash dissolution theory tested on 1 g samples.

Table 2.8: % Ni extractions and corresponding [H^+] for lower acidity extracts.

Extract Solutions	% Ni Extracted	[H^+] mol/l
9:1 4M $H_2SO_4/HNO_{3\,conc.}$	93.4	5.2
9:1 2M $H_2SO_4/HNO_{3\,conc.}$	90.0	3.4
9:1 1.5M $H_2SO_4/HNO_{3\,conc.}$	92.4	2.95
9:1 2M H_2SO_4/8M HNO_3	98.1	2.6

From the results shown in Table 2.8 the theoretical calculations were not disproven as the acid mixture 9:1 2M H_2SO_4/8M HNO_3 extracted more nickel than the concentrated 9:1 4M H_2SO_4/HNO_3 solution.

Although the larger sample size is theoretically more representative of the bulk material with less sample variation, the inhomogeneous nature of the ash is evident in the above results. Conflicting conclusions can be drawn from the 0.25 g and 1.0 g experiments, with respect to overall acidity and HNO_3 proportion for optimum extraction. Analysis of 1 g samples is theoretically more accurate with less sample variation, so for this discussion those results from larger sample sizes were considered of greater importance in making conclusions than the 0.25 g sample investigation results.

It is apparent that the percentage of Ni extracted reaches a plateau with respect to increasing overall acidity. This is determined from theoretical calculations of mols of ash product to be reacted and high percentage extractions for the samples: 1 g ash in 9:1 2M H_2SO_4/8M HNO_3, 0.25 g ash in 9:1 2M H_2SO_4/HNO_3 and 0.25 g ash in 9:1 4M H_2SO_4/8M HNO_3. To achieve a 95% or greater extraction of nickel, there is no need for an acid mixture such as 9:1 4M H_2SO_4/HNO_3 with [H^+] of 5.2 mol/l, since adequate extractions still occur using solutions with [H^+] of only 2.6 mol/l.

The greater ability of acid mixtures (compared to H_2SO_4) to extract nickel is not in doubt. However, the appropriate proportion of H_2SO_4 : HNO_3 (molar value) is questionable. From the results in sections 2.3.5.3, 2.3.5.4 and 2.3.9 a broad conclusion, that acid mixtures containing HNO_3 in 15-50% molar proportions perform an optimum extraction of nickel, was reached.

2.3.7 Effect of Ash on Extract Acidity

To establish what portion of the acid mixture is being neutralised during extractions, a 10ml solution of 9:1 4M H_2SO_4/HNO_3 was used to treat varying quantities of synthetic ash, with the following assumptions:

(1) with increasing ash sample weight (constant 10ml acid volume) the % Ni extracted is constant.

(2) H_2SO_4 reacts as a monoprotic acid.

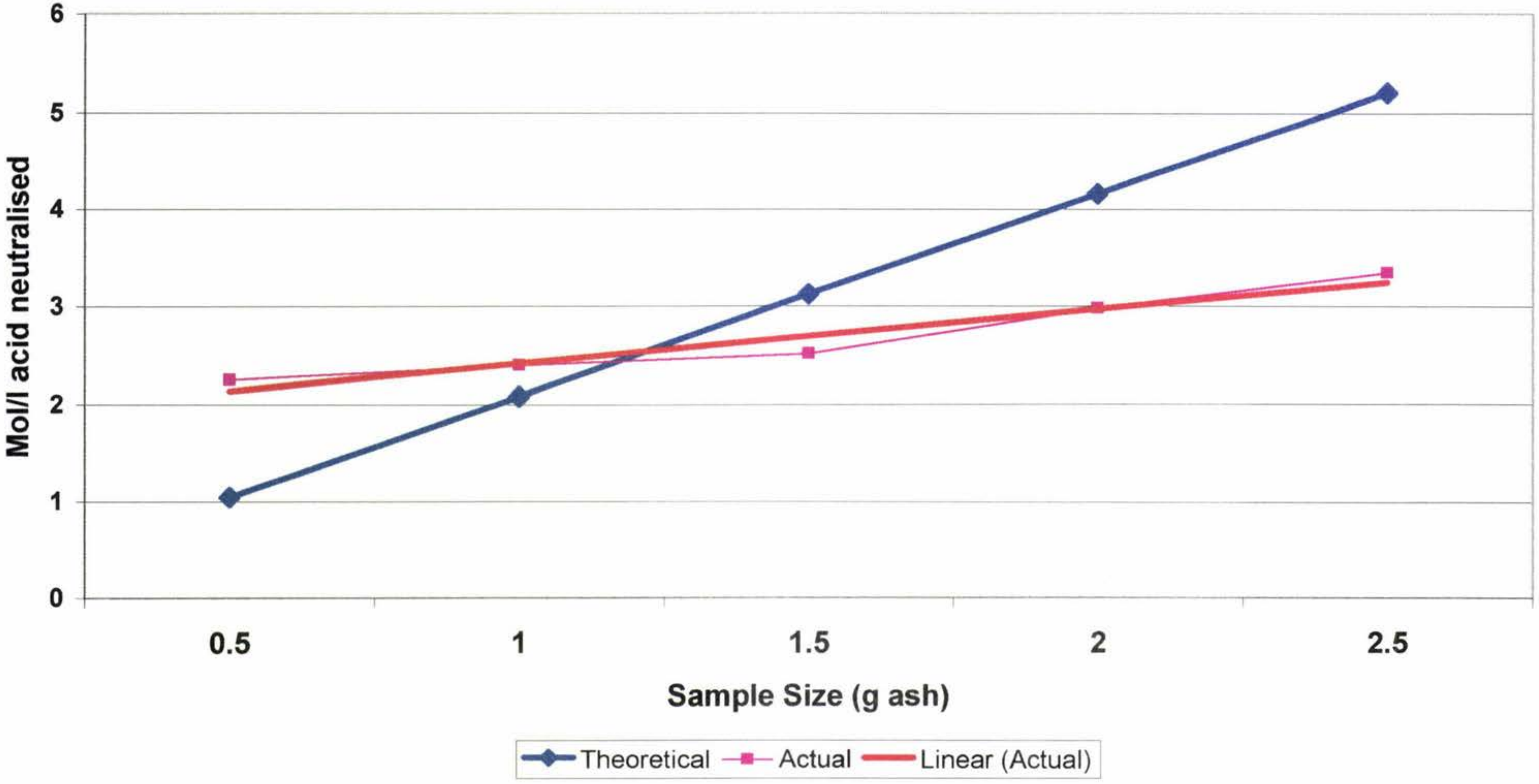
Table 2.9: The effects of varying quantities of ash and extract neutralisation.

g Ash	$[H^+]$ mol/l	expected mol/l H^+ reacted	Actual mol/l H^+ reacted
0.5	2.95	1.04	2.25
1.0	2.81	2.08	2.39
1.5	2.69	3.12	2.51
2.0	2.23	4.16	2.97
2.5	1.86	5.20	3.34

Figure 2.5 illustrates the differences in theoretical and actual acid neutralisation results. Although there is an increase in the amount of acid that is reacted, the results do not follow theoretical calculations for ash composition/acid neutralisation. The simple model used earlier assumes only $CaCO_3$ and NiO are present in the ash. The inclusion of major elements such as K, Fe, Al, P and Mg cause the expected amount of acid to be neutralised to rise to 2.5 from 2.0 mol/l H^+. This explains some of the deviation from theoretical for small samples i.e. 0.5 g ash/10 ml but does not effect the overall deviation from the theoretical values.

Linearity of the results implies that there is a trend in reactions with ash components, increasing with availability of the components. However these reactions are by no means as simple as the complete freeing of inorganic elements as predicted. A more adequate model should take into account solubility of ash components and reactions other than the dissociation of the elements in question e.g $CaSO_4$ formation.

Figure 2.5: Comparison of Theretical and Actual Acid Neutralisation During Ash Leaching



2.3.8 Large Volume (20 g ash per 100 ml Acid) Ash Extractions

The proportion of ash to acid was increased to produce a higher Ni concentration in the extract, as the greater the Ni concentration of an electroplating solution, the better more efficient the reduction of Ni^{2+} by electrolysis. This also improves the economy of the process by using less acid.

A solution made from 20 g ash per 100 ml of acid was estimated to be near the maximum for a Ni extraction from plant ash using the laboratory equipment available. This is due to the large volume of ash and remaining insoluble material causing mixing problems, potentially hindering nickel extraction.

Extract solutions were separated by centrifuge as the fine particle size and large volume of the ash residue inhibited filtration. This separation issue may need to be addressed for larger scale operations, as the collection of nickel-bearing solution is preferable to a portion of the solution being trapped within the centrifuged residue.

Where needed for later experiments, synthetic ash extracts were made using the specified method, and if necessary combined to give large volumes.

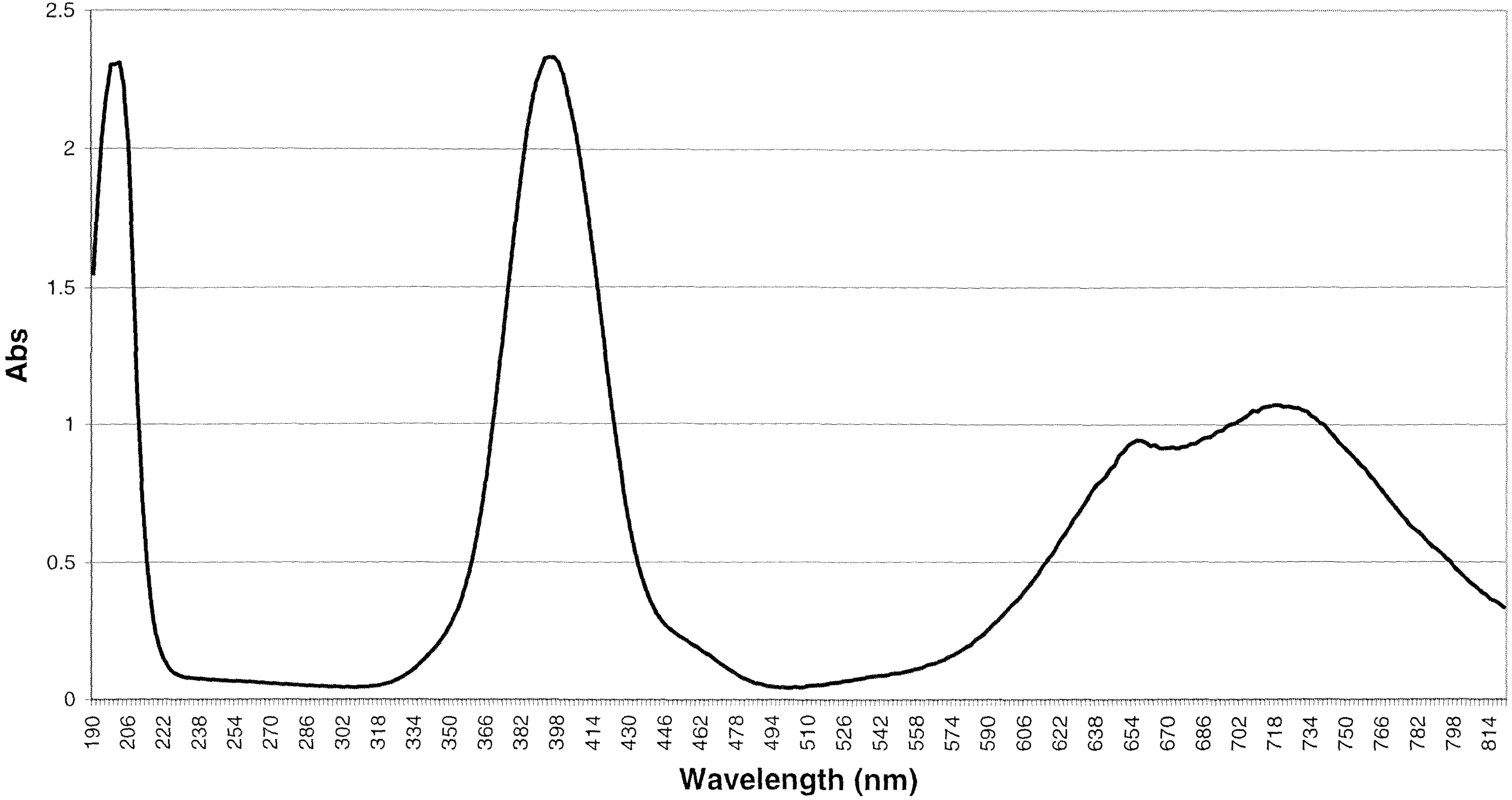
2.3.8.1 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extraction

The UV/Vis spectrum 190-820 nm for the extract (Fig. 2.6) clearly shows interference in the 190-400 nm range, given the comparison with a 0.5M $NiSO_4$ standard. It is unclear what properties of the extract cause this deviation from the Ni sulfate spectrum, and prohibit the 400 nm Ni peak from being used to monitor Ni concentrations.

Comparison of these extract spectra has shown that convenient and inexpensive monitoring of the extracts is possible using the 720nm peak. Analysis by ICP confirmed that such monitoring is an accurate means of determining Ni concentration.

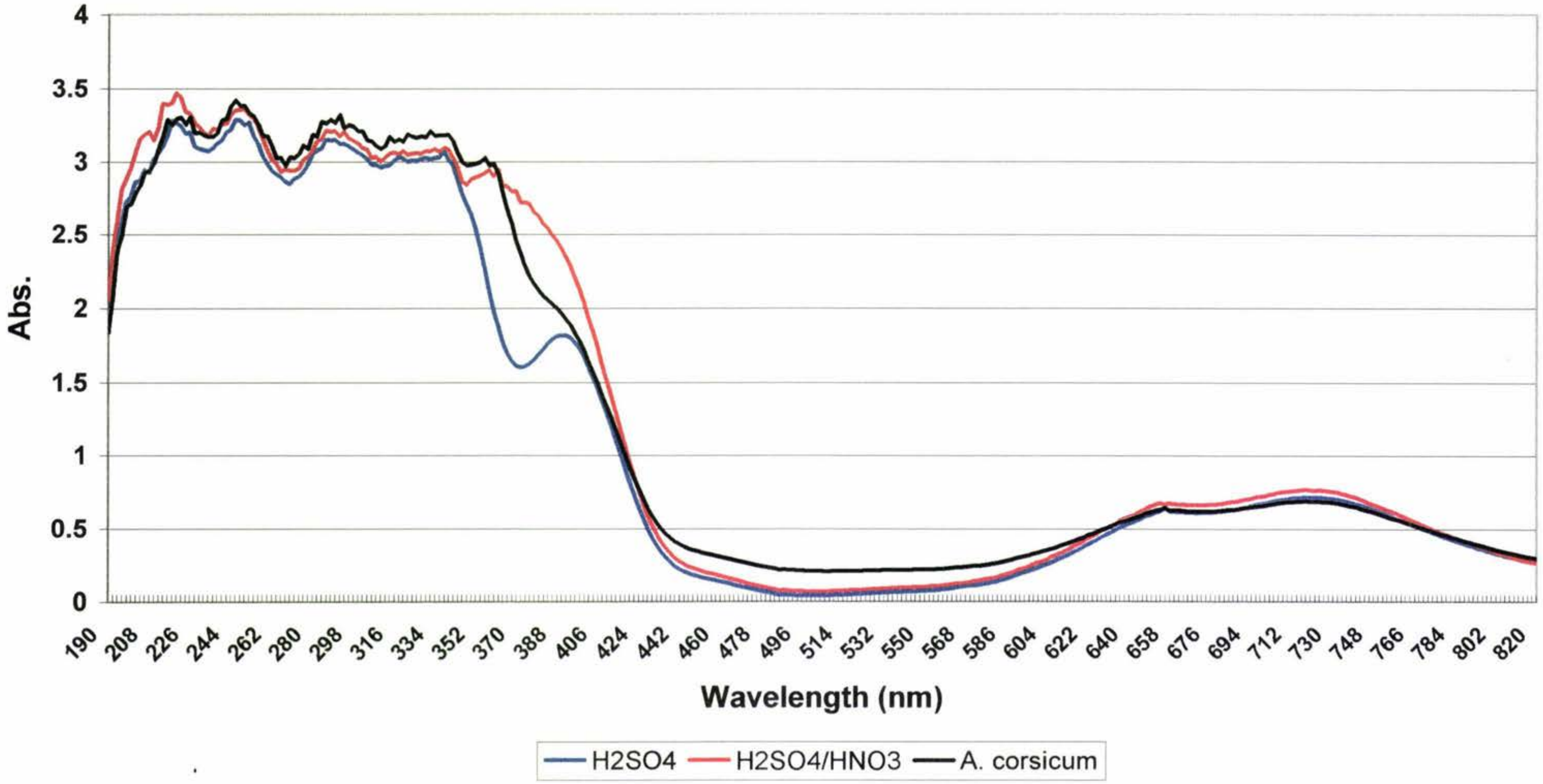
The acid mixture of 9:1 2M H_2SO_4/8M HNO_3 yielded 85 ml of 0.351 mol/l (20.60 g/l) Ni solution as determined by UV/Vis quantitative analysis at 720 nm, with ICP measuring 20.39 g/l. This corresponds to a 96.7% extraction, confirming the findings of previous investigations into acid mixtures and overall acidity. The remaining 15 ml of solution is trapped in the centrifuged insoluble material.

ICP results for the extract and comparison to those of the *A. corsicum* extract are shown in Table 2.10 and Fig. 2.7 with a discussion of these results in the *A. corsicum* Material Treatment section.



UV/Vis Spectrum (190-820nm) of 0.5 M $NiSO_4$ Solution

Figure 2.6: UV/Vis Spectrum for Synthetic Ash and *A.corsicum* Ash Extracts



The $[H^+]$ of the acid mixture extract was determined to 1.256 mol/l, implying that only 1.344 mol/l of the acid reacted. This is close to half the amount that reacted using an extraction of the same proportions i.e. 20g ash per 100 ml acid, but with 9:1 4M H_2SO_4/HNO_3 (twice the overall H^+ concentration).

2.3.8.2 4M H_2SO_4 Synthetic Ash Extraction

The 4M H_2SO_4 extraction yielded a solution of 0.332 mol/l (19.48 g/l) Ni solution as determined by the quantitative UV/Vis analysis at 720 nm. Given an ash nickel content of 10.65% this is representative of 91.5% extraction.

The UV/Vis spectra for this extract (Fig. 2.6), illustrates the degree to which the addition of nitric acid during leaching results in further impurity solubilisation.

2.3.8.3 *Alyssum corsicum* Material Treatment and 9:1 2M H_2SO_4/8M HNO_3 Extraction.

The Ni concentration of the 85 ml *A. corsicum* extract was 0.318 mol/l (18.7 g/l) as determined by UV/Vis quantitative analysis at 720 nm. This corresponded to a 90%+ extraction of Ni from the hyperaccumulator plant ash. The ICP (Table 2.10) value of 18.49 g/l confirmed this, again proving that UV/Vis analysis is sufficient for monitoring Ni content in these solutions. The remaining ICP results (Table 2.10 and Fig. 2.7) illustrate again the relative insoluble nature of Ca, due to its conversion to $CaSO_4$, compared to other major elements such as Ni, K and Mg.

In a comparison of synthetic ash extraction to *A. corsicum* ash extraction, it is found that the majority of elements extracted are in proportion to their relative abundance in the two ashes. Both K and Mg are present at half the *A. corsicum* extract concentrations in the synthetic ash extract, while Fe, P and Mn are increased proportional to their abundance.

The addition of 15 ml water to wash some of the nickel from the centrifuged residue (still containing 15 ml ash extract solution) allowed recovery of about half the remaining nickel in solution, at the expense of some dilution of the resulting solution. The final concentration of the now 100ml of extract was determined to be 0.295 mol/l· (17.3 g/l) Ni, however the overall yield of Ni from the ash increased from 85% before residue washing to 93% after residue washing.

Figure 2.7: Comparison of *A. Corsicum* Ash and Synthetic Ash 9:1 2M H_2SO_4/8M HNO_3 Extractions

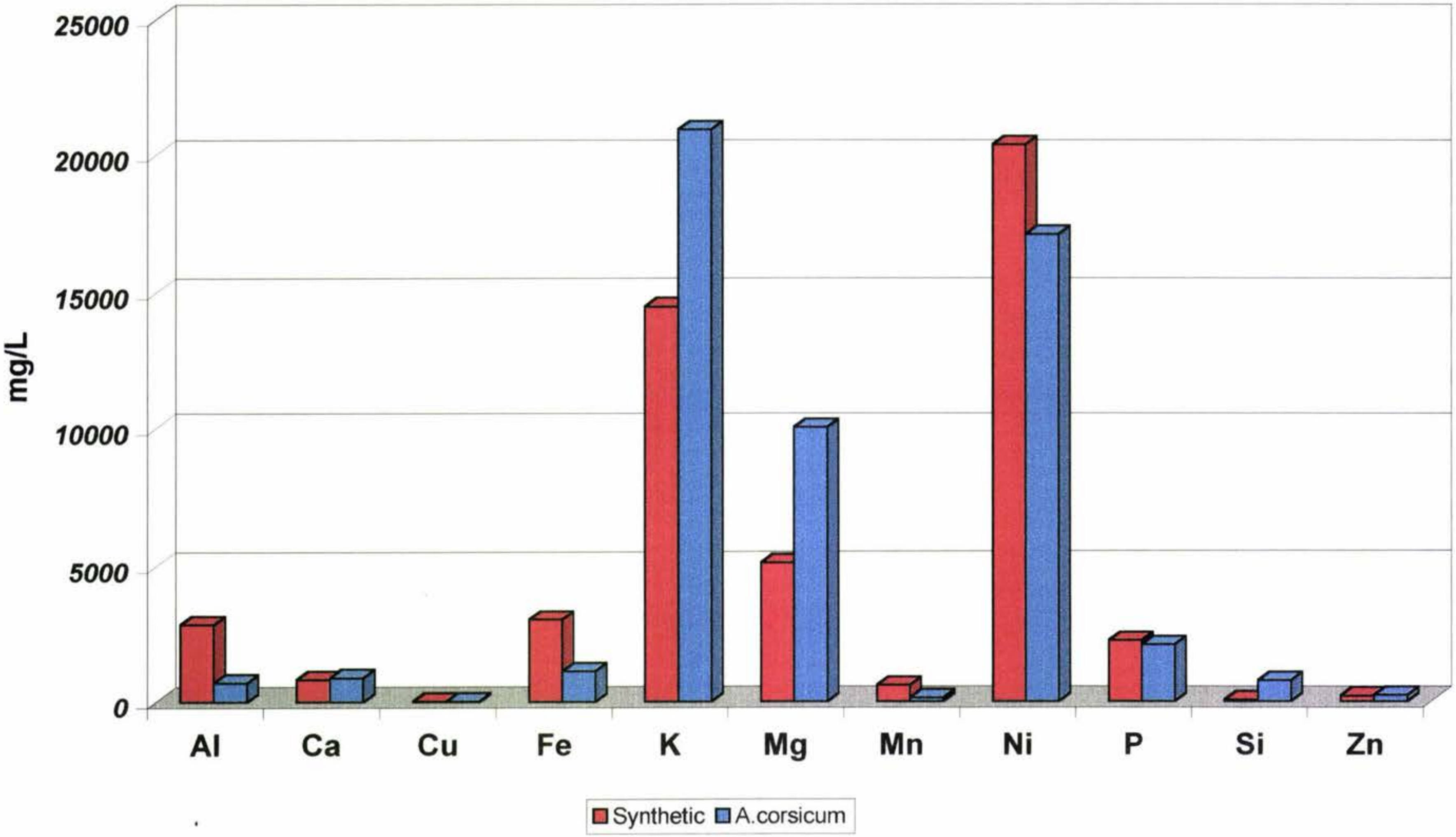


Table 2.10: ICP results for the 9:1 2M H_2SO_4/8M HNO_3 extract solutions of A. corsicum ash and synthetic ash.

Element	Concentration (μg/g)	
	A. corsicum	Synthetic Ash
Al	690	2850
Ca	875	810
Cu	10	15
Fe	1120	3050
K	20950	14500
Mg	10050	5160
Mn	140	600
Ni	18490	20390
P	2100	2250
S	38000	No analysis
Si	770	50
Zn	225	200

The ICP and UV/Vis results show this technique, for the extraction of Ni from both synthetic and *A. corsicum* ash to be comparable.

A 1:1 HF/HNO_3 extraction was used to ascertain the elemental composition of the insoluble residue. By comparing the results with the theoretical ash Ni-content and the extract solution, a more accurate determination of the nature of extraction and the proportions of leached products, was ascertained.

Table 2.11: Elemental composition of A. corsicum residue after acid extraction.

Element	Concentration (μg/g)
Al	1290
Ca	209100
Fe	3790
K	9580
Mg	4430
Mn	80
Ni	9400
P	210
Zn	150

The results shown in Table 2.11, for the concentrations of some elements present in the extracted ash residue, confirm primarily that an extraction of greater than 90% Ni occurred when leaching with 9:1 2M H_2SO_4/8M HNO_3. Given a theoretical Ni concentration of 11.4% in the ash, (from plant analysis and mass reduction) 91.7% of the nickel of plant origin has been solubilised. Also of importance is the large proportion of calcium present in the residue, due to its precipitation as insoluble $CaSO_4$. Levels of potassium and magnesium, high in the extract solution are also relatively low in the ash residue; again confirming the conclusions made for their high levels of extraction.

The nickel content of the residue material, 0.94%, is still relatively high compared to that of the synthetic ash residue, 0.17%. Incomplete removal of the Ni may be the result of incomplete combustion of the *A. corsicum* material, as the amount of Ni extracted showed little variation with the differing strengths of the acid used. The combustion of the *A. corsicum* material, weighing only 200 g and of fine nature may not have obtained the temperatures, or length of time at these temperatures, necessary for the complete removal of carbon from Ni complexes. The synthetic material, being of much larger volume and weight could have attained these higher temperatures thus resulting in an ash with a greater proportion of NiO present.

2.3.9 Composite Hyperaccumulator Plant Material

Due to the availability of smaller sized nickel-rich plant samples, it was possible to produce a composite material that contained all the unique hyperaccumulator properties. This was to be used exclusively for a nickel crystallisation investigation, with the extraction aimed toward such a goal.

Table 2.12: Elemental concentrations of hyperaccumulator composite plant material.

Element	Concentration (μg/g)
Ca	10980
Fe	85
K	3705
Mg	2560
Mn	95
Ni	5595
Zn	120

Analysis of a 0.2618 g sample of this material by ICP highlighted again the high Ni, K, Mg and Ca concentrations associated with these plants, as shown in Table 2.12. The relative exclusion of Zn and Fe during accumulation is also evident. To the above plant material, additional whole plant material, including leaves with greater than 1.0% Ni was added to give a stock with approximately 6600 μg/g Ni.

Ashing of the hyperaccumulator material was difficult as the supply of oxygen necessary for combustion was limited by the particle spacing. With the aid of ashless filter paper and a Bunsen burner, it was possible to initiate and maintain an adequate temperature for carbon removal, leaving the majority of the plant material as a white ash. The remaining carbon was removed by heating in a muffle furnace, ensuring an adequate extraction could be performed.

The plant composite's initial mass was 179.45 g; after combustion, with some loss of material associated with combustion, 8.40 g of ash was collected. Analysis of this ash by ICP (Table 2.13) determined the Ni content to be 8.59%. This corresponds to an approximately 13-fold increase in concentration of Ni, from plant material to ash.

Table 2.13: Elemental concentrations of hyperaccumulator composite ash.

Element	Concentration (μg/g)
Ca	184900
Fe	1730
K	105700
Mg	44800
Mn	1520
Ni	85900
P	4870
Zn	2230

2.3.10 Acid Extraction of Composite Hyperaccumulator Ash

For this extraction 4M H_2SO_4 was chosen because of the intention to use the solution to investigate sulfate crystallisation.

The proportions of acid/sample specified by previous extractions (1 litre acid per 200 g ash) were maintained to produce a solution with 15-20 g/l Ni, as maximising the Ni concentration was thought to be advantageous for nickel salt crystallisation (as well as electrowinning). A volume of 33 ml was recovered from the 41.5 ml of acid used in the extraction. Analysis of this solution by ICP (Table 2.14) determined the Ni concentration to be 20.2 g/l. This was approximately confirmed by the UV/Vis, which gave the concentration to be 0.357 mol/l (20.9 g/l).

Table 2.14: Elemental concentration of hyperaccumulator composite extract.

Element	Concentration (μg/g)
Ca	<25
Fe	400
K	20950
Mg	9800
Mn	280
Ni	20200
P	745
S	141000
Zn	720

Using the ICP determined concentration and the 41.5ml volume of acid, gives a total of 0.83 g Ni extracted from the ash. However, with the Ni concentration of the ash known to be 8.59%, and 8.30 g of ash used, only 0.71 g of Ni was available for extraction. Such a variation implies that during the refluxing of the acid/ash mixture, a loss of volume has occurred, resulting in the remaining Ni being concentrated. With this occurring, a greater proportion of the solution may remain trapped in the residue.

The UV/Vis spectrum of the composite ash extract, from 190-820 nm, showed the 400 nm and 720 nm peaks characteristic of a nickel sulfate solution. The unknown interference from 190-400 nm was also present, as was found in other Ni ash extracts.

Acidity of the extract was determined by pH measurement of a diluted solution. Leaching of the ash resulted in a neutralisation of the 4 mol/l H_2SO_4 to $[H^+] = 2.34$ mol/l.

Analysis of a 0.1705 g sample of the insoluble ash residue by ICP (Table 2.15), determined the Ni concentration to be 0.3% of the residue. Compared to the original 8.6% Ni content of the ash, this correlates to a 96.5% extraction of nickel from the ash. Such a low remaining Ni concentration compared to that of the *A. corsicum* ash again illustrates the inhibiting effects of incomplete combustion. The composite plant ash was heated a second time in a muffle furnace to ensure removal of all carbon, with the consequences being a better extraction of nickel (even without the addition of HNO_3).

Table 2.15: Elemental concentrations of hyperaccumulator composite residue after acid extraction.

Element	Concentration (μg/g)
Ca	276600
Fe	375
K	2070
Mg	<200
Mn	82
Ni	3000
Zn	100

The greater extractability of the inorganic elements is also reflected in the reduced residue concentrations of Mg and K.

The Ca concentrations are higher for the hyperaccumulator composite, compared to the *A. corsicum*, indicative of the effect nitric acid has on the extraction, allowing greater quantities of Ca to be removed from the ash.

2.4 CONCLUSION

The studies of Ni extraction using synthetic nickel-rich ash were sufficient to determine an effective and efficient method for the solubilisation of Ni from hyperaccumulator plant ash. The synthetic ash produced by open flame combustion was inhomogeneous in nature. NiO particles were concentrated in specific areas, as indicated by large variations observed in sample Ni concentrations. The extractability of metals from ash has been linked to firing temperatures, with crystalline, acid-insoluble mullites forming over 1200°C (Gilliam and Canon, 1980). Although these could cause some variation in Ni content results, the temperatures involved with plant ashing were not high enough to produce such compounds. It is suggested that carbon fixation can occur, the result of incomplete combustion, creating pockets of Ni (additional to the already distributed Ni) around large carbon particles that weren't completely combusted. When using small samples the effect would be an uneven distribution of Ni.

The problems of incomplete combustion are also apparent when comparing the *A. corsicum* and hyperaccumulator composite ash extracts and extract residues. The composite ash was heated a second time (after open flame combustion) to ensure complete removal of carbon, whereas the *A. corsicum* material was simply ashed by open flame combustion, with no such secondary treatment. The differences in extractability of mainly Ni, but also K and Mg were apparent. Extraction of the plant composite ash with 4M H_2SO_4 resulted in 96.5% of the nickel present being solubilised, to leave a residue with a Ni concentration of only 0.3%. The acid extraction of *A. corsicum* ash, using a theoretically better acid mixture, recovered only 91.7% of the nickel present, while the insoluble residue had a nickel concentration of 0.9%. This inhibited extraction may be attributed to incomplete combustion, with a minor portion of the nickel still being bound to carbon in a compound less soluble than NiO. X-ray powder diffraction spectra of the open-flame and controlled-combustion ash products indicated the majority of the nickel to be present as NiO in both cases. When ashing by open flame combustion the small sample size limits the obtainable temperature and high-temperature residence times, so that a small portion of the nickel remains bound to carbon. On a larger scale, this may not be such a problem owing to the greater 'particle' size and sheer volume of combustible material, enabling higher temperatures for longer periods. With respect to >90% Ni extractions, the degree of carbon removal is of key importance, with the degree of combustion vs. nickel return being a matter of economics.

The extractive ability of the three mineral acids used in leaching Ni from ash was demonstrated to be $HCl > H_2SO_4 > HNO_3$ and reinforced the findings of Gilliam and Canon (1980). This was concluded not only from the complete extraction by hot 2M HCl but also from the observed decrease in % Ni extracted when HNO_3 became the major acid component (>50 mole %) in a mixture of 4M H_2SO_4 and concentrated HNO_3.

A mixture of acids H_2SO_4 and HNO_3 was found to be more effective than leaching with H_2SO_4 on its own, if the proportion of HNO_3 was ~15-50%. This was thought to be the result of the different components of the ash being more soluble in different acids. Suggestions include:

(1) That the HNO_3 is more effective at directly oxidising the carbon than H_2SO_4, freeing the fixed Ni.

(2) HNO_3 extracts the Ni fixed to carbon in a better manner than H_2SO_4.

Heating of the acid during ash leaching, even for a short time, was shown to dramatically improve nickel extraction. Percentage extraction reaches a plateau with respect to leach time, as was also concluded by Gilliam and Canon (1980) in their studies of Al extraction from coal ash. Leach time and heating should be kept to a minimum as any further treatment beyond the initial plateau time results in no increase in Ni separation while potentially increasing both the concentration of impurities and the cost of the treatment. The best treatment time will vary with sample size and acid/sample proportions.

Percentage Ni extracted also reached a plateau with respect to increasing solution acidity above 2 mol/l H^+. Revised theoretical calculations based on ash composition and its complete dissolution in the acid predicted that 2.5 mol/l H^+ would be neutralised using 10 g ash in 100 ml acid. However pH analysis of ash extracts contradicted this model with unarguably linear results. The reactions during acid leaching are evidently more complex than first expected and more work is needed on establishing a suitable working model.

Extractability of the major inorganic elements (as a proportion of the elements concerned) follows the order $Ni > Mg \geq Fe \geq K > Ca$. The solubility of nickel proves advantageous as extractions with more dilute acids than theoretically required for dissolution of the ash, are still capable of >95% Ni extractions. Such dilute acid extractions have numerous benefits, the exclusion of less soluble impurities not the only one. As Ni electrodeposition is most effective with solutions of pH 4-5, there is a need to neutralise the ash extract. Excessive acid results in the need to use larger quantities of neutralising agents, so by minimising extract acidity, reagent costs of both acid and neutralising chemicals are minimised.

The low relative solubility of Ca is not the result of poor $CaCO_3$ solubility, but instead the reaction of free Ca^{2+} ions in the sulfate medium forming insoluble $CaSO_4$, while the presence of nitrates results in more soluble Ca nitrates forming, increasing the Ca content in the ash extract. For this reason the HNO_3 concentration must be kept to no greater than 30% molar proportions to avoid excess Ca in solution. This only marginally hinders Ni extraction but results are still above 95%.

The acid mixture 9:1 2M H_2SO_4/8M HNO_3 limits the inclusion of impurities such as Ca, performs a >95% Ni extraction and results in a residual $[H^+]$ of 1.35 mol/l, less acidic than other mixtures tested using the same ash/acid proportions. For these reasons it was chosen for use with the *A. corsicum* plant ash.

Trials with synthetic ash using 20 g ash/100 ml acid, compared 4M H_2SO_4 and 9:1 2M H_2SO_4/8M HNO_3 by UV/Vis analysis, with the latter proving most effective with 96.7% Ni extraction. This mixture when applied to hyperaccumulator plant ash was equally successful with comparable results to its synthetic ash analogue. However, further research has established that the presence of nitrates, to even 0.1 mol/l concentrations hinders electrodeposition of Ni (Murthy, 1996). While the solutions may be manipulated to counter this inhibition, the extraction of 96.5% Ni from the hyperaccumulator composite ash, using only 4M H_2SO_4 has shown that an adequate separation of Ni can be achieved using this single acid. With respect to nickel recovery by crystallisation, the use of this acid to produce a sulfate only medium is also advantageous, with the increased SO_4^{2-} concentration and lack of NO_3^- being of benefit when trying to crystallise a nickel sulfate salt. Although a greater degree of neutralisation would be required (if neutralisation is necessary), due to the remaining H^+ concentration, this disadvantage is of less importance than the potential problems associated with the presence of nitrates. For these reasons a nickel extraction using 4M H_2SO_4 can be considered the best first step in the treatment of the nickel-rich ash.

Chapter Three

Extract Neutralisation

3.1 INTRODUCTION

The acids used in Ni extraction experiments resulted in solutions with a large residual H^+ concentration. With respect to electrowinning nickel, the high activity of H^+ prohibits reduction of Ni^{2+} (refer Chapter Four: **Electrowinning**). Indeed, the electrodeposition of nickel is most commonly performed at pH 4-5, where Ni can be deposited preferentially over the evolution of H_2 gas (Dennis and Such, 1993).

From an investigation into sulfate salt crystallisation (refer Chapter Five: **Crystallisation and Precipitation**) it was apparent that by reducing the acidity of an extract, crystal growth can be promoted. For these reasons, there was a necessity to neutralise the ash extracts to pH values more favourable for nickel recovery.

Greater quantities of ash may be used to further neutralise the acid. However, it is unclear from the results as to whether this would be an efficient use of the nickel-rich ash. The percentage of nickel extracted could drop, resulting in the loss of potentially profitable nickel. An alternative to this is the neutralisation of the extracts with a suitable reagent.

Two reagents were considered: $CaCO_3$ and NaOH. Where the need is simply to reduce acidity, limestone is frequently used, owing to the cheap cost. However, such an additive would introduce contaminants into the ash extracts, and given the goal of extracting a relatively pure nickel product, this was not desirable. Purified $CaCO_3$ is industrially less common, but can still be considered as both inexpensive and readily available.

Sodium hydroxide has found uses in treating acidic wastewater, with recovery of metals by hydroxide precipitation (refer Chapter Five: **Crystallisation and Precipitation**). This reagent was also considered because it is inexpensive and readily available both in the lab and industry.

3.2 MATERIALS AND METHODS

3.2.1 Neutralisation of Synthetic Ash Extract (20 ml) with $CaCO_3$

To determine an acceptable quantity of $CaCO_3$ and the effects its addition has on ash extracts, neutralisation was first attempted on samples of the synthetic ash extract, which were produced where needed using the technique outlined in section 2.2.11.1. An initial sample size of 20 ml was used, followed by a larger 50 ml sample. Given the findings of these experiments, the process was attempted on a larger scale, before neutralisation of the *A. corsicum* extract was performed. This repetition ensured a better understanding of the neutralisation process, and reduced possible errors when treating the hyperaccumulator plant solution.

3.2.1.1 $CaCO_3$ Addition and UV/Vis analysis

The investigation of extract neutralisation by $CaCO_3$ addition, was carried out on the 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract. From its determined $[H^+]$ of 1.256 mol/l the theoretical quantity of $CaCO_3$ required to neutralise 20 ml solution to $[H^+] =$ 0.001 mol/l was calculated to be 1.255 g. $CaCO_3$ was added to the 20 ml solution in successive quantities to give a total mass of 0, 0.4, 0.8, 1.2 and 1.255 g $CaCO_3$. After each addition the sample was stirred for 5 min to ensure mixing, then centrifuged for 10 min at 4000 rpm to separate insoluble products. From the clear supernatant a UV/Vis spectrum (190-820 nm) was obtained using a Hewlett Packard UV/Vis spectrophotometer. Extracts were recombined with the insoluble material and shaken, before subsequent additions of $CaCO_3$.

On completion of $CaCO_3$ addition to 1.255 g and UV/Vis analysis, the neutralised solution was centrifuged for 10 min at 7000 rpm. From the mixture, 18 ml of solution was separated and the final $[H^+]$ determined.

3.2.1.2 Further $CaCO_3$ Addition

Owing to the incomplete neutralisation of the ash extract, further addition of $CaCO_3$ was required to reach H^+ concentration of 0.001 mol/l. To the 18 ml of remaining-extract (0.162 mol/l H^+), 0.1 g $CaCO_3$ was added, stirred for 5 min and centrifuged for 10 min at 4000 rpm. A pH measurement of the supernatant was taken and $[H^+]$ determined. Additional $CaCO_3$ was added, with the masses required estimated from previous changes in H^+ concentration. After each $CaCO_3$ addition, the mixture was stirred and centrifuged as above, and the $[H^+]$ was then measured.

3.2.1.3 Neutralisation of Synthetic Ash Extract (50 ml)

To a 50 ml sample of synthetic ash extract 4.37 g (0.875 mol/l) $CaCO_3$ was added, a quantity less than theoretically required to neutralise the solution to pH 3. The extract was stirred before being centrifuged for 10 min at 4000 rpm. The $[H^+]$ was measured to verify the extent of neutralisation, and an estimate made of the additional quantities of $CaCO_3$ required. Subsequent portions of the neutralising reagent were added with each being stirred and centrifuged at 4000 rpm for 10 min, before the $[H^+]$ was measured.

After a pH of approximately 3 was obtained, more $CaCO_3$ was added, with each addition aimed at neutralising the solution to pH 4.5.

3.2.1.4 Complete Synthetic Ash Extraction and Neutralisation with $CaCO_3$

The procedure outlined in Section 2.2.11.1 was employed to produce 200 ml of 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract (without washing), which was used to investigate both the neutralisation and volume of solution obtained after treatment with $CaCO_3$.

To this 200 ml of extract, 1.01 mol/l $CaCO_3$ was added to neutralise to the solution to pH 4.5, as determined from the 50 ml sample experiments (section 3.2.1.3). The solution was stirred to ensure mixing of the $CaCO_3$ then centrifuged for 10 min at 7000 rpm. From the precipitated and residual material 130 ml solution was recovered. The pH of this extract was found to be 4.45.

To recover a greater portion of the nickel, the insoluble material was washed with 70 ml double deionised water. The mixture was stirred and shaken to combine the water with nickel-rich solution trapped in the material. This was centrifuged for 10 min at 7000 rpm, separating 70 ml of now dilute nickel solution, which was added to the original 130 ml of neutralised extract to give a total of 200 ml neutralised extract. Two 0.5 ml samples were taken from the neutralised extract and diluted for ICP analysis. UV/Vis was used to determine the nickel concentration of the diluted extract, with the result being compared to that measured by ICP.

3.2.2 *Alyssum corsicum* Ash Extract Neutralisation

$CaCO_3$ in 1.01 mol/l proportions was added to 90 ml *A. corsicum* ash extract in order to neutralise the solution to pH 4.5 or higher given that the solution was slightly more dilute than the synthetic ash extract (due to residue washing). The mixture was stirred before being centrifuged for 10 min at 7000 rpm. After separation of the insoluble material, 75 ml of neutralised extract was recovered with the pH of this being measured. The remaining insoluble material was washed with 15 ml deionised water, with the mixture being shaken then centrifuged again for 5 min at 7000 rpm. The 15 ml of now dilute nickel solution was added to the original 75 ml of *A. corsicum* extract to give a total of 90 ml.

UV/Vis analysis was used to determine the nickel concentration and obtain a 190-820 nm spectra. Two 0.5 ml samples made up to 5 ml and 250 ml with deionised water were taken for ICP AES analysis.

3.2.3 Neutralisation by NaOH Addition

A brief investigation into the use of NaOH for neutralising ash extracts was carried out on a 4M H_2SO_4 synthetic-ash extract. New solutions were prepared and combined, with two 0.5 ml samples being taken and diluted for ICP analysis. A quantity of NaOH sufficient to neutralise the solution to pH 4.5 was added to 200 ml of the extract. This required 36.5 g NaOH (4.56 mol/l) which was stirred to ensure mixing. The resulting solution and insoluble material was centrifuged for 10 min at 7000 rpm with 175 ml of supernatant being collected. Deionised water (25 ml) was mixed with the insoluble material, centrifuged for 10 min at 7000 rpm and added to the original supernatant to give 200 ml. Samples of 0.5 ml were taken for ICP analysis and made up to 10 ml and 250 ml respectively, with the elemental concentrations being compared to those before neutralisation.

3.3 RESULTS AND DISCUSSION

3.3.1 Neutralisation by $CaCO_3$ Addition

3.3.1.1 $CaCO_3$ Addition and UV/Vis analysis

Investigation of the effect neutralisation has on the UV/Vis spectra of the ash extract, over wavelength range 190-820 nm, is shown in Fig. 3.1, with decline in the interference around the 400 nm Ni peak obvious.

The final H^+ concentration of the 20 ml synthetic ash extract after addition of 1.255g $CaCO_3$, was determined to be 0.162 mol/l, less than the of 0.001 mol/l expected. From this result it is apparent that the theoretical calculations based on the assumption that 1 mol CO_3^{2-} neutralises 2 mol H^+ are too simplistic for determining the changes in $[H^+]$, the end result being that further neutralisation is required.

The large volumes of insoluble white powdery material were impossible to distinguish from $CaCO_3$, but given the H_2SO_4 environment, were thought to be $CaSO_4$. This is the relatively insoluble product of freed Ca^{2+} ions binding to SO_4^{2-} ions present from the acid extraction.

As the $CaCO_3$ is added as a powder, it is believed that the insoluble $CaSO_4$ material may form on the surface of each particle inhibiting complete dissolution. Even with thorough mixing, it may not be possible to stop this from occurring. This may explain some of the apparent inefficiency of neutralisation using this type of reagent.

Probably of more importance in correcting the neutralisation model, are the reactions of sulfuric acid, especially with respect to highly acidic solutions. In such solutions H_2SO_4 does not completely dissociate, indeed SO_4^{2-} is a very minor species. This follows the reaction:

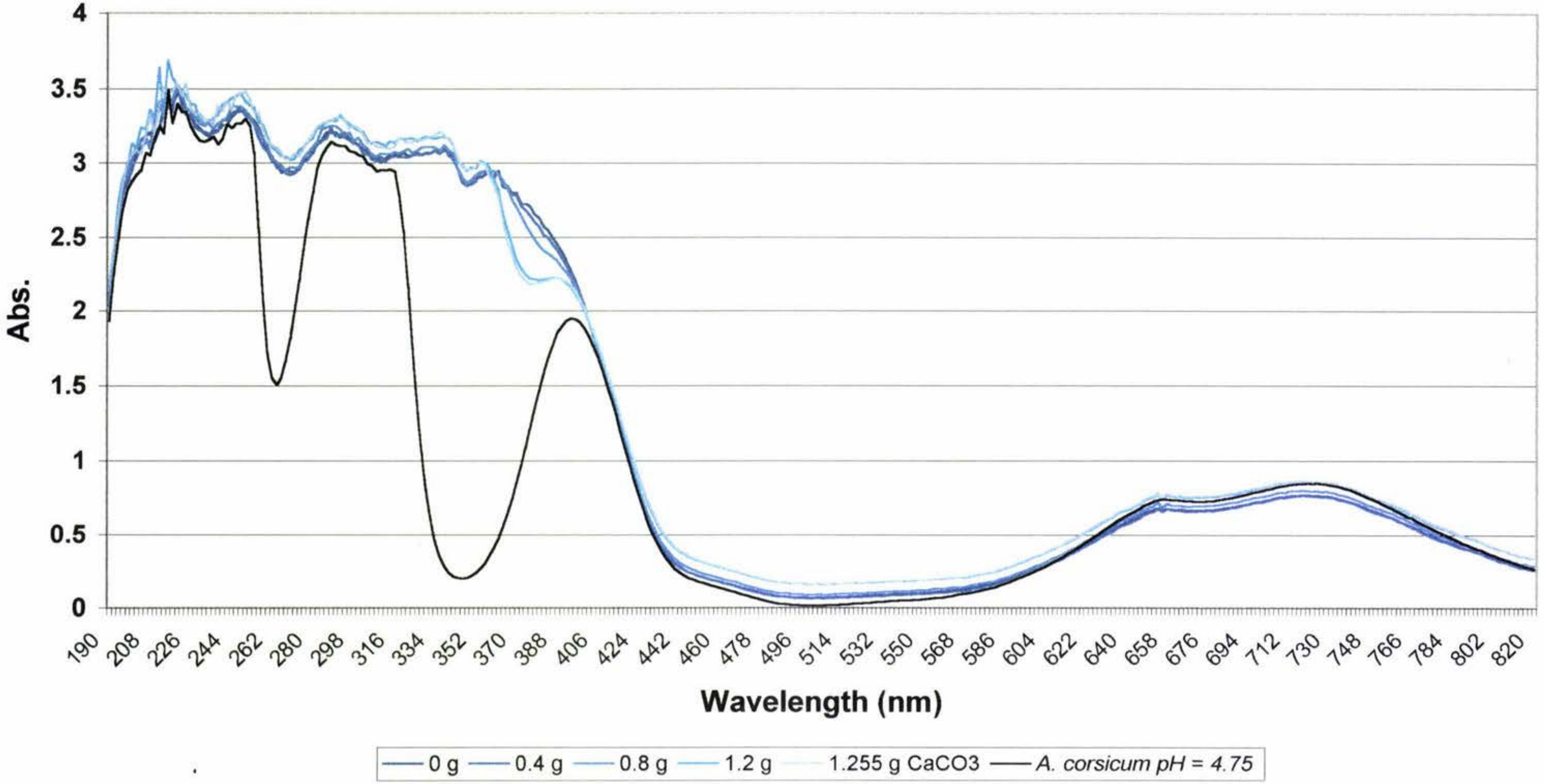
$$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$$

An equilibrium exists between bisulfate and sulfate, with the dissociation constant, K = 1×10^{-2} approximately.

$$HSO_4^- + H_2O \leftrightharpoons SO_4^{2-} + H_3O^+$$

This means in solutions where the pH is low and especially when it is pH 0 or below, much of the potentially available H^+ ions are still bound to the sulfate. As the acidity of the solution is reduced, more of the bisulfate is dissociated, freeing H^+ and

Fig 3.1: UV/Vis Spectra of Synthetic Ash During Neutralisation with $CaCO_3$ and *A. corsicum* Extract at pH 4.75



resulting in buffering of the pH. Therefore more neutralising reagent than predicted (from the measured H^+ concentration) would be required to achieve a given pH. It is difficult to calculate the required amount of neutralising reagent exactly, as the H^+ determinations required dilution of the extract to move the concentration into regions more easily measured. This too would effect the HSO_4^-/SO_4^{2-} equilibrium, resulting in more sulfate and a greater concentration of H^+ ions in solution, than would be if only dilution were taken into account. It should be noted that this does not account for all the apparent inefficiencies of $CaCO_3$ neutralisation, with further pH buffering evident.

3.3.1.2 Further $CaCO_3$ Addition

As neutralisation of the 20 ml extract sample was incomplete more $CaCO_3$ was added, with the degree of neutralisation determined after each addition. It was found that the efficiency of neutralisation (moles H^+ neutralised per moles $CaCO_3$ added) decreases as acidity of the ash extract decreases (Table 3.1).

Table 3.1: Neutralisation of a 20 ml sample synthetic ash extract by $CaCO_3$ addition.

$CaCO_3$ Added (mol/l)	Total $CaCO_3$ Added (mol/l)	$[H^+]$ (mol/l)	Ratio mols H^+ Neutralised /mols CO_3^{2-} Added
0	0	1.256	
0.626	0.626	0.162	1.745
0.055	0.682	0.126	0.654
0.187	0.869	0.023	0.547
0.034	0.904	0.006	0.514
0.009	0.913	0.003	0.238
0.016	0.930	0.001	0.148

In terms of an overall neutralisation from highly acidic (1.256 mol/l H^+) to pH = 3, each mole of CO_3^{2-} reacted with 1.349 mols H^+.

3.3.1.3 Neutralisation of Synthetic Ash Extract (50 ml)

Addition of 0.875 mol/l $CaCO_3$ resulted in pH 1.83 being obtained (Table 3.2). Subsequent additions showed that degree of neutralisation in differing solution volumes is the same for a given total $CaCO_3$ concentration, as is apparent by comparison of the 20 ml and 50 ml samples results. At pH 3, each has a $CaCO_3$ addition corresponding to approximately 0.93 mol per litre of starting solution.

In the region pH 4-4.5, the effectiveness of $CaCO_3$ was seen to drop to the point where the efficiency of H^+ neutralisation (as above), was to less than 1%.

It was determined that 1.01 mol/l $CaCO_3$ was required to neutralise this particular extract to pH 4.5. It is obvious that this quantity will change depending on the acid used and the ash composition, both of which determine the pH of the ash extract.

Table 3.2: Neutralisation of a 50ml sample synthetic ash extract by $CaCO_3$ addition.

$CaCO_3$ Added (mol/l)	Total $CaCO_3$ Added (mol/l)	pH	Ratio mols H^+ Neutralised /mols CO_3^{2-} Added
0.8750	0.8750	1.83	1.418
0.0248	0.8998	2.19	0.336
0.0287	0.9285	3.06	0.194
0.0080	0.9365	3.69	0.083
0.0160	0.9525	4.00	0.007
0.0583	1.0108	4.49	0.001

3.3.1.4 Complete Synthetic Ash Extraction and Neutralisation with $CaCO_3$

The 200 ml ash extract was neutralised to pH 4.45 by treatment with 1.01 mol/l $CaCO_3$. From this volume of extract only 130 ml was collected after centrifuging, a loss of 35% of the extract, the rest being trapped in the solid ($CaSO_4$/$CaCO_3$). The separated extract contained 45.5 mmol nickel (from the original nickel concentration of 0.35 mol/l), while the trapped portion held 24.5 mmol nickel. Washing of the $CaSO_4$ with 70 ml water, while diluting the extract, enabled a further 12.25 mmol nickel to be recovered. Concentration of the wash was calculated to be 0.175 mol/l Ni. The addition of this 70 ml diluted nickel solution to the original 130 ml extract gave a theoretical Ni concentration for the combined solution of 0.29 mol/l and a volume of 200 ml. This concentration corresponds to an 82.5% yield of nickel from the original extract (before neutralisation).

While washing with two 35 ml aliquots would result in an 84.4% yield, this was not considered, as the additional 2% gain in recovered nickel was not thought to be sufficient to justify an additional washing step in the overall process.

UV/Vis analysis confirmed these theoretical calculations with the neutralised and diluted ash extract having a concentration of 0.282 mol/l Ni. The ICP results shown in Table 3.3 (with comparison to previous results before neutralisation) found the Ni concentration to be marginally lower. Discussion of the changes in elemental concentration follow (section 3.3.2) owing to the similarity to the *A. corsicum* results.

Table 3.3: Elemental concentrations of 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract before and after neutralisation with $CaCO_3$.

Elements	µg/g @ pH = 0	µg/g @ pH = 4.45
Al	2850	25
Ca	810	824
Cu	15	5
Fe	3050	50
K	14500	12300
Mg	5160	4320
Mn	600	500
Ni	20390	16290
P	2250	320
Si	50	10
Zn	200	150

3.3.2 *Alyssum corsicum* Ash Extract Neutralisation

Addition of 1.01 mol/l $CaCO_3$, resulted in the *A. corsicum* extract being neutralised to pH 4.75. Analysis of the extract after addition of the 15 ml residue wash, using UV/Vis (at the 720 nm peak), showed the concentration to be 0.272 mol/l Ni. Results from ICP analysis shown in Table 3.4, confirm the nickel concentration determined by UV/Vis with 0.270 mol/l being measured.

Constant levels of Ca were observed during neutralisation, the result of Ca saturation in a sulfate/ nitrate environment. The removal of all the added Ca^{2+} ions in the form of $CaSO_4$ has a large effect on the sulfate concentration, changing the sulfate/nitrate ratio of the extract. In determining the loss of sulfate, it is assumed that all sulfur is present as SO_4^{2-}. Given the acid used for extraction, the original S concentration was 57700 µg/ml (69.2% SO_4^{2-}, 30.8% NO_3^-, as mole proportions). ICP results show that after the extraction only 38000 µg/ml remains (59.7% SO_4^{2-}). This is further reduced with $CaCO_3$ addition and solution dilution until only 14000 µg/ml remains (35.3% SO_4^{2-}).

Table 3.4: Elemental concentrations of A. corsicum extract before and after neutralisation.

Elements	μg/g @ pH = 0	μg/g @ pH = 4.75
Al	690	10
Ca	875	857
Cu	10	1
Fe	1120	1
K	20950	17200
Mg	10050	8950
Mn	140	100
Ni	18490	15850
P	2100	195
S	38000	14000
Si	770	8
Zn	225	40

Such a large drop in the sulfate concentration has an important impact on the ability to recover nickel by either electrowinning or sulfate crystallisation (refer relevant sections).

Of equal importance is the removal of many of the metals during neutralisation with $CaCO_3$. Such metals include Al, Cu, Fe and Zn, with P and Si while not metals also being removed to some extent. Aluminium and iron especially, are known to precipitate as hydroxides, even in mildly acidic solutions, while their phosphates may co-precipitate. Such reductions in concentration may be the cause for the observed decline in interference of the 400 nm peak in the UV/Vis spectra of the ash extracts upon neutralisation (Fig. 3.1).

3.3.3 Neutralisation by NaOH Addition

Extraction of the composite hyperaccumulator plant ash with 4 M H_2SO_4 resulted in a measured H^+ concentration of 2.34 mol/l. It can be assumed that the synthetic ash extract, using the same acid, would give a similar concentration. An addition of 4.56 mol/l NaOH was required to obtain a pH of 4.5, approximately twice the amount calculated, using the assumption of a 1:1 mol reaction for OH^- neutralising H^+. It was believed the pH buffering by the HSO_4^-/SO_4^{2-} equilibrium was at least partly responsible for this apparent inefficiency.

Elemental analysis (Table 3.5) showed that the neutralised ash extract had similar features to that of the *A. corsicum* extract in terms of impurity removal (with dilution taken into account). The key elements removed are Al and P, both reduced to less than 20 μg/ml. However, Fe and Zn were not excluded to the same degree in the case of NaOH addition, suggesting that the reactions forming their insoluble species are not entirely pH controlled. It is possible that some other physical parameter altered by the addition of $CaCO_3$ aided in their removal.

Table 3.5: Elemental concentrations of synthetic ash extract (4M H_2SO_4) before and after neutralisation with NaOH.

Elements	μg/ml @ pH = 0	μg/ml @ pH = 4.50
Al	2870	<20
Ca	215	205
Cd	2	2
Cu	2	2
Fe	3020	1820
K	11100	10770
Mg	4150	3870
Ni	20170	17880
P	2300	<20
S	107750	103250
Si	45	5
Sn	<6	<6
Zn	180	140

The quantity of insoluble material forming with NaOH addition was much less than that found during $CaCO_3$ addition, because $CaSO_4$ was not being precipitated. This reduces the problems of liquid/solid separation inherent with $CaSO_4$ production.

3.4 CONCLUSION

Theoretical calculations for the required amount of $CaCO_3$ to neutralise the ash extract, assumed that each mol of CO_3^{2-} would react with and neutralise two mols H^+ ions. The result of this reaction is to free Ca^{2+} ions and to produce CO_2 gas and H_2O. Neutralisation data showed that the ratio of mols H^+ neutralised per mol CO_3^{2-} added dropped dramatically as the pH increased, with efficiencies less than 1% observed above pH 4. The assumption of complete reaction by $CaCO_3$ proved to be simplistic. Indeed, the effect the HSO_4^-/SO_4^{2-} equilibrium has, with respect to pH buffering, is of importance when neutralising such strongly acidic H_2SO_4 solutions.

The introduction of $CaCO_3$ as a powder also causes considerable inefficiency, as it is thought that the reagent was not being completely dissolved. Instead, a layer of the insoluble $CaSO_4$ was thought to form on the outside of the particles, with greater effect as the pH increased.

Despite these inefficiencies and complications it was possible to determine that a $CaCO_3$ addition of approximately 1.01 mol/l (as fine powder), was sufficient to neutralise an ash extract, where 9:1 2M H_2SO_4/8M HNO_3 (200 g ash per litre acid) was used to leach the ash. The final result may vary to some extent, given the variance in ash composition.

The production of insoluble $CaSO_4$ from free Ca^{2+} and SO_4^{2-} ions causes numerous problems even on small-scale treatments. The large volumes of solid material generated during neutralisation trap a significant portion of the nickel-rich solution, thus necessitating a washing procedure to ensure an adequate nickel yield from the ash. This washing in turn results in the dilution of the overall extract, an undesired effect with electrowinning or crystallisation as the nickel separation procedure. Separation of a large quantity of such fine material becomes an issue when considering a large-scale operation. Disposal of the $CaSO_4$ however, is not so problematic, as the solid can be returned to the phytoextraction site as a fertiliser and to maintain the soils Ca levels.

Another important problem with respect to $CaSO_4$ production is the removal of a large proportion of the sulfate ions present in solution. From analysis of the *A. corsicum* extract, before and after neutralisation with $CaCO_3$, it was shown that 0.75 mol/l S was removed (mostly as a sulfate precipitate but also as lost solution) from the extract. This has a significant effect on both the electrowinning and crystallisation processes (refer relevant sections).

Treatment with NaOH greatly reduces the amount of insoluble material produced. While still requiring some separation it is unclear whether a washing step would be necessary or efficient.

Exclusion of numerous impurities, especially metals, was observed by ICP analysis. This was qualitatively confirmed by UV/Vis spectroscopy, with the reduction in interference around the 400 nm nickel peak. This shows that the neutralisation step acts as another purifying process, removing potentially problematic elements such as Fe. Combined with the product refinements made by the hyperaccumulation process and acid extraction, the end result is a solution with moderate concentrations (0.2-0.5 mol/l) of Ni, Mg and K. Such simplification of the medium is advantageous for any nickel separation process.

Although the neutralisation of an ash extract with NaOH is somewhat easier than with $CaCO_3$, the addition of sodium to high concentrations into the extract could be problematic in terms of disposal after nickel recovery. The extract solutions contain large amounts of potassium and magnesium, with both of these elements encouraging plant growth. Utilisation of this solution as a fertiliser would be advantageous, both in terms of recycling waste and improving the hyperaccumulator crop. However, a high concentration of Na ions discourages this application, as it would cause great damage to the soil ecology.

Chapter Four

Electrowinning

4.1 INTRODUCTION

4.1.1 Overview

Electrowinning is the recovery of a metal by electrochemical reduction of one of its compounds dissolved in a suitable solvent. Such a technique, similar to electroplating, is considered the most efficient way of recovering valuable metals from solution, potentially being selective and producing a pure product that can be marketed without further processing (Horner, 1992).

The process of electrowinning consists of three broad steps:

(1) The metal selected for recovery must be solubilised e.g. by leaching from ore.

(2) The metal-bearing solution is purified, if necessary, to remove other components more noble than the metal to be recovered, as these would be deposited in preference to the selected metal.

(3) The solution is placed in an electrolysis cell, where the metal is plated onto the cathode, with oxygen usually being produced at the anode.

4.1.2 Electrowinning Solution

The solubilisation of nickel was discussed in chapter two (**Ashing and Extraction**), with H_2SO_4 being selected for a number of reasons. This choice is also electrochemically advantageous, with the high mobility of the H^+ ions leading to good conductivity. Also, the sulfate ion is electrochemically inert under the expected operation conditions.

Boric acid is used as a buffering agent in many nickel electrodeposition solutions to help maintain the pH at the cathode at a suitable value, typically in the range 4-5. It is also added to aid in producing adherent metallic-nickel deposits. However, it is still unclear how H_3BO_3 improves nickel deposition. It has been suggested that a catalytic effect occurs with the nickel (Hoare, 1987), but it is more likely that the boric acid inhibits H^+ reduction, causing a decrease in the rate of H_2 evolution at the cathode surface. Less expensive and environmentally damaging alternatives to boric acid, such as acetic acid/sodium acetate mixtures are now being used successfully for electroplating and prove especially useful in high acidity solutions.

In many solutions prepared for nickel electroplating chloride ions are added either as HCl or a chloride salt to increase nickel diffusion and aid in anode consumption. However, electrowinning requires the use of an insoluble anode, and the presence of chloride ions has been reported to lead to the deterioration of such electrodes (Ni plating). There is also the possibility for Cl_2 evolution, with concomitant safety and environmental concerns. For these reasons, chloride is not commonly added to electrowinning solutions.

The nickel concentration has a significant effect on electrodeposition, relating to the activity of the Ni^{2+} ions and solution resistance. While commercial electroplating baths always contain in excess of 1 mol/l Ni, a hyperaccumulator extract usually only contains 0.35 mol/l Ni. Given the aim of electrowinning (the removal of as much nickel as possible from solution) it is apparent that much lower Ni concentrations must be workable. Avci (1989) reported the removal of nickel from wastewater down to as little as 2.5 mg/l using electrowinning. However, the current efficiency (refer 4.2.2) at such a concentration is less than 5%. The point at which the electrowinning process is terminated depends on the operational needs of the user, with the economics of power supply versus nickel return governing the decision.

With respect to recovery of nickel from hyperaccumulator plants the process of electrowinning, although essentially the same as for mineral processing, is simplified to some extent by the exclusion of all other metals more noble than nickel from the plant. This was the major reason electrowinning was considered (refer chapter one, **Introduction**). Counter to this simplification, are the higher concentrations of both potassium and magnesium than would be encountered in conventional electrowinning solutions which could prove to be problematic.

Purification of the hyperaccumulator ash extract was not undertaken since the hyperaccumulation, acid extraction and neutralisation were considered to have already performed sufficient exclusion of obvious nickel electrodeposition inhibitors, such as Cu and Zn.

4.1.3 Electrodeposition

The electrodeposition of nickel has been undertaken for over 100 years, and whether as electroplating or electrowinning processes, is considered by many as much art as it is science. For much of this time the processes were not understood and somewhat superstitious practices of using unusual additives, such as manure, were commonplace.

The fundamental process of nickel electrowinning requires two electrodes in a galvanic cell (working and counter) to be immersed in a nickel-bearing solution (normally of $NiSO_4$ or $NiCl_2$). Sufficient electric potential-difference is provided through a DC power supply to initiate the non-spontaneous electrochemical reactions, with reduction of solvated nickel occurring at the working electrode.

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$$

Oxidation of water occurs at the counter electrode.

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

From the standard reduction potentials for chemical reduction, it is apparent that in a solution where both Ni^{2+} ($E^\theta = -0.23$ V) and H^+ ($E^\theta = 0.00$ V) exist, it is in fact the hydrogen ion that should be reduced. However, because of the overpotential for hydrogen evolution, electrodeposition of nickel is often observed. The overpotential is the potential that must be applied to the cell over and above the theoretical potential required to liberate hydrogen. This is the result of differences in ion concentrations between the bulk-solution and electrode-surface, resistance of the electrolyte solution and also the activation energy required for a given reaction (kinetic effect) (Oldham and Myland, 1994). Overpotential may change with electrode material, current density and changes in concentration at the electrode surface (Oxford Concise Science Dictionary, 1997).

The yield of nickel (with respect to time) is limited predominantly by the current at which deposition takes place. If the current is too high, corresponding to a potential in excess of the hydrogen overpotential, then hydrogen evolution will occur. Alternatively, if the current is too low then the recovery of nickel is slow. The transport or diffusion of Ni^{2+} ions from the bulk solution to the surface of the electrode in turn limits the maximum workable current. If the rate at which nickel ions are supplied to the electrode is inadequate to maintain the nickel concentration at the electrode surface for a given current, then the cell potential increases (a response to polarisation of Ni^{2+} and increasing resistance). The efficiency of nickel recovery correspondingly decreases as H_2 evolution occurs. In such cases, the localised (at electrode surface) removal of H^+ ions from solution results in an increase in pH. If the pH increases sufficiently, then black nickel hydroxide is electrodeposited, a phenomenon known as burning or black stripe (Dennis and Such, 1993).

While achieving a good rate of nickel deposition is important, so too is the efficiency of the deposition process. In terms of energy requirement, electrowinning is possibly the most expensive industrial metal recovery technique. The theoretical quantity of metal produced by electrolysis is directly proportional to the amount of electricity supplied according to Faraday's law,

$$N = I\,t \,/\, n\,F$$

where N denotes the number of moles of species either reduced or oxidised (Atkins, 1994). However, because of chemical and electrochemical losses of energy, the process is never 100% efficient.

The economic efficiency of an electrolytic process for recovering metals depends to a large extent on the design of cells. Since the electrochemical reactions occur at an electrolyte-electrode interface, the possible output is directly proportional to the area of interface. Theoretically the yield of nickel can be improved by increasing the surface area of the electrodes, allowing greater overall current, owing to the reduced current density. The use of high surface-area electrodes is becoming more common, with advances into the use of materials such as nickel sponge (Coates, 1989).

Transport of Ni^{2+} to the cathode surface limits the maximum possible current. Since the nickel concentration cannot be readily increased in a plant extract, it is important for the cell design to maximise mass transport of the ions. Solution mixing, either through stirring or electrode rotation, aids in ion mobility. The layout of the cell can also determine the efficiency of solution mixing e.g. large plate-electrodes positioned close together inhibit adequate mixing, depleting metal ions between the plates.

While the electrochemical processes occurring at the cathode are of obvious importance, determining the nature and rate of nickel deposition, the oxidation occurring at the anode should not be overlooked. Considering that hydrogen evolution at the cathode should be avoided, there is no balance for the increase in H^+ ions being generated during the oxidation of H_2O to O_2. Even with species such as boric acid buffering the pH, there is a marked change in acidity over time. The electrogeneration of a more acidic solution, both increases the rate of reduction of H^+ to H_2 and decreases the efficiency of Ni deposition (Brillas et al., 1999). This rising acidity is normally controlled either by adding neutralising reagents or placing a diaphragm between the counter and working electrodes, thus maintaining the pH at the working electrode.

4.2 MATERIALS AND METHODS

4.2.1 Electrowinning Conditions

4.2.1.1 Electrolyte Solution

Unless specified otherwise, a 200 ml nickel sulfate solution, also containing boric acid, was used in all nickel electrowinning investigations. Based on the electroplating bath described by Watts (Dennis and Such, 1993), the nickel concentration varied from 1 mol/l to 0.5 mol/l, introduced as $NiSO_4.6H_2O$, depending on the experimental requirements. Boric acid concentrations were maintained at 20 g/l. Such solutions were slightly acidic with pH ranging from 4-5, before being adjusted to a pre-electrolysis value of 4.5 using NaOH or H_2SO_4. The solution was maintained at a temperature of 60°C.

4.2.1.2 Electrode Choice

Carbon-fibre cloth was used as the counter electrode. This avoided possible electrode degradation that can occur when oxidation takes place on carbon electrodes held together by binding agents, as is the case with most carbon rods. The surface area of the electrode was also greatly increased by using a carbon-fibre cloth, as compared to carbon rods.

Three types of working electrodes were investigated: copper plate, nickel plate and nickel sponge electrodes. Using the standard 0.5 mol/l Ni solution and conditions of 0.1 A at 60°C, the three were compared and copper plate chosen as most suitable. Nickel sponge, while increasing the potential surface area, consistently returned burnt deposits. This was due to the uneven (disjointed) nature of the material inhibiting adequate mass transport of the Ni^{2+} ions, and causing the reduction of H^+ ions; thus a localised pH increase (refer 4.1). Adequate deposits formed on the nickel plate electrodes where ion transport was not as hindered. However, this material was in short supply necessitating reuse of the electrodes, with successive layering of deposits. Flaking of these layers left an uneven and deteriorated electrode surface. The need for repetitive experiments with near identical working parameters prohibited this material from being used as working electrodes. Copper plate working-electrodes proved to produce excellent nickel deposits and a larger supply of this material permitted new working electrodes for each experiment. Each was scrubbed using a Teflon gauze pad to remove any tarnishing, then washed in methanol, dried and weighed using a four-figure balance. In this way, a clean electrode surface could be ensured and experiment conditions remained more alike between experiments than in the case of reusing electrodes.

4.2.1.3 Electrolysis Cell Construction and Electrical Set-up

A PTFE frame was used to hold the counter (4.5 cm x 4.3 cm) and working (4.5 cm x 4.3 cm x 0.1 cm) electrodes parallel, with a separation of 1.2 cm. Grooves were cut into this frame to facilitate easy removal and replacement of the working electrode for analysis. Holes drilled into the top of the frame, enabled tabs from the electrodes to protrude above the intended submersion line and be connected to a regulated DC power supply (Wonix, YW-APS305). For nickel solutions not derived from plant material, a 250 ml beaker was employed as the electrolysis vessel. This contained 200 ml of nickel-bearing solution in which the electrodes and frame, suspended from a retort stand, were completely immersed. No part of either electrode or frame was in contact with the outer vessel. A constant temperature (± 1°C) was obtained using a thermostat-controlled hot plate, with a digital thermometer suspended in the solution. A magnetic stirrer bar was also placed in the electrolysis vessel to provide constant stirring.

The electrowinning cell was connected to a power supply, with the current controlled by a variable resistor and measured using a multimeter. Potential was also monitored using a second multimeter.

4.2.2 Electrowinning

4.2.2.1 Current Efficiency and Visual Characteristics of Nickel Deposit

The current efficiency and visual characteristics of the nickel deposit were used, quantitatively and qualitatively respectively, to draw conclusions from the investigations. After each electrowinning period, the working electrode was removed, washed with double deionised water, washed a second time in methanol, then dried before being weighed on a four-figure balance.

The current efficiency, γ, is calculated as percentage of charge necessary to produce the amount of nickel recovered compared to the overall charge supplied by the power supply. This is determined by the calculation:

$$\gamma = \frac{m\,n\,F}{M_r\,I\,t} \times 100\%$$

m Mass of Ni deposited (g)

M_r Molar mass of Ni (g/mol)

n Number of electrons required to reduce Ni^{2+} i.e. 2

F Faraday's constant (96485 C/mol)

I Current (A or C/s)

t Time (s)

The overpotential for hydrogen evolution is greater on a copper electrode of this type than nickel. As the nickel was electrodeposited, and the working electrode underwent the transition from a copper to a nickel surface, the efficiency of Ni^{2+} reduction decreases. This phenomenon prohibits the current efficiencies for nickel deposits from different periods of deposition being compared. In the following investigations, current efficiencies between investigations were not compared.

Qualitative comparison of the visual characteristics of the nickel deposit was based on a number of immediately apparent properties. The deposits could be ranked by their lustre or shine, with dull deposits indicative of poor electrodeposition. The coverage of the deposit was also of importance, with an incomplete coverage of the underlying copper electrode also correlating to poor electrolysis (the period of electrodeposition was taken into account for this assessment). Likewise, any flaws such as pitting or burning were taken as signs of less than perfect electrodeposition.

4.2.2.2 Reproducibility of Nickel Deposit and Current Efficiency

The reproducibility of the electrowinning cell, with respect to the visual characteristics of the nickel deposit and corresponding current efficiency, was investigated using a 200 ml solution of 0.5 mol/l Ni and 20 g/l H_3BO_3, maintained at 60°C. Nine consecutive runs each of 30 minutes, with a current of 100 mA were undertaken. New working electrodes and solutions were made for each run. The visual characteristics of all nine working electrodes were compared and a statistical analysis performed on the their respective current efficiencies.

4.2.2.3 Effect of Increasing Current on Current Efficiencies

In a solution containing 1 mol/l Ni and 20 g/l H_3BO_3 at 60°C, the current efficiencies were determined and compared for 25 min periods of nickel electrodeposition at 100, 200, 300 and 400 mA.

4.2.2.4 Effect of Ni Concentration on Current Efficiencies

The electrowinning cell was used with solutions of Ni concentrations 0.05, 0.10, 0.40, 0.80 and 1.0 mol/l, with a boric acid concentration of 20 g/l. Temperature was maintained at 60°C with a deposition current of 100 mA, during nickel electrodeposition periods of 25 min. Initial acidity of the solutions was adjusted to pH 4.5. The current efficiencies and visual characteristics of the deposit were determined and compared for each Ni concentration.

4.2.2.5 Galvanostat Investigation – Comparison of Potential, Current and Temperature

A galvanostat was used to determine the relationship between potential and current for the electrowinning cell, using a 200 ml solution of 1 mol/l Ni and 20 g/l H_3BO_3 at pH 4.5. The current was increased in the progression: 0, 1, 2, 5, 10, 20, 50, 100, 150 and 200 mA, with each current being held for 30 seconds before being increased. Temperature was maintained during the experiment at 25°C. Subsequent experiments, using new solutions and working electrodes, were undertaken at higher temperatures, giving results of potential and current for the temperatures 25, 40, 50, 60 and 70°C.

During this process the oxidation reaction at the counter electrode involved the electrolysis of water.

$$H_2O \rightarrow {}^{1}/_{2}O_2 + 2H^+ + 2e^-$$

The effect of an alternative oxidation reaction, with respect to current and potential, was investigated by adding formaldehyde to the electrowinning solution. Oxidation at the counter electrode would then entail a two-stage process.

The above experiments were repeated using a solution containing 0.5 mol/l formaldehyde (introduced as 40% solution). Because of the 4e$^-$ reaction involved with the complete oxidation of HCHO, 0.5 mol/l was the theoretical requirement given a Ni concentration of 1 mol/l (2e$^-$ reduction). H_3BO_3 was also added to 20 g/l. Solutions and working electrodes were changed between each temperature alteration.

$$HCHO + H_2O \rightarrow HCOOH + 2H^+ + 2e^-$$

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^-$$

Nichrome wire (0.25 mm) was used as a pseudo reference electrode, positioned in solution approximately equidistant from the working and counter electrodes.

4.2.2.6 Linear Scan Voltammetry - Rotating Disc Electrode

Investigation of a number of the parameters of nickel electrodeposition was carried out with linear scan voltammetry, LSV, using a BAS rotating disk electrode (BAS RDE-1). As a steady state was not achievable, the study focused on the potential at which reduction was initiated and rate at which nickel was reduced. These results were then used to give some insight into the processes of Ni^{2+} reduction and identify favourable working conditions.

The parameters investigated with respect to nickel electrodeposition are shown in Table 4.1.

Table 4.1: Parameters investigated using LSV.

Parameter in Question							Compound Added
(A) Temperature (°C)	20	30	40	50	60		
(B) [Nickel] (mol/l)	0	0.05	0.10	0.20	0.35	0.50	$NiSO_4.6H_2.O$
(C) [Boric Acid] (g/l)	0	2.5	5.0	10.0	20.0	40.0	H_3BO_3
(D) [Chloride] (mol/l)	0	0.015	0.030	0.075	0.150		NaCl
(E) [Sulfate] (mol/l)	0.50	0.55	0.65				Na_2SO_4

LSV investigations were carried out using a series of rotation rates: 630, 1000, 1585, 2500, 4000, 6300 and 10000 rpm, for each change to solution.

A rotating disc working-electrode was constructed using Ni wire (99.99%) of 2.15 mm thickness surrounded by a threaded PEEK plastic-sleeve (6.40 mm x 24.20 mm); this left only the planar end of the nickel wire (3.63 mm^2) exposed to electrolysis. This was screwed onto the instrument (BAS RDE-1) with an electrical connection being made to the nickel wire within the sleeve. A carbon rod (2.5 mm x 20 mm) was used as the counter electrode, with a Ag/AgCl electrode being employed as the reference. During the electrolysis experiments these three electrodes were immersed in the solution to a depth of 15 mm. The temperature was measured with a thermocouple, which was also immersed in the electrolyte.

The nickel working-electrode was polished before use and again between each set of experiments; this ensured a clean surface for each set of experiments, giving greater reproducibility of results.

Solutions prepared for LSV were made to 500 ml, with nickel being introduced as $NiSO_4.6H_2O$. Unless stated otherwise the standard conditions of 60°C, $[Ni^{2+}] = 0.5$ mol/l and $[H_3BO_3] = 20$ g/l were used, with the initial pH adjusted to 4.5. Approximately 350 ml of the prepared solution was poured into a thermostat-controlled vessel, ensuring the temperature only fluctuated by ± 1°C.

4.2.3 Plant Extract Electrowinning

4.2.3.1 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

After neutralisation and liquid-solid separation by centrifuge, extract samples of the 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract were combined to give 200 ml of solution with a Ni concentration of 0.276 mol/l. H_3BO_3 was added to the solution at 20 g/l concentrations. The solution was adjusted to pH 4.5, and heated to 60°C. Electrodeposition was carried out at a current of 100 mA maintained for 25 min. This electrodeposition was repeated three times, with analysis of the solution, pH neutralisation to pH 4.5 and replacement of working electrode after each 25 min period.

The green powdery deposit forming on the working electrode in each case was dried in a vacuum desiccator. A sample of 0.1918 g was taken and dissolved in 100 ml of 2M HCl, then 1 ml diluted to 50 ml and analysed for Ni, Ca and Zn content using flame AAS. A second sample was taken and analysed by X-ray powder diffraction to investigate the structure of the powdery deposit.

4.2.3.2 Effect of Calcium on Electrowinning Solution

It was hypothesised that the inhibition of nickel reduction observed in the synthetic ash extract above, might be the result of calcium being present in the electrowinning solution. A 200 ml solution was made to investigate this hypothesis, with a Ni concentration of 0.35 mol/l and a H_3BO_3 concentration of 20 g/l. Calcium was added as $CaCl_2$ to give concentrations of 0, 0.1 and 0.5 g/l. The solution, heated to 60°C, was used with the electrowinning cell for 30 min at 100mA. Visual characteristics of the deposits and current efficiencies were compared after electrodeposition.

4.2.3.3 Simulation of 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

Owing to the limited volume of ash extract, a 200 ml solution was prepared to simulate the extract. An investigation into improving Ni electrodeposition was then carried out first on this simulated solution before being applied to the synthetic ash extract.

In addition to elemental concentrations, the simulated solution required similar sulfate and nitrate concentrations, which were thought to possibly contribute to the unknown inhibition of nickel electrodeposition. It was ascertained that sulfate proportions were reduced to 35.3 mole % , from the ICP analysis of the *A. corsicum* extract after neutralisation with $CaCO_3$ (theoretically the same for the synthetic ash extract), with nitrate being the remainder. Because of the dilution resulting from the addition of the synthetic ash residue wash solution, the sulfate and nitrate concentrations were less than would be found in the *A. corsicum* extract, with 0.34 mol/l and 0.61 mol/l respectively.

The pH was adjusted to 4.5 before electrowinning was undertaken. Elemental concentrations and compounds are given in Table 4.2.

Table 4.2: Elemental concentrations in simulated synthetic ash extract solution.

Element	Elemental Concentration (g/l)	Compound Added
Ca	0.8	$Ca(NO_3)_2$
K	12.3	KNO_3
Mg	4.3	$MgSO_4$
Mn	0.5	$MnSO_4.H_2O$
Ni	16.2	$NiSO_4$ and $Ni(NO_3)_2$
Zn	0.2	$ZnSO_4$

Proportions of sulfate and nitrate compounds were used to give the respective elemental concentrations as specified above. Boric acid was also added to a 20 g/l concentration. It was necessary to determine whether electrowinning from this solution gave the same result as found for the plant extract, so the solution was heated to 60°C and electrodeposition at 100 mA undertaken for a period of 25 min. The green precipitate formed on the working electrode, verifying that the solution was adequately similar to the synthetic ash extract. This enabled further experiments to be carried out using the same solution formula. The simulated solution was found to have a pH of 2.55 after the period of electrodeposition.

A second solution was made using the above elemental concentrations and acidity adjusted to pH 3.5. The solution was tested again for electrowinning, at 100 mA, 60°C and a period of 25 min, with an identical green deposit observed. A third solution was treated in the same manner, but neutralised to pH 5.5 before electrowinning was undertaken. Only small quantities of green precipitate were observed in this case, with a burnt, incomplete deposit forming underneath. From a fourth solution, neutralised to pH 6, electrowinning resulted in the same burnt, incomplete deposit.

To another solution using the elemental concentrations as specified above, with pH adjusted to 4.5, Na_2SO_4 was added to give a concentration of 1.0 mol/l. The solution was filtered to remove insoluble material, before the pH was measured and determined to be 5.77 then adjusted to pH 4.5. This solution was used for electrowinning in the same manner as above, with the result being a shiny, metallic nickel deposit with near perfect visual characteristics.

4.2.3.4 Addition of Na_2SO_4 to the 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

Owing to the findings of the above investigation using a simulated ash extract solution, Na_2SO_4 was added to 200 ml 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract to give a concentration of 1.0 mol/l. The solution was filtered to remove insoluble material and adjusted to pH 4.5. Electrowinning was carried out for 30 min at a current of 100 mA and a temperature of 60°C. The copper working electrode was removed after this period and the current efficiency determined.

4.2.3.5 Simulated Sulfate Ash Extract Solution

To determine any inhibiting effects the presence of nitrates has on Ni electrodeposition a 200ml solution was made mimicking the 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract as above, but with elements added as sulfate salts only. This gives a total sulfate concentration of 0.80 mol/l. The solution was neutralised to pH 4.5 and electrowinning performed for 30 min in an identical fashion to previous experiments. This resulted in a burnt metallic deposit. Further solutions were prepared as above with $NaNO_3$ and Na_2SO_4 added where appropriate to give total nitrate and sulfate concentrations as shown in Table 4.3:

Table 4.3: Simulated solution with varying sulfate and nitrate additions.

Total $[SO_4^{2-}]$ (mol/l)	Total $[NO_3^-]$ (mol/l)
0.80	0
0.80	0.30
0.80	0.50
1.00	0.30
1.34	0.50

The pH of each solution was adjusted to 4.5 before electrowinning was undertaken for 30 min in the same manner as above, at the end of which the visual characteristics of the working electrodes were assessed.

4.2.3.6 Electrowinning from the *A. corsicum* Extract

After neutralisation, H_3BO_3 was added to the 100 ml *A. corsicum* extract to give a concentration of 20 g/l, and the acidity of the solution adjusted to pH 4.5 using NaOH and H_2SO_4. The conductivity of the extract was measured using a conductivity meter (Orion Research model 701 A/ digital ionalyzer) and compared to that of a typical Watts solution, containing 1 mol/l $NiSO_4.6H_2O$ and 20 g/l H_3BO_3. These were found to be 62.7 mS/cm and 45.0 mS/cm respectively.

After this analysis the 100 ml *A. corsicum* extract was heated to 60°C in a 150 ml beaker. Electrowinning was carried out for 10 min at a current of 40 mA. This current was used to give the same current density as in the other electrowinning investigations, as the solution did not completely cover the electrodes.

A green Ni hydroxide deposit was observed as predicted, indicative of the nitrate content of the solution. Na_2SO_4 and $NaNO_3$ were added to the solution to give the overall concentrations as shown in Table 4.4.

Table 4.4: Nitrate and sulfate additions to A. corsicum extract.

Total $[Na_2SO_4]$ (mol/l)	Total $[NaNO_3]$ (mol/l)	pH
0	0	4.5
0.35	0	4.5
0.70	0	**3.5**
0.70	0	**4.5**
0.70	0	**5.5**
1.00	0	4.5
1.00	0.10	4.5
1.00	0.20	4.5
1.00	0.25	4.5
1.00	0.30	4.5

Electrodeposition was carried out for periods of 10 min in each case, with the pH adjusted to an initial value of 4.5 unless stated otherwise. The current efficiency was determined for the last period of electrowinning, as the deposit was near perfect and considered representative of the type that would be produced using hyperaccumulator extract solutions on an industrial scale.

4.3 RESULTS

4.3.1 Electrowinning

4.3.1.1 Reproducibility of Current Efficiency and Visual Characteristics of Nickel Deposit

The visual characteristics of the nickel deposited onto the nine copper working electrodes were almost identical. No significant variation could be seen by eye, with all deposits having a good metallic lustre, complete coverage and no blemishes. These results, while encouraging in terms of finding a reproducible result, emphasise that this is a very simplistic qualitative comparison.

While some deviation of percentage current efficiencies occurred, the majority were within a narrow range. Given this variance, the current efficiencies should be used only as a guide for assessing electrodeposition. In experiments where the electrodeposition period is not repeated numerous times, it may not be possible to compare results that differ by less than 5%. This variance is most likely the result of differences on the surface of the working electrode, causing differing growth rates of the nickel deposit.

The current efficiencies for the nine periods of electrodeposition are shown in Table 4.5.

Table 4.5: Current efficiencies for nine identical electrodeposition experiments.

	#	Current Efficiency %
	1	84.3
	2	82.4
	3	83.7
	4	90.5
	5	75.9
	6	84.1
	7	75.3
	8	82.9
	9	82.6
Mean	82.4	
s	4.6	

The qualitative visual characteristics and percentage current efficiencies of a nickel deposit, produced from the electrowinning cell, were used to compare solutions and identify which was best suited for nickel recovery. The degree to which such techniques can determine subtle differences is however in question. For this reason the findings of such investigations were treated more as a guide.

4.3.1.2 Effect of Increasing Current on Current Efficiency

An increase in current resulted in an increase in potential, closer to the hydrogen overpotential limit. With this rising potential a greater proportion of the current supplied is used to produce H_2 gas. This was evident using the electrowinning cell, with the electrode observations and current efficiencies shown in Table 4.6 illustrating the equilibrium shift between H^+ and Ni^{2+} reduction. The potential was not increased enough to cause the extreme result of 0% Ni recovery efficiency.

Table 4.6: Effects of increasing current on electrowinning cell.

Current (mA)	Current Efficiency %	Degree of H_2 Gas Formation
100	88	None
200	77	Small and Limited
300	57	Moderate (bubbles forming)
400	40	Significant Gas Production

A current efficiency of approximately 90% or greater is desired for an electrodeposition process, so as to not waste energy on hydrogen evolution. Although the removal of H^+ ions may counteract to some extent the acidification occurring at the counter electrode, a complete hydrolysis of the water would be required to obtain a stable pH.

4.3.1.3 Effect of Ni Concentration on Current Efficiency

When the concentration of nickel in solution drops sufficiently, an increase in potential is observed to maintain a fixed current. This is the result of increased resistance in the solution and a decreased supply of ions to the electrode surface. When the supply of Ni^{2+} ions is limited, the reduction of H^+ becomes more favourable and a greater proportion of the current is utilised in its reduction. This was evident in the decreasing current efficiencies shown in Table 4.7, although the investigation also illustrated that adequate nickel deposits could be obtained without excessive loss of energy (as hydrogen), when concentrations dropped as low as 0.05 mol/l Ni.

Table 4.7: Effect of Ni concentration on current efficiencies.

[Ni] mol/l	Current Efficiency %	Deposit Appearance
0.05	88	Shiny Metallic / Adherent Ni
0.10	91	Shiny Metallic / Adherent Ni
0.40	95	Shiny Metallic / Adherent Ni
0.80	97	Shiny Metallic / Adherent Ni
1.00	96	Shiny Metallic / Adherent Ni

While the current efficiency was found to decline at the lower concentrations it is unclear whether this is the result of decreased activity of the Ni^{2+} ion or variance in cell performance. Avci (1989) reported steadily decreasing current efficiencies when concentrations were less than 0.03 mol/l, with sharper decreases observed below 0.01 mol/l Ni. However, it is difficult to compare results in this manner as the cell design, affecting mass transport of Ni^{2+}, plays a major role in determining current efficiencies, especially at low concentrations. Indeed, the electrochemical recovery of metals from dilute solutions is limited by the occurrence of polarisation in the diffusion layer, leading to a low mass-transfer rate.

4.3.1.4 Galvanostat Investigation – Comparison of Potential, Current and Temperature

Using a reference electrode, and a galvanostat, it was possible to determine the potential of the working (E_{neg}) and counter (E_{pos}) electrodes separately, and the overall cell potential, E_{cell}. Using the standard conditions of 60°C as an example (Fig. 4.1), the separate electrodes were shown to change in potential uniformly with an increase in current. Such a similar change in potential with current, implies that any inefficiency of electrodeposition is not the responsibility of any one reaction, but instead both the oxidation and reduction reactions.

The potential E_{cell} was shown to decrease with an increase in temperature, from 25-70°C (Fig. 4.2). This overall potential decrease was shown to be consistent over the range of currents scanned, with a difference of 0.25 V occurring between 25°C and 70°C at 200 mA. The lower potentials observed when temperature is increasing, are the result of greater mobility of the ions in solution. This relationship can be expressed with the Stokes-Einstein equation (Atkins, 1994):

$$D = kT / 6\pi a \eta$$

Where D = diffusion coefficient
k = constant
T = temperature (K)
a = spherical radius of ion
η = viscosity of solvent

From this equation, diffusion should increase proportionally with temperature provided the ionic hydrodynamic radius does not alter.

Fig. 4.1: Cell and Electrode Potentials with Varying Current for Watts Solution at 60 degrees C

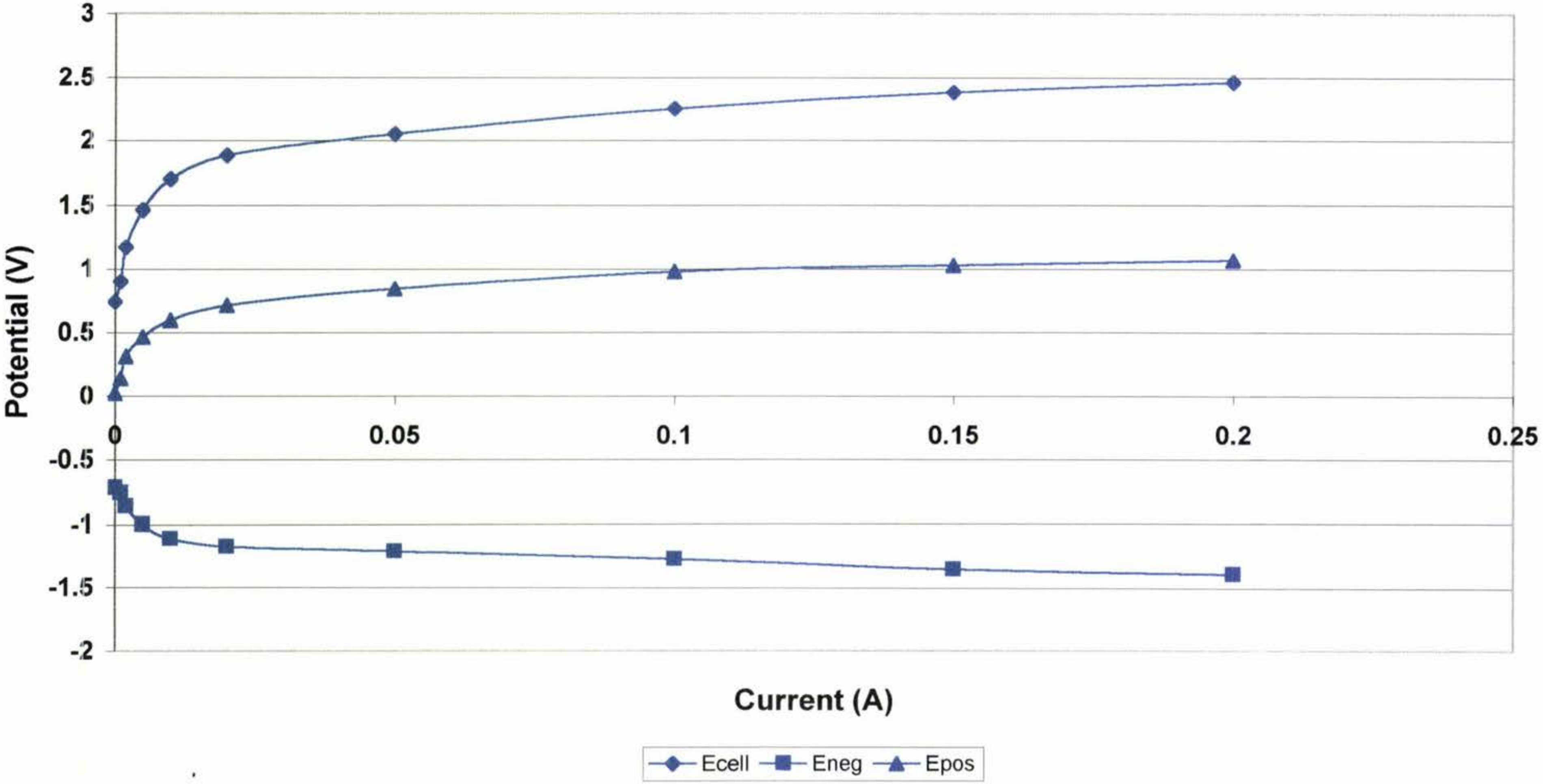


Fig. 4.2: Comparison of Ecell and Potential with Varying Temperatures

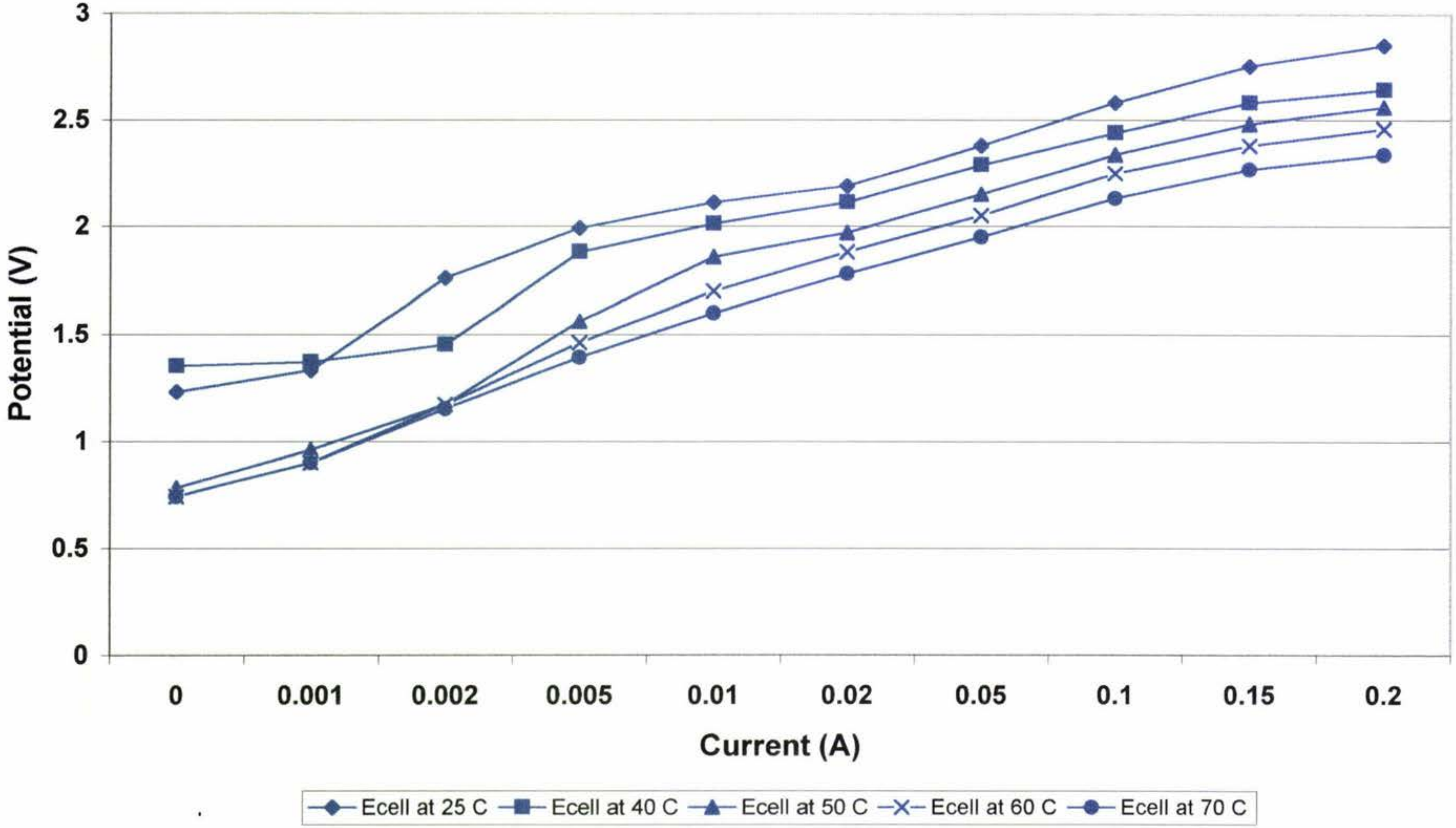
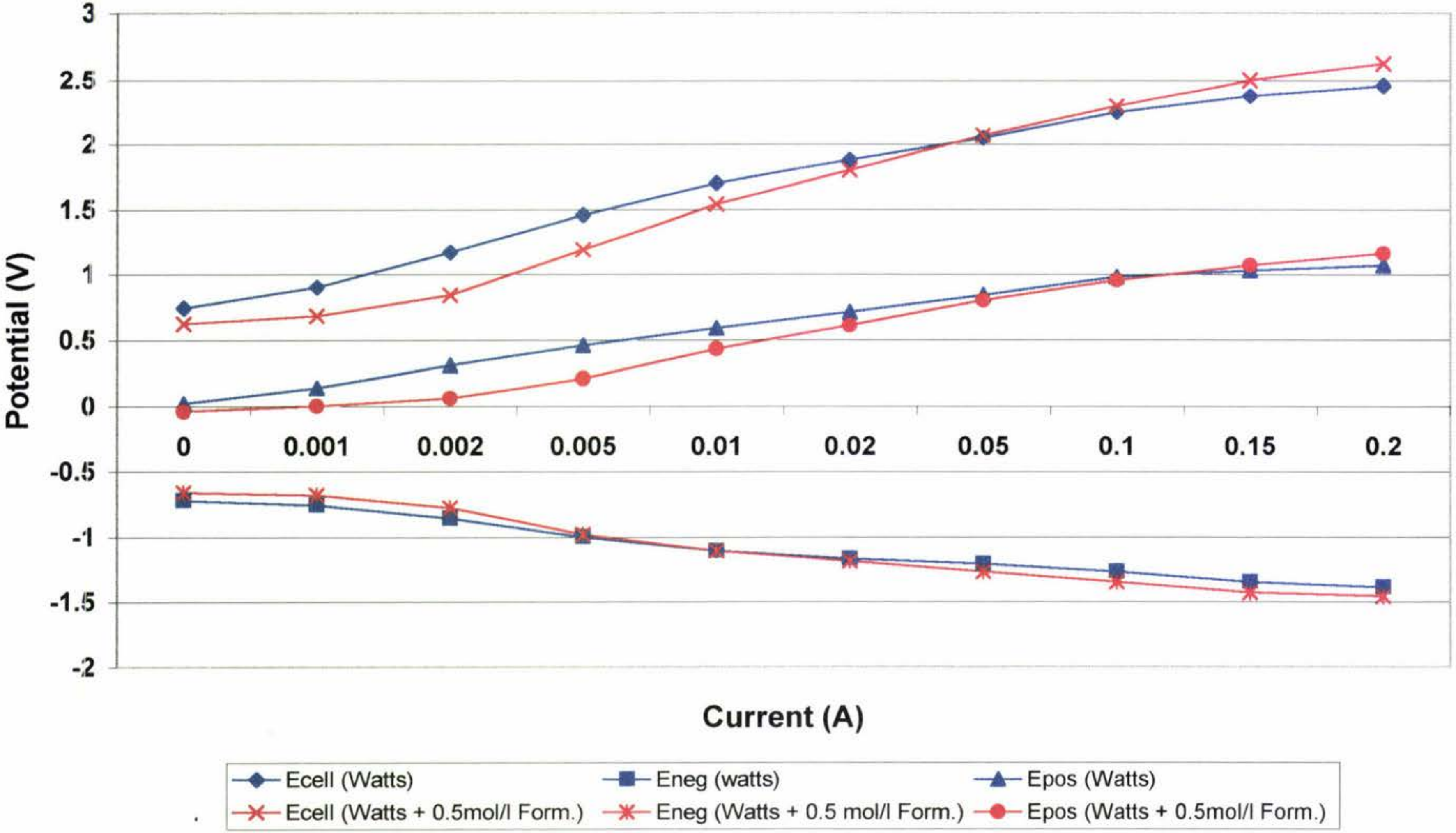


Fig. 4.3: Comparison of Cell and Electrode Potentials vs. Current for Watts and Watts + 0.5mol/l Formaldehyde at 60 degrees C



When determining the most efficient means of carrying out electrowinning in a commercial sense, it is important to balance the energy input with product output, thus minimising energy waste. An increase in temperature results in greater efficiencies of nickel production by decreasing the cell potential for a given current, thus increasing current efficiency (especially at higher currents) and reducing electricity usage for a given current. However, this decrease in potential and the relevant increase in efficiencies, incurs additional costs in the form of heating the solution. Indeed it may be necessary to sacrifice some of the electrodeposition efficiency, to save costs on energy required for heating the solution.

The introduction of formaldehyde into the electrolysis solution, offering an alternative oxidation reaction to the splitting of water, should have had its greatest and possibly only effect on E_{pos}, the counter electrode potential. In fact, results similar to that of the conventional solution were seen, with minor differences occurring in both E_{pos} and E_{neg} (Fig. 4.3). It is difficult to determine whether such small differences are the result of different electrochemical processes or instead simply due the to variability of the electrowinning cell results. The same decrease in potential with increasing temperature was observed, excluding the result at 70°C, indicative of greater ion mobility. With respect to the oxidation process (E_{pos}), the addition of formaldehyde had the largest effect at relatively low currents (<50 mA), where potential was lower than the solution without formaldehyde. It may be that the poorer diffusion of HCOH, compared to H_2O, results in a reduced concentration at the electrode surface. Under such conditions the oxidation of water may become more favourable, accounting for the potentials being similar to that found without formaldehyde.

4.3.1.5 Linear Scan Voltammetry – Rotating Disc Electrode

The rate at which nickel electrodeposition occurs determines the yield of nickel metal for a given time. For the process to be efficient it is important to maximise the current, with respect to the potential (refer 4.3.2.4). This is especially important considering the limited range of potential where nickel reduction occurs instead of hydrogen evolution.

The rate of nickel reduction is proportional to the slope of a graph 'current vs. potential' (Figures 4.4-4.10), with the potential at which Ni reduction is initiated also contributing to the rate of reduction i.e. the smaller the initial potential, the greater the possible current assuming the slope is constant.

The key to increasing the current for a given potential is to decrease the electrical resistance of the solution, increase Ni^{2+} mobility (mass transport), or decrease the energy necessary for an electrochemical reaction to occur.

(A) Temperature Dependence

Figure 4.4 clearly shows an increase in the rate of reduction as the temperature is increased up to 60° C. Such an effect is the result of the overpotential for Ni^{2+} reduction lowering as the ion mobility increases and the additional energy supplied by the higher temperatures reduces the activation energy necessary for the electrochemical reduction of nickel. Such high temperatures (50-60°C) are favourable for nickel electrodeposition and commonly used in industrial electroplating operations.

(B) Nickel Concentration Dependence

It is apparent that the nickel concentration of an electrolysis solution of this type would be of importance in determining (and affecting) current and potential. Figure 4.5 shows the relationship between rate of reduction and the nickel concentration of the solution, with dramatically increased rates at higher concentrations.

The nickel concentration affects the resistance of the solution, with greater conductivity achieved at high concentrations. Also, at lower concentrations there is a greater Ni^{2+} polarisation, caused by differences between the electrode-surface and bulk solution nickel concentrations, given a constant rate of ion diffusion.

In a solution where the nickel concentration was 0.5 mol/l, it was found that only marginal difference was observed in the rate of reduction when the speed of electrode rotation was changed (Fig. 4.6). This suggests that at 0.5 mol/l Ni (bulk solution concentration) and even at low mass transport rates, the differences in electrode-surface and bulk-solution nickel concentrations are small, so polarisation caused by such discrepancies would likewise be small. When the concentration is smaller, it was found that greater variation in reduction rates existed, as electrode rotation was changed (Figure 4.7). This is indicative of the increased polarisation suggested, as the nickel concentration decreases. However, the overall effect is small.

Fig. 4.4: Effect of Temperature on Current and Potential at 4000 rpm and 0.5 M $NiSO_4$

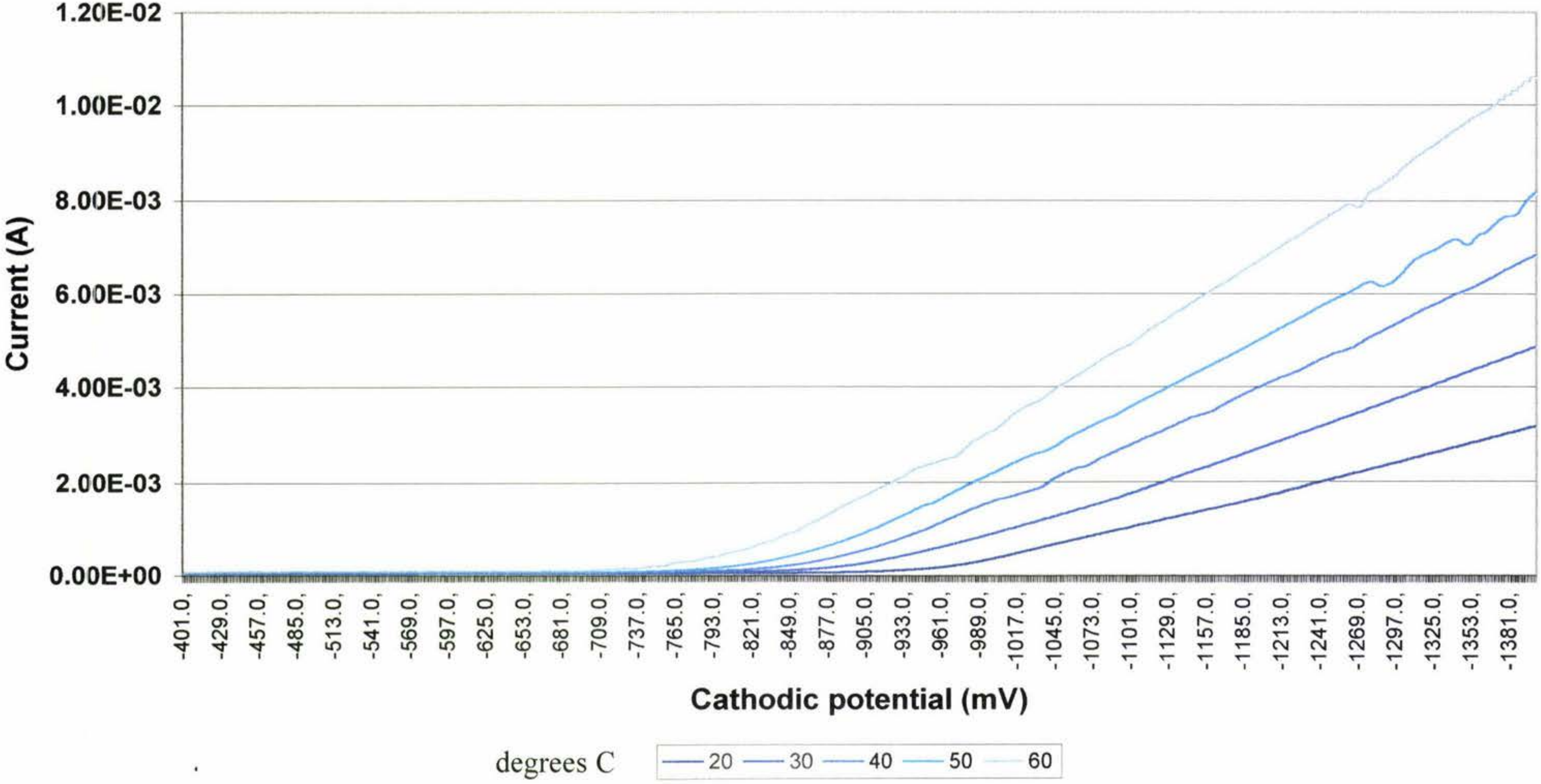


Fig. 4.5: Effect of Nickel Concentration on Current and Potential at 4000 rpm and 60 degrees C

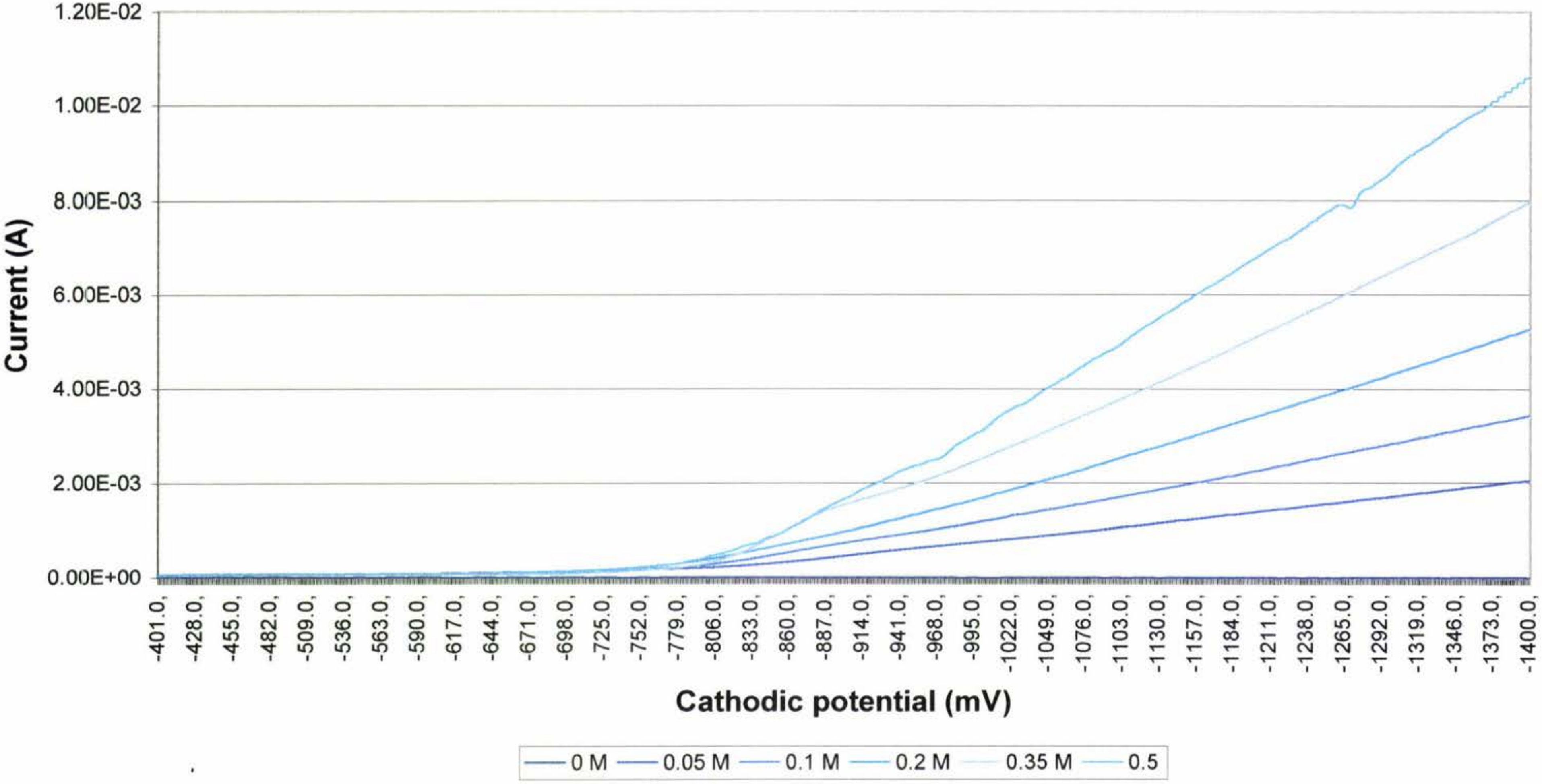


Fig. 4.6: Effect of Rotation Rates on Current and Potential for 0.50 M Ni at 60 degrees C

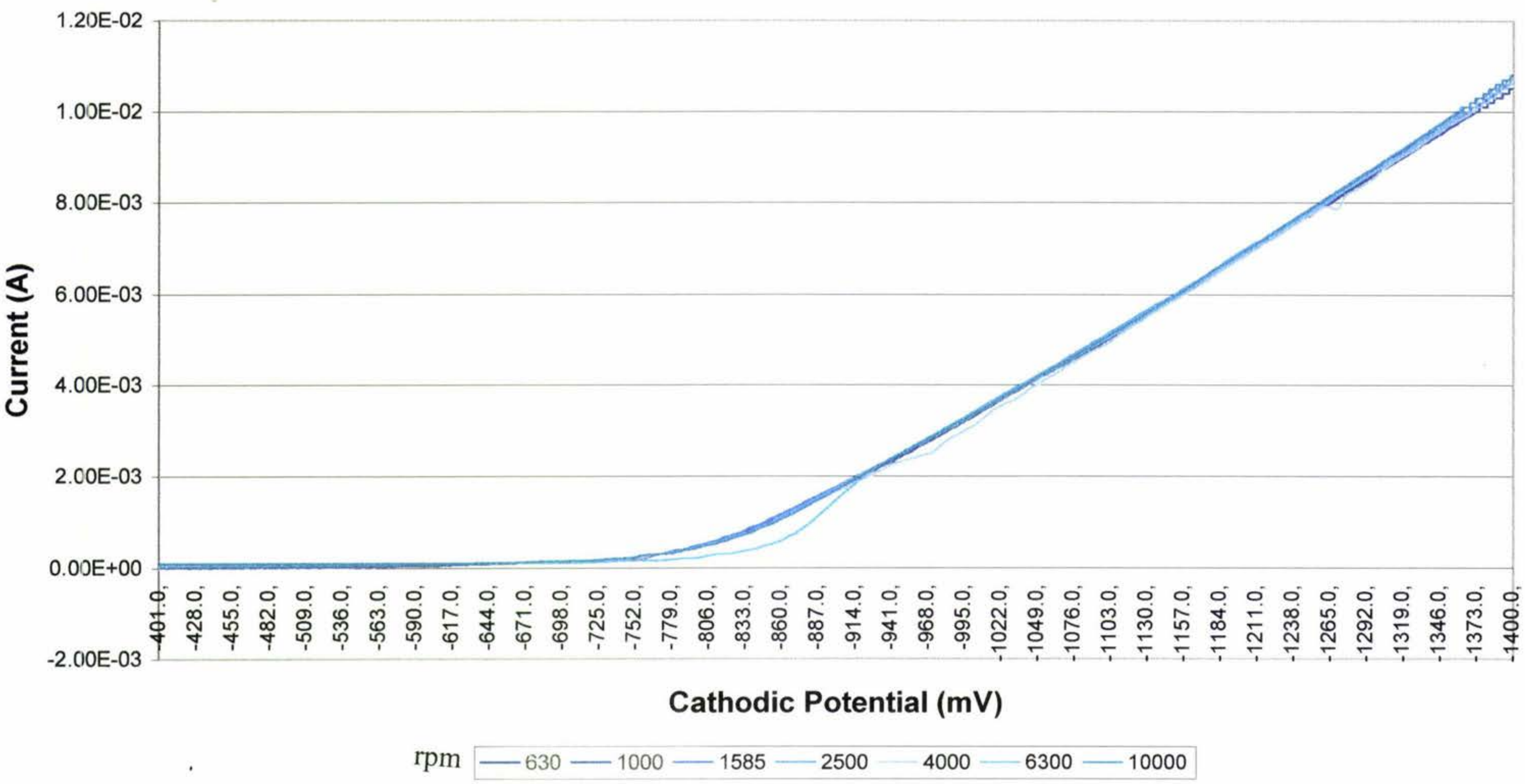


Fig. 4.7: Effect of Rotation Rates on Current and Potential for 0.05 M Ni at 60 degrees C

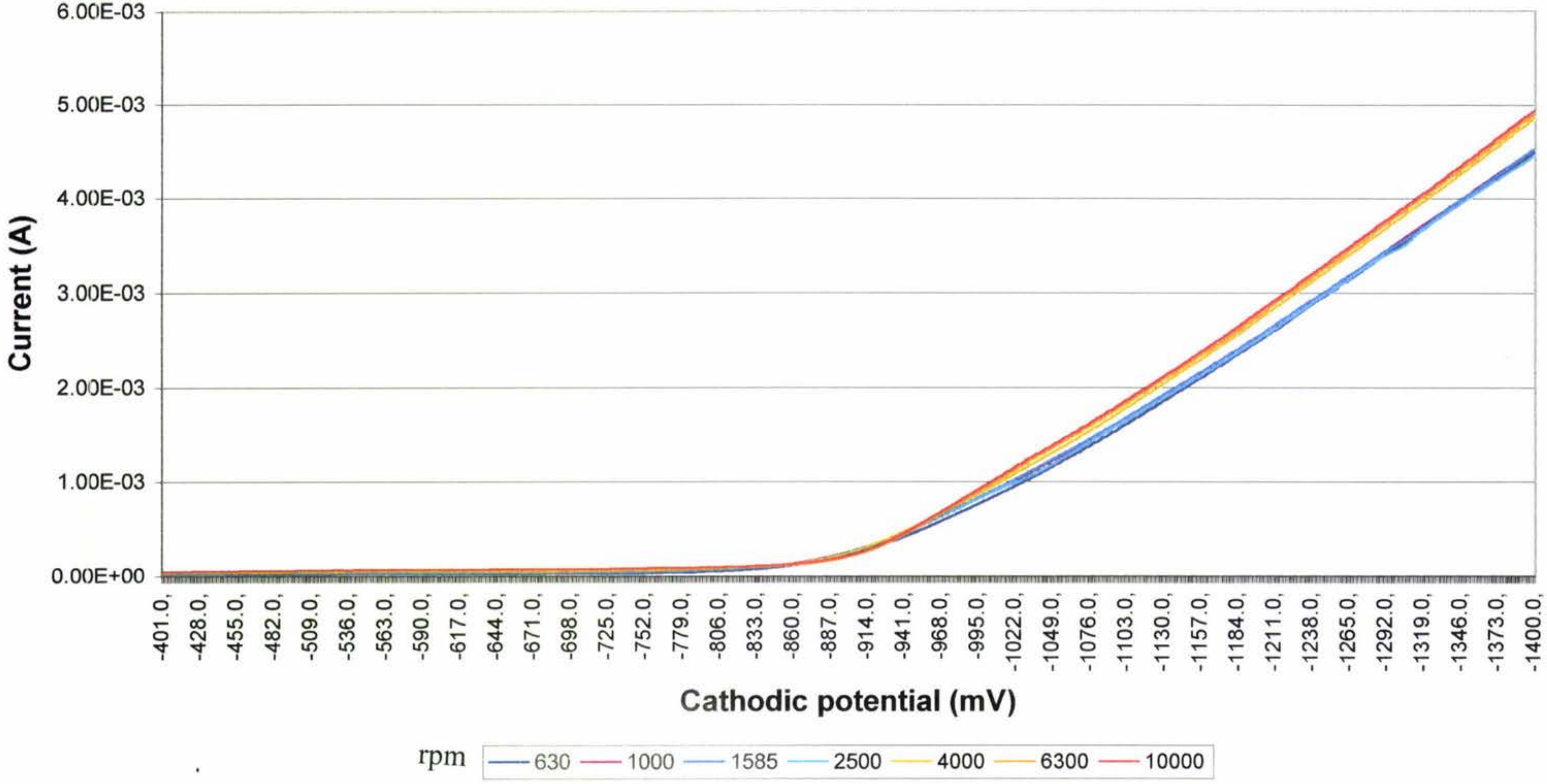


Fig. 4.8: Effect of Boric Acid Concentration on Current and Potential at 4000 rpm and 60 degrees C

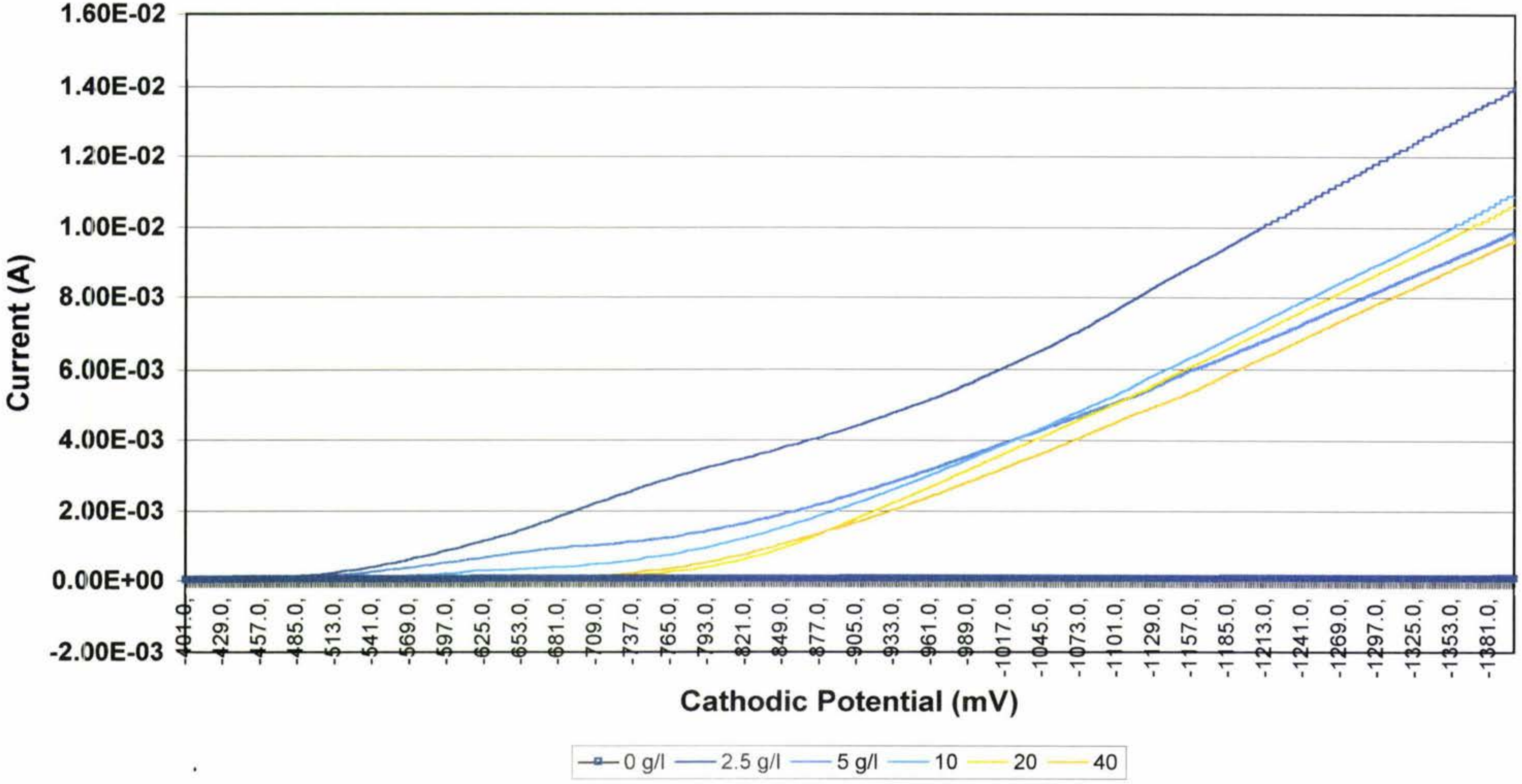


Fig. 4.9: Effect of Chloride Concentration on Current and Potential at 4000 rpm and 60 degrees C

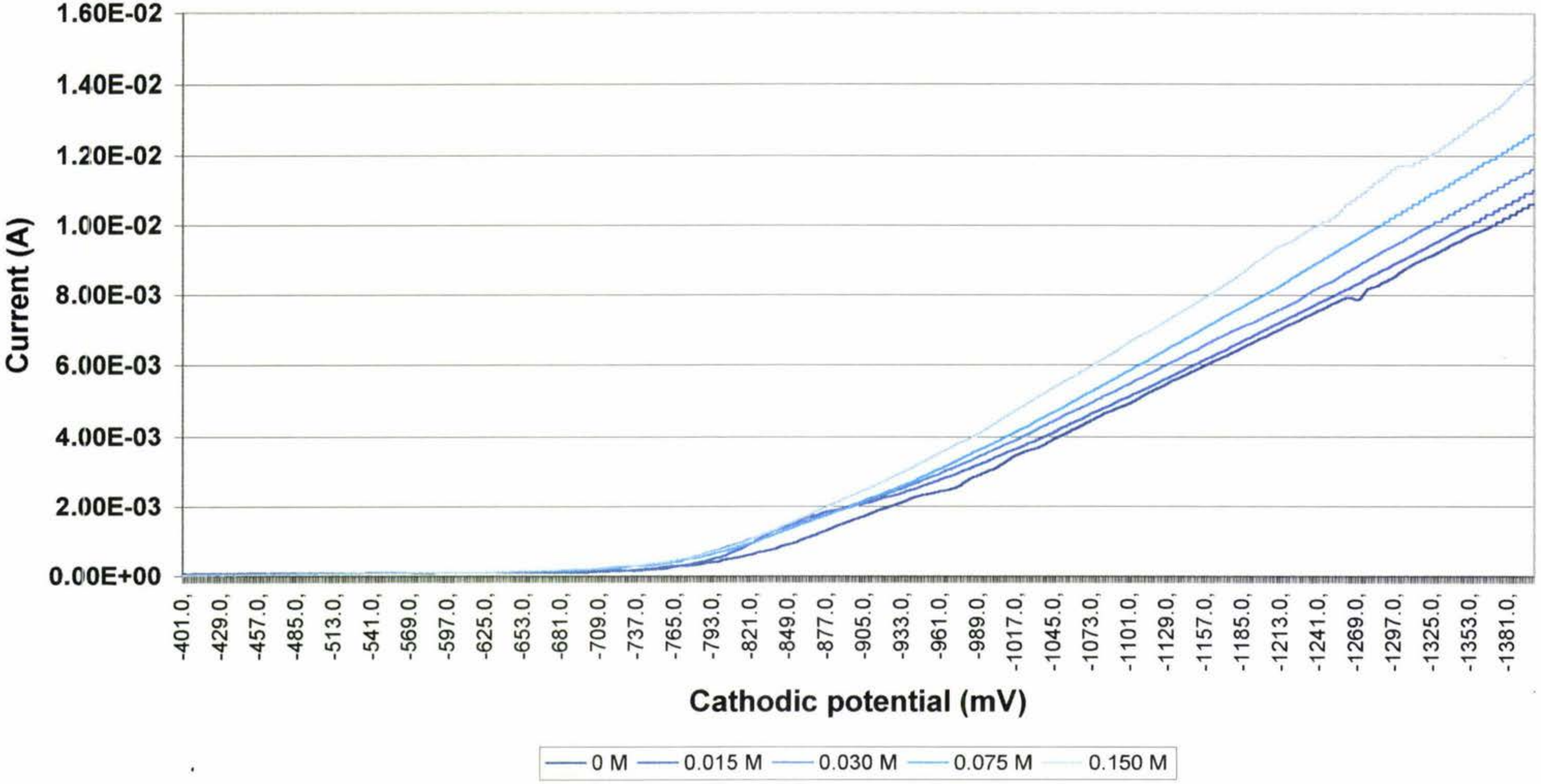
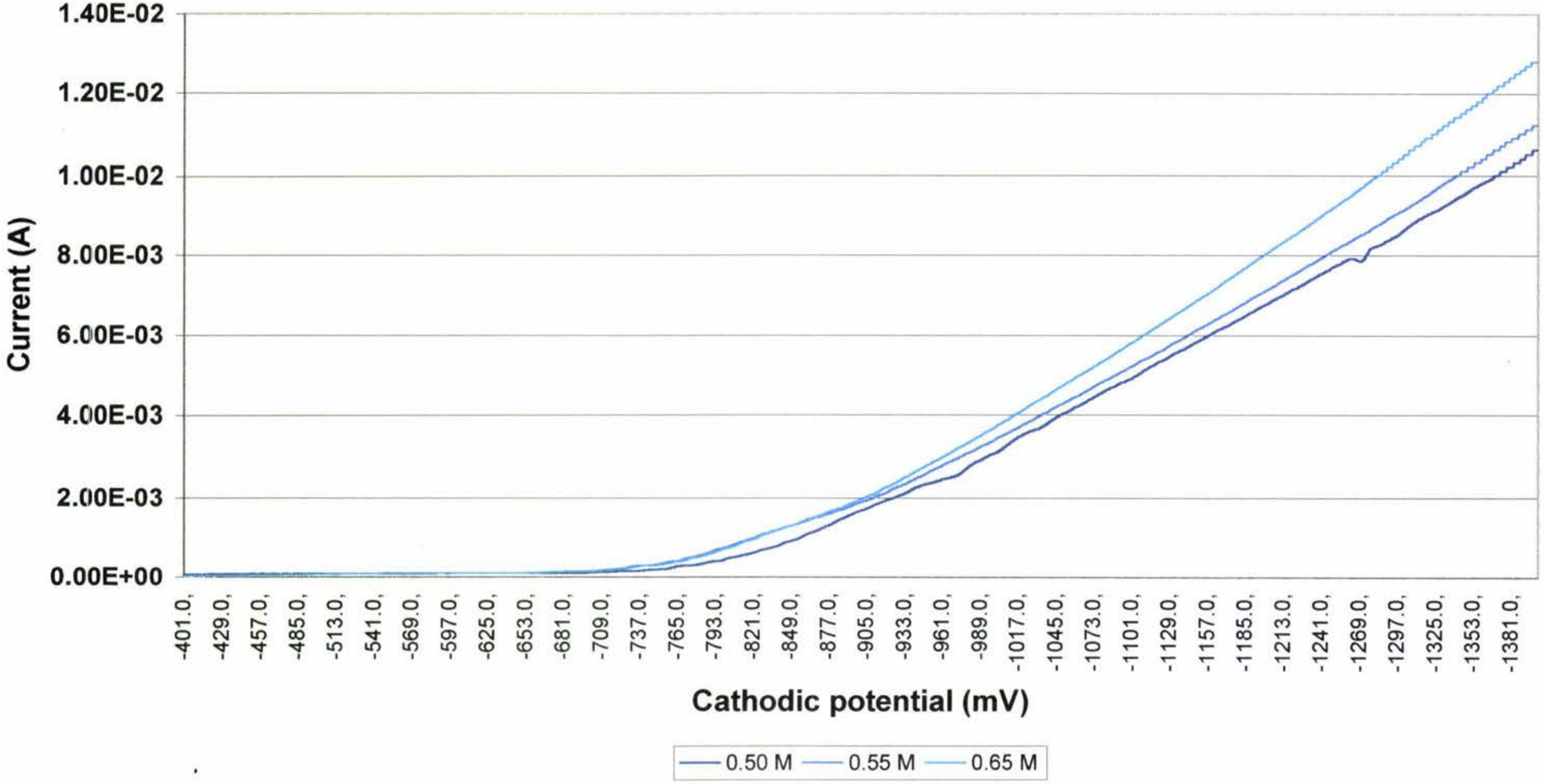


Fig. 4.10: Effect of Sulfate Concentration on Current and Potential at 4000 rpm and 60 degrees C



(C) Boric Acid Dependence

In a nickel solution where no H_3BO_3 is present, the reduction of Ni^{2+} does not occur in the potential range investigated (Figure 4.8), whereas it was found that the presence of as little as 2.5 g/l boric acid enabled the nickel reduction to occur (refer 4.1). As the H_3BO_3 concentration increased there was no major change in the slope of the graphs. However, it was observed that the potential at which nickel reduction initially occurred moved more cathodic, reducing the overall rate of the nickel reduction. Karwars et al. (1988) concluded that boric acid aided nickel deposition by adhering to the electrode and blocking surface sites for H^+ reduction, with a bridging effect occurring with nickel allowing Ni^{2+} reduction. Using such a model, it is apparent that by increasing the H_3BO_3 concentration more of the electrode surface is blocked. It is possible that with fewer sites for deposition the overall rate of Ni^{2+} reduction would be less.

(D) Chloride and (E) Sulfate Dependence

The rate of nickel reduction was found to increase as both the chloride and sulfate concentrations increased (Fig. 4.9 and 4.10). By raising the concentration of these supporting electrolytes, the solution conductivity can be increased, thus reducing the resistance of the solution.

In the plant extract solutions to be used in this electrowinning investigation, the concentration of sulfate is expected to be in excess of the nickel concentration, lending this resistance-reducing characteristic to the electrodeposition process.

4.3.2 Plant Extract Electrowinning

4.3.2.1 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

After periods of electrolysis of 25 min the acidity of the solution was found to have changed to pH 2.6-3.0 from the initial value of 4.5, the result of oxidation of H_2O at the counter electrode.

The deposit was not metallic nickel as expected. Instead, a green powdery deposit formed on the copper surface. This easily washed off leaving the copper surface beneath relatively unblemished. Analysis of this powdery material by flame AAS determined it to be 16.1% Ni, 0.8% Ca and 0.9% Zn.

XRPD analysis of the same material (Fig. 4.11) showed that it was predominantly amorphous, with only minor peaks evident. These small peaks corresponded to the nickel oxide hydroxide $4Ni(OH)_2$-NiOOH. However, it is thought that compounds of other elements present in solution may also be involved, such as KOH, $Mg(OH)_2$ and $CaSO_4$. Also, when Zn is present it is known to be included in the composition of the hydroxide films at cathode surfaces during nickel hydroxide formation (Ernst, 1969).

4.3.2.2 Effect of Calcium on Electrowinning Solution

To investigate the hypothesis that calcium may be having an inhibiting effect, electrowinning solutions were prepared containing calcium. Working electrodes after electrodeposition, all had good metallic-nickel deposits, and current efficiencies ranged 90-95% with no apparent inhibition of nickel deposition. These results disproved the above hypothesis. Ernst et al. (1969) reported that presence of the metals Cd, Cu, Fe, Mg and Sn as additives had no inhibiting effect on nickel deposition from a Watts solution, with Zn having only a weak inhibiting effect.

The presence of these elements, other than Ni, was evidently not responsible for the formation of the nickel hydroxide deposit.

4.3.2.3 Simulation of 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

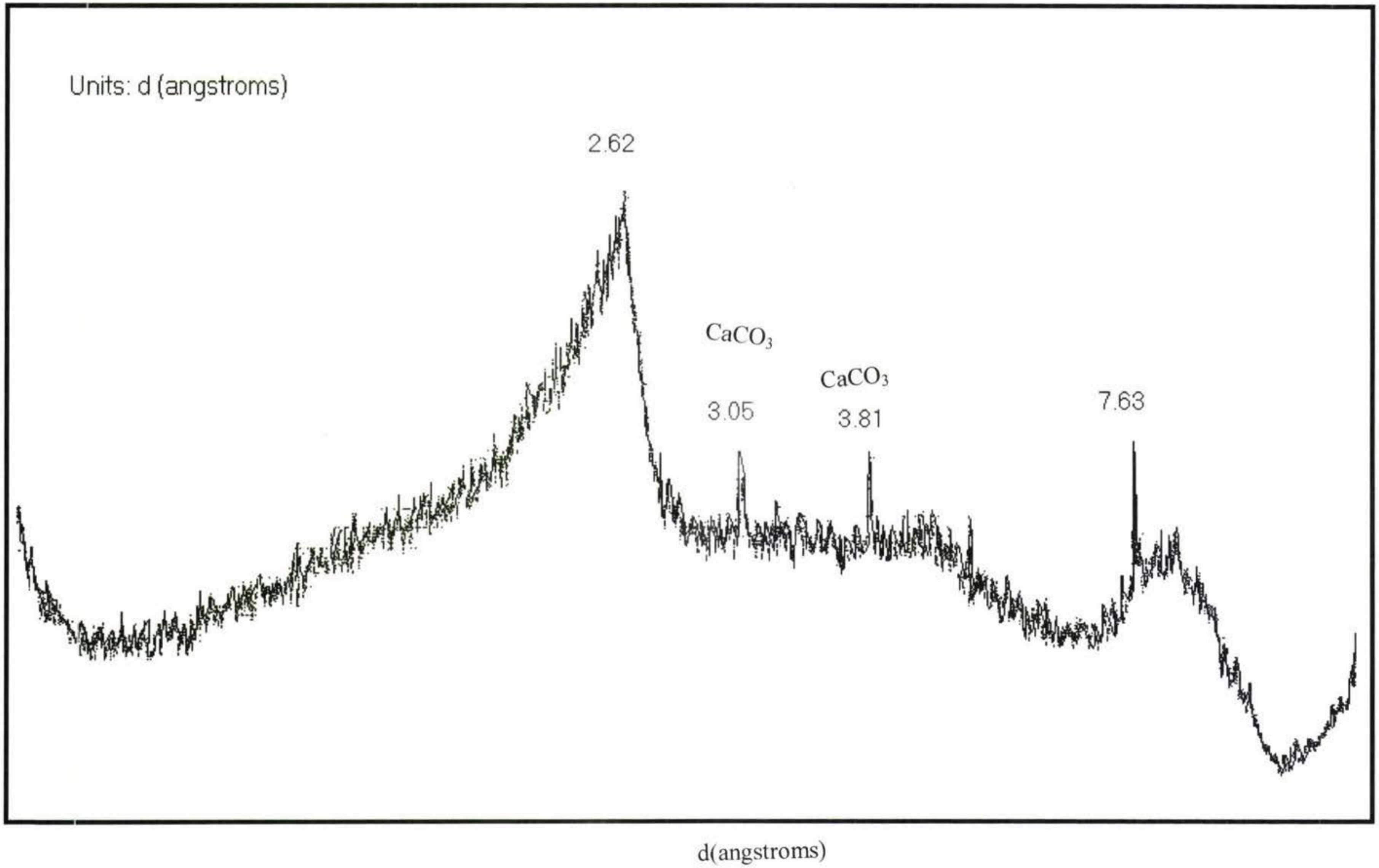
To investigate possible explanations for the poor electrodeposition and indeed if there was a means of correcting the problem, a solution was made to simulate the ash extract. The same amorphous powder was found to occur when electrowinning was attempted with this solution also. As elemental interference had already been ruled out as causing the green deposit, it could be only concluded that the sulfate and nitrate concentrations or some relationship of these concentrations played an important role.

Acidity or H^+ concentration of the solution also plays a major part in determining the nature of the deposit as confirmed when an increase in pH of the simulated solution resulted in a decrease in the quantity of the green deposit forming.

Most nickel electrolysis solutions use sulfate to act as Ni^{2+} counter ions. Because of the depletion of sulfate in the ash extract solutions during neutralisation with $CaCO_3$, it was hypothesised that the conductivity was reduced and diffusion of Ni^{2+} to the working electrode was being inhibited.

To counteract the low sulfate/high nitrate problem and to increase electrical conductivity, sulfate was introduced to the system as Na_2SO_4. This resulted in a good

Figure 4.11: X-ray spectra of amorphous electrowinning deposit. Small defined peaks correlating to a nickel hydroxide product.


Units: d (angstroms)
2.62
CaCO$_3$
CaCO$_3$
3.05
3.81
7.63
d(angstroms)

metallic nickel deposit, verifying the assumption that the sulfate concentration is of importance.

4.3.2.4 Addition of $NaSO_4$ to 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

The method for achieving a satisfactory nickel deposit by sulfate addition, as determined with the simulated ash extract solution, was tested on the ash extract. The addition of 1.0 mol/l Na_2SO_4 into the solution proved equally successful. A metallic nickel deposit formed on the working electrode, with no signs of burning or pitting. The current efficiency for this period of electrodeposition was determined to be 94%.

4.3.2.5 Simulated Sulfate Solution

Murthy (1996) reported that the presence of nitrates in a nickel plating solution leads to the deposition of nickel hydroxide, with this being the aim of some electrolysis processes. The nitrate concentration in the ash extracts is significant where the 9:1 2M H_2SO_4/8M HNO_3 mixture was used, and it was hypothesised that this was the most likely the cause of the observed green nickel hydroxide deposit.

This hypothesis was assessed by first investigating a sulfate only solution. The major elements were added to appropriate concentrations as their sulfate salts, giving a total SO_4^{2-} concentration of 0.80 mol/l. The visual characteristics of the deposit after electrodeposition for this initial solution and further solutions containing Na_2SO_4 and/or $NaNO_3$ are shown in Table 4.8.

Table 4.8: Total sulfate/ nitrate concentrations in simulated sulfate solution.

$[SO_4^{2-}]$ mol/l	$[NO_3^-]$ mol/l	Deposit Appearance
0.80	0	Burnt Metallic
1.00	0	Burnt Metallic
0.80	0.30	Green Powder
0.80	0.50	Green Powder
1.00	0.30	Shiny Metallic / Adherent Ni
1.34	0.50	Shiny Metallic / Adherent Ni

In a solution where only sulfate is present, the deposit is incomplete and burnt or blackened. Originally thought to be caused by insufficient sulfate concentration, when more was added the result was the same. This implies that there is another factor, other than having sufficient sulfate, to produce a good nickel deposit.

When nitrate was added to the original solution, the green powdery deposit was observed, further evidence that the presence of nitrate is responsible for the same type of deposit as in the 9:1 2M H_2SO_4/8M HNO_3 ash extract. However, when added in certain quantities to solutions where Na_2SO_4 had already been added (with a blackened deposit forming) it resulted in a good nickel deposit. From such unusual observations it can be suggested that a window between sulfate and nitrate concentrations exists, from which a good nickel deposit can form. On the high nitrate side, a green Ni hydroxide deposit forms, while on the high sulfate side, a blackened metallic deposit is seen. It is unclear from the results why this should occur, but it may be speculated, that in sulfate-only solutions, the conductivity is increased enough (resulting in a decrease in hydrogen overpotential) to allow H^+ reduction at the currents used. When nitrate is added, it in some way reduces this effect and if balanced against the sulfate concentration, may allow Ni^{2+} to be reduced. If the nitrate concentration is increased to the point where it is outside the nickel reduction window, then the hydroxide deposit is observed.

4.3.2.6 Electrowinning from the *A. corsicum* Extract

Using the findings from the previous experiments, the *A. corsicum* extract (pH = 4.5) was used with the electroplating cell. With the limited volume of extract (100 ml) and the need to cover the electrode surfaces as much as possible, the solution was placed in a 150 ml beaker. This smaller sized vessel limited solution mixing more than a 250 ml beaker would. The current was adjusted to take into account the smaller surface area of the electrodes immersed in the solution, thus the current density was maintained at that used in the other experiments, where the whole electrode was immersed. The results of this investigation, with varying quantities of Na_2SO_4 and $NaNO_3$ are shown in Table 4.9.

The initial electrodeposition period resulted in the green Ni hydroxide deposit, characteristic of excess nitrate, as found for the 9:1 2M H_2SO_4/8M HNO_3 extract which had also been neutralised with $CaCO_3$.

The addition of sulfate as Na_2SO_4 proved to arrest the formation of the green hydroxide, but when added in apparent excess, resulted in the characteristic burnt or blackened deposit.

Table 4.9: Electrowinning from A. corsicum extract.

$[Na_2SO_4]$ mol/l	$[NaNO_3]$ mol/l	pH	Deposit Appearance
0	0	4.5	Green Powder
0.35	0	4.5	Some Green Powder
0.70	0	**3.5**	Dull Ni (burning and pitting)
0.70	0	**4.5**	Burnt Ni
0.70	0	**5.5**	Black Metallic
1.00	0	4.5	Dull Ni (burnt)
1.00	0.10	4.5	Dull Ni (some burning)
1.00	0.20	4.5	Ni Deposit (small portion burnt)
1.00	0.25	4.5	Shiny Metallic / Adherent Ni
1.00	0.30	4.5	Shiny Metallic / Adherent Ni

Of importance was the observed differences in deposit when acidity was varied. It is known that an increase in the H^+ concentration inhibits the production of a metallic nickel deposit, but in this case, where there is an apparent excess of sulfate, a drop in pH actually aided in producing a better deposit. It should be noted that the reverse was true for the simulated extract solution, where a decrease in the observed effects of excess nitrate were found as the pH was increased.

Following the hypothesis established from the sulfate-only solution, $NaNO_3$ was added to balance the sulfate/nitrate concentrations and establish the window for good Ni deposition. This proved successful, with an excellent nickel deposit, of hyperaccumulator plant origin, forming. The current efficiency for this final period of deposition was determined to be 95%.

4.4 CONCLUSION

The electrodeposition of nickel is considered by many as being as much art as science. This investigation of using electrowinning to recover nickel from hyperaccumulator extract solutions was meant to determine its feasibility and identify conditions under which nickel electrodeposition may be best conducted, and did not include the determination of specific electrochemical processes and reactions. The investigation was successful in this respect, with current efficiencies of greater than 90% being obtained for electrowinning of plant-derived nickel. While the purity of the deposit was not ascertained, the visually unblemished nature of the deposit (combined with the high current efficiency) implies the product may be relatively pure.

The electrodeposition of nickel is controlled by a number of physical and chemical parameters, with most affecting the delivery of Ni^{2+} ions to the working electrode surface and reaction activation energies. Where temperature and solution mixing are low, the mobility of the nickel ions is reduced, limiting transport to the electrode. Decline of the nickel concentration has the same effect, increasing the nickel overpotential, reducing the rate of nickel deposition and hence the maximum workable current (for a greater than 90% current efficiency).

Boric acid aids in the electrodeposition of Ni^{2+}, with its absence from the electrowinning solution resulting in no nickel deposition occurring. The manner in which it does this is still unclear.

The pH is another controlling factor; where this is too low, hydrogen evolution becomes more favourable than nickel deposition, reducing the current efficiency. Where it is too high, metal hydroxides are likely to precipitate out of solution. Of special note, with respect to solution pH, are the apparent localised changes at the electrode surfaces. When hydrogen evolution occurs at the working electrode, the removal of H^+ ions from the solution-electrode interface layer, results in a localised increase in the pH. This then causes black nickel hydroxide to be deposited during nickel electrodeposition, otherwise known as burning. This is an unusual situation, with the black hydroxide forming on the electrode when the acidity of the bulk solution is high. This is important as the electrochemical processes at the counter electrode produce H^+.

The elementally refined nature of the as extract solution proved favourable for such electrochemical processing, with nickel apparently being deposited preferentially over the other extract constituents. While low concentrations of zinc were present in the hyperaccumulator solution, this caused no obvious deleterious effects. The major concern was originally that the high potassium and magnesium concentrations would in some way hinder the electrochemical reduction of nickel, although this was not observed. Indeed it was found by Liu et al. (1989), that the presence of potassium sulfate actually aided in nickel electrodeposition.

The largest inhibition of the electrowinning process came not from the hyperaccumulator plants, but instead the acids used in leaching the ash, and to some extent the reagents used for extract neutralisation (refer chapter two **Ashing and**

Extraction). Sulfuric acid was rightly chosen, owing to the electrochemically inert nature of the sulfate, although, an excess of sulfate resulted in burnt deposits, implying it was in fact not inert. However, it is suggested that the increase in conductivity caused by high sulfate concentrations results in a decrease in the overpotential for both hydrogen and nickel reduction, to the point where H_2 evolution is possible at the currents used for electrowinning, thus burnt deposits are observed. When nitrates are present in excess, the result was considerably worse, with no metallic-nickel deposition and instead the formation of a green nickel hydroxide powder on the working electrode. The study of how these two species affect nickel electrodeposition is beyond the scope of this investigation, with no relevant literature found that might suggest a reason for the result. Given that hydroxides form as the result of an excess of nitrate, it may be hypothesised that this species actively promotes H^+ reduction. Alternatively, it may interact with the boric acid in solution, limiting the controlling effect the buffer has on H^+ reduction.

It was found that good nickel deposits were obtainable if the sulfate and nitrate concentrations were within a certain range, with the proportion of sulfate to nitrate necessary apparently changing with varying concentrations of the species. This unusual balance of the two species creates a window where nickel deposition can occur successfully, and implies the two species interact to promote H^+ reduction (or H_3BO_3 inhibition).

The difference in products observed when either sulfate or nitrate was in excess, being burnt deposits and green hydroxide formation respectively, allowed for easy qualitative determination of solution conditions, and determined whether further sulfate or nitrate addition was necessary. For a typical hyperaccumulator ash, such as that of the *A. corsicum* material, leached with 9:1 2M H_2SO_4/8M HNO_3 and neutralised to pH 4.5 with $CaCO_3$, there is a need to increase the sulfate concentration. Using the synthetic ash, the addition of 1 mol/l Na_2SO_4 proved adequate; however less was required for the hyperaccumulator extract before the sulfate was in excess, necessitating $NaNO_3$ addition.

The required amount of sulfate would be lower in the case where $CaCO_3$ was not employed as a neutralising reagent, as $CaSO_4$ precipitation (responsible for removing 0.75 mol/l SO_4^{2-}) would not occur. Indeed, given the findings of this investigation it may be that the proportion of sulfate to nitrate in a 9:1 2M H_2SO_4/8M HNO_3 hyperaccumulator extract, neutralised with NaOH, is ideal for nickel electrowinning.

Alternatively, using a H_2SO_4 extraction, the excess sulfate (and resulting decrease in hydrogen overpotential) might be controlled by the addition of further H_3BO_3.

While the recovery of plant-derived nickel was encouraging, the simple nature of the cell design, small scale and lack of electrochemical process knowledge make it difficult to conclude whether electrowinning on an industrial scale is feasible, although it is certainly possible. Much work is required, primarily into the electrochemical effects of sulfate and nitrate, before such a conclusion can be made. Cell design should also be reviewed on a larger scale to maximise mass transport and include an electrode-separating diaphragm, to control acidity and allow for the acid generated at the counter electrode to be reused in the ash leaching process.

Chapter Five

Crystallisation and Precipitation

5.1 INTRODUCTION

5.1.1 Overview

A number of techniques used in the nickel refining industry utilise chemical treatment of a nickel solution to produce a medium or compound of higher purity than the starting material.

The problem of nickel separation from solutions of plant origin is primarily the same as for other multimetal media i.e. the exclusion of other metals during the recovery of a nickel compound. Chemically this can be approached by utilising the differing solubility properties of the various metals when forming certain compounds. A common example is the removal of iron from solutions by aeration to produce insoluble iron oxides. When applied to nickel phytoextraction the problem of metal separation is simplified, because the plant has already excluded heavy metals other than nickel. However, high concentrations of both Mg and K are typical owing to the hyperaccumulator origin of the medium, with the similarities in atomic radii of Mg and Ni causing particular problems.

Many multi-step processes have been suggested for the removal of nickel from various systems. The majority of these use either sulfate crystallisation, hydroxide, carbonate, sulfide or oxalate precipitation.

5.1.2 Nickel Sulfate

In many waste solutions metals are solubilised in an acid medium, commonly H_2SO_4. From these it is possible to recover the nickel as nickel sulfate, a water-soluble nickel salt. As the concentration of H_2SO_4 increases, the nickel sulfate becomes less soluble. The recovery is based on this principle, with treatment consisting of evaporating a large portion of the water from solution, resulting in an increase in sulfuric acid concentration. This forces the $NiSO_4$ to crystallise out. Although the process can be taken to the point where all Ni is removed, it is not commonly done in this way. This is because the process is energy-intensive and slower settling rates are observed with increasing densities of the solution (Rajcevic, 1990).

5.1.3 Nickel Hydroxide

Precipitation of nickel as an insoluble hydroxide has long been used as a means of decontaminating solutions, particularly where complex chemical compounds are not involved and economic recovery is not a consideration (Dean et al., 1972). Typical treatment involves the use of lime or sodium hydroxide to produce an alkaline pH, from which the nickel hydroxide is precipitated, settled then filtered. Optimum pH for nickel removal is approximately 10.5, with concentrations reported as low as 0.3 mg Ni/l after treatment. The use of lime to perform this extraction was reported to produce removal efficiencies as high as 90.5% (Robinson, 1980). Precipitating metals as hydroxides has the advantage of selectively removing metals depending on the pH, with metals precipitating in the following order with increasing pH: Fe^{3+}, Al^{3+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} (Dean et al., 1972). Nickel hydroxide is appreciably more soluble than those of Cd, Co and Zn (approximately 0.13 g/l at room temperature). The review of metal separation techniques by Brooks (1991) challenged this specificity, saying that owing to the potential for coprecipitation and the ion-exchange characteristics of colloidal hydroxide precipitates, even distinct differences in pH are no guarantee of avoiding mixed precipitates when metal mixtures are in solution. The filtration of nickel hydroxide is a major problem owing to its gelatinous nature and large volumes.

Nickel hydroxides are used primarily in the manufacture of nickel – cadmium batteries (Antonsen, 1992), although they may be decomposed at 230°C to yield water and nickel oxide.

5.1.4 Nickel Carbonate

Nickel carbonate can be precipitated by the addition of sodium carbonate to a nickel-bearing solution, forming a dense sludge, which can be separated by filtration. This occurs at a lower pH than that required with hydroxide formation, but the technique is often used in conjunction with hydroxide precipitation, to extract a greater portion of nickel from waste solutions. The addition of sodium carbonate to a nickel-bearing solution, is the most common means of initiating precipitation of a basic nickel carbonate, $2NiCO_3.3Ni(OH)_2.4H_2O$. This compound is used in preparing catalysts, in the preparation of coloured glass and as a neutralising agent in nickel electroplating solutions (Antonsen, 1992).

5.1.5 Nickel Sulfide

Most metal sulfides are very insoluble and the precipitating of nickel sulfide is probably the most frequently used hydrometallurgical extraction approach for economic nickel recovery. Primarily employed in the nickel refining industry, NiS can be precipitated by the addition of sulfides to nickel-containing solutions. Such sulfide may be added in many forms, the most common of which are as solid sodium sulfide or gaseous hydrogen sulfide. McAnally et al. (1984) reported that this technique has numerous advantages over other precipitation/crystallisation processes including:

(1) Excellent removal efficiency due to low solubility of nickel sulfides.
(2) Sulfide addition can precipitate nickel complexed with most complexing agents.
(3) Sulfide precipitates exhibit less of an amphoteric nature than hydroxide precipitates and have less tendency to resolubilise.
(4) Lower precipitate volumes than that found with hydroxide precipitation.

As with most industrial processes there are problems associated with sulfide treatment of solutions. Most of these relate to the toxicity of excessive sulfide concentrations in solution and the formation of H_2S gas. Problems of this nature are easily controlled in an industrial environment through pH and sulfide concentration control. The optimum sulfide : nickel mole ratio was estimated by Robinson (1980) to be 1.0-2.5, with such an addition resulting in residual nickel concentrations of 4 mg/l at pH 8.5, corresponding to an approximate 99% nickel removal.

Nickel sulfide is used as a feedstock in smelting, or in the case of high purity precipitates, can be directly cast into electrodes for nickel electrowinning. As the nickel industry is already geared to process sulfide ores and sulfide products, there is a large existing market for such a precipitate.

5.1.6 Nickel Oxalate

The addition of oxalic acid to waste nickel solutions, such as electroplating baths, has proven to be an efficient means of recovering nickel in the form of an insoluble Ni oxalate (Brooks, 1989). Nickel extractions as high as 99.9% have been reported with this method being employed as both a means of recovering nickel for resale and decontamination of the waste solution (Brooks, 1987).

This extraction occurs best at slightly acidic to neutral pH values, with an excess of oxalic acid required to the theoretical stoichiometric requirement (Brooks, 1989). The precipitate separates and settles easily from the solution making filtration a relatively simple process compared to most other nickel precipitates already suggested.

The limitations of this process are determined by the nature of the solution, with treatment of solutions containing organic compounds such as citric acid and EDTA, frequently employed in electroplating to enhance deposit formation, being inefficient. These soluble compounds can sequester the Ni^{2+} ions away from the oxalate group, hindering their extraction. For this reason they need to be destroyed before an oxalic acid treatment can be effective. Techniques such as aeration and addition of an oxidant such as H_2O_2 are commonly used to break down these organic complexing agents (Brooks, 1989).

The metals Zn, Co and Cu are also amenable to this type of oxalate extraction, owing to the insoluble nature of their oxalates. In a process where the goal is simply heavy metal extraction for the decontamination of wastewater, metal coprecipitation is advantageous, but such is not the case for economic nickel recovery. The presence of these metals would result in an impure product, limiting saleability.

Nickel oxalate is used as a catalyst, with highly purified compounds costing approximately $A 250 per 50 g. While this may not be a large market, there are alternatives for its use. A purified product could be heated to decompose the organic oxalate group leaving a pure NiO product. This may be subsequently sold or refined to produce high purity nickel metal. It is unclear however, whether such refining of the nickel oxalate could be considered as an economical option.

5.1.7 Nickel Recovery from Hyperaccumulator Plant Solutions

The key to choosing an acceptable Ni precipitation/crystallisation method for a phytoextraction operation, is in producing a product that maximises cost recovery.

Even with an excellent extraction of nickel from solution, the technique can only be considered if the resulting product has a monetary value sufficient to make the operation economical.

Although there are numerous techniques offering greater than 90% nickel extraction, there is little point in any process requiring further refining if the product is to be used in a smelting operation. If such were the case, it would be preferable to use the ash or bio-ore directly for smelting. Indeed, it would be advantageous for the product to be directly marketable with no additional processing.

Nickel sulfide, hydroxide and carbonate are all relatively low-cost products, with the requirement of further processing to produce a satisfactory product. For this reason the present investigation concentrated on sulfate crystallisation and oxalate precipitation.

When potassium is present in solution, as is the case with a solution of plant origin, it is found that the nickel potassium sulfate double salt is crystallised preferentially over nickel sulfate. This is due to the much lower solubility of the double salt, which has a solubility of only 7 g/l at 0°C. The relative ease with which it crystallised out of solution (section 5.2.1) suggested that a relatively easy and inexpensive method for nickel extraction could be determined. Such a process could take advantage of high potassium concentrations, a fundamental hyperaccumulator extract property and due to the refinements carried out by previous processes, produce a relatively pure product.

The application of the nickel oxalate recovery technique with respect to hyperaccumulator plants, is a simpler process than when utilised in nickel waste treatment, although the principles are the same. The hyperaccumulator extracts lack heavy metals other than nickel, the result of selectivity by the hyperaccumulation, acid extraction and neutralisation processes (where applied). This allows a nickel oxalate precipitate relatively free of Zn, Co and Cu to be produced.

The plant extract solution does not require any pre-treatment for organic complexing agents before oxalic acid addition. The ashing of plant material has ensured that any such interfering compounds have been destroyed and no addition has occurred afterwards. The culmination of these two major advantages, with respect to oxalic addition to hyperaccumulator extracts, reduces extraction costs while increasing potential yields and monetary returns.

5.2 MATERIALS AND METHODS

5.2.1 Nickel Potassium Double Salt Investigation

5.2.1.1 (A) Investigation of Ni-rich Crystals from *A. corsicum* Extract.

Green/blue cubic crystals (1-3 mm) were observed to be forming in the refrigerated *A. corsicum* extract. A number of crystals were extracted from the solution and washed with 95% ethanol before being dried in a vacuum desiccator, leaving a white powdery material on the surface of the blue/green crystals. A sample crystal weighing 0.0871 g was dissolved in 100 ml double deionised water. This sample solution was diluted to make a second solution, with both being analysed by ICP-AES.

A representative crystal was chosen for X-ray powder diffraction analysis to determine its crystalline structure.

(B) Pure $K_2Ni(SO_4)_2.6H_2O$ Production for XRPD Comparison

Pure $K_2Ni(SO_4)_2.6H_2O$ was crystallised from 200 ml solution containing 0.5 mol/l $NiSO_4$ and K_2SO_4. The solution was heated first, to dissolve the single salts, then refrigerated for 24 hours to aid in crystallising the nickel potassium double salt. The blue/green crystals were separated using vacuum filtration, dried, then analysed by X-ray powder diffraction. This gave a comparison for the XRPD analysis of the crystals separated from the *A. corsicum* extract (A).

(C) Crystals from Simulated Hyperaccumulator Extract.

A 200 ml solution, containing Ni, Mg, K, Ca and Zn at concentrations present in the *A. corsicum* extract (pH 4.75),was made using their sulfate salts to simulate a H_2SO_4 extract.

The solution was heated to 70°C to dissolve all the components, then refrigerated for 48 hours to encourage crystal growth. The crystals were collected by vacuum filtration and dried in a desiccator. These crystals were compared to those from both (A) and pure $K_2Ni(SO_4)_2.6H_2O$ crystals (B), using XRPD.

5.2.1.2 Determination of Magnesium in White Powder Material

Crystals weighing 0.0838 g, with little white powdery material were chosen from the (B) crystals. These were dissolved in 100 ml of double deionised water for determination of Mg concentrations by flame AAS. A second sample of crystals weighing 0.0818 g, with greater proportions of the white powder, was taken and analysed in the same manner. This was to qualitatively determine whether the Mg is contained predominantly in the white outer material as opposed to within the Ni crystal lattice.

5.2.1.3 Addition of K_2SO_4 to Simulated Hyperaccumulator Solution

A 200 ml solution, with Ni, Mg and K concentrations similar to those of the *A. corsicum* extract (pH 4.75) was created using the sulfate salts of each element: 0.250 M Ni^{2+}(introduced as $NiSO_4.6H_2O$), 0.368 M Mg^{2+} and 0.440 M K^+ (introduced as anhydrous sulfates).

The solution was refrigerated for 2 days to encourage crystallisation of the nickel potassium double salt. After crystallisation a 0.5 ml sample was taken, diluted to 100 ml with double deionised water and analysed for Ni using flame AAS.

Additional K_2SO_4 in 0.05 mol/l portions was added to the solution without removal of the crystals, heated to 70°C and stirred to ensure that the added material and existing crystals were dissolved. The solution was refrigerated for 2 days, with crystallisation of $K_2Ni(SO_4)_2.6H_2O$ again evident. Each time, a 0.5 ml sample was taken and made up to 100 ml for flame AAS analysis of Ni. Additions of K_2SO_4 were conducted to give total added concentrations of 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50 mol/l K_2SO_4. All materials including $K_2Ni(SO_4)_2.6H_2O$ crystals were re-dissolved by heating and stirring with each successive K_2SO_4 addition. Refrigeration and sampling was conducted in the above manner.

5.2.1.4 Nickel Salt Crystallisation from 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

The solution from the 9:1 2M H_2SO_4/8M HNO_3 extraction of synthetic nickel-rich ash was made up to 200 ml in a measuring flask, because of loss of volume from electrowinning experiments. A 0.5 ml sample was taken and diluted for AAS Ni analysis. The pH of the bulk solution was measured at pH 4.5.

The solution was heated to 70°C before the addition of 20 g (corresponding to 0.573 mol/l) K_2SO_4. A small quantity of insoluble material was filtered off using filter paper and the remaining 195 ml of ash extract solution was refrigerated for 24 hours, after which time a 0.5 ml sample was taken and made up to 100 ml. From this, 5 ml was taken and diluted to 25 ml for flame AAS Ni analysis.

The solution was returned to the refrigerator for a further 24 hours. A sample of 0.5 ml was taken and made to 250 ml for Ni analysis before the remaining solution was again returned to the refrigerator for 24 hours. At a total of 72 hours, a similar sample was taken.

The solution was filtered using vacuum filtration and filter paper to collect the insoluble crystals. This material was subsequently dried and weighed.

The filtrate was collected, now with a volume of 160 ml, heated, and another 0.2 mol/l K_2SO_4 added. The solution was seeded with a 1 mm $K_2Ni(SO_4)_2.6H_2O$ crystal and returned to the refrigerator for another 72 hours. A sample of 0.5 ml was taken after this time and diluted to 250 ml with deionised water for Ni analysis using AAS.

5.2.1.5 Sulfate Concentration Increase by H_2SO_4 Addition

A simulated hyperaccumulator extract was made to a volume of 200 ml in a 400 ml beaker, containing the three major inorganic elements Ni, Mg and K as their sulfate salts (refer 5.2.3). In an attempt to increase the sulfate concentration, H_2SO_4 was added to the solution, giving SO_4^{2-} concentrations of 1, 2, 4 and 8 mol/l (assuming complete dissociation of the acid). The volume maintained at 200 ml by evaporation. The solution was heated and stirred to dissolve any crystals, followed by refrigeration for 48 hours. After each successive H_2SO_4 addition and refrigeration, a 0.5 ml sample was taken and diluted to 50 ml. The analysis of these samples proved to be unnecessary as no solid crystallised in this experiment.

5.2.1.6 Treatment of Hyperaccumulator Composite Extract

Refrigeration of the 33 ml, strongly acidic plant composite extract for 24 hours resulted in the crystallisation of a small number of $K_2Ni(SO_4)_2.6H_2O$ crystals. To encourage removal of greater than 90% of the Ni by double salt crystallisation, 2.87 g K_2SO_4 was added, giving 0.5 mol/l. This was done to the solution without prior neutralisation. The solution was heated and stirred to dissolve all material, then returned to the refrigerator for 48 hours. A sample of 0.5 ml was taken and diluted to 250 ml for ICP elemental analysis.

Potassium was added to the 31 ml solution in the form of 4.00 g KOH, corresponding to the theoretical requirement to neutralise the solution to approximately pH 5 (2.23 mol/l). The solution was heated and the pellets stirred in to completely dissolve them, leaving no residue, then refrigerated for 2 days. A sample of 0.5 ml was taken after this period (and subsequent crystallisation) then diluted to 50 ml for ICP elemental analysis and pH determination. All crystallised material was filtered in a Buchner funnel, collected, dried and weighed.

A sample $K_2Ni(SO_4)_2.6H_2O$ crystal of 0.0820 g was taken from the recovered material and dissolved in 50 ml 2M HCl for ICP elemental analysis.

5.2.2 Nickel Oxalate Investigation

5.2.2.1 Initial Oxalic Acid Study

A simulated hyperaccumulator solution with Ni, Mg and K (as sulfate salts) at concentrations of 0.250, 0.368 and 0.440 mol/l respectively (refer 5.2.3), was made to a volume of 200 ml. To this room temperature solution, solid oxalic acid was added to 0.625 mol/l, corresponding to an oxalic acid : nickel mol ratio of 2.5. The mixture was stirred continuously until all the acid was dissolved, then left to stand. A fine light blue precipitate formed almost immediately, decolourising the solution. The beaker was left covered overnight and a 1 ml sample taken the next day and diluted to 100 ml for Ni analysis by AAS. To recover the insoluble material the solution was filtered, with the precipitate being dried in a vacuum desiccator and weighed using a four-figure balance. The remaining solution was placed in the refrigerator and left for 5 days, by which time a further small quantity of precipitate had formed. A second 1 ml sample was taken and diluted for nickel analysis. The solution was returned to the refrigerator for another 24 hours, then a third 1 ml sample taken, diluted and analysed. A sample of 0.1012 g was removed from the dried precipitate and dissolved in 100 ml 2M HCl, then diluted 1 ml to 50 ml for analysis of Ni, Mg and K by flame AAS. A portion of the remaining precipitate weighing 3.0012 g was washed with 3 aliquots of 50 ml double deionised water in a Buchner funnel using vacuum filtration. Once dry this was removed and weighed. A 0.1353 g sample was taken and dissolved in 100 ml 2M HCl, then diluted for AAS analysis of Ni, Mg and K.

5.2.2.2 Addition of Oxalic Acid to Simulated Hyperaccumulator Extract

A simulated hyperaccumulator solution of 200 ml was made with Ni, Mg, K as in section 5.2.3, and a Ca concentration of 0.020 mol/l, introduced as $CaCl_2$. This mixture was stirred and heated to 70°C to dissolve all components, then allowed to cool to room temperature. Oxalic acid was added in quantities corresponding to an oxalic acid : nickel mol ratio of 1.0. This was stirred to dissolve all acid crystals then left to stand for 2 days, with the solution covered to protect against evaporation. A 0.5 ml sample was taken from the settled solution and diluted to 100 ml for AAS analysis of Ni and Mg. Oxalic acid was added in additional 0.1 oxalic acid : nickel mol ratio quantities to give a range of ratios from 1.0 to 1.9. With each addition the solution was stirred vigorously to dissolve the oxalic acid then left to stand and sampled in the same manner as stated previously.

Acidity of the solution was maintained before oxalic addition at pH 5 with the use of 2M H_2SO_4 and 2M KOH.

5.2.2.3 $K_2Ni(SO_4)_2.6H_2O$ Crystallisation and Secondary Nickel Oxalate Recovery.

After establishing that the nickel concentration could be reduced to 1.5 g/l through the crystallisation of $K_2Ni(SO_4)_2.6H_2O$, an investigation was carried out to use nickel oxalate precipitation to remove the remaining portion of nickel present. This was undertaken using a simulated hyperaccumulator solution with the Ni, Mg and K present as their sulfate salts in concentrations 0.25, 0.368 and 0.440 mol/l respectively, made up to 200 ml in a beaker. Two steps were used in extracting the nickel by crystallisation/precipitation:

Step one - Addition of K_2SO_4 to concentrations of 0.5 mol/l, as outlined for previous experiments. The solution was heated to dissolve all material, then refrigerated for 2 days to encourage crystallisation. After this time a 1 ml sample was taken from the solution and diluted to 50 ml, followed by another tenfold dilution. This sample was analysed by flame AAS for Ni concentration. The nickel solution was then filtered to recover the blue/green crystals, which were subsequently weighed using a four-figure balance.

A single crystal, weighing 0.3998 g was collected and placed in a 400 ml beaker. This was dissolved in water before 5 ml of 1:1 water and conc. HCl was added, and subsequently made up to 200 ml. The mixture was heated to 75°C and 200 ml of 1% dimethylglyoxime in ethanol was added. Dilute ammonia (1:1 water and conc. ammonia) was added dropwise to the solution with constant stirring until precipitation of the red solid $Ni(C_4H_7O_2N_2)_2$ occurred, then in slight excess. This was allowed to stand and cool for 1 hour, before being filtered in a previously weighed sintered glass filter. The precipitate was washed with cold water and dried at 115°C for 50 minutes. After cooling the filter and precipitate were then weighed and hence the precipitate mass determined.

Step two – Oxalic acid was added to the now dilute 190 ml simulated Ni extract at room temperature, with concentrations corresponding to a 1.3 oxalic : Ni mole ratio. The solution was stirred to dissolve all oxalic acid then left to stand for 2 days. After this period a 1 ml sample was taken and diluted for Ni analysis by flame AAS. Given the results, an additional 0.95 g of oxalic acid was added, stirred to dissolve then left for 2 days to precipitate and settle. Another 1 ml sample was taken, diluted and analysed for Ni. Further oxalic acid, weighing 0.665 g to give a total of 0.1 mol/l, was added and treated in the same manner as previous additions. A 1 ml sample was again taken and analysed for Ni content.

Acidity was maintained at pH 5 using KOH and H_2SO_4, to ensure no new elemental components were introduced.

5.3 RESULTS AND DISCUSSION

5.3.1 Nickel Potassium Double Salt Investigation

5.3.1.1 X-ray Powder Diffraction Analysis of A, B and C Crystals *(refer section* 5.2.1.1*)*

Analysis of the blue/green crystals (A) observed to grow in the *A. corsicum* extract, was undertaken using X-ray powder diffraction to determine both crystallinity and structural composition. The resulting spectra with many sharp peaks (Fig. 5.2), showed a clearly defined crystalline structure. Assignment of these peaks to chemical and mineral compounds was limited by the mineralogical database available. However, $K_2Ni(SO_4)_2.6H_2O$ was identified.

Decolourisation of the ash extract implied that a large portion of the crystalline material should be bearing nickel. The absence of peaks characterising other possible nickel compounds lead to the tentative assignment of the crystals as being a nickel potassium sulfate double salt.

The X-ray spectra of the pure crystals of $K_2Ni(SO_4)_2.6H_2O$ (B) was used as a comparison to aid in establishing the validity of the assignment given to the (A) crystals. By comparing the peaks, those still unassigned could be identified as either impurities or contributing to the $K_2Ni(SO_4)_2.6H_2O$ spectra.

The X-ray spectra for (B) proved to be well defined, also with many peaks. On comparison these proved to match almost exactly those of the X-ray spectra for crystals (A), thus confirming its assignment.

Of note were the visual characteristics of the crystals (Fig. 5.1). Both the (A) and simulated hyperaccumulator crystals (C) possessed a white powdery substance over the surface, while the (B) crystals did not. The main difference between the solutions from which the different crystals were grown was the absence of magnesium from that producing the pure salt. Thus it was thought that this powder was a magnesium compound.

Comparison of (C) crystals with those of plant origin by X-ray powder diffraction showed the products to be almost identical, with all major peaks present and only slight variance in intensities. The production of this simulated material was useful for further experiments, as the mass of crystals from *A. corsicum* was limited.

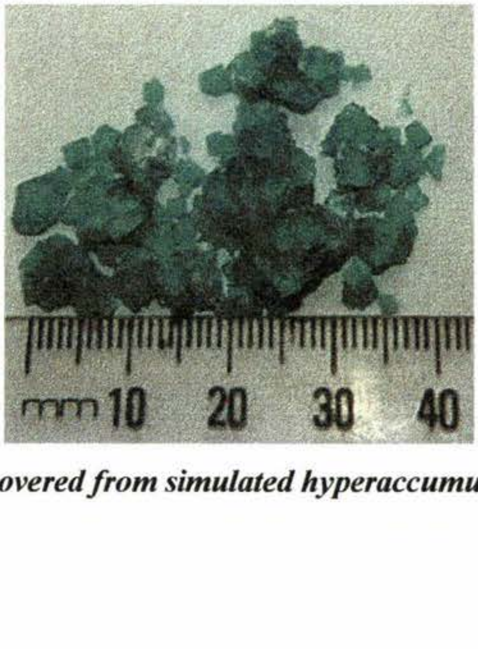
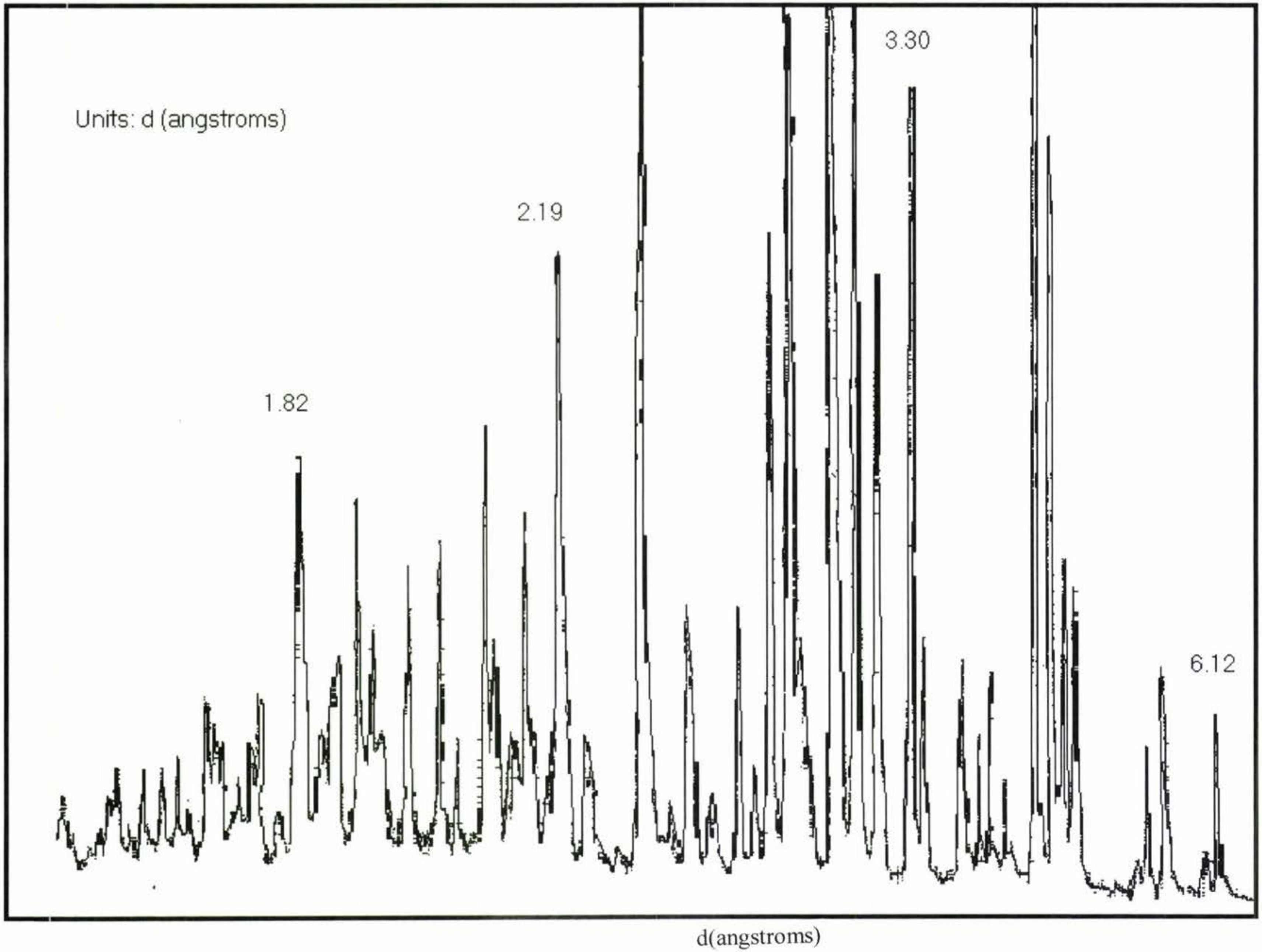


Figure 5.1: Crystals recovered from simulated hyperaccumulator solution.

Figure 5.2: X-ray spectra of crystals recovered from *A. corsicum* extract. Representative of the spectra obtained from A, B and C crystals.


Units: d (angstroms)
3.30
2.19
1.82
6.12
d(angstroms)

The elemental investigation of the (A) crystals with ICP, was useful, not so much in identifying the crystal compound, but as a validation of the characterisation made by X-ray powder diffraction. The mole ratios of the major elements Ni, K and S were used to aid in this classification, with a ratio of 1 : 2 : 2 expected. The ICP analysis also identified the presence of impurities, while their proportions with respect to Ni, K and S gave some clue as to the nature of the crystal compound.

Table 5.1: Interpretation of ICP results for <u>A. corsicum</u> extract crystals.

Element	% Mass	Mols (x 10^{-4})	M/Ni mole ratio
Ca	0.18	0.04	0.02
K	18.83	4.19	2.50
Mg	0.85	0.30	0.18
Ni	11.30	1.68	1.00
S	12.51	3.40	2.02

The results shown in Table 5.1 demonstrate the relationship between the components of $K_2Ni(SO_4)_2.6H_2O$, with a 1.00 : 2.02 : 2.50 ratio of Ni : S : K close to that expected. The deviation from ideal is due mainly to the presence of a Mg impurity, expected to be the Mg analogue, $K_2Mg(SO_4)_2.6H_2O$ of the Ni salt or, considering the little remaining S after Ni complex formation, as some other potassium magnesium double salt. This impurity would then make up 14.1% (as $K_2Mg(SO_4)_2.6H_2O$) of the total mass of the crystals, with a majority (84.1%) being taken up by $K_2Ni(SO_4)_2.6H_2O$. The remaining 1.8% was thought to be due to the presence of other less abundant compounds e.g. Ca, Zn or P based, or due to analytical error.

5.3.1.2 Determination of Magnesium in White Powder Material

In choosing two sample groups, one with less and the other with greater portions of outer white material, it was hoped to qualitatively determine whether the Mg was formed as a separate compound i.e. as the white powder, or held within the nickel potassium sulfate lattice. Sample analysis determined Mg concentrations corresponding to 0.68% and 1.13% respectively for the lesser and greater white-powder portioned samples. Using the assumption that the magnesium is present as

$K_2Mg(SO_4)_2.6H_2O$, these results would yield 11.2% versus 18.7% of the total mass as the magnesium salt for the samples.

It can be concluded that the white material contains a larger proportion of precipitated Mg compound than exists within the Ni crystalline material. It cannot however, be determined whether it is exclusively held within this outer material. Possibilities for the presence of Mg as an insoluble compound include:

(1) Being precipitated after the crystallisation of the nickel salt, giving a Mg compound outer layer.

(2) Formed as a distinctive compound during the nickel crystal growth and thus trapped within the nickel material, but with growth continuing after Ni crystallisation to form the outer layer.

(3) Incorporation of Mg atoms into the potassium nickel sulfate lattice. Mg may be substituting Ni at random sites, with a secondary compound forming the outer layer of white material.

The analysis does not exactly support the assumption that all of the Mg is present as a $K_2Mg(SO_4)_2.6H_2O$ salt. While being only partly soluble in cold water, there is no definite proof as to the form of the Mg. ICP analysis of the Ni crystals determined adequate sulfur concentrations for Ni crystallisation only, however, analytical uncertainties possible in such an analysis mean the presence of further sulfates cannot be discounted.

In the ash extract solution, no white precipitate is observed. This material is only apparent after the blue/green crystals have been extracted and dried. While it may be bound to the larger crystals but not obvious because of their small particle size and lack of colour, it is possible that the material is still soluble and is only precipitated when the solution surrounding the nickel crystals is dried. It remains insoluble in ethanol.

5.3.1.3 Addition of K_2SO_4 to a Simulated Hyperaccumulator Solution

The addition of K_2SO_4 to a solution from which $K_2Ni(SO_4)_2.6H_2O$ was already crystallising was thought to encourage further crystallisation by a common ion effect. As K_2SO_4 is more soluble in cold water than the $K_2Ni(SO_4)_2.6H_2O$ and this compound has already reached saturation, an increase in concentration of K^+ and SO_4^{2-} should cause more Ni to be extracted as the double salt. This theory was tested using a simulated hyperaccumulator extract, with sampling and AAS analysis of the solution after K_2SO_4 addition.

Table 5.2: Ni concentration after $K_2Ni(SO_4)_2.6H_2O$ crystallisation and K_2SO_4 addition.

$[K_2SO_4]$ added (mol/l)	Residual [Ni] (g/l)	% Ni extraction
initial	14.70	
0	11.30	23.1
0.05	9.43	35.8
0.10	8.39	42.9
0.15	6.38	56.6
0.20	4.16	71.7
0.25	4.07	72.3
0.30	3.85	73.8
0.35	4.06	72.4
0.40	2.74	81.4
0.45	2.08	85.9
0.50	1.42	90.3

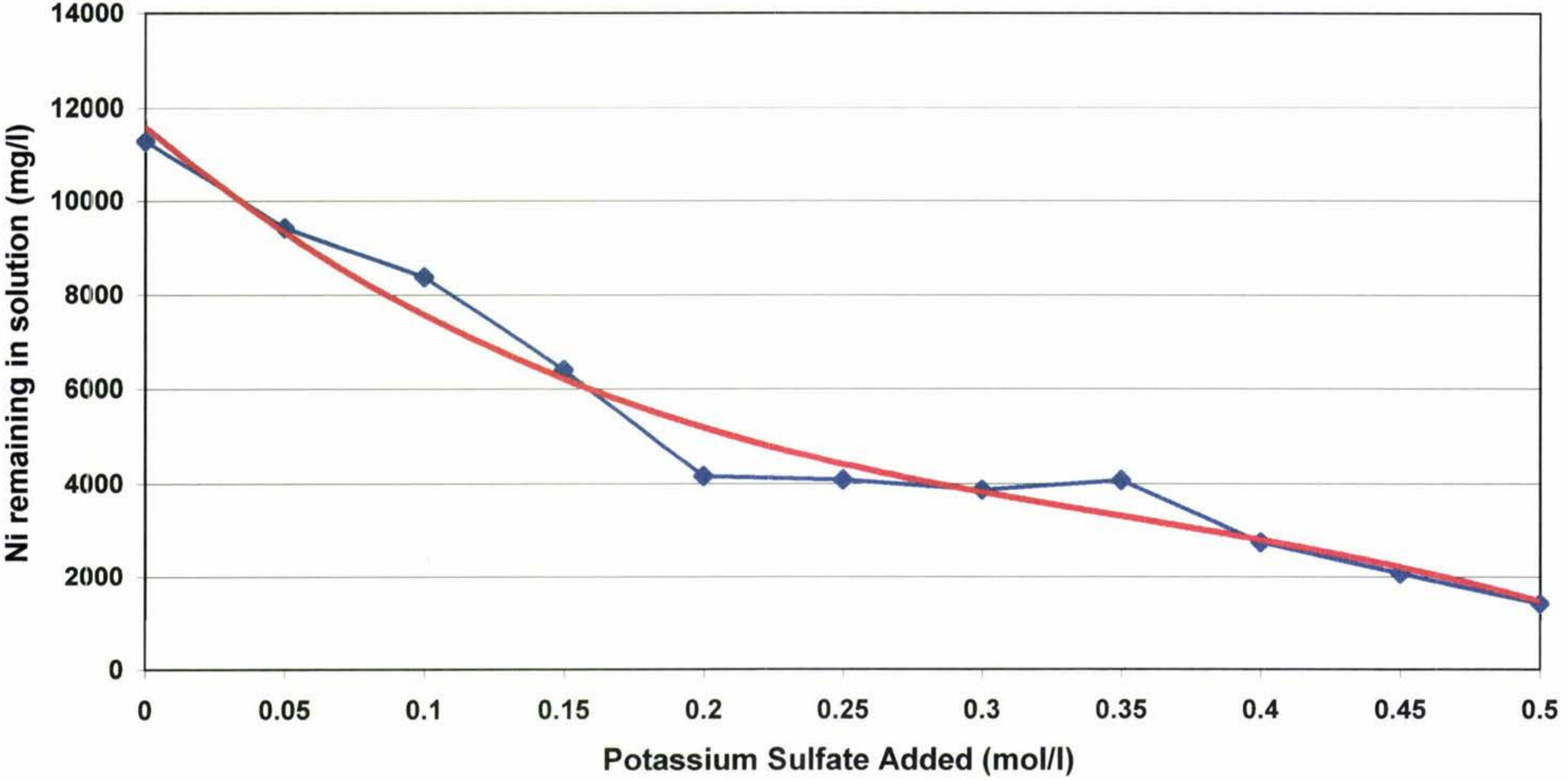
The results shown in Table 5.2, demonstrate the induced crystallisation observed when K_2SO_4 is added, supporting the above hypotheses. The extraction of Ni was increased from 23.1%, with conditions similar to those present in the ash extract, to 90% with the addition of 0.5 mol/l K_2SO_4 (Fig. 5.3). The remaining solution, containing only 1.42 g Ni/l was almost completely decolourised, with large 1-7 mm blue/green Ni double salt crystals covering the bottom of the beaker.

The inconsistencies in the results can be explained by simple variations in growth rates of the crystals, with such variations possibly being the result of differences in heating and cooling.

5.3.1.4 Nickel Salt Crystallisation from 9:1 2M H_2SO_4/8M HNO_3 Synthetic Ash Extract

A quantity of K_2SO_4 greater than that of the endpoint in the simulated hyperaccumulator solution, was added to the 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract. By sampling the solution after longer periods of refrigeration, the optimum time for $K_2Ni(SO_4)_2.6H_2O$ crystal growth could be determined. It should be noted that this solution had already received an increase in sulfate from the electrowinning

Fig. 5.3: Concentration of Ni Remaining in Simulated Hyperaccumulator Solution After Nickel Salt Crystallisation



investigation, with a total concentration of approximately 1.34 mol/l SO_4^{2-}. Nitrate was also present.

Table 5.3: Ni concentration after $K_2Ni(SO_4)_2.6H_2O$ crystallisation for increasing periods of refrigeration.

Time Refrigerated (hours)	Residual Ni Concentration (g/l)
0	16.12
24	2.24
48	2.18
72	1.97
168	2.04

The Ni concentration was found to be 0.274 mol/l (16.12 g/l), marginally less than before electrowinning because of dilutions and nickel electrodeposition. From the results shown in Table 5.3, it was evident that the majority of crystal growth occurs during the first 24 hours of refrigeration, with an 86.1% extraction of Ni occurring. From this period, the first sign of crystal growth was observed between 9-12 hours after the solution had been placed in the refrigerator. Additional cooling after the first 24 hour period only results in as much as an extra 0.27 g Ni/l in the form of $K_2Ni(SO_4)_2.6H_2O$, being extracted from solution. Whether this further extraction is advantageous or if the optimum is at most 24 hours is a matter of economics. For all remaining experiments the period of 48 hours was chosen as standard, to reduce unnecessary experiment length and because this investigation showed crystal growth still occurring during the later 24 hours of the 2-day period.

After the crystals had developed over 7 days, they were separated from the solution and dried. A total of 21.20 g of crystalline material was collected. The difference in Ni concentrations between the starting solution and that of the filtrate after crystallisation was 0.241 mol/l, which corresponds to the amount of Ni in the crystals. Assuming that all 21.20 g of the extracted crystals was $K_2Ni(SO_4)_2.6H_2O$, with a molar mass of 437.13 g/mol, this would correspond to 0.243 mol/l of the nickel double salt. While this does not take into account the impurity of the salts or the loss of material through extraction, it is still an accurate comparison for the amount lost from solution and further proof of the nature of the nickel crystals.

The remaining 160 ml of filtrate was treated with more K_2SO_4, an additional 0.2 mol/l giving a total of 0.773 mol/l K_2SO_4, in the hope of crystallising the remaining 1.9 g/l Ni. After 2 days refrigeration it was observed that while a small quantity of blue/green nickel crystals had formed, a much larger volume of fine white crystals had grown. Analysis of the solution determined the Ni concentration to be 1.87 g Ni/l, only marginally less than that before the second K_2SO_4 addition, with the overall nickel extraction of 88.4%. It is suggested that the nickel concentration had dropped too low for further crystallisation of the nickel double salt and instead K_2SO_4 saturation resulted in crystallisation of K_2SO_4. This is supported by the work of Caven and Johnston (1926), who produced a phase diagram for the K_2SO_4-$NiSO_4$-H_2O system at 25°C (Fig. 5.4). This showed that crystallisation of the nickel potassium sulfate salt was possible down to very low nickel concentrations (0.02 mol/l). Below this, K_2SO_4 was observed to crystallise. Their results illustrated how the solubility of nickel sulfate increased with increasing quantities of potassium sulfate, and likewise for the potassium salt when the concentration of nickel sulfate was increased. Also of importance is that for a given nickel sulfate concentration, the double salt can be crystallised (over a wide range of $NiSO_4$ concentrations – 0.03 to 2.8 mol/l) by adding a relatively small amount of K_2SO_4. However, as the nickel concentration drops close to its lower limit (for $K_2Ni(SO_4)_2.6H_2O$ crystallisation), the amount of potassium sulfate necessary to promote double salt crystal growth increases, to the point (as stated above) where only K_2SO_4 is recovered.

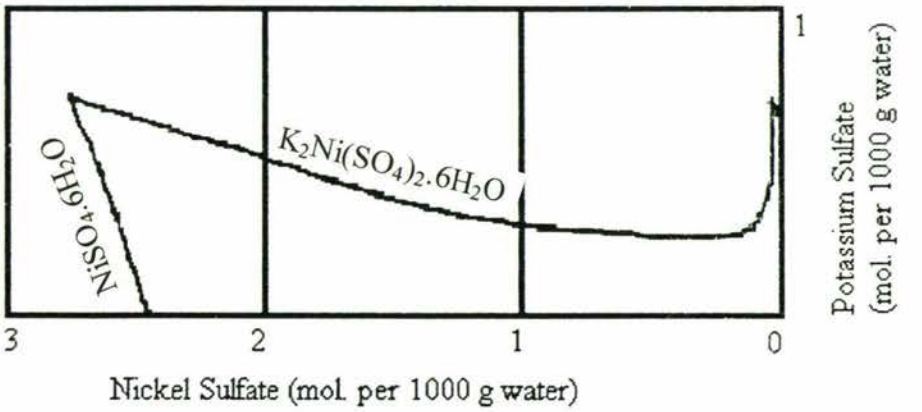


Figure 5.4: Phase diagram for $NiSO_4$-K_2SO_4-H_2O system. Caven and Johnston (1926)

5.3.1.5 Sulfate Concentration Increase by H_2SO_4 Addition

From the previous investigation into induced crystallisation by the common ion effect, it was hypothesised that the separation of Ni by $K_2Ni(SO_4)_2.6H_2O$ crystallisation could be enhanced not only by K_2SO_4 addition, but also by H_2SO_4 addition (using the assumption that this would add SO_4^{2-}). The K/Ni ratio of the simulated hyperaccumulator solution was marginally less than 2:1 (0.440 compared to 0.250), but was still sufficient to enable further crystallisation of the nickel potassium double salt.

The initial sulfate concentration from the addition of Ni, Mg and K as their common sulfate salts was 0.838 mol/l. At this concentration a moderate quantity of the nickel crystals was observed, as with the ash extract solutions. Upon addition of H_2SO_4 to give a proposed total SO_4^{2-} concentration of 1.00 mol/l, the crystals were observed to be of a finer nature, with sizes of 0.2-1.0 mm. Also, a decline in the quantity of crystals was observed. Subsequent addition of H_2SO_4 to give 2 mol/l sulfate produced no crystals after refrigeration. This continued for the remainder of the experiment up to 8 mol/l sulfate, where the absence of crystals was still observed.

Given these results it was not considered necessary to perform a Ni analysis on the samples, as the Ni concentration would only show a drop from the sampling.

It is evident that the reduction in crystallisation is caused by an increase in acidity. As the H^+ concentration increases the equilibrium,

$$HSO_4^- + H_2O \leftrightharpoons SO_4^{2-} + H_3O^+$$

is pushed to the left to produce more HSO_4^-, to the point where in highly acidic solutions virtually no SO_4^{2-} is present. This causes the observed reduction in $K_2Ni(SO_4)_2.6H_2O$ crystallisation. If the pH were to be maintained constant an increase in sulfate concentration should encourage crystal growth.

It is apparent that for techniques utilising H_2SO_4 concentration to crystallise $NiSO_4$, it is more the removal of water than any increase in SO_4^{2-} that results in the salt crystallising. If the concentration of H_2SO_4 were taken to the point where no water remained in solution, the crystallisation of the sulfate salt would be assured (Rajcević et al., 1990). However, such an evaporation is energy intensive and could not be considered as a means of encouraging crystallisation. The addition of potassium with SO_4^{2-}, or even potassium alone, may be more effective at crystallisation inducement.

5.3.1.6 Treatment of Hyperaccumulator Composite Extract

Crystallisation of $K_2Ni(SO_4)_2.6H_2O$ from the hyperaccumulator composite extract appeared to initially contradict the findings of the previous investigation, where crystal growth was not observed with increasing acidity. With a H^+ concentration of 2.34 mol/l, this was clearly in the range where crystallisation was being inhibited. However, ICP analysis of the hyperaccumulator composite and *A. corsicum* extracts (Table 5.4) at pH~0, determined that their Ni, Mg and K concentrations were similar. The key difference between the two was the S concentration, with the composite extract being 141000 μg S/ml compared to a substantially smaller 38000 μg S/ml of the *A. corsicum* extract. In a solution of such strong acidity as found with the hyperaccumulator composite extract, SO_4^{2-} should only be present as a very minor species. But, owing to the large excess of sulfur with respect to H^+, it can be assumed that the SO_4^{2-} concentration is larger in the composite extract than would be found in a purely H_2SO_4 solution, or the *A. corsicum* extract, explaining why sulfate crystallisation is observed.

Table 5.4: Elemental concentrations of composite ash extract before and after K_2SO_4 addition and comparison to A. corsicum.

Element	Concentration (μg/g)		
	Hyperaccumulator After K_2SO_4	Hyperaccumulators Before K_2SO_4	*A. corsicum* @ pH~0
Fe	450	400	1120
K	35950	20950	20950
Mg	7400	9800	10050
Mn	350	280	140
Ni	4600	20200	18490
P	<200	745	2100
S	167000	141000	38000
Zn	200	720	225

The addition of K has been shown to encourage crystallisation of the double salt. For this reason, 0.5 mol/l K_2SO_4 was added directly to the highly acidic extract before neutralisation, in the same proportions previously required for a greater than 90% Ni recovery as a sulfate salt. After mixing and refrigeration, a large quantity of the blue/green crystals had formed. ICP analysis of the remaining solution, with results shown in Table 5.4, determined the remaining Ni concentration to be 4.6 g/l, representative of a 77.2% Ni separation. As expected, a smaller portion of Mg was also removed.

The strong acidity of this extract appeared to dominate the HSO_4^- / SO_4^{2-} equilibrium, hindering a Ni extraction, equivalent to the less acidic solutions (>90%).

Potassium was added in the form of KOH to promote further crystallisation of $K_2Ni(SO_4)_2.6H_2O$ in two ways:

(1) Increase the potassium concentration, forcing $K_2Ni(SO_4)_2.6H_2O$ to be crystallised out of solution by a common ion effect.

(2) Move the pH to more neutral regions, where HSO_4^- becomes converted to SO_4^{2-}, and where crystallisation of $K_2Ni(SO_4)_2.6H_2O$ is known to occur more readily.

The addition of KOH also ensured that no further impurities such as Ca or Na were introduced into the solution from other reagents.

After refrigeration an almost complete decolouration of the extract solution was observed, with many small blue/green $K_2Ni(SO_4)_2.6H_2O$ crystals having been formed. A large volume of small needle-like white crystals, assumed to be K_2SO_4, had also crystallised.

Table 5.5: Elemental concentrations of composite extract after KOH addition.

Element	Concentration (μg/g)
Fe	360
K	79900
Mg	5900
Mn	290
Ni	530
P	1880
S	14600
Zn	60

Analysis of the solution after this additional crystallisation determined the Ni concentration to be only 0.53 g/l (Table 5.5), representative of a 97.4% recovery of nickel as $K_2Ni(SO_4)_2.6H_2O$. This was greater than all previous nickel separations using crystallisation. Even after the KOH addition the solution was still acidic, with a $[H^+]$ of 1.35 mol/l. Evidently, given a sufficient sulfate and potassium concentration, this level of acidity does not hinder $K_2Ni(SO_4)_2.6H_2O$ crystallisation. In fact, a much smaller amount of KOH would be adequate to encourage almost complete removal of nickel from solution, as the production of K_2SO_4 implies an excess has been added. From filtration of the extract, 7.6465 g of crystalline material was collected. Analysis of a representative crystal by ICP (Table 5.6), showed a Ni concentration indicative of 78.1% of the mass consisting of the double salt.

Table 5.6: Elemental concentrations of $K_2Ni(SO_4)_2.6H_2O$ crystals recovered from hyperaccumulator composite extract.

Element	% Mass of Crystalline Material
Ca	<0.01
Fe	0.03
K	14.69
Mg	0.60
Ni	10.49
P	<0.01
S	18.17
Zn	0.23

All other elemental constituents of the crystals were present in similar concentrations to that found in the nickel crystals from the *A. corsicum* extract. The main exception was sulfur, which was found to be at concentrations significantly higher than that necessary to bind nickel as $K_2Ni(SO_4)_2.6H_2O$. Evidently excess potassium and magnesium would be present as sulfate salts, either together as a double salt or individually.

5.3.2 Nickel Oxalate Investigation

5.3.2.1 Initial Oxalic Acid Study

The oxalate: Ni mole ratio of 2.5 was higher than that described by Brooks (1989), in order to ensure removal of as much Ni as a nickel oxalate as possible. The precipitation of this compound is rapid, with the majority of the material forming in the first half-hour. Extraction after an overnight standing period, resulted in 18.40 g material being collected. Analysis of the solution after precipitation determined the Ni concentration to be 0.64 g Ni/l, from the original 14.7 g Ni/l, corresponding to a

95.6% extraction as nickel oxalate. This removal of nickel should result in a mass of 8.75 g nickel oxalate (47.6% of precipitate mass as $Ni(COO)_2.2H_2O$). This leaves a 9.65 g (52.4%) portion of the insoluble material unaccounted for. It should be noted that such calculations do not take into account the possibility that some proportion of the nickel precipitate may be monohydrate nickel oxalate, which would effect the total mass of nickel oxalate present.

From the AAS analysis of elemental concentrations, with the results shown in Table 5.7, it is apparent that both K and Mg have been precipitated in some form. The determined nickel oxalate content of 45.6% is close to the figure calculated for loss of nickel from solution. Using the assumptions that Ni and Mg are present as dihydrate oxalate compounds, with K present as $KHC_2O_4.H_2O$ (less soluble than the K_2 oxalate), and the known concentrations for these elements, this still leaves 27.9% of the material as unknown. The most probable origin for this unknown portion is from reactions of the oxalic acid, either to form less soluble organic compounds or more simply being recrystallised.

Table 5.7: Elemental concentrations of oxalate precipitate.

Element	Concentration (mg/g)	% of Sample Assuming as Oxalate
Ni	146.4	45.6
K	34.7	13.6
Mg	22.2	12.9

After washing a 3.00 g precipitate sample with water, there was a reduction in mass to 1.88 g. The elemental analysis of this washed product, Table 5.8, showed a dramatic increase in the Ni concentration relative to both magnesium and potassium.

Table 5.8: Elemental concentrations of washed oxalate precipitate.

Element	Concentration (mg/g)	% of Sample Assuming as Oxalate
Ni	22.9	71.4
K	5.3	2.0
Mg	17.2	10.5

With the reduction in mass came a decrease in both Mg and K concentrations, with a drop of 51.6% and 90.4% respectively. The unknown portion of the precipitate was also dramatically reduced to the point where only 16.1% of the precipitate is unknown. Such reductions imply that the compounds are precipitated not so much because they are insoluble in water, but because the solution was super-saturated with oxalic acid.

Nickel content however remained constant, with the water-insoluble nickel oxalate remaining to make up a larger proportion of the precipitate. In terms of mass balance, 1.368 g of nickel oxalate was assumed to be present before washing, while 1.343 g is present after three consecutive water washes. The slight deviation from complete conservation can be accounted to slight loss of material in filtration and collection.

With refrigeration and more standing time, increased precipitation was observed. Analysis of the solution showed an increase in percentage nickel extraction from 95.6% after 1 day, to 99.3% nickel recovery after 5 days standing and refrigeration. A further 1-day refrigeration, in addition to the previous 6 days, resulted in an increase to 99.4% nickel extraction as an oxalate.

5.3.2.2 Addition of Oxalic Acid to a Simulated Hyperaccumulator Extract

The titration of a simulated hyperaccumulator solution with oxalic acid was used to show the most efficient proportions of the acid required to extract 95-99% Ni as an oxalate. The pH was maintained at a value of 5 as described by Brooks (1987), who used oxalic acid: nickel ratios of 1.5 at pH 5-6 to extract 92.5 to 99.9% of Ni from industrial waste solutions. A period of 2 days standing time at room temperature was considered the most efficient use of both time and electricity, potentially important when considering a larger scale operation.

The addition of oxalic acid to 1 : 1 mols with Ni has the result of reacting with the majority of free Ni (Table 5.9), creating the insoluble nickel oxalate. Figure 5.5 illustrates this decline in nickel concentration and clearly shows the reduced returns with subsequent oxalic addition to higher concentrations.

It is apparent that oxalic acid may be employed to separate nickel from solution. Whether this is an efficient extraction and the degree to which the extraction should be carried out is a matter of both goals and economics.

Figure 5.5: Concentration of Nickel remaining in simulated hyperaccumulator solution after nickel oxalate precipitation.

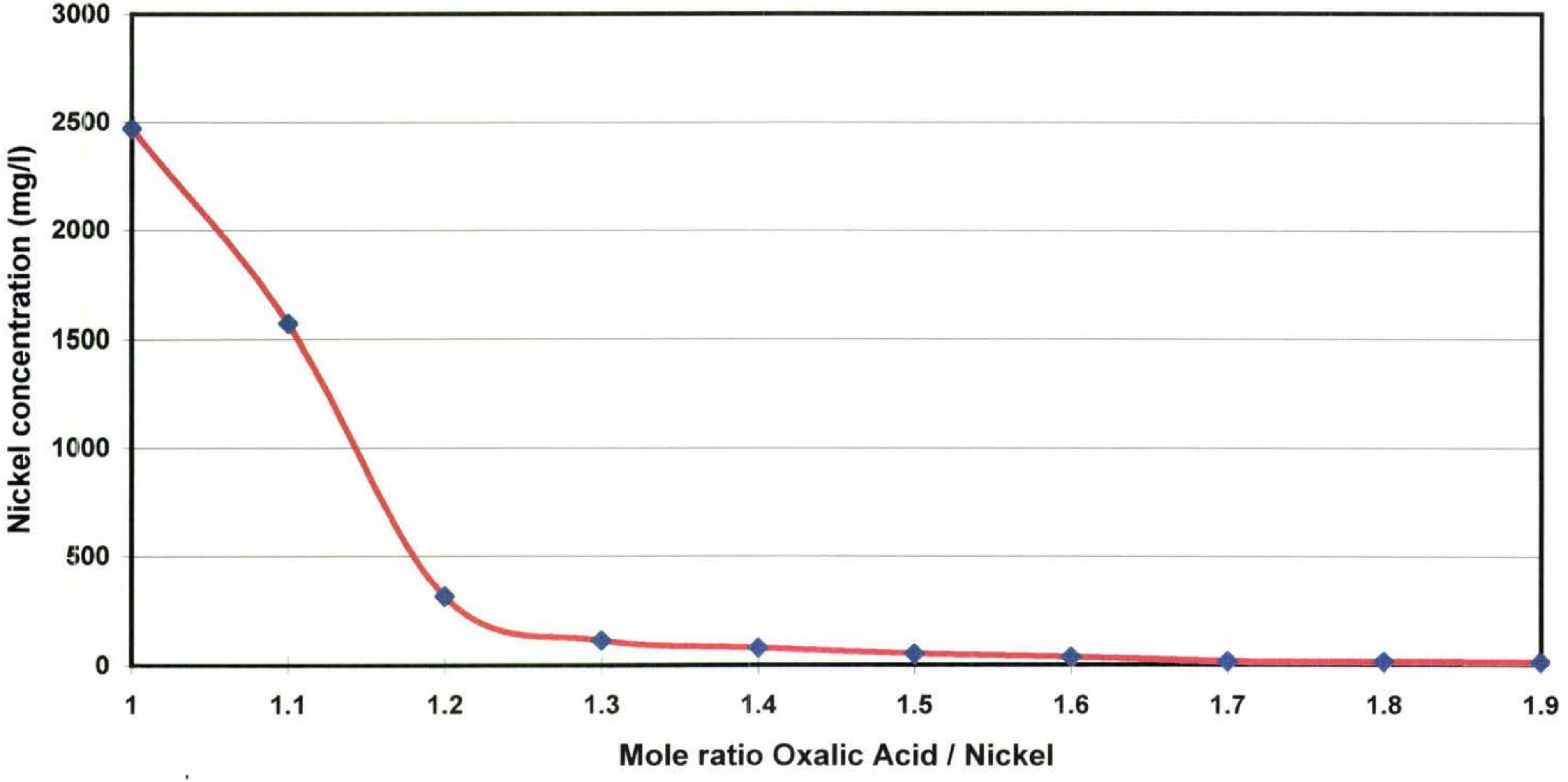

3000
2500
2000
1500
1000
500
0
Nickel concentration (mg/l)
1
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
Mole ratio Oxalic Acid / Nickel

Table 5.9: Titration of synthetic extract solution with oxalic acid and the resulting Ni extraction.

Oxalic Acid: Ni Mole Ratio	Residual [Ni] (g/l)	% Ni Extraction	Residual [Mg] (g/l)
initial	14.700		8.942
1.0	2.468	83.21	6.040
1.1	1.570	89.32	5.112
1.2	0.312	97.88	5.030
1.3	0.112	99.24	4.968
1.4	0.077	99.48	4.786
1.5	0.050	99.66	4.520
1.6	0.037	99.75	4.248
1.7	0.016	99.89	4.242
1.8	0.014	99.90	4.237
1.9	0.012	99.92	4.236

For the purposes of this study, with the aim being nickel recovery for phytoextraction cost recovery, the addition of oxalic acid to concentrations 1.3 times that of the Ni was considered sufficient. At this point a 99.2% extraction has been achieved. The use of more oxalic acid to concentrations as high as 1.9 times that of Ni results in only an increased yield of 0.5%. Alternatively, reducing the oxalic concentration to only 1.2 mol oxalic : Ni, results in the loss of 1.3% of the possible yield.

The figure of 1.5 mols oxalic : Ni stated by Brooks (1987) was employed not only to recover Ni for recycling, but also as partial purification of the waste solution, making disposal possible. Oxalic addition is capable of removing Ni down to 12 mg/l concentrations (Table 5.9), however, it would be preferable to use another more efficient means if the goal was to decontaminate the solution.

Although this investigation only used a simulated hyperaccumulator solution, the results may be used as a guideline for further extractions. Percentage Ni extractions will vary with the content of the solutions and conditions of the plant extract treatment.

The extraction of Mg from solution is apparent in the results, with greater than 50% being removed with excessive oxalic acid addition. The mass proportions of Ni : Mg lost from solution for the 1.9 oxalic acid : nickel mol ratio are 0.32 g Mg for each 1 g Ni. This is confirmed in the previous investigation, where approximately the same proportions can be found when comparing Mg and Ni content of the oxalate precipitate.

5.3.2.3 $K_2Ni(SO_4)_2.6H_2O$ Crystallisation and Secondary Nickel Oxalate Recovery.

The aim of this investigation was to test a nickel recovery process, with the initial and major part of the extraction being achieved by crystallisation of $K_2Ni(SO_4)_2.6H_2O$. The second step, involving oxalic acid addition, was to remove any remaining Ni to concentrations that would be acceptable for return to the phytoextraction site, or disposal as wastewater. Oxalic acid was used only as a secondary step because of the greater expense of reagents and filtration associated with the nickel oxalate. Also, because the crystallisation of the nickel potassium sulfate occurs from the ash solution even without chemical aid.

The addition of 0.5 M K_2SO_4 and subsequent refrigeration resulted in 26.80 g of crystals being extracted. Predominantly blue/green cubic crystals with an outer powdery white material, these crystals ranged in size up to 4 mm.

Analysis of the solution showed the remaining Ni concentration to be 1.598 g/l (0.027 M) from the original 14.67 g/l (0.250 M), indicative of a loss of 2.615 g of Ni from solution. This represents an extraction of 89.1 %, in agreement with previous extractions and their remaining Ni content. Assuming all this nickel is present as the nickel potassium sulfate salt, with a molar mass of 437.13 g/mol, this corresponds to a mass of 19.50 g $K_2Ni(SO_4)_2.6H_2O$. Thus by mass balance the filtered crystals, extracted from solution, have a theoretical purity of 72.7 % with respect to the nickel salt.

The determination of nickel content in the blue/green crystals was established using dimethylglyoxime to precipitate a nickel dimethylglyoximate from solution. With a known 20.3 % Ni in the dimethylglyoximate and a recorded mass of 0.1904 g this corresponded to a mass of 0.0387 g Ni from the 0.3998 g sample. With the assumption that all Ni is present as $K_2Ni(SO_4)_2.6H_2O$ (Mr = 437.13 g/mol) this implies a purity of recovered nickel crystals of 72.0[illegible] %. This is in good agreement with the mass balance determination, from the loss of Ni from solution.

Filtration and treatment of the 200 ml simulated hyperaccumulator solution left a volume of 195 ml for further treatment. Oxalic acid addition to the filtered solution was in mole proportions 1.3 times that of the 0.027 mol/l Ni present. The application of oxalic acid to a dilute solution, at mole ratios found acceptable for nickel recovery from a 0.250 mol/l nickel solution, was to be tested. If successful, such a nickel recovery could then be treated as the second stage in a complete Ni extraction process.

After the solution was left to stand for two days a fine light blue precipitate was observed. Analysis of the solution showed the Ni concentration to be 0.93 g/l, much greater than the 0.31 g/l found for the same mol ratio used on a 0.250 mol/l Ni solution. This is most likely because of inadequate saturation of the oxalate group throughout the solution, allowing a greater proportion of Ni^{2+} ions to remain unbound. To encourage further precipitation the concentration of oxalic acid was increased by 0.04 mol/l, thus increasing the mole ratio of oxalic acid : nickel to 2.77. With standing for a further 48 hours, more precipitate was observed. Analysis of the solution gave the Ni concentration to be 0.37 g/l. Addition of oxalic acid again, to give a total concentration of 0.1 mol/l, resulted in the solution having a final Ni concentration of 0.20 g/l. The resulting precipitate yield after filtration and washing with water was 1.1943 g. Given the loss of 0.024 M nickel from solution (corresponding to 0.272 g Ni) and assuming its presence as a dihydrate oxalate, this gives a mass of 0.848 g $Ni(COO)_2.2H_2O$, thus a purity of 71.0 % for the nickel oxalate precipitate.

5.4 CONCLUSION

First reported by Tutton in 1893 (Caven and Johnston, 1926), nickel potassium sulfate is one of a number of salts following the $M_1M_2(SO_4)_2.6H_2O$ notation referred to as Tutton's salts. In a solution of $NiSO_4$ and K_2SO_4, over a wide range of concentrations, $K_2Ni(SO_4)_2.6H_2O$ is found to crystallise preferentially over either nickel sulfate or potassium sulfate. From the work of Caven and Johnston (1926) it is apparent that the crystallisation of the double salt is influenced more by the potassium sulfate, as at concentrations of greater than 2.5 mol/l Ni and less than 1 mol/l K, the double salt still crystallises. The preferential crystallisation of $K_2Ni(SO_4)_2.6H_2O$ over its components is due to the greatly different solubilities of the three compounds in cold water, with the double salt being soluble only to 7 g/l (0.8 g Ni/l) at 0°C. This relatively insoluble nature of $K_2Ni(SO_4)_2.6H_2O$ at colder temperatures, enables the salt to be crystallised easily, without the excessive energy demands of evaporation to initiate crystal formation, as with the industrial crystallisation of $NiSO_4.7H_2O$

It is believed that this is the first such occurrence of the crystallisation of $K_2Ni(SO_4)_2.6H_2O$ being used to recover nickel from solution. It appears that this method is ideally suited to hyperaccumulator ash extracts, owing to the naturally high abundance of both nickel and potassium, and the relative ease of extracting both elements from the plant ash using H_2SO_4.

Crystal growth is a sensitive function of a number of parameters, with both potassium and sulfate concentrations being of importance. Acidity of the solution is also a major controlling factor through its influence on the HSO_4^-/SO_4^{2-} balance, as evident when better yields of $K_2Ni(SO_4)_2.6H_2O$ crystals are obtained from neutralised solutions.

The influence of potassium is apparent in the comparison of the hyperaccumulator composite extract and the synthetic ash extract. Both were leached with 4M H_2SO_4, and differed only in their potassium concentrations, with the hyperaccumulator extract having approximately twice as much potassium. From this potassium-rich solution, $K_2Ni(SO_4)_2.6H_2O$ crystal growth was observed before neutralisation, whereas crystal growth was only seen in the synthetic solution after neutralisation (and subsequent increase in sulfate concentration).

While crystal formation occurred in hyperaccumulator extracts without chemical aid (except neutralisation in some cases), the degree of nickel separation was insufficient for economic purposes. To encourage further crystallisation of $K_2Ni(SO_4)_2.6H_2O$, the concentration of potassium and/or sulfate ions can be increased (common ion effect).

As stated previously, the sulfate concentration may be increased by the neutralisation of the solution. With a drop in H^+ concentration, the HSO_4^-/ SO_4^{2-} equilibrium is driven to convert a greater proportion of the HSO_4^- into SO_4^{2-}. The benefits of such an increase are apparent. By using a relatively concentrated acid such as 4M H_2SO_4 to dissolve the ash, the total available sulfate concentration is increased. However, there is a need for greater neutralisation to realise the higher sulfate levels. Indeed it may be that by using a less concentrated acid (still capable of performing an adequate nickel extraction) the necessary sulfate concentration required to produce a given $K_2Ni(SO_4)_2.6H_2O$ yield, may be more easily obtainable.

The addition of K_2SO_4 improved nickel crystallisation, with both the additions of potassium and sulfate favouring crystal growth. The addition of 0.5 mol/l K_2SO_4 to simulated hyperaccumulator solutions, with low sulfate concentrations, resulted in a greater than 90% recovery of the nickel and a remaining Ni concentration of approximately 1.5 g/l. Slightly higher residual Ni concentrations were observed for the 9:1 2M H_2SO_4/8M HNO_3 synthetic ash extract, probably owing to relatively high nitrate concentration. When such a K_2SO_4 addition is made to a solution with an already high sulfate concentration, it is more likely that any induced crystallisation is the response of potassium addition. Indeed, it was shown that the sulfate concentration of a 4M H_2SO_4 extract was sufficient, when saturated with potassium, to allow crystallisation of almost all nickel, and still be large enough to support crystallisation of potassium sulfate as well.

KOH may also be used as an additive to induce $K_2Ni(SO_4)_2.6H_2O$ crystallisation, with its addition encouraging growth in two ways. Firstly, the addition of potassium improves crystal growth by way of the common ion effect. Secondly, the hydroxide reduces the solutions acidity, allowing for a greater sulfate concentration.

The use of KOH was thought to be more beneficial than K_2SO_4, especially when considering solutions with already high sulfur concentrations (4M H_2SO_4 extraction). In such solutions the addition of further sulfate is less effective, instead adjustment of the pH to less acidic values and hence conversion of some of the existing sulfur into SO_4^{2-} (from HSO_4^-) is likely to be of greater benefit. Compared to K_2SO_4, a greater proportion of the mass of KOH is potassium, allowing for better potassium saturation of the solution for a given weight of reagent. The requirement for a smaller quantity of reagent, the cheaper cost of KOH is economically advantageous.

Saturation of the hyperaccumulator composite extract with potassium, added as KOH, resulted in an almost complete recovery of nickel as $K_2Ni(SO_4)_2.6H_2O$, with a 97.4% extraction. Of equal importance was that it did so with the H^+ concentration still greater than 1 mol/l. Thus, nickel can be recovered as a double salt, without the need for a separate neutralisation process. The implied savings in processing costs are large, as after recovery of the nickel, the remaining extract may be treated as a waste water and disposed of, or neutralised in the most cost effective and convenient manner.

The blue/green cubic crystals recovered from the hyperaccumulator extracts were determined to have a purity of 70-85% $K_2Ni(SO_4)_2.6H_2O$. The remaining portion is made up primarily by an unknown Mg contaminant, with the majority of this thought to be in the outer white powdery material present even after the crystals are washed and dried.

Also observed from the hyperaccumulator composite extract was the crystallisation of K_2SO_4, owing to potassium saturation and removal of the less soluble $K_2Ni(SO_4)_2.6H_2O$. The sulfate concentration of the remaining solution after nickel removal is still high. From such a solution, where potassium is at saturation concentration, any further addition of KOH results in crystallisation of K_2SO_4 as well as an increase in pH. Therefore neutralisation of the solution by KOH addition, could also yield a significant quantity of potassium sulfate, a product easily marketed, or usable as a fertiliser at the phytoextraction site.

A method for obtaining purified nickel sulfate from an impure double salt of nickel has been suggested by Nozima et al. (1974). This entails re-dissolving the crystals in water then adding aqueous ammonia and bubbling O_2 through the solution to precipitate Fe, V and Cu. Ni^{2+} ions are then extracted by addition of a naphthenic acid and kerosine mixture. This separates Ni from unwanted Mg and Ca. The nickel is then back-extracted by addition of 2M H_2SO_4 to recover 100% of the $NiSO_4$. It is unclear from the report whether potassium would be removed if the method were applied to the nickel potassium double salt. In any case the result would be a pure nickel salt product. Alternatively this technique could be applied directly to the neutralised extract, eliminating the nickel crystallisation step.

Decomposition of $K_2Ni(SO_4)_2.6H_2O$ occurs in two steps with the final products being NiO and K_2SO_4 (Lukashev et al., 1979). This gives an alternative to direct sale of the double salt, as NiO could be recovered (after leaching of the K_2SO_4). However, nickel oxide of such quality, would probably find use only as a feedstock for smelting, and if such were the case, the unprocessed ash would be a more economical product.

The double salt, while not commonly marketed, has been used as a pigment dye and has recently found uses in filtering and detecting UV light (Singh et al. 1998).

The presence of K_2SO_4 in a $NiSO_4$-based electroplating bath was found to aid in producing an adherent and black stripe-free nickel deposit by increasing the electrical conductivity and throwing power (Liu, 1989). Concentrations up to 18 g/l were reported to be favourable. This could be another potential market for $K_2Ni(SO_4)_2.6H_2O$, as its presence would not only supply the potassium required for such improvements, but also increase the Ni concentration (reducing the need for $NiSO_4$).

Further work into the production and uses of the potassium nickel double salt, should focus on improving the purity of the product. As the main impurity as a magnesium compound a pre-nickel-recovery process that preferentially removes Mg from solution would be of great benefit. Alternatively, a purification process of the nickel double salt could be investigated, starting initially with a recrystallisation study.

The precipitation of nickel as a nickel oxalate, as used in the treatment of waste-water to remove certain heavy metals, proved to be an excellent means of recovering nickel from a phytoextraction based solution. Such a process is made easier by the refined nature of the solution, with a nickel extraction of greater than 99% possible at near-neutral pH. For treatment of a neutralised extract, with a Ni concentration of 0.25-0.35 mol/l, addition of oxalic acid to 1.3 times the molar concentration of Ni, was considered optimum in terms of returned product for the reagents used. This resulted in a 99.2% nickel recovery with only 0.31g/l Ni remaining in solution. Assuming a dihydrate species, the final product after washing with water was 71% nickel oxalate. Oxalic acid addition was also investigated as a secondary nickel recovery step after $K_2Ni(SO_4)_2.6H_2O$ crystallisation to reduce nickel content and potentially help recover costs of processing. When applied to a dilute ash extract solution with Ni concentrations ranging from 0.026-0.009 mol/l (depending on processing) the addition of oxalic acid to a concentration of 0.1 mol/l was required to remove much of the remaining nickel, leaving only 0.003 mol/l Ni in solution.

As a stand-alone process, oxalic acid addition to precipitate nickel oxalate is an effective and relatively easy means of recovering nickel. It is however limited by the cost of reagents and the need to neutralise the solution to pH 5-6, in order for an adequate extraction to occur. With respect to the use of oxalic acid as a secondary nickel recovery technique, the poor product returns (0.023-0.006 mol nickel oxalate per litre processed) and need for neutralisation inhibit its use. Another problem with its use as a secondary nickel recovery, is the incomplete removal of nickel, which may still need to be recovered in order for the solution to be disposed of. Thus a third nickel extraction would be required, adding to overall costs.

Limitations on the discharge of nickel-bearing wastewater are normally set to 1 mg Ni/l (USEPA, 1993). This is to reduce the possible toxic effects that high metal concentrations can have on plant and animal life. Such restrictions mean the used nickel solution may not be disposed of unless proper permission has been obtained. Alternatives include returning the solution directly or after dilution, to the site of phytoextraction (in the case of phytomining). With high K, Mg and SO_4^{2-}

concentrations, the used extract could make an ideal fertiliser for the hyperaccumulator crops. The extract, containing approximately 0.2-0.5g Ni/l may also be treated to remove the remainder of the nickel, through conventional hydroxide or sulfide precipitation. One of these more thorough techniques could be used an alternative to the oxalic acid addition, reducing the number of nickel recovery steps to two and reducing processing and product handling costs. Precipitation of any remaining nickel as a hydroxide, could be the simplest means of final nickel separation, as KOH can be used to neutralise the solution and to produce K_2SO_4. This also avoids the more complicated requirements of sulfide addition. If the sulfate concentration were to be depleted, then further neutralisation could be carried out using a reagent cheaper than KOH, such as limestone. Nickel hydroxide could then be collected and treated as in conventional wastewater processing.

Chapter Six

Conclusion

6.1 Overview

Nickel hyperaccumulator plants such as those of the genus *Alyssum*, have the remarkable ability to extract large quantities of nickel (up to 2% of their dry weight) from the metalliferous soils they grow in. It has been suggested that this characteristic could be utilised in a commercial extraction operation, either as phytoremediation or phytomining.

Another significant feature of the plants is the apparent nickel refining that the accumulation process achieves. Many other metals within the soil (except magnesium) are substantially excluded from the plant material, resulting in a more refined medium than the soil. Combustion of the plant material results in a bio-ore, with nickel content far in excess of economic grade Ni ore and little in the way of elements that would potentially inhibit Ni recovery. Such a material could be exploited, using a more specific nickel recovery process than smelting to produce a more pure product, with potentially greater monetary returns. This study focused on the possibility of electrowinning and crystallisation, as a means of recovering nickel from hyperaccumulator ash. Although these recovery techniques were considered separately, the initial stages were the same, with the nickel first undergoing concentration (ashing), then solubilisation (ash leaching).

6.2 Combustion

The combustion of hyperaccumulator plants whether through open-flame or controlled-temperature methods was shown by X-ray powder diffraction to produce similar ash products, each containing nickel in an oxide form. However, in the case where open-flame combustion was used the resulting ash was inhomogeneous with respect to nickel, caused by incomplete combustion. This was thought to be due to the small scale of the ashing, with short high-temperature residence times. On a larger scale this might not be such a problem, indeed the advantages of recovering energy from the process, out-weigh the possible problems caused by ash inhomogeneity.

An approximate ten-fold reduction in the mass of the hyperaccumulator material was observed upon ashing, corresponding to a ten-fold increase in nickel concentration in the medium, with the ash commonly being 10-15% Ni.

6.3 Acid Leaching

In leaching the nickel-rich ash, H_2SO_4 was used as the main acid, owing to its low cost and the common usage of a sulfate medium for both nickel separation techniques investigated. The extractive properties of acids, with respect to nickel, were found to follow the order $HCl > H_2SO_4 > HNO_3$, confirming the findings of Gilliam and Canon (1980). HCl was not seriously considered for ash leaching owing to problems associated with chloride ions. Future work could focus on the use of this acid, with the crystallisation of a nickel chloride species being the overall goal.

Mixtures of sulfuric and nitric acid, such as 9:1 2M H_2SO_4/8M HNO_3 recovered marginally more nickel from the ash than either acid alone. However they also extracted greater quantities of other elements such as Ca. The presence of a large excess of nitrate in the ash extracts was found to inhibit nickel electrowinning. For these reasons a simple 4M H_2SO_4 extraction was considered most favourable for further processing of the solution.

Acid leaching was found to be improved when higher temperatures and mixing were employed, with nickel recoveries being greater than for any other elements.

Solubilisation of nickel from the ash ranged from 90-99% during leaching, depending on the nature of the ash and whether incomplete combustion had occurred. This resulted in solutions of 0.30 to 0.35 mol/l Ni. In each case, however, a portion of the solubilised nickel was held within the residue (predominantly made up of precipitated $CaSO_4$).

The leaching, like the hyperaccumulation process, performed additional refining of the medium by extracting nickel preferentially over other ash components. Elements such as Fe and Zn, already in only minor concentrations, were excluded more so, while Ca was precipitated as $CaSO_4$ after reacting with the sulfuric acid. This left an acidic solution containing predominantly Ni, Mg and K in a sulfate (or sulfate/nitrate) medium.

6.4 Neutralisation

Neutralisation of the acidic extract was investigated as nickel electrowinning required a more neutral pH than that of the leachates. $CaCO_3$ and NaOH were used (because of their low cost) with significantly more reagent than calculated required to obtain a pH of 4.5. This was probably caused by the buffering action of the HSO_4^-/SO_4^{2-} equilibrium and the formation of insoluble calcium sulfate on the surface of the $CaCO_3$ particles (incomplete dissolution).

The introduction of sodium into the extracts, while considered only a spectator ion for techniques such as electrowinning, prohibits any remaining solution from being disposed of on soil. The use of $CaCO_3$ produced different problems, resulting in the removal of approximately 0.75 mol/l sulfate as $CaSO_4$.

6.5 Electrowinning

Although the electrowinning proved successful, with nickel being recovered from a hyperaccumulator extract at good current efficiencies, it is apparent that engineering concerns and unknown chemical/electrochemical processes, both of which were beyond the scope of this investigation, complicate the process.

Hyperaccumulator-based solutions offer the advantage of a ready-purified medium from which nickel electrodeposition can be easily conducted. It was shown through the use of both simulated and actual plant extracts, that the elemental concentrations of solution components such as K, Mg, Zn, Ca, etc. were not sufficient to prohibit nickel recovery by this method. Indeed it was the species SO_4^{2-} and NO_3^-, present from the acid extraction, that proved to have the largest effect, with excesses of either resulting in the inhibition of nickel electrodeposition. It was found that sulfate and nitrate counteracted each other, with the excesses of either being arrested by an increase in the concentration of the opposite species. In balancing their concentrations a window occurred from which a good nickel deposit was obtainable.

Much work on both electrowinning cell design and especially the electrochemical processes is needed before this method of nickel separation can be seriously considered for a large-scale phytoextraction operation.

6.6 Crystallisation and Precipitation

The recovery of nickel by either crystallisation or precipitation of a nickel compound is by no means novel, being used extensively in industries such as wastewater treatment and nickel refining. However, the utilisation of the insoluble nature of potassium nickel sulfate, $K_2Ni(SO_4)_2.6H_2O$, in this investigation of nickel separation, is thought to be a first.

The $K_2Ni(SO_4)_2.6H_2O$ salt crystallises preferentially from solutions over a large range of nickel and potassium sulfate concentrations, making this method of nickel recovery ideal for hyperaccumulator ash extracts, where these species are found in abundance.

Although crystal growth occurred in the hyperaccumulator ash extracts without chemical aid, it was necessary to encourage further crystallisation in order to achieve an efficient recovery of nickel, greater than 95%. This was undertaken by means of the common ion effect, with both potassium and sulfate addition being investigated. While K_2SO_4 addition proved successful on neutralised extracts and simulated hyperaccumulator solutions, it was found that KOH actually promoted $K_2Ni(SO_4)_2.6H_2O$ crystal growth more efficiently, making a separate neutralisation step unnecessary. It did so by both increasing the potassium concentration and by means of neutralisation, forcing a greater proportion of HSO_4^- to be dissociated to SO_4^{2-} (thus sulfate concentration increases). In this manner the nickel could be adequately removed in still highly acidic solutions (greater than 1 mol/l H^+).

From the hyperaccumulator extracts used, it was found that 95-98% of the nickel could be removed from solution using KOH to aid crystallisation, leaving as little as 1.3 g/l in solution. The blue/green $K_2Ni(SO_4)_2.6H_2O$ crystals were easily separated, owing to their large size (1-7 mm), with analysis determining the potassium nickel sulfate content to be 70-85%, depending on the solution used. The remaining portion of the crystal material was found to be predominantly an unknown magnesium compound, which also formed a white powder on the surface of the blue/green nickel salt. Smaller concentrations of elements such as zinc and calcium were also observed.

The use of oxalic acid to precipitate nickel oxalates proved equally successful at removing nickel, with extractions of greater than 99%. However, the additional step of neutralising the solution to pH 5-6 before treatment and the reagent cost (with respect to product return), made its choice as either a primary or even secondary nickel recovery method uneconomical.

Treatment of the remaining solution, after $K_2Ni(SO_4)_2.6H_2O$ recovery, is determined primarily by the means in which it is to be disposed, with the ideal being the return of the solution to the phytoextraction site to act as a fertiliser.

6.7 Final Assessment

It can be concluded that the most effective and efficient means of recovering nickel from a hyperaccumulator plant crop is as follows.

(1) Ashing of plant material by means of open flame combustion, with recovery of energy as either heat or electricity.

(2) Leaching of the ash with 4M H_2SO_4 under reflux (~96% Ni solubilisation).

(3) Recovery of the solution, limited to about 93% of this, even with a small addition of water wash, because of trapping of solution in the residue.

(4) Addition of KOH and possible refrigeration to promote $K_2Ni(SO_4)_2.6H_2O$ crystallisation (~98% Ni recovery with a compound purity of 85%)

(5) After liquid/solid separation, either KOH or limestone addition to neutralise the acidity (and produce K_2SO_4 in the case of KOH addition), then return of the remaining solution to the phytoextraction site.

(6) Sale of $K_2Ni(SO_4)_2.6H_2O$ directly or further processing to purify.

With the *A. corsicum* crop return of 9 tonnes /ha (Robinson, 1997) with an average Ni content of 1%, and using the extraction figures as above (assuming no other loss of Ni and compound impurities) this process would produce an estimated 690 kg of the nickel double salt from a 1 ha crop.

Such a process appears feasible, but with the overall aim being monetary return to recuperate the costs of the phytoextraction (and potentially make a profit), the key to success will be in identifying a market for the nickel compound. If this is achieved nickel phytoextraction may be an economically viable and indeed beneficial option for soil decontamination or the mining of low-grade ore.

Appendix

A.1 Flame Atomic Absorption Spectroscopy

Standards were prepared for flame AAS by dilution of a 1004 μg Ni/ml ICP standard with double deionised water. Solutions of 2.42, 4.84, 7.27, 9.70 and 19.40 μg/ml nickel were produced in this manner, with water acting as the blank. The resulting standard curve proved to be linear.

Sample solutions prepared for analysis were diluted with double deionised water until the measured nickel concentration was within the range of 2.5-10.0 μg/ml Ni. This ensured an accurate determination of the nickel content.

For all flame AAS analysis a GBC 905AA instrument was used.

A.2 Ultraviolet-Visible Spectroscopy

Standards for quantitative determination of Ni concentration at 720 nm wavelength, were prepared by dissolving appropriate quantities of $NiSO_4.6H_2O$ (99.99%) in double deionised water. A four-figure balance was used when weighing the nickel sulfate, with solutions of 0.05, 0.10, 0.20, 0.30, 0.40 and 0.50 mol/l nickel being produced.

When both obtaining the UV/Vis spectra (190-820 nm) and determining the Ni concentration at 720 nm, a Hewlett Packard 8452A Diode Array spectrophotometer was used.

A.3 pH Determinations

Measurement of pH was performed using a Denver model 50 instrument with a combination glass electrode.

Standards with pH values of 1.00 and 2.00 were prepared with 25 ml 0.2 M KCl and 67.0 or 6.5 ml (respectively for pH 1 or 2) 0.2 M HCl.

Standards with pH values of 3.00 and 4.00 were prepared with 50 ml 0.1 M potassium hydrogen phthalate and 22.3 or 0.1 ml 0.1 M HCl respectively.

Standard with pH 5.00 was prepared with 50 ml 0.1 M potassium hydrogen phthalate and 22.6 ml 0.1 M NaOH.

Standard with pH 6.00 was prepared with 50 ml 0.1 M potassium dihydrogen phthalate and 5.6 ml 0.1 M NaOH.

A.4 Inductively Coupled Plasma – Atomic Emission Spectroscopy

Multi-element analysis of sample solutions was performed on a Varian Vista AX CLD simultaneous ICP-AES. The instrument was situated at Grasslands Research Centre, Palmerston North, New Zealand, with analysis being performed by AgResearch Analytical Laboratory Staff.

References

Anderson, C. W. N., Brooks, R. R., Stewart, R. B. and Simcock, R. (1998). Harvesting a crop of gold in plants. *Nature* **395**: 553-554.

Antonsen, D. H. (1992). Nickel compounds. In Howe-Grant, M. and Kraschwitz, J. (Eds.) Encyclopedia of chemical technology 4th edition. USA. John Wiley and Sons Inc.

Atkins, P. W. (1994). Physical Chemistry 5th edition. Oxford, England. Oxford University Press.

Avci, E. (1989). Electrolytic recovery of nickel from dilute solutions. *Separation Sci. and Tech.* **24(3 & 4)**: 317-324.

Baker, A. J. M. (1981). Accumulators and excluders – strategies in the response of plants to heavy metals. *J. Plant Nutr.* **3**: 643-654.

Baker, A. J. M. and Brooks, R. R. (1989). Terrestrial higher plants which hyperaccumulate metallic elements – a review of their distribution, ecology and phytochemistry. *Biorecovery* **1**: 81-126.

Baker, A. J. M., Proctor, J., van Balgooy, M. M. J. and Reeves, R. D. (1992). Hyperaccumulation of nickel by the flora of the ultramafics of Palawan, Republic of the Philipines. In Baker, A. J. M., Proctor, J. and Reeves, R. D. (Eds.) The vegetation of ultramafic (serpentine) soils. Hampshire, UK. Intercept Ltd.

Baker, A. J. M., Reeves, R. D. and Hajar, A. S. M. (1994). Heavy metal accumulation and tolerance in British populations of *Thlaspi caerulescens* J. & C. Presl (Brassicaceae). *New Phytol.* **127**: 61-68.

Baker, A. J. M., McGrath, S. P., Reeves, R. D. and Smith, J. A. C. (1997). Metal hyperaccumulator plants: A review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils. In Banuelos, G. S. and Terry,

N. (Eds) Proceedings of the symposium on phytoremediation, fourth international conference on the biogeochemistry of trace elements, 23-26 June 1997, Berkeley, CA.

Blaylock, M. J., Salt, D. E., Dushenkov, S., Zakharova, O., Gussman, C., Kapulnik, Y., Ensley, B. D. and Raskin, I. (1997). Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. *Environ. Sci. Technol.* **31**: 860-865.
Boca Raton, Florida. CRC Press. pp. 85-107.

Bowen, H. J. M., Cawse, P. A. and Thick, J. (1962). The distribution of some inorganic elements in plant tissue extracts. *J. Exp. Bot.* **13**: 257-267

Brillas, E. Rambla, J. and Casado, J. (1999). Nickel electrowinning using a Pt catalysed hydrogen-diffusion anode. Part I: Effect of chloride and sulfate ions and a magnetic field. *J. Applied Electrochemistry.* **29**: 1367-1376.

Brooks, C. S. (1987). Nickel metal recovery from metal finishing industry wastes. Proceedings of the 42nd Industrial Waste Conference. Purdue University, Indiana, USA. Lewis Publishers Inc. pp. 847-852.

Brooks, C. S. (1989). Metal recovery from electroless plating wastes. *Metal Finishing* **87(5)**:33-36.

Brooks, C. S. (1991). Metal recovery from industrial waste. Michigan, USA. Lewis Publishers.

Brooks, R. R. (1987). Serpentine and its vegetation. Portland, OR. Dioscorides Press.

Brooks, R. R. (1998). Plants that hyperaccumulate heavy metals: Their role in phytoremediation, microbiology, archaeology, mineral exploration and phytomining. United Kingdom. CAB International.

Caven, R. M. and Johnston, W. (1926). Equilibrium in the systems nickel sulphate-potassium sulphate-water, zinc sulphate-potassium sulphate-water, and manganese sulphate-potassium sulphate-water at 25°. *J. Chem. Soc.* 2628-2632.

Chaney, R. L., (1983). Plant uptake of inorganic waste constituents. In Parr, J. F., Marsh, P. B. and Kla, J. M. (Eds.) Land treatment of hazardous wastes. Park Ridge, NJ. Noyes Data Corp. pp. 50-76.

Chaney, R. L., Angle, S. J., Li, Y., Baker, A. J. M., Reeves, R. D., Roseberg, R. J., Volk, V. V., Kukier, U., Peters, C., Zdimal, K. and Nelkin, J. P. (1999). Phytoextraction of soil nickel using *Alyssum* species. Proceedings of the 5th international conference on the biogeochemistry of trace elements, 11-15 July 1999, Vienna, Austria. pp. 14-15.

Chaney, R. L., Li, Y., Brown, S. L., Homer, F. A., Malik, M., Angle, J. S., Baker, J. M., Reeves, R. D. and Chin, M. (1997). Improving metal hyperaccumulator wild plants to develop commercial phytoextraction systems: Approaches and progress. Proceedings of the symposium on phytoremediation, fourth international conference on the biogeochemistry of trace elements, 23-26 June 1997, Berkeley, CA. pp. 129-158.

Coates, D., Paul, G. and Daugherty, P. (1989). Advances in lightweight nickel electrode technology. *Space Electrochem. Res. Technol.* (SERT) pp. 259-67.

Dean, J. G., Bosqui, F. L. and Lanouette, K. H. (1972). Removing heavy metals from waste water. *Env. Sci. & Tech.* **6(6)**:518-522.

Dennis, J. K. and Such, T. E. (1993). Nickel and chromium plating. Cambridge, England. Woodhead Publishing Ltd.

Dennis, J. K. and Such, T. E. (1993). Nickel and chromium plating 3rd edition. Cambridge, England. Woodhead Publishing Ltd.

Ernst, R., Knoedler, A., Disam, A. and Kawase, H. (1969). Effect of electrolyte additives on the processes in the phase boundary layer in nickel deposition. *Forschungsinst., Edelmetal. und Metallchem., Schwaebisch Gmuend, Ger. Metalloberflaeche*. **23(10)**: 293-302.

Ernst, W. H. O., Verkleij, J. A. C. and Schat, H. (1992). Metal tolerance in plants. *Acta. Bot. Neerl.* **41**(3): 229-248.

Gabbrielli, R., Gremigni, P., Bonzi Morassi, L., Pandolfini, T. and Medeghini, P. (1997). Some aspects of Ni tolerance in *Alyssum bertolonii* Desv.: strategies of metal distribution and accumulation. In Jaffré, T., Reeves, R. D. and Becquer, T. (Eds.) Écologie des milieux sur roches ultramafiques et sur sols metallifères. New Caledonia. Documents Scientifiques et Techniques, ORSTOM. pp. 225-227.

Gabbrielli, R., Pandolfini, T., Vergnano, O. and Palandri, M. R. (1990). Comparison of two serpentine species with different nickel tolerance strategies. *Plant Soil.* **122**: 271-277.

Gilliam, T. M. and Canon, R. M. (1980). Removal of metals from coal ash. AIAA proceedings 15th intersociety energy conversion engineering conference, Seattle, Washington 1980. The American Institute of Aeronautics and Astronautics. pp. 970-977.

Hoare, J. P. (1987). Boric acid as a catalyst in nickel plating solutions. *J. Electrochem. Soc.* **134(12)**: 3102-3103

Horner, J. (1992). Electroplating. In Howe-Grant, M. and Kraschwitz, J. (Eds.) Encyclopedia of chemical technology 4th edition. USA. John Wiley and Sons Inc.

Jaffré, T., Brooks, R. R., Lee, J. and Reeves, R. D. (1976) *Sebertia acuminata*: a hyperaccumulator of nickel from New Caledonia. *Science* **193**: 579-580.

Karwars, C. and Hepel, T. (1988). Influence of boric acid on electrodeposition and stripping of Ni-Zn alloys. *J. Electrochem. Soc.* **135(4)**: 839-844.

Keynes, M. (1976). Mineral deposits/ prepared by an Open University course team. Open University Press.

Krämer, U., Cotter-Howells, J. D., Charnock, J. M., Baker, A. J. M. and Smith, J. A. C. (1996). Free histidine as a metal chelator in plants that accumulate metal. *Nature* **379**: 635-638.

Kumer, P. B. A. N., Dushenkov, S., Salt, D. E. and Raskin, I. (1994) Crop brassicas and phytoremediation – a novel environmental technology. *Cruciferae Newsletter* **16**: 18-19.

Lee, J., Reeves, R. D., Brooks, R. R. and Jaffré, T. (1977). Isolation and identification of a citrato-complex of nickel from nickel-accumulating plants. *Phytochemistry*. **16**: 1503-1505.

Lee, J., Reeves, R. D., Brooks, R. R. and Jaffré, T. (1978). The relation between nickel and citric acid in some nickel-accumulating plants. *Phytochemistry*. **17**: 1033-1035.

Liu, G. (1989). Discussion on conductive salts for dull nickel plating caused by the wrong additive. *Diandu Yu Huanbao* **9(6)**: 39-40.

Lukashev, E. A., Selivanova, N. M. and Orlova, V. T. (1979). Study of potassium and nickel double sulfates. *Zh. Neorg. Khim.* **24(4)**:964-972.

McAnally, S., Benefield, L. and Reed, R. B. (1984). Nickel removal from a synthetic nickel-plating wastewater using sulfide and carbonate for precipitation and coprecipitation. *Sep. Sci. and Tech.* **19(2-3)**:191-217.

Minguzzi, C. and Vergnano, O. (1948). Il contenuto di nichel nelle ceneri di *Alyssum bertolonii* Desv. *Atti Soc. Toscana Sci. Nat.* **55**: 49-77

Murthy, M., Nagarajan, G. S., Weidner, J. W. and Van Zee, J. W. (1996). A model for the galvanostatic deposition of nickel hydroxide. *J. Electrochem. Soc.* **143(7)**: 2319-2327.

Nicks, L. J. and Chambers, M. F. (1995). Farming for metals? *Min. Environ. Manage.* **Sep**: 15-18.

Nozima, S., Nada, T., Itow, J. and Suzuki, K. (1974). Purified nickel sulfate from an impure double salt of nickel. Patent: JP 72-117996 19721127.

Oldham, K. B. and Myland, J. C. (1994). Fundamentals of electrochemical science. Toronto, Canada. Academic Press, Inc.

Osmond, C. B. (1976). Ion absorption and carbon metabolism in cells of higher plants. In Lüttge, U. and Pitman, M. G. (Eds.) Encyclopedia of plant physiology (new series), vol. 2A. Berlin. Springer-Verlag. pp. 347-372.

Oxford Concise Science Dictionary. (1997). Oxford, England. Oxford University Press

Rajcevic, H. P. (1990). A hydrometallurgical process for the treatment of industrial wastes. *Plating and Surface Finishing.* **July**: 22-25.

Raskin, I., Kumar, N., Dushenkov, S. and Salt, D. E. (1994). Bioconcentration of heavy metals by plants. *Current Opinion in Biotechnology.* **5**: 285-290.

Reeves, R. D. (1992). Hyperaccumulation of nickel by serpentine plants. In Baker, A. J. M., Proctor, J. and Reeves, R. D. (Eds.) The vegetation of ultramafic (serpentine) soils. United kingdom. Intercept Ltd. pp. 253-277.

Reeves, R. D. and Baker, A. J. M. (2000). Metal-accumulating plants. In Raskin, I. and Ensley, B. D. (Eds.) Phytoremediation of toxic metals: using plants to clean up the environment. John Wiley & Sons Inc., pp. 193-229.

Robinson, A. K. (1980). Sulfide precipitation of heavy metals. Cincinnati, USA. USEPA: 600/2-80-139.

Robinson, B. H. (1997). The phytoextraction of heavy metals from metalliferous soils. PhD Thesis, Massey University.

Robinson, B. H., Chiarucci, A., Brooks, R. R., Petit, D., Kirkman, J. H., Gregg, P. E. H. and De Dominicis, V. (1997). The nickel hyperaccumulator plant *Alyssum bertolonii* as a potential agent for phytoremediation and phytomining nickel. *J. Geochem. Explor.* **59**: 75-86.

Schlegel, H. G., Cosson, J–P. and Baker, A. J. M. (1991). Nickel-hyperaccumulating plants provide a niche for nickel-resistant bacteria. *Bot. Acta* **104**: 18-25.

Singh, N. B., Partlow, W. D., Strauch, S., Albert, M., Jackovitz, J. F. and Coffey, D. W. (1998). Crystals for ultraviolet light filters. Patent: US 96-709398 19960830.

Thurman, D. A. and Rankin, J. L. (1982). The role of organic acids in zinc tolerance in *Deschampsia caespitosa*. *New Phytol.* **91**: 629-635.

Tundermann, J. H., Tien, J. K. and Howsen, T. E. (1992). Nickel and nickel alloys. In Howe-Grant, M. and Krashwitz, J. J. (Eds.) Encyclopaedia of chemical technology, 4th edition. John Wiley & Sons Inc., US.

United States Environmental Protection Agency (1993). Toxics release inventory. Washington D. C. USEPA/745/R-93/003.

Vázquez, M. D., Poschenrieder, J., Barceló, J., Baker, A. J. M., Hatton, P. and Cope, G. H. (1994). Compartmentation of zinc in roots and leaves of the zinc hyperaccumulator *Thlaspi caerulescens*. *Bot. Acta.* **107**: 243-250.

Vergnano Gambi, O., Gabbrielli, R. and Pancaro, L. (1982). Nickel, chromium and cobalt in plants from Italian serpentine areas. *Acta Oecol. Plant.* **3**: 291-306.