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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.

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