Phytomining: a win-win partnership between agronomy and chemical engineering to recycle metals dispersed in soil. GPE

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PHYTOMINING: A WIN-WIN PARTNERSHIP BETWEEN AGRONOMY AND CHEMICAL ENGINEERING TO RECYCLE METALS DISPERSED IN SOILS

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Abstract. Huge areas in the world are covered by soils containing high contents of metal. Phytomining aims at recovering these metals by growing hyperaccumulating plants and treating the metal-rich biomass by pyrometallurgical or hydrometallurgical processes. This contribution is an overview of the results we have obtained for several years in Ni phytomining. Hyperaccumulating plants, *Alyssum murale*, are grown in the Balkans (Albania) and high Ni yields are reached: 100 kg Ni per ha. Once harvested and dried, *A. murale* biomass is incinerated and the ashes are treated by a hydrometallurgical process that we have designed and patented to produce a high value added salt: sulfate and ammonium nickel double salt hexahydrate, used for electrolytic surface treatment. The process steps are described and the main results presented. Our results have demonstrated the feasibility of the synthesis of this nickel double salt after phytoextraction. This process is currently up-scaled to the pilot scale. A start-up project has been launched to develop this activity with two directions: the production of Ni salt and consulting activity for phytoextraction.

Key-words. phytoextraction, nickel, hyperaccumulating plant, hydrometallurgy, secondary resources

INTRODUCTION

Soils and wastes with high metal content are a source of compounds of industrial interest. But metal concentrations are generally too low for conventional mining and metallurgical recovery. In these conditions, phytomining offers a great interest. Phytomining is based on the properties of some plants, called hyperaccumulating plants or hyperaccumulators: these plants are able not only to tolerate but also to accumulate metals contained in soils and transfer them from their roots to their aerial parts. Metals are then extracted from soils and concentrated in the biomass. Biomass can be treated by pyrometallurgical or hydrometallurgical processes to recover metals or to produce high added value metal salts.

Nickel is the most hyperaccumulated metal, *ca* 400 plant species able to hyperaccumulate Ni have been reported worldwide[1]. These plants easily contain 10 g Ni kg^{-1} (1 wt %) in their tissues[2] provided they were grown on soils having a high enough content of available Ni[3,4]. Among them, 45 belong to the genus *Alyssum* (e.g. *Alyssum murale*, *Alyssum bertolonii*, *etc.*). Besides, huge areas of ultramafic rocks, naturally rich in metals such as Ni, are present in numerous places around the world (e.g. Mediterranean countries, New Caledonia, Canada, Brazil, Cuba, The United States)[5,6,7]. These serpentine soils contain 1 to 7 g Ni kg^{-1}; they have a low fertility and are generally abandoned by agriculture. For these lands, "freezing" has been so far the most economically viable management solution, although it is unsatisfactory from health and environmental aspects. Then, an agronomic approach aiming at growing Ni hyperaccumulators has a great interest for such regions, since it gives a value to these abandoned soils, and gradually decreases their toxicity and increases their fertility. The feasibility of growing Ni hyperaccumulators to reach high yields of Ni have been demonstrated[8,9]. Field trials that we have performed in Albania have shown that was possible to produce 1 t dry biomass per ha, corresponding to more than 110 kg Ni[9].

Once harvested and dried, biomass can be incinerated at moderate temperature, around 600°C, and the produced ashes can be considered as a bio-ore, containing 20 wt % Ni. Ashes can be treated by pyrometallurgical or hydrometallurgical processes to produce metal or high added value products such as catalysts or nickel salts[13-16] (Fig. 1).

Ni recycling has an economic interest since Ni has a relatively high value, despite it has recently dropped (*ca* 14 000 USD t^{-1}, London Metal Exchange); the value of Ni salts drastically increase with their purity.

This contribution aims at presenting an overview of the research we have been performing in this area for a few years, concerning plant growing (briefly) and the process we have designed to obtain a high purity Ni salt, sulfate and ammonium Ni double salt hexahydrate. This salt is used for electrolytic surface treatment and chemical synthesis.

Figure 1. Schematic representation of Ni phytomining to produce the double salt

MATERIALS AND METHODS

Ni phytoextraction by native plants of the Balkans

Ultramafic outcrops are widespread in the Balkans. Our work has focused mainly on *Alyssum murale*[2,7,9] but we have also investigated other species from the Brassicaceae: *Leptoplax emarginata* (Boiss.) and *Bornmuellera tymphaea* (Hausskn.). *L. emarginata*, *B. tymphea*, *A. murale*, *A. markgrafii* and *A. bertolonii* were collected in Albania and in Greece[2]. All these species are able to accumulate in average more than 10 g Ni per kg of dry biomass considering the whole plants (stem, flowers and leaves)[2]. The highest concentrations were recorded in the leaves of *L. emarginata* where they reached more than 30 g Ni per kg of dry biomass.

Small quantities of *L. emarginata* and *B. tymphea* were collected from spots where they have grown spontaneously. On the contrary, we have used high quantities of *A. murale* grown in Albania (1 t of biomass per year) in Pojskë (Pogradec, East of Albania), in the region of Pogradec, latitude 40°59'55.28"N; longitude 20°38'0,92"E. Plants were harvested at the middle of the flowering stage, when the Ni content in the aerial part is the highest. These harvests were possible after a plant cultivation following the pioneering work on phytoextraction agronomy[9,10].

Sampling, preparation and incineration of Ni hyperaccumulators

Plants were collected by hand, sun dried, sent from Pogradec to Nancy and kept at ambient temperature (20°C). Flowers, stems, seeds and leaves were separated and oven dried at 70°C for 24 h; the dry plant parts were weighed crushed and finely ground (Prep'line 850 grinder). Ni content was measured in each part of the plants separately and in average[2,13] . Ground plants were incinerated in a furnace (model 1400 furnace, Barnstead Thermolyne). The best conditions have been determined by trying two temperatures. A temperature of 550°C (and more generally up to 700°C) is well adapted, since it allows the destruction of organic matter but Ni is not volatilized.

Chemical analysis

Solid matrices (crushed plants and ashes) were first mineralized: aliquots (0.1 – 0.2 g) were contacted with 8.5 mL HNO_3 (≥ 65%) and 1.5 mL H_2O_2 (50%) before microwave digestion (Milestone StartD Digestion System). Then all the solutions were analysed by plasma emission spectroscopy (ICP-AES, Thermo iCAP 6000 Series ICP scientific Emission Spectrometer), a multi-element solution (SCP sciences) being used for standardization. Ashes and salt were characterised by XRD.

Hydrometallurgical process

The process is described in Figure 2. After incineration, ashes are washed with water. Then Ni is solubilised with 1.9 M sulphuric acid (150 g ashes L^{-1}). The filtered leachate is neutralized with sodium hydroxide 5 M to reach a pH of 5. Water is evaporated at 100°C to reduce the volume by a factor of 3. The cooled supernatant is pumped, the solid residue is washed with water. Ni is recovered by crystallisation with ammonium sulfate at 0°C. This recovery is based on the low solubility of ammonium disulfate salt $Ni(NH_4)_2(SO_4)_2.6H_2O$ at 0°C which is 1.4 g salt per 100 g of water.

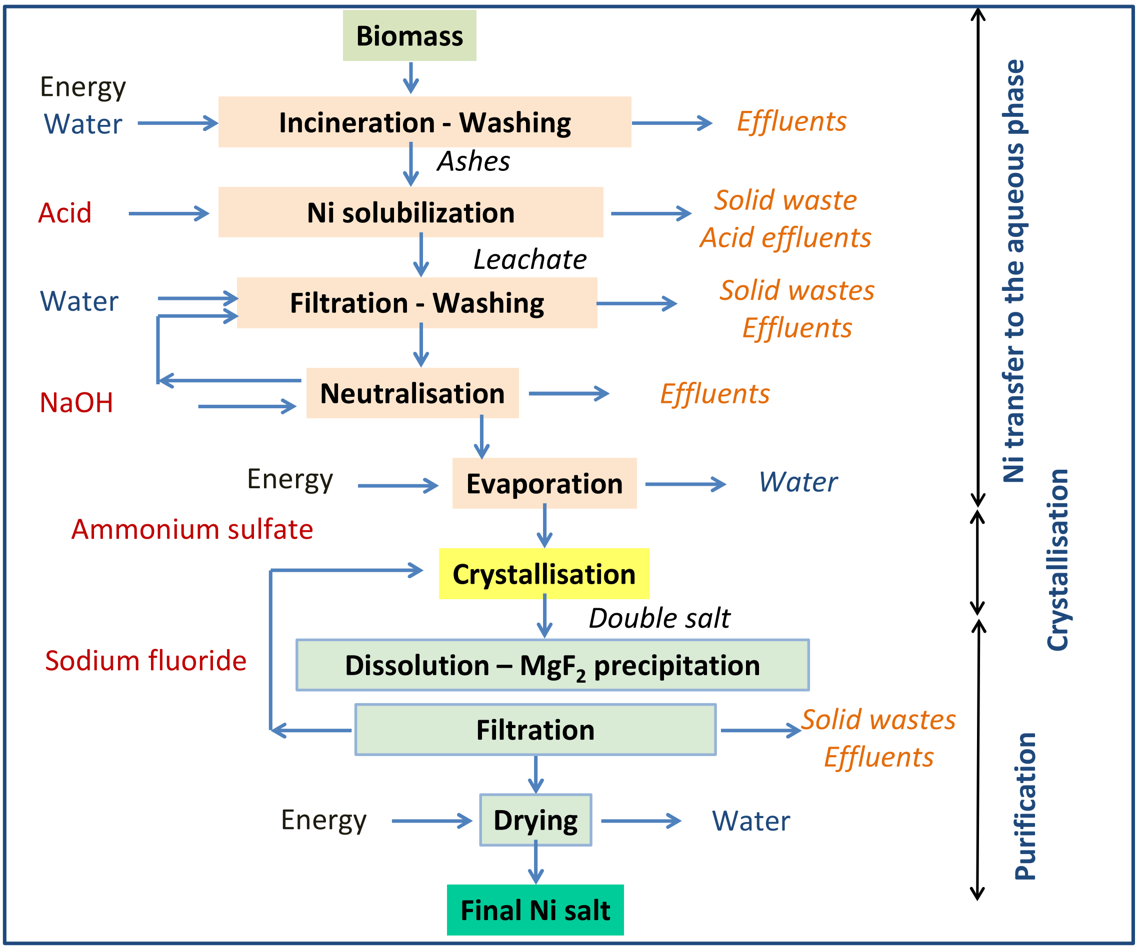

Figure 2. Presentation of the hydrometallurgical process to obtain the Ni double salt

In order to reach a high purity salt, the crystallized salt is dissolved in water and a crystallisation step was done with sodium fluoride to precipitate magnesium fluoride to remove magnesium in excess. The MgF_2 residue was separated and the double salt crystallisation was performed a second time at 0°C. All the details concerning the process are given in reference[13].

RESULTS

Metal contents in the plants and ashes

In all the plants that were used for the process, the overall Ni content was about 10 g Ni per kg of dry biomass. In the results obtained by Barbaroux[13,16], Ni concentration was 9.7 g Ni per kg of dry biomass. The other major elements were Ca, K and Mg at respective concentrations of 8.4, 7.6 and 3.9 g kg^{-1}. Trace elements were present at very concentrations[2,13,16]. Incineration at 550°C reduced the mass with a factor of 6.6 and concentrates all the elements. Metal mass balance between dry plants and ashes were met, showing there was no metal loss[2].

Ni double salt production

The ash washing step with water enabled us to reduce significantly the concentration of potassium in the ashes. The acid leaching has been tested in different conditions of acid concentrations, temperature and duration. With the concentration given here, the totality of Ni was transferred from the ashes to the solution. The leachate contained 10.16 g Ni L^{-1} but the concentrations of the major elements were relatively high as well: 0.58 g Ca L^{-}1, 1.16 g K L^{-1} and 5.98 g Mg L^{-1}. Non negligible concentrations of Fe (0.61 g L^{-1}), Al (0.19 g L^{-1}) and Co (7.51 mg L^{-1}) were also recorded.

The pH adjustment and the evaporation step maintained high concentrations of Ni, Ca and Mg while Fe concentration was significantly lowered because of iron hydroxide precipitation.

The first crystallization with ammonium sulfate led to recovery rates of 64.7% for Ni, 41.3% for Mg, 72.0% for K and only 16.9% for Ca. Then crystallisation was not specific to Ni. For this reason, a further step was added to remove Mg. The precipitation step with sodium fluoride enabled us to remove a very high fraction of Mg: after removing the MgF_2 residue, the Ni concentration in the supernatant was 9.1 g L^{-1} while Mg concentration had dropped to 0.04 g L^{-1}.

The second crystallization step with ammonium sulfate led to the salt where the concentrations were 132 g Ni kg^{-1}, 2.3 g K kg^{-1}, 0.70 g Mg kg^{-1}, while the other elements were at concentrations lower than 1 g kg^{-1}.

The XRD patterns of the salts after the second crystallisation step with ammonium sulfate is shown in Figure 3.

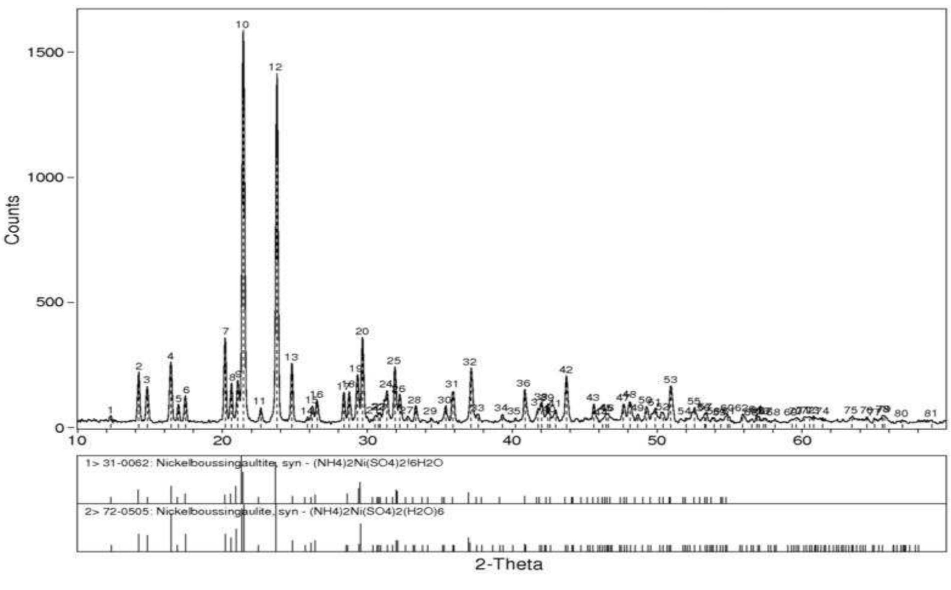

Figure 3. XRD pattern of the purified Ni double salt

DISCUSSION

These results have shown the feasibility of the production of the sulfate and ammonium nickel double salt hexahydrate from the biomass of the hyperaccumulating plant *Alyssum murale.* In this overview, the process has not been yet optimised. But even in these conditions, we have performed a detailed economic study and it was proved that the process led to a high benefit.

Since the patent deposition, further work has been done on the hydrometallurgical process in two main directions. The first one was to optimize the process and increase salt purity. As was shown in the results, the most difficult steps are the removal of K, Ca and above all Mg. We have found new pathways to increase the removal of these elements. For instance, a higher amount of K can be eliminated during ashes washing. In the same way, progress has been made in Mg removal, avoiding the use of sodium fluoride. We are also working on the minimisation of effluent and solid waste release, with the idea of recycling at each step. In these conditions, the process is currently optimised and the results are currently in acquisition and finalisation. The second direction was upscaling. A pilot has been designed and is currently in construction to prove the feasibility of the process at a higher scale in the objective to go to the industrialisation. Besides, the economic study is being refined to take into account the changes in the process. A life cycle assessment is beginning to quantify the impact of the process on the environment.

Actually, this presentation has most focused on the hydrometallurgical process but in all our studies, we consider the global chain, which combines the phytoextraction and the hydrometallurgical steps. As a matter of fact, the cultivation of hyperaccumulating plants in regions covered by serpentine soils offers many advantages. It gives a new value to these lands characterized by a low fertility and provides a new income to the farmers. Since it is non-destructive, metal removal would improve soil quality and make it useful for further food production use. Also, it would preserve and develop other ecosystem services from low value lands (e.g. regulation services: soil quality; carbon storage; cultural services: aesthetic, social stability). Apart from natural soils, phytoextraction can also be applied to the decontamination of soils that have been contaminated by metals after industrial or mining activities. It should be successfully applied to the revegetation of sterile mine heaps.

CONCLUSIONS AND PERSPECTIVES

In this contribution, we have given an example of the potentialities of phytomining through the example of the production of the nickel double salt from the biomass of *Alyssum murale*, native species of the Balkans. But many other perspectives can be considered. At first, many other plants of other regions of the world, e.g. under tropical climate (Cuba, Brazil, South China, etc.) should give very interesting results regarding phytomining. Plants can be selected to attain very high Ni extraction rates.

Besides, we could envisage other Ni products. The production of Ni metal has been shown feasible but other Ni salts of high added value could be produced as well.

Then, other elements than Ni could be of interest for phytomining, provided that (1) hyperaccumulating plants exist (2) they can be grown to attain sufficient rates, that means a high concentration of the element in the biomass and high biomass production and (3) the synthesis of high added value products is feasible. For instance, hyperaccumulating plants are known for Zn, Cd, As, Cu and some other metals, the challenge would be the extraction of other elements. This method would enable us to extract valuable elements from secondary resources in which they are dispersed.

In 2013, we have just launched a start-up project, accompanied by the "Incubateur Lorrain" of Nancy University. We are examining the possibility of creating a company, with two activities (1) the production of Ni salts by phytomining and (2) consulting for phytoextraction. A market analysis is being conducted to evaluate the interest of this creation.

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