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# Increasing purity of ammonium nickel sulfate hexahydrate and production sustainability in a nickel phytomining process

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## ABSTRACT

Phytomining, now called agromining, consists of growing hyperaccumulator plants in order to farm metals and recover them from the biomass. This technology enables us to extract metals from secondary resources (e.g. metal containing-soils, mineral wastes, polluted soils) and manufacture high-value products. It has proved feasible for nickel, since more than 400 hyperaccumulators have been identified worldwide, able to accumulate at least 1% Ni in their tissues. Moreover, Ni is a target metal with a relatively high economic value.

We have recently designed and patented a method for the synthesis of a nickel salt, ammonium nickel sulfate hexahydrate (ANSH:  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ), from the biomass of the hyperaccumulator plant *Alyssum murale*, grown in the Balkans. In this contribution, the process has been improved in order to save water, energy and chemicals, while producing a high purity salt. The biomass is dried and ashed, potassium is removed by washing ash with pure water following a cross-current pathway, nickel is extracted by acid leaching (2M  $\text{H}_2\text{SO}_4$ , 95 °C, 2 h, mass fraction of 10%). The leachate is neutralized by  $\text{Ca}(\text{OH})_2$  to reach a pH of 4–5 and magnesium is removed by precipitating  $\text{MgF}_2$  after addition of NaF. Then volume is reduced by evaporation and ANSH crystallization is run at 2 °C for 4 h. The crystals are dissolved and a second crystallization is run. The final ANSH was characterized by combined techniques (ICP-AES, XRD and gravimetric analysis), and the purity was  $99.1 \pm 0.2\%$ .

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## 1. Introduction

Phytomining consists of growing metal hyperaccumulator plants in order to farm metals and recover them from biomass (Chaney et al.,

2007). Hyperaccumulator plants accumulate high concentrations of metals in their aerial parts (Jaffre et al., 1976; Baker and Brooks, 1989; Anderson et al., 1999; van der Ent et al., 2012). They can be used as miners to extract metals from secondary resources not suitable for

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mining, like ultramafic soils, mineral wastes, polluted soils and so on. Among the metals that can be hyperaccumulated, nickel (Ni) has a particular interest since more than 400 nickel hyperaccumulators have been identified worldwide, and Ni has a relatively high economic value. Ni phytomining has gained growing interest in the last years and the term “agromining” has even been proposed (van der Ent et al., 2015).

Extensive literature is available on Ni hyperaccumulator plants, their identification, ecophysiology, and the investigation of metal speciation in the plant tissues (Baker et al., 2000; Montargès-Pelletier et al., 2008). Also, their agronomy has been widely investigated, in order to reach high yields of plants and therefore of metals (Chaney et al., 2005; Bani et al., 2009; Tang et al., 2012; Bhargava et al., 2012; Bani et al., 2015). Field experiments carried out in Albania with the plant *Alyssum murale* enable us to obtain ca 120 kg Ni per hectare (Bani et al., 2015).

The feasibility of extracting metals directly from hyperaccumulators by hydrothermal processes has been demonstrated (Le Clercq et al., 2001; Yang et al., 2009a, 2009b). However, plants are most often incinerated to obtain ash, in which Ni is ten to twenty times more concentrated than in the plant (Zhang et al., 2014). Actually, ash can be considered as a real bio-ore. This bio-ore can be directly introduced into a smelter to produce Ni metal by pyro-metallurgy (Chaney et al., 2007). Also several contributions have proved that this bio-ore could be processed by hydrometallurgy, to produce Ni metal (Tennakone et al., 2007; Barbaroux et al., 2011), catalysts for organic chemistry (Losfeld et al., 2012a, 2012b) or high-value salts for electroplating (Barbaroux, 2010; Barbaroux et al., 2012; Mercier et al., 2012). We have designed and patented a hydrometallurgical process for producing ammonium nickel sulfate hexahydrate (ANSH) salt from *A. murale* ashes (Barbaroux et al., 2012; Mercier et al., 2012; Barbaroux, 2010). This process consists of the following stages: (i) ash is washed with water to remove potassium; (ii) the washed ash is leached with a sulfuric acid solution (1.9 M, 150 g ash L<sup>-1</sup>, 95 °C, 2 h), the Ni-rich leachate also contains magnesium, calcium and iron; (iii) the leachate pH is increased to 5.0 by sodium hydroxide addition and the liquid is partly evaporated, iron hydroxide is precipitated; (iv) ANSH crystallization is performed by addition of ammonium sulfate (2 °C, 6 h); (v) ANSH is purified by salt dissolution, precipitation of magnesium fluoride after sodium fluoride addition and ANSH is recrystallized. ANSH purity was 88.8%.

The aim of the present work is to improve this process, in order to save water, chemicals and energy. Each stage of the process was re-visited and significant improvements are proposed to optimize the process and produce a salt of higher purity.

## 2. Materials and methods

### 2.1. Sampling plants and ashes

*A. murale* was harvested in Albania on an ultramafic soil (Pojské: 40°59'55"N; 20°38'55"E) in June, 2012 (750 kg). Plants were collected manually, air-dried and stored. They were ground to 2 mm in batches of 40 kg with an industrial grinder and kept at an ambient temperature of 20 °C ± 2 °C. The ground plants were burnt on a stainless steel plate (15 cm × 25 cm) in a furnace (model 1400 furnace, Barnstead Thermolyne) at 550 °C for 2 h. The ashes were stored in a sealed container.

### 2.2. Chemicals

Sulfuric acid (95–97%), ethanol (99.8%), ammonium hydroxide (25% NH<sub>3</sub>), ANSH salt (99.999%) (salt #1) and ANSH salt (98%) (salt #2) were provided by Sigma-Aldrich, ammonium sulfate (99.5%) and dimethylglyoxime (H<sub>2</sub>DMG) (99.0%) by Fluka, sodium hydroxide (99% by Merck), calcium hydroxide (96% by BDH Prolabo and sodium fluoride NaF (analytical reagent grade) by Fisher Scientific.

### 2.3. Potassium removal from the ash

Preliminary experiments consisted of washing the raw ash with deionized water under mechanical stirring with a three-blade turbine (Heidolph Bioblock Scientific). Three mass fractions of ash (10, 15 and 20%) and three rotation speeds (500, 1000 and 2000 rpm) were tested. Supernatant samples (1 mL) were taken at the beginning of the agitation and after 1, 5, 10, and 15 min.

The first washing method (M#1) consisted of washing the ash twice, each time with deionized water with an intermediate filtration stage. All the filtrations were performed on a set-up composed of a Büchner funnel (Labbox) and a vacuum pump (Fischer Scientific), using ashless filter papers (Sartorius, 391). The ash was successively called A<sub>10</sub> (raw ash), A<sub>11</sub> (after the 1st stage) and A<sub>12</sub> (at the end). The filtrates were called PE<sub>11</sub> and PE<sub>12</sub>.

The second method (M#2), a so-called cross-current method, has been designed to minimize water consumption. It consisted of 3 following steps (Fig. 1): a 1st batch of raw ash A<sub>10</sub> was washed as in M#1. The second batch of raw ash A<sub>20</sub> was washed with PE<sub>12</sub> to give A<sub>21</sub> and PE<sub>21</sub> and ash A<sub>21</sub> was washed with deionized water to give A<sub>22</sub> and PE<sub>22</sub>. The third batch was a repetition of the second one: raw ash A<sub>30</sub> was washed with PE<sub>22</sub> to give A<sub>31</sub> and PE<sub>31</sub> then A<sub>31</sub> was washed with deionized water to give A<sub>32</sub> and PE<sub>32</sub>. The elemental composition of each solution was measured by ICP-AES.

### 2.4. Acid leaching

Acid leaching was conducted by mixing 5 or 10 g washed ash with H<sub>2</sub>SO<sub>4</sub> (1, 2, and 3 M) at a mass fraction of 10%. Mixing was performed under magnetic stirring on a heating plate (Fisherbrand) at 70 and 95 °C for 1–4 h. The temperature was monitored with a silicon temperature sensor (Thermometer HD860). To compensate for water evaporation, deionized water was added every 20 min to keep the total volume constant. Samples (1 mL) were withdrawn after 1, 2, 3 and 4 h, filtered and analyzed.

### 2.5. Purification of the Ni-rich leachate

The acid leachate L<sub>1</sub> was neutralized by adding, drop by drop, a suspension of Ca(OH)<sub>2</sub> (10 or 20 wt%) under magnetic agitation. This reaction was conducted for 1 h until pH reached 4–5 (pH meter Mettler Toledo, DG 111-SC). The suspension was filtered and the leachate was called L<sub>2</sub>.

To precipitate MgF<sub>2</sub>, a mass of NaF corresponding to an excess of 10% was added under magnetic stirring at room temperature (20 °C) for 30 min to dissolve all NaF. The suspension was filtered and the filtrate L<sub>3</sub> brought to 100 °C on a heating plate to evaporate water. Volume was reduced by a factor of 2–3, and the final solution was called L<sub>4</sub>.

### 2.6. Crystallization

To crystallize ANSH, a mass of ammonium sulfate corresponding to an excess of 20% was added to L<sub>4</sub>. The suspension was heated at 60 °C to dissolve the solid and kept at room temperature. Crystallization was performed in a jacketed reactor under magnetic stirring. The cooling fluid (ASCAGEL MEG: monoethylene glycol based antifreeze) was maintained at 0 °C by a cooling bath (Bioblock Scientific). The suspension was filtered. Crystals were washed with 5–10 mL of cold deionized

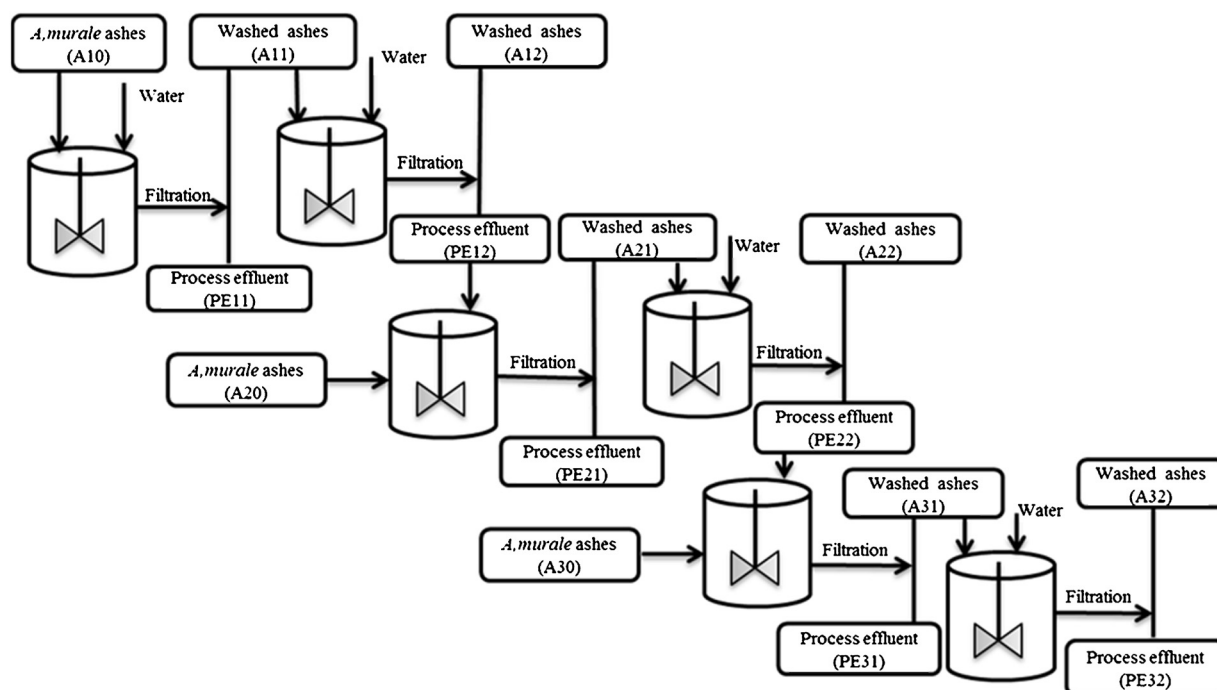


Fig. 1 – Process diagram of simulating countercurrent washing.

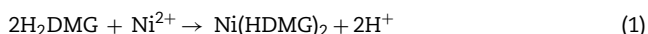
water (<5 °C). To increase crystal purity, a second crystallization was performed at 0 °C, after having dissolved the crystals in deionized water; the suspension was filtered.

## 2.7. Chemical analysis and characterizations

Biomass and ashes were analyzed by ICP-AES after mineralization and by X-ray diffraction (XRD) with the procedures already described (Zhang et al., 2014). Solutions were analyzed by ICP-AES (Zhang et al., 2014). Crystals were characterized by ICP-AES after dissolution, XRD and gravimetric analysis. For ICP-AES analysis, solutions were prepared by dissolving 0.1 g of ANSH crystals into 200 mL of deionized water. Reference solutions were prepared in the same condition with the commercial salts, salt#1 and salt #2.

XRD analysis of crystals was carried out on (Rigaku–Miniflex II diffractometer), with a scan range from 10° to 80° at a scanning speed of 1.0° min<sup>-1</sup>. Cu K $\alpha$  radiation was used with 30 kV and 15 mA.

Gravimetric analysis consisted of performing the precipitation of Ni<sup>2+</sup> with dimethylglyoxime (H<sub>2</sub>DMG) following the reaction given in Eq. (1):



Ca 0.5–0.6 g of ANSH were precisely weighed, put in a 250 mL beaker, dissolved in 50 mL of deionized water at 60 °C. The reagent, 50 mL of ethanol containing 10 g L<sup>-1</sup> of H<sub>2</sub>DMG was added, and concentrated ammonia (25% NH<sub>3</sub>) was added, drop by drop, to reach pH 9. The red complex of Ni(HDMG)<sub>2</sub> appeared. The reaction was run for 20–30 min under magnetic stirring and the suspension was filtered. The solid Ni(HDMG)<sub>2</sub> was washed with deionized water and dried at 105 °C in the oven until it reached a constant weight.

All the characterizations were done in triplicate, allowing calculating standard deviation for each result.

## 3. Results and discussion

### 3.1. Concentrations of the major elements in the ash

Preparations of *A. murale* and ash production have been previously detailed as well as plant and ash characterization (Zhang et al., 2014). The major elements present in the plant have been concentrated in the ash to reach 12.7, 12.5, 10.7, 3.0 and 0.5 wt% for Ni, Ca, K, Mg and Fe respectively. These values were consistent with the ones previously obtained (Barbaroux et al., 2012; Zhang et al., 2014).

### 3.2. Potassium removal from the ash

Two parameters were tested to improve potassium removal: the solid fraction (10, 15, 20%) and the stirring speed (500, 1000, 2000 rpm). The highest solid fraction was 20% since, after that, it is difficult to immerse the ash. K removal was not significantly affected by both parameters, with a removal rate of 63.3 ± 5.4% after a single washing step. This means that the dissolution of potassium species is not limited by solubility or by diffusion mechanisms.

The comparison of XRD analysis of the raw and washed ashes (Fig. 2a and b) clearly shows the disappearance after washing of the peaks marked 1, 2 and 3 corresponding to K<sub>2</sub>CO<sub>3</sub>. Final concentrations of K (<20 g L<sup>-1</sup>) were significantly lower than K<sub>2</sub>CO<sub>3</sub> aqueous solubility (110 g in 100 g water at 20 °C (Linke, 1965)), which proves that K removal was not limited by solubility.

Method M#1 was tested with successive washing steps. The second and third ones enable us to remove respectively 12.9 ± 1.2% and ca 3%. Despite additional washing steps, it is not possible to eliminate more than 80%. This means that other K compounds are present in the ashes. Two washing steps are a good compromise with a total removal of 76.1 ± 6.9%. Thus, K concentration in the ash was reduced from 101.1 g kg<sup>-1</sup> in A<sub>10</sub> to 23.7 g kg<sup>-1</sup> in A<sub>12</sub>, and K concentration in

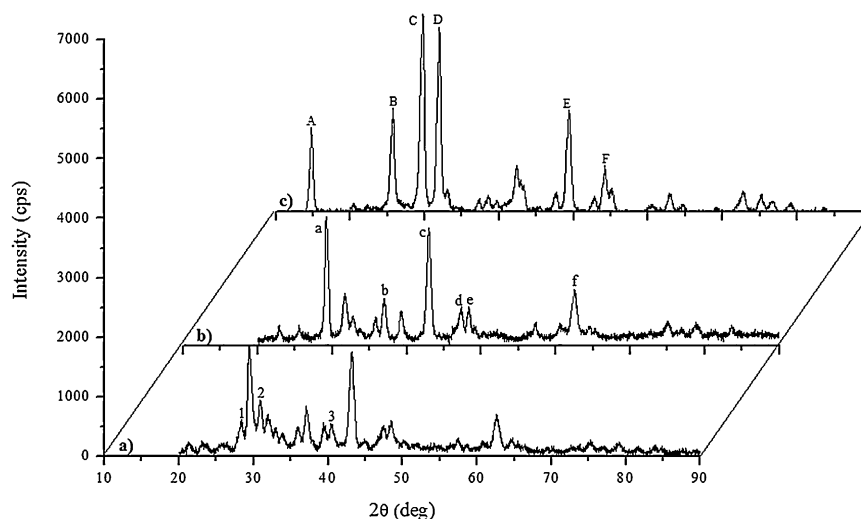


Fig. 2 – X-ray diffraction patterns of (a) raw ashes ( $A_{10}$ ), ashes (b) after washing ( $A_{12}$ ) and (c) after acidic leaching ( $SW_1$ ).

Table 1 – Mass balance of the whole process.

	Recovery (%)				
	K	Ca	Mg	Ni	Fe
Process effluent 1 ( $PE_1$ )	$79.5 \pm 4.2$	$0.2 \pm 0.0$	$2.3 \pm 0.3$	$0.5 \pm 0.0$	$0.3 \pm 0.2$
Process effluent 1 ( $PE_2$ )	$10.1 \pm 2.0$	$1.8 \pm 0.0$	$1.4 \pm 0.2$	$0.0 \pm 0.0$	$0.0 \pm 0.0$
Acid leachate ( $L_1$ )	$17.6 \pm 1.9$	$6.2 \pm 1.2$	$105.8 \pm 0.6$	$97.8 \pm 0.5$	$96.4 \pm 1.2$
Solid waste ( $SW_1$ )	$0.8 \pm 0.3$	$87.9 \pm 3.5$	$2.4 \pm 1.0$	$11.7 \pm 0.8$	$18.2 \pm 1.0$
Treated leachate ( $L_2$ )	$16.1 \pm 1.5$	$9.2 \pm 1.8$	$110.2 \pm 3.7$	$97.1 \pm 0.7$	$2.3 \pm 0.4$
Solid waste ( $SW_2$ )	$1.4 \pm 0.5$	$160.5 \pm 8.9$	$4.1 \pm 1.6$	$4.5 \pm 1.2$	$95.5 \pm 5.3$
Treated leachate ( $L_3$ )	$17.8 \pm 1.8$	$1.5 \pm 0.3$	$22.5 \pm 4.1$	$93.5 \pm 1.9$	$2.4 \pm 1.0$
Solid waste ( $SW_3$ )	$0.9 \pm 0.2$	$8.5 \pm 4.1$	$84.8 \pm 6.0$	$1.1 \pm 0.0$	$6.5 \pm 1.6$
After evaporation ( $L_4$ )	$16.0 \pm 1.3$	$1.3 \pm 0.3$	$15.0 \pm 5.0$	$93.5 \pm 3.3$	$0.3 \pm 0.2$
Crystals	$7.2 \pm 0.6$	$0.0 \pm 0.0$	$3.7 \pm 1.3$	$64.1 \pm 1.4$	$0.0 \pm 0.0$
Effluents	$9.9 \pm 2.8$	$1.2 \pm 0.3$	$10.7 \pm 3.7$	$26.8 \pm 0.9$	$0.2 \pm 0.1$

the effluent ( $PE_1$ ) was  $15.9 \pm 0.8 \text{ g L}^{-1}$  and  $3.3 \pm 0.2 \text{ g L}^{-1}$  in  $PE_2$ . The mass reduction of raw ashes was 19.1%.

Studies of dissolution kinetics were done at the highest mass fraction (20%) and lowest stirring speed (500 rpm), to assess the optimal washing time. These two parameters were chosen following the previous experiments, to minimize water and energy consumption. Fig. 3 shows that the dissolution plateau is very quickly reached (in less than 5 min). A rapid washing step (fixed to 10 min) is optimal to avoid the reprecipitation of Ca and Mg, and remove all elements efficiently.

Method M#1 required at least 8 mL of deionized water to wash 1 g ashes. In comparison, method M#2, inspired from cross-current washing (Fig. 1), only needed 5.3 mL of deionized water. The last effluent  $PE_{32}$  can also be used to wash new raw ashes  $A_{40}$ . Therefore, one third of the volume of deionized water was saved. Moreover, for 25 g ash washed in 100 mL water, K concentration was higher in the effluent  $PE_{31}$  ( $23.9 \text{ g L}^{-1}$ , Fig. 2c) than in the washing solution of method M#1 (the maximum was of  $18.5 \text{ g L}^{-1}$ , Fig. 2a). And K removal rate from the ash was about  $81.7 \pm 5.0\%$ , which was almost the same as with M#2.

At this step, the mass of the ash has decreased from 30.0 to 22.0 g. The mass balance on the main elements is given in Table 1. Ni, Ca, Mg and Fe have been concentrated in the ashes at 176, 182, 41 and  $4.7 \text{ mg g}^{-1}$  and K removed at about  $89.6 \pm 6.2\%$  (Table 1). The effluents mainly contained K and could be reused as a fertilizing solution in agriculture.

### 3.3. Acid leaching

Three parameters may influence leaching effectiveness: acid concentration, temperature and duration. Previously, we found that leaching with 1.9 M  $\text{H}_2\text{SO}_4$ , at  $95^\circ\text{C}$  for 4 h, with a solid fraction of 13%, enabled us to extract 96% Ni (Barbaroux

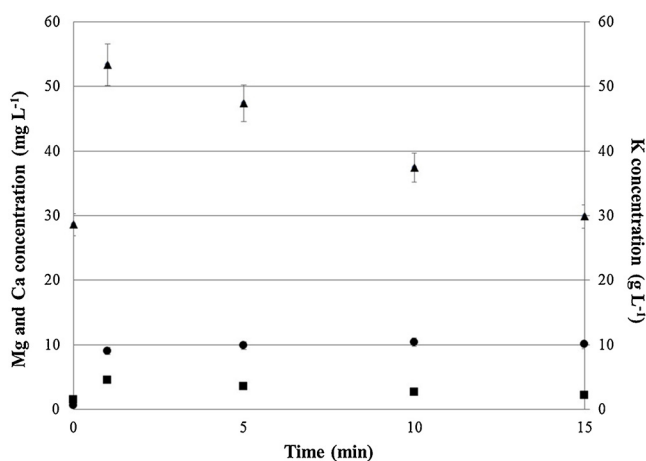


Fig. 3 – Evolution of K (●), Ca (▲) and Mg (■) concentrations in the ash washing solutions after the one step washing (method M#1) at 20 wt% ash with a stirring speed of 500 rpm.

**Table 2 – Ni extraction from *A. murale* ashes.**

H <sub>2</sub> SO <sub>4</sub> (M)	Temperature (°C)	Extraction (Ni %)			
		Time (h)			
		1	2	3	4
1	70	56.8 ± 4.0	61.8 ± 4.3	69.2 ± 4.8	78.8 ± 5.5
2	70	67.1 ± 5.4	78.8 ± 6.3	80.1 ± 6.4	94.0 ± 7.5
3	70	74.8 ± 6.0	88.0 ± 7.0	98.7 ± 7.9	100.2 ± 7.5
2	95	95.9 ± 7.7	99.4 ± 7.9	100.6 ± 7.9	101.9 ± 8.1

et al., 2012). Here, experiments were run at a solid mass fraction of 10% and parameters were tested as presented in Table 2. The lower temperature and acid concentration did not allow a total extraction. To reach a total extraction, concentrated acid or high temperature had to be used. Actually, a high acid concentration would lead to higher sulfate concentration in the leachate. Therefore, it was preferable to increase temperature. The best conditions were then 95 °C, 2 M H<sub>2</sub>SO<sub>4</sub>, 2 h, for an ash mass fraction of 10%. They were close to the previous conditions except that the heating duration was halved, which represents energy and equipment use saving.

The comparison between XRD analysis of the washed ashes (A<sub>12</sub>) and the ashes after acid leaching (SW<sub>1</sub>) has shown the disappearance of peaks (a–f) corresponding to CaCO<sub>3</sub> and MgCO<sub>3</sub> (Fig. 2b). In SW<sub>1</sub>, peaks (A–F) corresponding to CaSO<sub>4</sub>·2H<sub>2</sub>O were recorded (Fig. 2c) and no peaks matched with MgSO<sub>4</sub> and NiSO<sub>4</sub>, which was another evidence of Ni transfer from the washed ashes (A<sub>12</sub>) into leachate (L<sub>1</sub>).

### 3.4. Purification of the Ni-rich leachate

Leachate (L<sub>1</sub>) needed to be neutralized as it contained an excess of H<sub>2</sub>SO<sub>4</sub>. It also contained 0.43 g L<sup>-1</sup> of iron that can be removed in the form of FeOOH. The previous neutralizing agent, NaOH 5 M, generated a significant amount of Na<sub>2</sub>SO<sub>4</sub> at the first crystallization step since the solubility of Na<sub>2</sub>SO<sub>4</sub> is 4.8 g per 100 g of water at 0 °C, while ANSH solubility is 1.4 g per 100 g of water at 0 °C (Barbaroux et al., 2012). The addition of NaOH 5 M to L<sub>1</sub> (obtained from 30 g of raw ashes A<sub>10</sub>) would produce at the same time 34.6 g Na<sub>2</sub>SO<sub>4</sub> and 24.3 g of ANSH.

Here, NaOH was replaced by Ca(OH)<sub>2</sub>, which made CaSO<sub>4</sub> precipitate since the solubility of CaSO<sub>4</sub> is 0.205 g per 100 g of water at 25 °C (Lide, 2003). Fe(OH)<sub>3</sub> also precipitated, since its solubility is 2.097 × 10<sup>-9</sup> g per 100 g of water at 15 °C (IUPAC-NIST Solubility Database, Version 1.0). The suspension was filtered, producing the neutralized leachate (L<sub>2</sub>) and a solid waste (SW<sub>2</sub>) mainly composed of CaSO<sub>4</sub> and containing Fe(OH)<sub>3</sub>.

Preliminary experiments have shown that the mass fraction of Ca(OH)<sub>2</sub> should not be too high, to avoid a dramatic increase in viscosity. With a mass fraction of 10%, the leachate was neutralized to pH 4.5 and 95.5 ± 5.3% of Fe was removed

(Table 1). After that, Mg was removed from (L<sub>2</sub>) by precipitating MgF<sub>2</sub> by NaF addition. After filtration, 84.8 ± 6.0% of Mg was removed (Table 1). Then the solution was evaporated to concentrate Ni in the solution. 93.5 ± 3.3% of nickel was recovered in the purified leachate (L<sub>4</sub>) (Table 1).

### 3.5. ANSH crystallization

Initially, ANSH was crystallized without stirring. This time, the solution was stirred (magnetic stirring). At the end, crystal purity (based on Ni content) was assessed by several techniques and compared with salts #1 and #2. For salt #1, a purity of 99.6 ± 0.3% was obtained by ICP-AES and 99.7 ± 0.1% by gravimetric analysis. For salt #2, 98.8 ± 1.0% and 98.6 ± 0.2%. These results showed that these techniques were reliable. Therefore, they were used to analyze our crystals.

The elemental concentrations in the crystals measured by ICP-AES after each crystallization step are given in Table 3. The purity was 92.4 ± 2.0% after the first step and reached 100.6 ± 1.0% after the second one. Uncertainty was due not only to measurement but also to sample heterogeneity, the sample weight was small (0.1 g), to avoid further dilution. Therefore, the standard deviation was rather high. Gravimetric analysis was performed to decrease uncertainty. The results were of the same order: 89.2 ± 1.0% after the first step and 99.1 ± 0.4% after the second one.

Moreover XRD patterns (peaks at 2-theta of 16.46°, 21.50°, 23.60°, 29.50°, 31.99°, 36.97°, 40.86° and 41.90°) were consistent with the peaks of ANSH from AMS data (Treushnikov et al., 1978). Therefore, this new process enables us to directly obtain the targeted salt with the same purity as previously obtained (88.8% (Barbaroux et al., 2012)). However, in this case, it is just after the first crystallization step. After the second one, the purity drastically increases to reach more than 99%.

### 3.6. The new process flow sheet

The flow sheet of the new process is presented in Fig. 4. The main differences compared to the previous one (Barbaroux et al., 2012) are as follows. Firstly, leaching duration was halved, which saves energy. Secondly, for neutralization, 10% suspension of Ca(OH)<sub>2</sub> was used instead of NaOH (5 M), which

**Table 3 – Elemental concentrations in the crystals after the first (1st) and second (2nd) crystallization steps.**

Elements	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	Zn	
Concentration (mg g <sup>-1</sup> )	1st	<DL	0.18 ± 0.14	<DL	0.03 ± 0.01	<DL	<DL	0.03 ± 0.03	17.65 ± 3.41	2.85 ± 2.01	<DL	0.52 ± 0.33	137.36 ± 1.28	0.79 ± 0.04	0.02 ± 0.00	0.88 ± 0.04
	2nd	<DL	0.03 ± 0.03	<DL	0.03 ± 0.00	<DL	<DL	<DL	18.80 ± 2.99	0.87 ± 0.64	<DL	<DL	149.43 ± 1.06	0.77 ± 0.45	0.03 ± 0.00	0.95 ± 0.02

Detection limits (DL): <0.2 μg g<sup>-1</sup> for Na and <0.02 μg g<sup>-1</sup> for other elements.

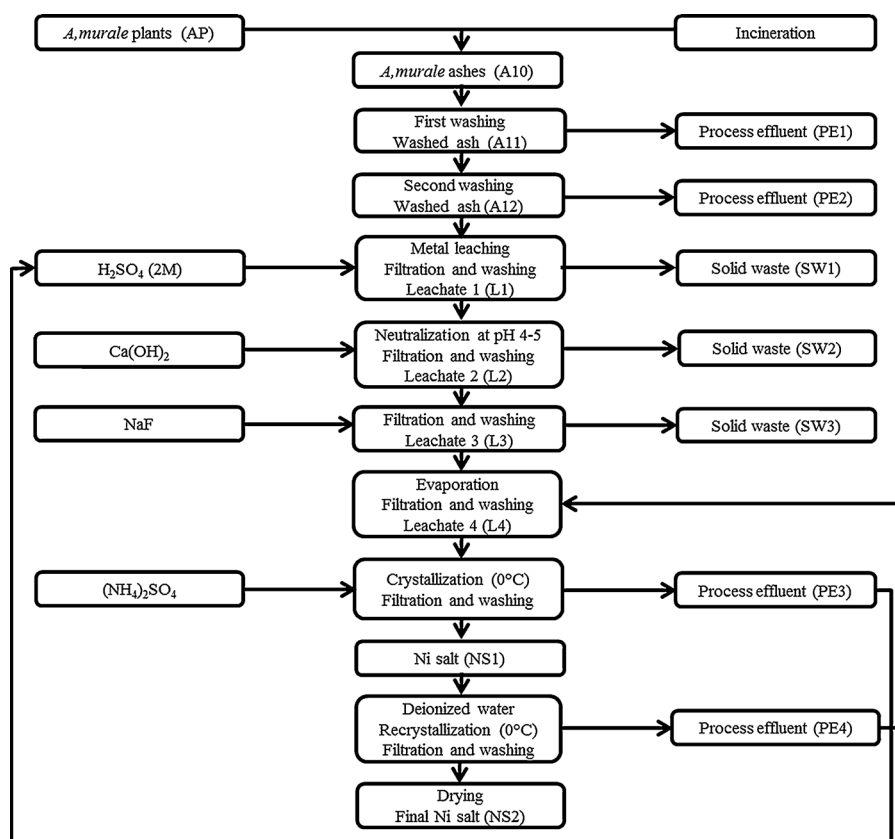


Fig. 4 – The new flow sheet of the process to produce ANSH salt from ashes of *A. murale*.

not only reduced the economic cost, but also avoided the production of a large quantity of  $\text{Na}_2\text{SO}_4$ . In addition, almost all excess  $\text{H}_2\text{SO}_4$  was precipitated from solution in the form of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Also,  $95.5 \pm 5.3\%$  of Fe was eliminated from the raw ashes. Thirdly, magnesium was removed before ANSH crystallization, and the removal rate was  $84.8 \pm 6.0\%$ . It just took one step to reduce the volume of the pure leachate ( $L_4$ ), to concentrate Ni before crystallization. And also, a single addition of ammonium sulfate was sufficient and lowered the production cost. To finish, ANSH crystals were produced and characterized by XRD analysis, ICP-AES and gravimetric analysis. The purity reached  $99.1 \pm 0.2\%$ , which was higher than previously.

The mass balance (Table 1) was obtained from the general results. The whole process was repeated 3 times. We found that at least  $89.6 \pm 6.2\%$  of K was removed from the raw ashes, and this ratio can be improved by using more water to wash the raw ashes. Using  $\text{Ca}(\text{OH})_2$  can increase the pH and eliminate  $95.5 \pm 5.3\%$  of Fe from the raw ashes. The addition of NaF can precipitate  $84.8 \pm 6.0\%$  of Mg from the leachate  $L_2$ . The yield of Ni was  $64.1 \pm 1.4\%$  in the crystals; the rest of the Ni ( $26.8 \pm 0.9\%$ ) was still in the effluents. It could be recycled and recovered, so that the total Ni yield could attain more than  $90.9 \pm 2.3\%$ . The method to increase the yield is ongoing.

#### 4. Conclusions

This study details the improvements of the process that we designed to produce ANSH from the hyperaccumulator plant *A. murale*. The process has been simplified and the number of steps decreased. Therefore, water, energy and chemical reagent consumption has been reduced.

The economic feasibility has been proven (Barbaroux, 2010) and the process is currently upscaled to the pilot scale. A life cycle assessment is ongoing to evaluate the environmental impacts of the phytomining process, from the plant cultivation to the ANSH production. This work should lead to the production of a commercially viable product with a high purity. At the moment, this approach is being extended and other processes are investigated to produce other Ni salts from *A. murale* and other hyperaccumulator plants.

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