Impact of Recrystallization on the Purity of ANSH Crystals Produced from Ni Hyperaccumulator Plant

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The industrial development will influence the demand and price of nickel in the coming years which opens the possibility for the use of innovative ways for its exploitation from secondary resources. Phytomining of nickel is a prospective in situ technology that uses plants with natural hyperaccumulating capabilities for this element. This study represents application of currently established and developed hydrometallurgical methods on wild populations of nickel hyperaccumulator from Serbia and explores the impact of recrystallization on the purity of the final product. The study confirms that nickel salts (ammonium nickel sulfate hexahydrate) can be synthesized from the Odontarrhena muralis that is naturally occurring on the ultramafic sites in West Serbia. Due to the small starting mass for the harvested biomass the preliminary experiments were separated into two series, which yielded 7,3g and 5,2g nickel salts of 60% and 73% purity, respectively, before recrystallization. However after recrystallization their purity was maximized reaching analytical levels of purity 99,9%, whereas their mass was reduced to 5,45g and 3,89g. More comprehensive studies with larger biomass and proper cultivation on ultramafic soil are needed in future to fully explore the potential for the development of Ni phytomining in Serbia.

Key Words: *Hyperaccumulator, Biomass metallurgy, Phytomining, Nickel extraction*

1. INTRODUCTION

In order to address key resource needs in the production of metallic raw materials and implement circular economy, growing global interest was shifted to their extraction from secondary resources. Important raw materials are frequently extracted from secondary resources using novel and environmentally friendly techniques that aim to be as sustainable as feasible. One such in situ technology is phytomining, which makes use of plants' capacity to store metals in their biomass. Nickel is a strategically valuable resource because it is primarily used as an alloying material for stainless steel, giving it the ductility and strength

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needed for deformation into desired products. It is also used as an alloying element in brass and bronze. Additionally, nickels greatest application is in metal coatings (nickel plating) due to its exceptional anticorrosive characteristics.

Besides these two most widespread applications, nickel is also used as a component in batteries, electric vehicles, magnets, and various other products.

Nickel phytomining is based on the use of identified plant species with the ability to hyperaccumulate this element in its organs. In order to be considered a Ni hyperaccumulator a plant must have the ability to accumulate nikel in quantities exceeding 0.1% (1000 ppm) of dry mass [1], primarily in its above-ground parts. The most well-known nickel hyperaccumulators include species such as Rinorea bengalensis [2], Thlaspi goesigense [3], Berkheya coddii [4], Alyssum bertolonii [5], Odontarrhena muralis (syn. Allysum murale) [6], Blepharidium guatemalense [7], and others.

In addition to the extraction of nickel (Ni), case studies concerning phytomining have also been conducted for:

Copper (Cu) and Cobalt (Co) [8], Selenium (Se) [9], Thallium (Tl) and other noble metals [10], Manganese (Mn) [11], Arsenic (As) [12], Cadmium (Cd) and Zinc (Zn) [13], as well as rare earth elements [14]. Odontarrhena muralis (syn. Alyssum murale) is one of the most well-known Ni hyperaccumulators, and this species has been used to assess the feasibility and impact of phytoextraction in various parts of Europe, due to its high biomass production and ability to grow in diverse environmental conditions [15]. Research by Tumi et al. [16] shows that populations of Odontarrhena muralis from ultramafic habitats in Serbia demonstrate a significant capability for nickel accumulation (up to 6,793 $mg \cdot kg^{-1}$ in aboveground parts and up to 13,160 $mg \cdot kg^{-1}$ in leaves), making them suitable for extraction purposes.

The extraction of Ni from hyperaccumulating plants, hyperaccumulators (HA), can be carried out by pyrometallurgical or hydrometallurgical processes. Research on hydrometallurgical approach has developed in two directions: the first route where the HA biomass is dried, grounded, and used as raw material for leaching, and the second route where the ground biomass is burned to ash, being used as raw material for leaching after washing and purification [6, 13, 15]. The second route has proven much more popular, leading to numerous studies aimed at improving process efficiency. Since the next step after grinding the HA biomass is burning it to ash, it is necessary to determine the optimal temperature and burning time to achieve the appropriate ash composition while transitioning Ni into an inorganic state.

Regarding temperature and time, Zhang et al. [17] concluded that a temperature of 550°C is sufficient and that the optimal burning time for converting the entire initial quantity of dry HA biomass to ash varies depending on the furnace used and the combustion conditions. Vaughan et al. [18] investigated the impact of thermal treatment of ash in a reducing CO/Ar atmosphere at temperatures of 700°C and 950°C on two Ni leaching systems using H_2SO_4 and NH_4OH solutions. Similarly to the combustion of all plant-derived biomasses, the predominant elements in the ash residues are Ca and K, in the form of various compounds, predominantly carbonates (K_2CO_3, $CaCO_3$, $K_2Ca(CO_3)_2$). To reduce the amount of acid required for leaching, washing is initially carried out to remove water-soluble salts.

This washing with water has been primarily effective in removing K salts (K_2CO_3, K_2SO_4 and KCl), as confirmed by various studies [18, 19, 20].

The main goal of the hydrometallurgical process is to obtain a concentrated alkaline solution of nickel ions, from which a wide range of products can be derived, including metallic Ni or nickel salts. Zhang et al. [20] built upon the methodology developed by Barbaroux et al. [20, 34] and improved the process of synthesizing ammonium nickel sulfate hexahydrate (ANSH) by introducing innovations such as two-stage ash washing, reducing leaching time to 2 hours, and replacing NaOH with $Ca(OH)_2$ for neutralizing the alkaline solution.

Vaughan et al. [18] developed a rough method for synthesizing $Ni(OH)_2$ which has broad applications. Vaughan's and Zhang's processes have many similarities, but Vaughan's method is unique in terms that it utilizes a concentrated K_2CO_3 solution formed during ash washing instead of traditional bases used in industrial $Ni(OH)_2$ production.

Zhang's processes involves additional steps of purifying the alkaline solution with sodium fluoride (NaF) and multiple recrystallizations of ANSH to achieve high purity. Additionally,despite ANSH being an expensive component, its market is small.

However, recrystallization is a common and well developed method used to purify solid substances. The procedure begins with dissolving the substance in a suitable solvent, in Zhang's processes this is low-cost and easily obtainable distilled water. In essence when the substance is soluble at high temperatures but less at low ones this allows the material to recrystallize as the solution cools. After the substance is dissolved, the solution is filtered while still at high temperature removing all insoluble pollutants. By means of recrystallizations the formed crystals are increased in purity because the pollutants remain dissolved in the solvent.

Our study follows Zhang's process as it is more adequate, affordable and produces Ni salts of high quality. However, our methodology for recrystallization is more simplified and efficient. The main goal of this study is to determine the source of the low initial purity of the synthesized crystals and reveal how recrystallization will impact the increase of purity at the cost of crystals mass.

2. MATERIALS AND METHODS

During the summer of July 2019, HA plant species O. muralis was sampled from the ultramafic locality of Mount Maljen, Tometino polje. HA samples were air-dried to constant weight. Combustion was carried out in a muffle furnace (Nabertherm Muffle Furnace L3/11/B410, Germany), at thetemperature of 550°C, for a duration of 4 hours. The content of chemical elements in dry biomass, ash, rinsed ash, effluents after ash rinsing, leaching solution before and after purification, and solid residue after leaching was determined using atomic absorption spectrometry (AAS) (PinAAcle 900T PerkinElmer, Inc, Norwalk, CT, USA), while the content of chemical elements in ANSH salt was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (Spectro Genesis).

Mineral phase composition of the samples was determined by using X-ray diffraction (XRD). XRD patterns were obtained on an automated diffra-ctometer (PHILIPS PW-1710, Eindhoven, Netherlands) using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. Diffraction data were collected in the 2 h Bragg angle range from 4 to 65°, counting for 1 s (qualitative identification) at every 0.02°step. Divergence and receiving slits were fixed at 1 and 0.1, respectively.

All XRD measurements were performed at room temperature in a stationary sample holder. Scanning electron microscopy (SEM) analyses were performed using a JEOL JSM–6610LV scanning electron microscope (JEOL Inc., USA) equipped with an INCA energy–dispersive X–ray analysis unit (EDS). An acceleration voltage of 20 kV was used. The analyzed samples were coated with a fine layer of gold dust to be visible under the microscope. The ash mass was divided into two parts (series 1 and series 2), both subjected to the process proposed by Zhang et al. [20], which involves: two-step rinsing of the ash with deionized water to remove soluble salts, leaching of the rinsed ash in 2M sulfuric acid at 95°C for 2 hours, neutralization of the leach solution with iron removal by adding $Ca(OH)_2$, purification of the neutral solution by adding NaF for magnesium precipitation, and finally ANSH crystallization by adding ammonium sulfate to the purified solution. After the crystals were weighted and analyzed from each series they were dissolved separately in 50ml of distilled water. Unlike the recrystallization applied by Zhang et al. [20], the dissolving and cooling was performed only one time making the process cheaper and simpler. The solution was heated to evaporate the remaining water and after it was filtered it was left to cool overnight.

3. RESULTS AND DISCUSSION

The air-dried HA samples were reduced by 93% from the initial mass (Table 1), which is consistent with literature values [21].

Table 1. Mass balance of combusting dry plant biomass into ash

Combustion batch	1st	2nd	3rd	4th	Sum
Dry plant (g)	287	416	238	268	1209
Ash (g)	23	28	19	22	92

The elemental content of Ni in the dry plant biomass was about 2.917 ppm while it increased tenfold in the ash to 30.100 ppm, which is consistent with literature data from other researchers on various types of nickel hyperaccumulators [17, 19, 20, 21]. During the washing step of the process, the greatest loss of mass is due to the dissolution of potassium and calcium salts. The mass fraction of ash during washing with deionized water was 20%, regardless of the washing step and series, as the optimal mixing ratio for this process, according to Zhang et al. [20], was 1:4.

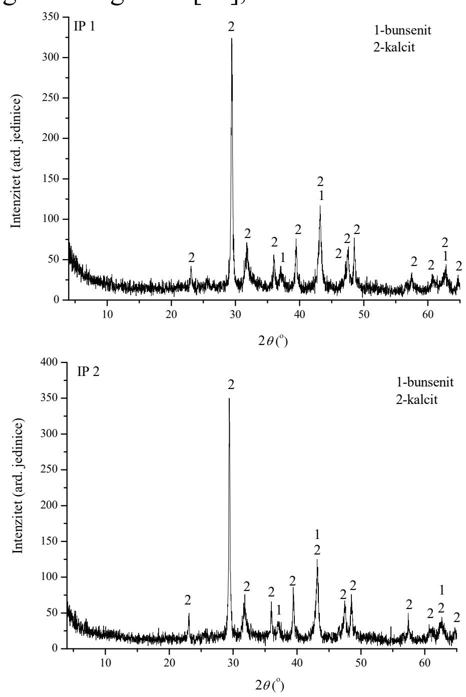

Figure 1 - XRD patterns of washed ashes for each series: S1 (IP 1) and S2 [22] (IP2)

There were no significant differences between the series during the washing process, as can be seen from the XRD analyses of washed ashes for both series (Figure 1) that confirmed to the presence of calcite ($CaCO_3$) and bunsenite (NiO). The results of the leaching for both series of experiments are presented in Table 2. We can observe the change in elemental content in the starting material, washed ash (WA), as well as the effect of leaching on the content in the leachate (L) and the solid waste (SW) that remains after leaching.

Table 2. Elemental content for washed ash, leachate and solid waste for both series

Elemental content (ppm)	First series (S1)			Second series (S2) [41]		
	Washed ash	Leachate	Solid waste	Washed ash	Leachate	Solid waste
Ni	47500	4500	2740	39980	8500	3990
Mg	52700	8100	3500	48500	15200	4600
K	30000	2585	1120	38500	3430	1320
Fe	2850	223	379	2220	262	342
Ca	235000	630	92300	217400	530	132200

The results of XRD analyses of the solid residues from leaching for both series show that the only phase present in the solid waste after leaching is gypsum ($CaSO_4{\cdot}2H_2O$). The XRD findings are confirmed by the EDS analyses of SW for both series.

Therefore it can be concluded that Ni, previously bounded in the form of NiO within the washed ash has been leached out. The detected Ni in the solid waste is dispersed throughout in small quantities likely bound by stronger organic ligands that the sulfuric acid could not break down.

After leaching with sulfuric acid, the next step is the neutralization and purification removing iron ions from the leachate solution using a suspension of Ca(OH)2. This step is not only characteristic for Zhang's method [20] but was also used by Vaughan in his research [18]. After the gypsum is removed from the leach solution using a vacuum pump, is the removal of Mg from the leaching solution by adding NaF in excess of 10% for MgF_2 precipitation.

One of the technical limitations in this study was that the elemental content was not determined in between the purification steps due to limited amount of starting materials. As discussed in a previously published study [22], the presence of Ca in the leach solution was not taken into account during this process. For the first series the Ni content in the leachate solution dropped from 4.500 ppm to 3.800 ppm after purification and neutralization steps, while for the second series the drop was more significant 8.500 ppm to 5.400 ppm. Zhang [20] emphasizes that if a 20% suspension of $Ca(OH)_2$ is used, due to the viscosity of the mixture, nickel can become trapped within the $CaSO_4$ precipitate and be lost from the leachate solution, which can explain the drop in Ni concentration. The final step is the precipitation of ANSH by adding ammonium sulfate, the purity of ANSH salt is calculated relative to the theoretical nickel concentration expected in the salt. For comparison, Zhang synthesized ANSH with 99,1% purity (Ni: 149,13±1,06 mg/g) from O. murale biomass [20], while Barbaroux synthesized ANSH with 88.8% purity (Ni: 132±3,13 mg/g) [19].

The first series S1 produced 7,3 g of ANSH with 60% purity (Ni: 87,73±0.84 mg/g), and the second series S2 produced 5,2 g of ANSH with 73% purity (Ni: 109,67±1.04 mg/g) before recrystallization. However, after recrystallization both series showed a maximal increase in purity to 99.9%; for the first series 5,45g (Ni: 150,21±1.08 mg/g) and for the second series 9,34g (Ni: 150,32±1.11 mg/g).

This means that the collective mass of the crystals decreased form 12,5g to 9,34g but the highest purity was obtained. Therefore from around 1200g of dry plant mass and 90g of ash it is possible to produce 9,37g of ANSH crystals of highest purity.

The difference between the series in mass and in purity after synthesis can be attributed to the content of P to Mg in the ANSH crystal product. Mainly magnesium competes with nickel for the ammonia ions during the crystallization of Ni(NH4)2(SO4)2·6H2O because it precipitates in the form of Struvite (MgNH4PO4·6H2O).

Since the first series has a higher concentration of Mg compared to Ni in the solution [22], it is reasonable that it would precipitate a larger mass of ANSH but with lower purity, which is further supported by the fact that the ANSH crystals from the first series contain five times more P (Table 3).

However, after recrystallization even though Mg is still present in the crystals the content of P is significantly reduced, and that lead to the high increase in purity. The difference in purity between the series before and after recrystallization is clearly visually evident from color and clarity in Figures 2 and 3.

Table 3. Element content of final ANSH salt product for both series.

First series								
Element content of crystal (mg/g)	Ca	Fe	K	Mg	Ni	P	Zn	Na
Before Recrystallization	0,74 ±0,10	0,44 ±0,24	24,61 ±0,54	19,39 ±0,44	87,73 ±0,84	1,81 ±0,14	0,74 ±0,24	10,72 ±0,26
After Recrystallization	0,33 ±0,10	0,25 ±0,24	36,54 ±0,54	10,14 ±0,44	150,21 ±1,08	0,01 ±0,14	1,22 ±0,24	0,10 ±0,26
Second series								
Element content of crystal (mg/g)	Ca	Fe	K	Mg	Ni	P	Zn	Na
Before Recrystallization [22]	<0,01	0,35 ±0,25	24,49 ±0,54	20,87 ±0,44	109,67 ±1,04	0,34 ±0,06	0,97 ±0,22	0,06 ±0,002
After Recrystallization	0,41 ±0,10	0,12 ±0,25	31,32 ±0,54	6,39 ±0,44	150,32 ±1,11	<0,01	1,20 ±0,22	0,12 ±0,02

Figure 2 - ANSH crystals before and after recrystallization for series 1

Figure 3 - ANSH crystals before and after recrystallization for series 2

The difference in purity between the series before and after recrystallization was the same on the microscopic level, as it is seen in Figures 4 and 5.

The EDS analysis confirmed the presence of P in the crystals before recrystallization and in Figure 6 we can see the similarities of pure crystals with the area spectrum 1 in Figure 7. The pale particles that can be seen in Figure 4 are confirmed by EDS analysis to be potassium fluoride KF, while the small needles have a higher content of Ca and Al.

This presence of KF can indicate that the removal of Mg during the purification process by addition of NaF wasn't inhibited by Ca, as previously believed [22]. Future research should focus on investigating this particular step in order to ensure greater efficacy of the purification process.

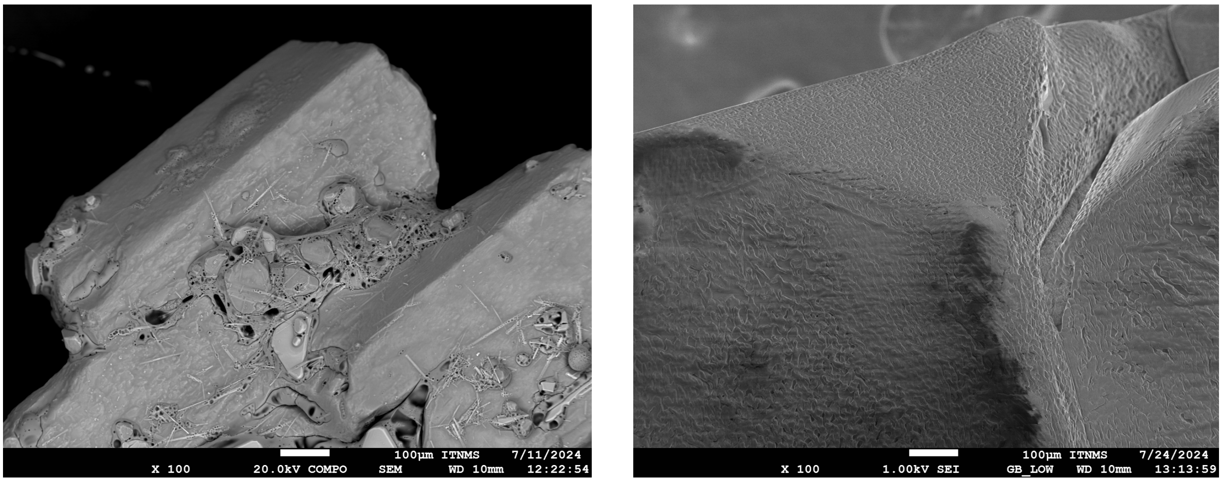

Figure 4 - SEM micrograph ANSH crystals before and after recrystallization for series 1

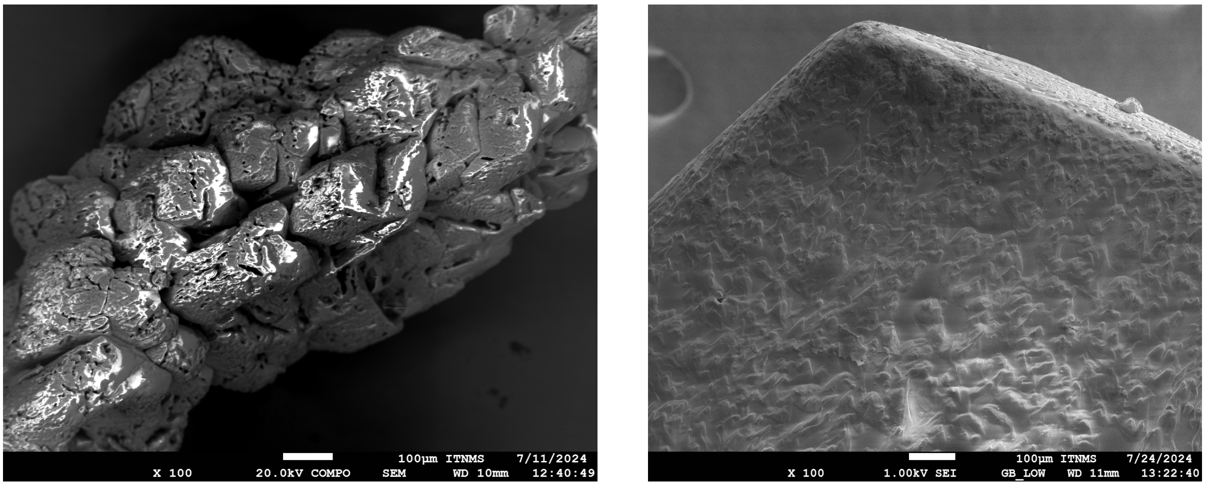

Figure 5 - SEM micrograph ANSH crystals before and after recrystallization for series 2

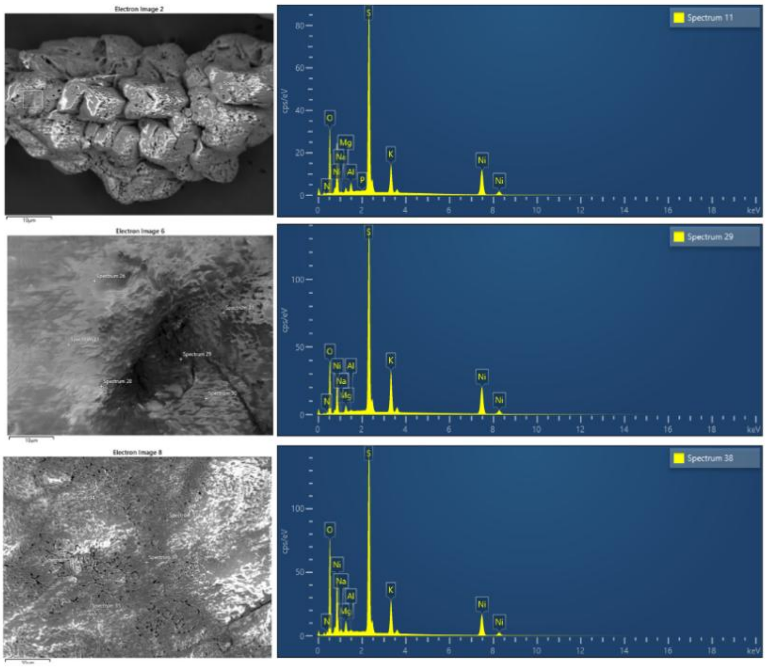

Figure 6 - EDS spectrum analysis of ANSH crystals of greater purity over 70%

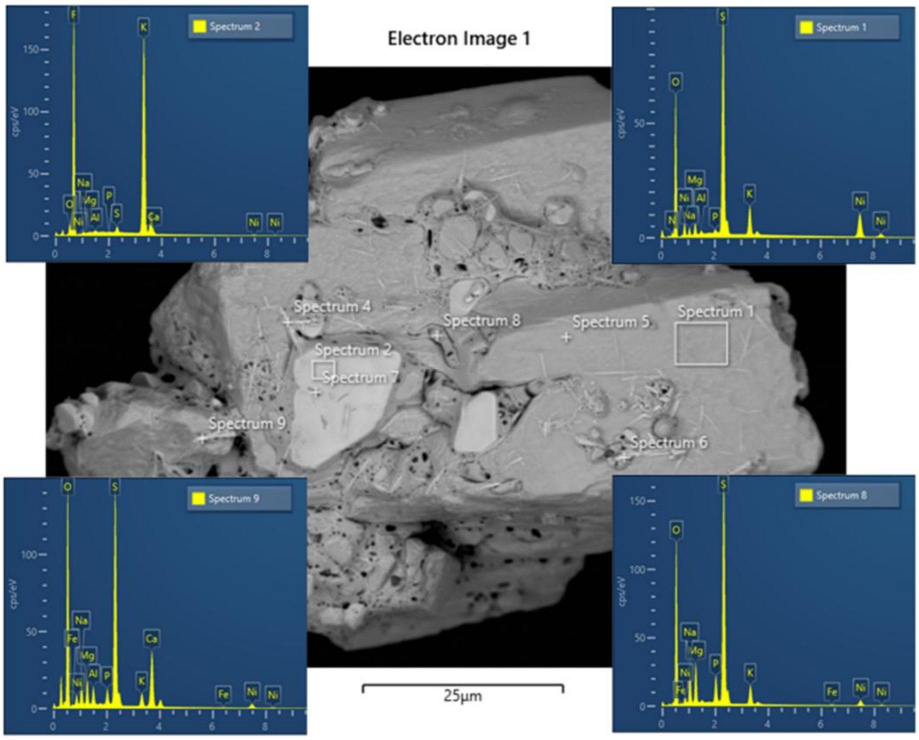

Figure 7 - EDS spectrum analysis of ANSH crystals with the lowest purity of 60%

4. CONCLUSION

Phytomining is a new technique using hyperaccumulating plants whose biomass is utilized as bio-ore for metal extraction. This study presents a preliminary analysis of the established methods and achieved results in hydrometallurgical processes for nickel phytomining, as well as the potential for Serbia to join the growing trend of phytomining biotechnology research, with its natural, geological, and technological resources. This emerging field is rapidly expanding in countries capable of growing and cultivating native hyperaccumulator plant species.

Our research has proven that it is possible to synthesize nickel salts of analytical purity from the species Odontarrhena muralis (syn. Alyssum murale), a nickel hyperaccumulator growing on Serbia's ultramafic soils. Due to operational constraints in applying the technological process and the small quantity of initial biomass, nickel salts with purities of 60% and 73% were obtained before recrystallization with the combined mass of 12,5g. After recrystallization their mass was reduced by 25% but their purity was increased to around 99,9%. Therefore from the starting mass of 90 g of Ni HA ash as a bio-ore it is possible to synthesize 9,37g of ANSH crystals of highest purity. The overall lower purity after initial synthesis is contributed to the coprecipitation of Struvite and ANSH due to the presence of phosphorus. Additionally the lowest purity of 60% can also be contributed to small particles of KF, therefore the removal step of Mg during the purification process by addition of NaF should be investigated in greater detail.

To achieve this, it is necessary to collect significantly more initial biomass, consider the possibilities of cultivating hyperaccumulators at ultramafic soils in Serbia. Thus, being able to further investigate various range of products that can be derived from hyperaccumulators and the associated technologies (combustion, thermal treatment of ash, purification of the leach solution, and processing of the final product). Finally, assessing the demand for these products in Serbia and the region, all the while paying special attention to sustainable development and environmental protection. Additionally, it should be noted that despite low financial viability of currently employed extraction processes, further development and enhancing of extraction technologies, phytomining could significantly contribute to nickel and nickel salt production in the coming years.

5. ACKNOWLEDGEMENT

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REZIME

UTICAJ REKRISTALIZACIJE NA ČISTOĆU KRISTALA ANSH DOBIJENIH IZ NI HIPERAKUMULIRAJUĆE BILJKE

Usled industrijskog razvoja i ponude i potražnje za niklom u bliskoj budućnosti otvara se mogućnost za upotrebu inovativnih načina ekplotacije ovog metala iz alternativnih sirovina. Fitorudarenje nikla je perspektivna in situ tehnologija koja koristi prirodne sposobnosti biljke da hiperakumulira ovaj hemijski elemement. Ova studija predstavlja primenu trenutno zastupljenih i razvijenih hidrometaluških postupaka na divljoj populaciji hiperakumulatora iz Srbije, kao i uticaj rekristalizacije na čistoću krajnjeg proizvoda. Potvrđeno je da se so nikla ANSH (amonijum sulfat nikl heksahidrat) može sintetizovanoti iz vrste Odontarrhena muralis koja prirodno rate na ultramafitskom zemljištu istočne Srbije. Usled male količine početne mase uzorkovane biomase, prelimenarni eksperimenti podeljeni su u dve serije. Pre reklistalizacije prva serija proizvela je 7,3g ANSH 60% čistoće dok je druga serija proizvela 5,2g ANSH 73% čistoće. Međutim nakon reklistalizacije čistoće obe serije su porasle do analitičko čistog nivoa od 99,9% dok su im mase redukovane na 5,45g za prvi i 3,89g za drugu seriju. Potrebno je izvesti mnogo sveobuhvatnije studije sa većom polaznom količinom biomase kao i uz primenu propisnih agronomskih tehnika na ultramafitskom zemljištu kako bi se u buduće razvio pun potencijal fitorudarenja nikla u Srbiji.

Ključne reči: *hiperakumulatori, metalurgija biomasse, fitorudarenje, ekstrakcija Ni*