NEW APPROACHES FOR OBTAINING SELENIUM (Se) FROM NATURAL RESOURCES

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Abstract: *In the last few years, application of selenium has increased significantly due to its unique possibilities to acts as an antioxidant and as an anticancer reagent in human body. Due to this, selenium is one of the most important chemical elements for human health. Recently, selenium usage in microelectronics was significantly increased as semiconductors with characteristic electronic properties. The selenium is the least abundant element in earth crust, but as the application fields of selenium are widely opened, the needs of this element are larger. This opens new views in the field of improving existing and developing new technologies for extraction of selenium.*

In this work, a new technology for extraction of selenium from natural resources was developed, by combining the advantages and removing the disadvantages and weaknesses of the existing technologies. The sediments near mineral water springs and used water filters with content from 0.0656 to 0.9291 % wt. of Se were used as mineral selenium resources. Also, the plants such as Astralagus bisulcatus and Stanleya pinnata with content of Se around 100 mg·kg^{-1} biomass were used as a plant resources. The technology presented in this work is a combination of pyrometallurgical and chemical methods in order to obtain intermediates reach with selenium, and further chemical and electrochemical extraction of selenium from these intermediates was done. The analyzes were performed using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). The results have shown that from mineral resources can be extracted pure red technical selenium with analytical grade up to 48.3 % of Se. From the plant resources can be obtained enriched selenium intermediates with analytical grade from 1.367 to 1.604 % wt. of Se which are potential material for medicine applications.

Key words: SELENIUM, Se – INTERMEDIATES, MINERAL RESOURCES, PLANT RESOURCES, ICP-AES.

1. Introduction

Selenium is a nonmetallic element was firstly discovered by Jöns Jakob Berzelius in 1817 [1]. Its name comes from the Greek word for the moon (*Selene*). The reserves of selenium in earth crust is with quantity of around 500 mg·t^{-1}. Its presence in the soil depends on variety of factors such as the presence in parent minerals of the soil and the possibility of removing or adding the selenium by the process of leaching during soil formation [2]. The chemistry of this unique material is most similar to the sulfur but unlike sulfur, selenium is much stronger oxidant and proved to be better antioxidant. Selenium was recognized as very active in cancer protection and may have multimodal mechanism in cells transformations prevention [3]. The two molecules are qualitatively the same but Se provides systematically a better coupling link than S, whatever the tunneling conditions are, and due to this better electronic properties [4]. Selenium is widely used as an additive to glass. Also, it is used as a pigment for ceramics, paint and plastics. Selenium has a photovoltaic and a photoconductive action and therefore it is useful in photocells, solar cells and photocopiers. It can convert AC electricity to DC electricity, so it is extensively used in rectifiers. In ferrous metallurgy, it is used as an alloying element in stainless steels. Very important applications of selenium are in medicine, nutrition, livestock feeds and cosmetics [5].

According to the existing technologies, selenium is the most widely produced from anode sludge obtained during electro-refination of copper. Anode sludge has complex chemical composition and consequently, the existing technologies are very complex and expensive. Also the produced selenium contains a lot of impurities that needs to be removed in order to be used in fields of electronics, medicine, pharmacology, nutrition and cosmetics. To achieve the needed purity, additional electrorefining is necessary, making the finalproduct more expensive. In order to produce less expensive selenium or selenium intermediates, there is a need of optimization, and simplification of the existing technologies, finding new sources of selenium or develop a new technologies which are less complex than existing ones.

The selenium produced by the existing technologies contains hazardous heavy metals, limiting its application for human health. The main goal of this work is optimization and simplification of the existing methods for selenium and/or selenium intermediates production from natural resources. A new methods for production of selenium from mineral and plant resources were developed by combining the pyrometallurgical, chemical and electrochemical methods.

2. Experimental

2.1 Materials and analysis

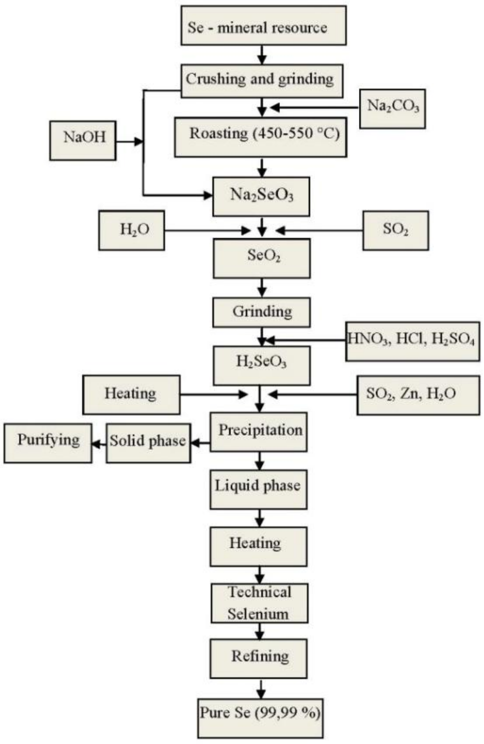
As a natural resources of selenium were used such as sediments found near mineral water springs and waste water filters with content from 0.0656 to 0.9291 % wt. of Se, and plants reach with selenium such as *Astralagus bisulcatus* and *Stanleya pinnata* with content of Se around 100 mg·kg^{-1} in the biomass. Hydrogen peroxide (H_2O_2), selenium dioxide (SeO_2), nitric acid (HNO_3), hydrochloric acid (HCl), sulfuric dioxide (SO_2), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and zinc (Zn) were used as received from *Merck KGaA*, Darmstadt, Germany. For the electrolysis, metal electrodes based on aluminum, copper and zinc were used. The analysis of Selenium content was done using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES).

2.2 Processing

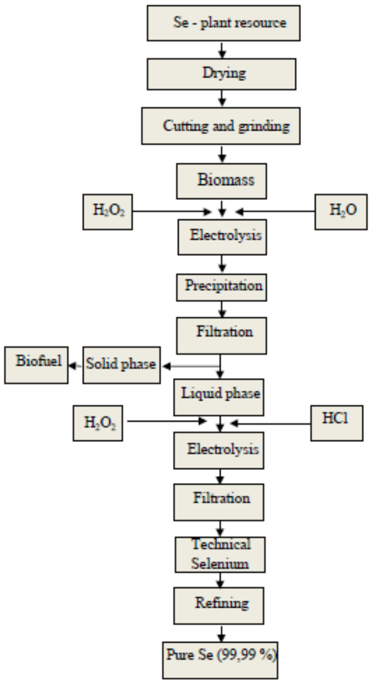
For production of selenium from natural resources, the materials should contains of minimum 0.05 % Se. Firstly, production of selenium from mineral resources will be presented, and further the production of selenium from plant resources.

The sediments obtained near mineral water springs and waste water filters are with content up than 0.0656 % of Se, and they represents a good materials for extracting this element. Developed new technology is presented in Figure 1-*a*. Processing of selenium containing resources starts with crushing the material under 25 mm and then grinding under 0.25 mm. In order to obtain sodium selenite, grinded material was treated with sodium carbonate and further, roasted at temperatures around 500 °C. The process is given with chemical reaction 1 presented in Table 1. Depending on the Se-resource chemistry, the material can be also treated with NaOH, but these results will not be commented in this work. After roasting, the obtained product was treated with H_2O, SO_2 and the produced sodium selenite was converted to selenium dioxide, where sodium bisulfite was obtained as a byproduct. This process is given with chemical reaction 2 in Table 1. The obtained product was grinded and immersed in acid solution to be converted to selenium acid and by products such as $NaNO_3$, H_2SO_4, NaCl, Na_2SO_4, NO_x, SO_2 and H_2O. This is presented with chemical reactions 3-*a*, *b*, *c* and *d* shown in Table 1. Gases are accepted trough special filters and were purified and neutralized. The by-products under the heating in the presence of SO_2, Zn and H_2O precipitated and were removed from the dispersion. This is presented with chemical reactions 4-*a*, *b* and *c* in Table 1. The liquid phase reach with selenium was heated and selenium with technical purity was obtained. Further and the last process was refining of the technical selenium to produce ultra-pure selenium.

Technology for production of selenium from plants, the is presented in Figure 1-*b*. Selenium reach plant resources should contain as much as possible selenium. Used materials in this work contain around 100 mg selenium per kilogram biomass. The biomass was treated with H_2O_2 and H_2O. In reaction with H_2O_2 elemental selenium from plants was transformed to SeO_2. During the electrolysis process in presence of H_2O, SeO_2 was transformed to selenium acid (H_2SeO_3). This is shown with chemical reactions in Table 2. After 24 h, the dispersion was filtered, and the liquid phase reach with selenium was treated again electrolytically. In order to maintain low pH value of the electrolyte, HCl and H_2O_2 were additionally added. As result of the electrolysis process, red and grey selenium were precipitated at the bottom of the electrolytic cell. After 24 h, the dispersion was filtered. The obtained selenium was further refined in order to produce ultra-pure selenium product. These results are not presented in this work, but only the results for production of the intermediates reach with selenium.



a)



b)

***Figure 1**: Scheme of the technology for production of selenium from mineral resources a), and from bio-resources b)*

***Table 1:** Chemical reactions of the processes presented in Figure 1-a.*

No.	Chemical reaction	Process
1	$SeO_2 + Na_2CO_3 = Na_2SeO_3 + CO_2$	Roasting
2	$Na_2SeO_3 + 2SO_2 + H_2O = SeO_2 + 2NaHSO_3$	Chemical treatment
3	*a*) $2SeO_2 + 2HNO_3 + H_2O = 2H_2SeO_3 + 2NO_x$ *b*) $NaHSO_3 + 3HNO_3 = NaNO_3 + H_2SO_4 + 2NO_2 + H_2O$ *c*) $NaHSO_3 + HCl = SO_2 + H_2O + NaCl$ *d*) $NaHSO_3 + H_2SO_4 = Na_2SO_4 + SO_2 + H_2O$	*a*) Selenous acid obtaining *b*, *c*, and *d*) Sodium nitrate, sulfuric acid, Sodium chloride and Sodium sulfate is obtained from Sodium bisulfate
4	*a*) $4HCl + 2Zn + H_2SeO_3 = 3H_2O + \mathbf{Se} + 2ZnCl_2$ *b*) $H_2SeO_3 + SO_2 + H_2O = \mathbf{Se} + H_2SO_4$ *c*) $H_2SeO_3 + H_2O = HSeO_3^- + H_3O^+$	*a* and *b*) Precipitation and obtaining of technical selenium *c*) Protonation of the solution

***Table 2**: Chemical reactions of the processes presented in Figure 1-b.*

No.	Chemical reaction	Process
1	*a*) $H_2SeO_3 + H_2O = HSeO_3^- + H_3O^+$	*a*) Protonation of the solution
2	*b*) $Se + 2H_2O_2 = SeO_2 + 2H_2O$	*b*) Extraction of selenium from plants
	c) $SeO_2 + H_2O = H_2SeO_3$	c) Production of selenous acid from plants

3. Results and discussion

3.1 Selenium obtained from mineral resources

In Table 3 are presented results from ICP-AES analysis for the used material form mineral resources. These results show that mineral resources near mineral water springs are with variable chemistry. For the technology presented in this work, these variations do not affect on the final results. In table 4 are presented results obtained from the technology presented at Figure 1-*a*. In the Figure 2-*a* is presented the produced red selenium with technical purity.

The results in Table 4 shows that for the presented technology at the scheme in Figure 1-*a*, technical red selenium with content of up to 53.573 % Se can be obtained. Analyzing the rest impurities in the produced technical red selenium and the chemical reactions presented in Table 1, one can be noted that hydronium ion is produced through the processes and protonation of the solution occurs. This changes the conditions in the electrolysis process and could not be achieved further increase of Se content. For this reason, further sequential electrolysis was performed in order to produce ultra-pure selenium [6-8]. These results are confidential and they are not presented in this work.

3.2 Selenium obtained from plant resources

In table 5 are presented result from ICP-AES analysis from the obtained material from plant resources. The biomass obtained from plant resources using technology presented in Figure 1-*b*, shows that selenium content varies. For the proposed technology, these variations did not affect on the selenium yield in the process of electrolysis. Great amount of present copper, aluminum and zinc is result of the used electrodes in the process of electrolysis. In order to use these materials for production of ultra pure selenium for electronic applications there are not significant restrictions. The presence of toxic elements in these intermediates is at the lower limits but still there are some disadvantages that should be eliminated in the production process. The obtained selenium intermediates are presented in Figure 2-*b*.

In order to use these selenium intermediates for medicine applications, elements such as aluminum, copper and zinc should be eliminated from the material. This can be achieved by using another type of electrodes in the process of electrolysis. Analyzing the chemical compound of the obtained intermediates, these materials can be potential materials for producing selenium reach drinking water can be used as a supplements in a food and other medical products, but with some modifications that need to be done before their use.

a) *b)*

Figure 2: *Obtained red technical selenium from mineral resources a), and selenium intermediates from plant resources b)*

Table 3: *ICP-AES for used materials from mineral resources.*

Element	Al	As	B	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	Pb	Ti	Zn	Se
1. % Wt.	11.11	0.01	0.009	0.002	1.28	0.02	3.49	0.69	0.21	0.19	0.07	0.0005	1.37	0.023	0.007	0.01	0.08	**0.929**
2. % Wt.	3.13	0.09	0.083	0.194	28.3	0.01	0.34	1.36	3.06	6.56	0.27	0.0028	0.68	0.009	0.001	0.03	0.14	**0.065**

Table 4: *ICP-AES for the obtained technical red selenium from mineral resources.*

Element	Al	Ag	Ba	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Sb	Ti	Zn	V	Se
1. % Wt.	9.47	0.0076	0.0182	0.047	0.115	4.97	0.91	0.026	0.026	0.017	0.015	0.008	0.052	0.0066	**53.573**
2. % Wt.	6.88	0.0074	0.004	0.032	0.058	6.84	1.37	0.091	0.029	0.015	0.019	0.018	0.089	0.0057	**48.296**

Table 5: *ICP-AES of the biomass obtained from plant resources*

Element	Al	Ag	As	Bi	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Sr	Ti	Zn	V	**Se**
1. % Wt.	10.382	0.0075	0.0837	0.006	0.84	0.006	0.027	12.81	0.12	1.94	0.03	0.021	0.354	0.04	0.005	0.02	2.53	0.007	**1.36**
Element	Al	Ag	As	Cd	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Sr	Ti	Zn	V	**Se**
2. % Wt.	14.42	0.0071	/	0.005	0.944	0.007	0.048	5.67	0.14	3.41	0.03	0.02	0.29	0.02	0.006	0.02	2.49	0.006	**1.604**
Element	Al	Ag	Bi	Tl	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Sr	Ti	Zn	V	**Se**
3. % Wt.	4.5	0.0078	0.02	0.007	2.69	0.009	0.009	6.63	0.06	/	0.04	0.02	0.09	0.04	0.01	0.015	0.32	0.005	**0.139**

4. Conclusion

From the presented results in this work, several conclusions could be drawn:

- Here are presented new combined technologies for production of technical red selenium from mineral resources and selenium intermediates from natural plant resources.

- These technologies were combined process of chemical, hydrometallurgical, pyrometallurgical and electrometallurgical procedures.

- Due to the process of formation of hydronium ion and protonation of the electrolyte, the process of electrolysis was facilitated, and the yield of selenium increased.

-The obtained results showed that produced material from mineral resources was red technical selenium with content of Se from 48.293 to 53.573 % wt which is attributed to the developed technology and the concentration in the selenium source. From the selenium bio-sources, such as plants, intermediates reach with selenium were obtained, with content of Se from 0.139 to 1.604 % wt. with potential applications in food or medical products.

References

[1] Jaime Wisniak, Jöns Jacob Berzelius A Guide to the Perplexed Chemist, *The Chemical Educator* **5**, (2000) pp. 343-350.

[2] Raymond J. Shamberger, Environmental Occurrence of Selenium. *In: Biochemistry of Selenium. Biochemistry of the Elements*, **2**, Springer, Boston, MA (1983) pp. 167-183.

[3] C. Ip H.E. Ganther, Comparison of selenium and sulfur analogs in cancer prevention, *Carcinogenesis* **13**, 7, (1992) pp. 1167-1170.

[4] L. Patrone, S. Palacin, J. P. Bourgoin, Direct comparison of the electronic coupling efficiency of sulfur and selenium alligator clips for molecules adsorbed onto gold electrodes, *Applied Surface Science* (2003) pp. **212-213, pp.** 446-451.

[5] Irene Rosenfeld Orville A. Beath, Selenium - Geobotany, Biochemistry, Toxicity, and Nutrition**,** e-Book ISBN: 9781483275901, *Academic Press, Elsevier*, (1964).

[6] Monika Khetarpal, Deepika Bhandari, and N. S. Saxena, Collective Excitations and Thermodynamic Properties of Liquid Selenium: A Transition from Short Chain Polymer to Real Polymer System, Phys. Stat. Sol. (b) **29**, (1998) pp. 209.

[7] James E. Hoffmann, Recovering Selenium and Tellurium from Copper Refinery Slimes, *Fourth Biennial Workshop on* organometallic vapor phase epitaxy, October 8-11, • Monterey, California USA, (1989).

[8] Geert Cornelisa, Sofie Poppe, Tom Van Gerven, Eric Van den Broeck, Michiel Ceulemans, Carlo Vandecasteele, Geochemical modelling of arsenic and selenium leaching in alkaline water treatment sludge from the production of non-ferrous metals, *Journal of Hazardous Materials* **159** (2008) pp. 271-279.