

Plant Biosphere - Natural Extractor and Concentrator of Rhenium from Soils and Waters

OGNYAN BOZHKOV, CHRISTINA TZVETKOVA AND TEMENUZHKA BLAGOEVA
 Laboratory of Analytical Chemistry and Laboratory of Inorganic Salts,
 Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
 Acad. G. Bontchev Str., bl.11, Sofia,
 BULGARIA

Abstract: -The plant Biosphere was shown to be a natural biocollector and concentrator of dispersed rhenium in environment. The bioaccumulation and preconcentration of rhenium in plants can be used for its recovery from soils and waters from ore dressing and work processing regions. A new approach to the development of a procedure for rhenium phytorecovery is proposed. Regional investigations on the degree of rhenium accumulation in different kinds of plants growing in the vicinity of the ore dressing mines Asarel- Medet and copper processing Medet in Bulgaria were carried out. The results showed that the plant Biosphere in these vicinities was enriched in different but considerable amounts of rhenium, which exceeded its natural spread in Earth's crust 1400 to 44000 times. The content of rhenium in the vegetation growing along the river exceeds its content in flowing rivers 395-times. It was shown that the concentration of rhenium in green and dry yellow leaves from the same vegetation was equal. This evidences that the dry leaves can also be used as a source for rhenium recovery. The basic advantage of Re is that this metal is preferably accumulated (more than 98%) in green over ground parts of all kinds of plants. It is very easy to harvest the green plant mass containing rhenium at soil level, collect it together with green and dry leaves, to incinerate or treat them in different ways to concentrate rhenium.

Key- Words: - rhenium, plant Biosphere, extraction, soils, waters, ore dressing regions

1 Introduction

Rhenium is one of the rarest elements in the earth's crust (its occurrence amounts to 7×10^{-8} %). It belongs to the ten most expensive metals on Earth. The two most important applications of rhenium are in high-temperature super alloys and platinum rhenium catalysts. High temperature super alloys are used in turbine components of aircraft engines and other aerospace applications. Platinum rhenium catalysts are used to produce lead-free gasoline. Rhenium is not found free in nature and does not form minerals of its own. The average rhenium content in its main carrier minerals is as follows: pyrite 0.3 g/t, chalcopyrite 0.6 g/t, and molybdenite 114 g/t [1]. Rhenium was recovered as a by-product from porphyry copper- molybdenum or porphyry copper concentrates that were processed to recover the rhenium using pyro- and hydrometallurgical technologies. The rhenium world production is not sufficient to meet the requirements of industry. Therefore, the search for new rhenium sources continues.

2 Dispersion of rhenium in the environment of ore dressing and work processing regions

The existing technologies for enrichment of rhenium-containing ores and rhenium extraction from concentrates are not sufficiently effective. In these processes part of the rhenium is lost and dispersed in the environment (soils and waters) through emission of volatile Re_2O_7 and waste industrial solutions and waters (ReO_4^-) [2, 8]. The problem is how to extract and collect the dispersed rhenium without polluting and damaging the environment.

3 Plant Biosphere - a new source for rhenium recovery

3.1 Data about rhenium accumulation in plants

In the past decade, easy accumulation of rhenium in all kinds of terrestrial and some kinds of marine plants was established in amounts exceeding its natural occurrence in soils and seawater [3]. The rhenium content in ash from some plants growing in copper or molybdenum ore dressing regions in Russia was found to vary from 0.13 to 170 g/t, exceeding the background levels from 25 to 34 000 times [4]. In the same work, the authors found that the content of rhenium in plants growing above ore deposits in a depth of 600-700 m exceeded its concentration in primary ore. They concluded that in the vicinity of ore deposits the plants are enriched in rhenium forming rhenium aureoles [4]. Green algae *Briopsis maxima* were found to be a hyper accumulator of rhenium from waters of Pacific Ocean. The concentration factor was calculated to be 7.4×10^5 on wet basis from the rhenium concentration (7.42 pg/ml) in Pacific Ocean seawater [3]. In general, we can assume that rhenium accumulates in various species of terrestrial and marine plants that can be used as a source for its recovery from soils and waters.

3.2 Study of rhenium accumulation in plants

For developing a procedure for rhenium recovery from soils and waters by plants it is necessary to study the processes of its bioaccumulation in vegetation. That is why, we developed some procedures (field test and laboratory variants) for its determination in a wide concentration interval (from 3 to $n \times 10^3$ ng.g⁻¹) [5, 6]. Our investigations show that more than 98% of Re is accumulated in the green part of plants, while in roots Re is practically absent [7]. It is known that the most stable chemical form of Re in the surface environment (soils and waters) is ReO_4^- , which is considered to be highly mobile in biogeochemical cycles [3]. Our laboratory study [5] on the dynamics of rhenium accumulation in leaves of green geranium (*Pelargonium*) from soils spiked with rhenium (as perrhenate) shows that after one week the concentration of rhenium increases from 1 µg/g in soils to 20 µg Re per 1 g of raw leaves (respectively to 1667 µg Re per 1g ash). In three weeks, the rhenium content in leaves increased up to 110 µg Re per g of raw leaves (respectively up to 9167 µg Re per 1g ash) and did not increase any more with time. Similar experiments were carried out with aqueous solutions of rhenium and have shown that a leaf of green geranium (1 g weight) extracts 55

µg Re per 1 g of raw leaves (4583 µg Re per 1g ash, respectively). from a solution with $C_{\text{Re}} = 40$ µg Re/ml for 7 days, and 110 µg Re per 1 g of raw leaves (to 9167 µg Re per 1g ash, respectively) for 12 days. The results show that rhenium is gradually accumulated by green geranium and reaches the limit concentrations. By ashing of plants, Re is preconcentrated more than 83-times.

3.2.1 Mechanism of gradual bioaccumulation of rhenium in vegetation

On the basis of the study of processes of bioaccumulation of rhenium in plants, Bozhkov and Tzvetkova [3] supposed the following mechanism, which explains the gradual accumulation of rhenium in green leaves. Perrhenate ions present in the soil are sucked by the root fibrils together with water and other nutrient ions. Mineral substances and water are further transported through the xylem to the stem, branches and finally to leaves. Reaching the leaves, water and mineral salts (including perrhenate) penetrate the plant cell through the semi-penetrable cell coat and plasmatic membrane and enter the leaf cytoplasm by diffusion, since the salt concentration in the cell liquid is higher than the concentration of the aqueous salt solution coming from the root. The cell swells and water in the cytoplasm presses the cytoplasm to the cell coat. Water and salts (including perrhenate ions) enter the cell until the pressure of the cytoplasm to the cell coat is equalized with the pressure of the entering water (i.e. the turgor pressure is increased). The increased turgor pressure reduces the cell sucking ability, thus preventing penetration of water and mineral salts (including perrhenate ions). This is the way the perrhenate ions are accumulated in the green plants. Water content and salt concentration in the cell sap continuously change due to transpiration of water from the leaves and formation of organic substances by photosynthesis. These processes cause repeated decrease in turgor pressure, the latter restoring the sucking ability of the cell this resulting in resumed penetration of water and mineral substances including perrhenate ions. The process is constantly repeated, yielding gradual accumulation of rhenium in plants.

3.3 Approach to the development of a procedure for rhenium phytorecovery

This property of Re can be used for development of a method for its extraction from contaminated soils and waters by growing suitable plants. We propose the following approach to development of a procedure for rhenium phytorecovery:

1. To carry out regional investigations on the degree of rhenium accumulation in different kinds of plants growing near the ore dressing. The regions with the highest degree of rhenium accumulation in plants are a new potential source for its recovery.
2. To choose the best plant bio collector of rhenium (rapid and highest degree of Re accumulation by natural way)!
3. To develop a procedure for effective Re extraction from plants and obtaining pure ammonium perrhenate.

3.3.1 Regional investigation on the rhenium distribution in the environment of ore dressing and work processing regions

The present study shows our regional investigations on the distribution of rhenium in plants and waters from the ore dressing regions Asarel and Medet in Bulgaria and from the plant mass around the metallurgical ore processing region of Medet, Bulgaria. The ore deposit in the mine of Asarel is pyrite and chalcopyrite. The old mine Medet processed copper-molybdenum ore. The most often used plants for recultivation of mining regions in Bulgaria are birch and acacia. The sampling was performed in the beginning of November 2006 (see Fig.1) Plant samples were collected from the mines and from the spoils in them. The water of the river Maresh flowing from a spoil in mine Asarel as well as the vegetation growing near the river were also analyzed for rhenium content. The soils from spoil were also analyzed for rhenium content by a method developed by us for thermal extraction of rhenium from natural materials with subsequent kinetic determination [8].

3.4 Results and discussion

The rhenium content in green and dry leaves of the same plants was compared. The samples were analyzed using a field test and in the laboratory [6]. The results of the analyses are summarized in Tables 1 and 2.

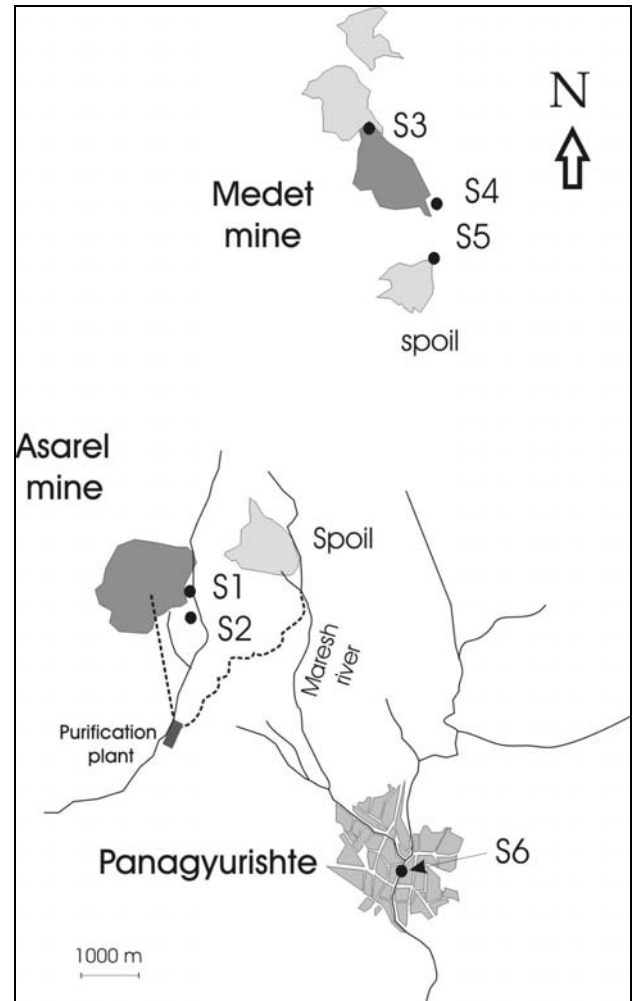


Fig. 1 Map of the ore-dressing regions Asarel and Medet and sampling sites, marked as S1...S6

The results in Tables 1 and 2 reveal that rhenium is not uniformly distributed in the mining regions but its content in the vegetation growing there exceeds its Clark level from several thousand to tens of thousands. If one accepts that the mean rhenium content in pyrite and chalcopyrite ores from mine Asarel is 0.3 g Re/t and 0.6 g Re/t respectively, then the rhenium content in the vegetation near the mine exceeds ten times and more that in the basic ore. On the other hand, the concentration of rhenium in leaves of acacia exceeds more than 100 times its concentration in soil. The results reveal that acacia leaves accumulate greater amounts of rhenium than do birch leaves.

Table1. Concentration of rhenium in plants from the ore dressing region Asarel –Medet

Sampling site, Sample type	C _{Re} µg/g ash	Ratio C _{Re} /Clark*
S1, green leaves of acacia	9.2	13143
S2, green leaves of birch	4.1	5857
S3, Leaves of acacia	9.45	13500
S4, Leaves of acacia	3.6	5142
S5, Leaves of birch	0.975	1393
S6, Riverside of r. Maresh-green and yellow dry leaves of <i>Arctostaphylos</i>	30.8	44000

*The Clark of Rhenium in the Earth’s crust is 7.10⁻⁴ µg/g

Table 2 Comparison of the rhenium concentration in plants with its background level

Sampling site	Sample type	C _{Re} found in µg/g	Ratio C _{Re} plant/ C _{Re} background
S1	soil	0.090	102.2
S1	green leaves of acacia	9.2	
S6	water from r. Maresh	0.078	394.8
S6	riverside of r. Maresh- leaves of <i>Arctostaphylos</i>	30.8	

The rhenium content in the vegetation growing inside the mine (S3) exceeds about 2.6 times that on the spoils (S4). Analyses for Re content in waters of the river Maresh flowing from the spoils of mine Asarel show that the Re content in it is 0.078µg Re. ml⁻¹. Analysis the vegetation along the river and mainly of the green and yellow dry leaves of *Arctostaphylos*

shows that the rhenium content in both cases is the same and equal to 30.8 µg Re g⁻¹ ash, the latter being 394 times higher than that in running water. This evidences that the vegetation along the river is also a biocollector of rhenium, which can be used for its extraction from polluted waters. On the other hand, the equal concentrations of rhenium in green and dry yellow leaves confirm that rhenium does not play a significant role in the plant metabolism since it is liberated with the falling leaves. Finally, dry yellow leaves appear to be a new potential source of rhenium.

With a view to studying the anthropogenic pollution of the environment with rhenium as Re₂O₇ emissions from the pyrometallurgical treatment of copper concentrates a plant sample of leaves of acacia and birch was taken directly below the chimney and 600 m from the chimney. The plant sample of leaves of birch outside of the ore processing regions (20-km west from the pyrometallurgical area) was analyzed for rhenium content. The results are summarized in Table 3

Table 3 Rhenium content in plant mass from the work processing region Medet

Sample Type	C _{Re} µg/g ash	Ratio C _{Re} / Clark
Leaves of acacia*	26.49	37843
Leaves of birch **	18,67	26671
Leaves of birch ***	0.15	214

*collected at a 600 m distance from the chimney of the copper works “Medet”

**growing in front of the copper works “Medet”

*** collected outside the ore-dressing regions 20-km to the west

The results in Table 3 also indicate that the anthropogenic pollution of the environment with rhenium due to emissions of the copper processing works Medet is significant. It is interesting that the vegetation growing in unpolluted regions is also enriched in rhenium and exceeds its Clark level 214 times.

4 Conclusions

All results obtained by us evidence that the plant Biosphere in vicinity of ore dressing and processing works appears to be a natural biocollector and concentrator of dispersed rhenium and a new potential source for rhenium recovery from soils and wastewaters. Our investigations aimed at studying the best plant biocollector of Re are still in progress. The green mass of plants growing in areas of ore processing and mining could be harvested, green and dry leaves collected and then incinerated or treated in different ways to preconcentrate rhenium. Our studies can be used as a basis for developing a cheap, simple and environmentally friendly biotechnological scheme for rhenium phytoextraction from soils and waters in areas of ore processing and mining.

References:

- [1] L. Borisova and A. Ermakov, *Analytical Chemistry of Rhenium (in Russian)*, Nauka, Moscow, 1974.
- [2] M. Magyar, Rhenium, *U. S. Geological Survey Minerals Yearbook*, 2003, pp. 621- 624.
- [3] O. Bozhkov, Chr. Tzvetkova, L. Borisova, V. Ermakov and V. Ryabukhin, Study of rhenium accumulation in plants, *Trends in Inorganic Chemistry*, review, Vol. 9, 2006, pp. 1- 10.
- [4] S. Kalinin, M. Asanov, K. Sulejmanov and E. Fain, Biogeochemical aureols of rhenium in ore dressing regions (in Russian), *Vestn. A N Kaz. SSR*, Vol. 10, 1986, pp. 48- 51.
- [5] O. Bozhkov and L. Borisova, Bioaccumulation of rhenium in green plants. New possibility for its recovery, *Proceedings of International Conference Modern Management of Mine Producing, Geology and Environment Protection*, 2001, pp. 411- 419
- [6] O. Bozhkov and L. Borisova, Extraction and Determination of Trace Amounts of Rhenium in Plants, *Intern. J. Environ. Anal. Chem.*, Vol. 83, N 2, 2003, pp. 135- 141.
- [7] L. Borisova, Yu. Demin, N. Gatinskaya, V. Ermakov, V. Ryabukhin and O. Bozhkov, Determination of Rhenium in Plant Materials, *J. Anal. Chem.*, Vol. 60, N 1, 2005, pp. 86- 91.
- [8] O. Bozhkov and L. Borisova, Vacuum Thermal Extraction of Rhenium from Natural Materials with Subsequent Kinetic Determination, *J. Anal. Chem.*, Vol. 54, N 10, 1999, pp. 931- 934.

Acknowledgments:

The authors appreciate the financial support of the Bulgarian Ministry of Education and Science, Project TK-X-1602/06 and EC FP6, Project INCO- CT- 2005- 016414