Phytomining: New Method for Rhenium

Rhenium (Re) is one of the rarest elements in the Earth’s crust ($7 \times 10^{-8}\%$), and is one of the ten most expensive metals on the world market\(^1\). It has unique physicochemical properties that allow its use in preparation of high-temperature superalloys; rhenium improves the physicochemical properties of Ni-Re, W-Re, Pt-Re, and other superalloys. The main application of Re is Ni-Re alloy in preparing turbine blades for aircraft engines and gas turbines. The main world producers of Re are Chile, Kazakhstan, France, Germany, Russia, U.S., China, Great Britain, the Netherlands, and Poland\(^1\).

The main consumers of Re world production are: Rolls Royce (28%), General Electric (28%), and Pratt & Whitney (12%) in the manufacture of superalloys used in aerospace industry and energetics. Re-Pt alloys account for 14% of Re use as catalysts for the production of lead-free gasoline. High-temperature thermocouples, x-ray sources, self-cleaning electrical contacts, and other products consume 18% Re. About 80% of Re is obtained as a by-product of the pyro- and hydrometallurgical treatment of molybdenum and copper ores and concentrates, and 20% is obtained from Re-containing wastes, such as alloys and catalysts.

The world production of Re in 2008 was 45 tons, while the annual demand of Re is about 60 tons\(^1\). Because world production of Re cannot meet industry needs, there is a continual search for new Re sources and new, more effective technologies for its production. Current technologies for producing rhenium containing concentrates and extracting Re from them are not effective enough. During these processes, part of the rhenium is lost and dispersed as volatile Re$_2$O$_7$ in surrounding soils and as ReO$_4^-$ ions in industrial waste solutions and water\(^2\). The scattered rhenium in the environment around copper and molybdenum mines and copper processing factories is a potential source for rhenium production.

How can this rhenium be collected profitably?

The unique property of rhenium to accumulate and concentrate in the green parts of all kinds of vegetation can be used to this aim. The plant biosphere is a natural collector and concentrator of Re from the surface environment (soils and waters)\(^3\). The most mobile and bioavailable species of rhenium in the surface environment is ReO$_4^-$ ions\(^4\). The vegetation in areas of copper mines and copper processing works is enriched in rhenium in amounts many times exceeding its natural occurrence\(^5\). It is known that rhenium occurs in copper and molybdenum sulfide ores as the water insoluble ReS$_2$\(^6\).

There are sources of bioavailable ReO$_4^-$ ions in these areas. This is the oxidation zone of ore deposits and dissolved oxygen in underground, hydrothermal, and surface waters. Some oxidation steps of the technology for producing copper and molybdenum concentrates by bacterial leaching with acidithiobacillus ferrooxidans in H$_2$SO$_4$ solution in presence of Fe$^{3+}$ ions also generate ReO$_4^-$ ions, which are dispersed in the surface environment of copper mine regions through waste waters and rain fall\(^7,8\). Volatile Re$_2$O$_7$ is generated during roasting of the concentrate, which is dispersed as a gas emission in the environment and settles on the soils, where in contact with water, it easily transforms to ReO$_4^-$ ions\(^9\).

Asarel open pit copper mine, Bulgaria. Phytomining rhenium is an inexpensive, environmentally friendly green technology.
Taking into account these considerations, one can predict regions with the potential for rhenium phytomin- ing. The most important first step is to investigate the rhenium distribution in the vegetation in these areas and to find locations with industrial importance of Re concentration in the plant mass, which, say the authors is about 500 g Re/t ash.

Phytomining of rhenium

Phytomining is defined as the uptake and preconcentration of bioavailable metal species from the environment into the plant biomass in a natural way\(^9,10\). Preconditions for rhenium phytomining and production are:

- Find locations with rhenium concentration in vegetation of industrial importance.
- For Re extraction from soils, sow the area with the plant species that is a hyperaccumulator of Re; i.e., capable of accumulating 1000+ g Re/1 t hay\(^9\). The Re hyperaccumulator should be wide spread, unpretentious for growing, have a large amount of green mass, and be easy to harvest.
- Apply simple procedures for its extraction from vegetation and control the amounts of main ash elements (e.g., K, Mg, and Ca) in the leachates.
- Purify Re-containing solutions from impurities using an inexpensive, effective procedure to obtain ammonium perrhenate.

Investigative results on Re distribution in the vegetation in the vicinity of three copper mines in Bulgaria showed that rhenium was not uniformly distributed in the areas. In all cases, the metal concentration in the plants exceeded its natural spread from one hundred to several thousands times. Different plant species displayed different capacities for Re accumulation. The highest Re concentrations were found in vegetation of the area of the open pit Asarel mine\(^5\) shown in Fig. 1 and Table 1.

Vegetation growing close to the depot of oxide copper concentrate had levels of Re concentration in the vegetation of industrial importance (acacia leaves with 1686 μg Re/g ash). Re concentration in the aqueous extract of the soil near the acacia was 5 μg Re/g soil\(^11\); the concentration of bioavailable Re (as water soluble perrhenate) in the soil. The enrichment factor (CRe in leaves/CRe in soil) of acacia leaves is 337.2. However, tree species are unsuitable for the technological extraction of Re from soils and waters, the difficulty arising from the collection of the green mass. The plant species, which accumulates 1000 or more g metal/1 t dry mass, is a hyperaccumulator\(^9,10\).

Re phytomining requires a plant hyperaccumulator of Re that should be simple to cultivate and grow fast; have a great amount of green mass, which is a precondition for hyperaccumulation of Re; and be easy to harvest and grow again after cutting. Experiments were conducted on a laboratory scale to determine the capacity for rhenium bioaccumulation of different plant species, based on the above criteria.

| TABLE 1 — HIGHEST RE CONCENTRATIONS FOUND IN THE VEGETATION AROUND ASAREL MINE |
|---------------------------------------------|---------|---------|
| Sampling site/sample type                  | CRe mg/g ash (a) | CRe/Clark Ratio value (a) |
| S1/leaves of flowering clover              | 2.30     | 3286    |
| S1/ acacia leaves                          | 0.59     | 843     |
| S2/oak leaves                              | 7.20     | 10,286  |
| S2/beech leaves                            | 1.61     | 2300    |
| S2/drainage water from lake                | 0.12 mg/ml | 171     |
| S3/river water                             | 0.04 mg/ml | 57.1    |
| S3/elder leaves                            | 30.8     | 44,000  |
| S4/acacia leaves 5 m from depot            | 1686     | 2.41 x10^6 |
| S4/soil 5 m from depot                     | 5.0      | 7143    |
| S5/acacia leaves                           | 13.2     | 18,857  |

Re phytoextraction from soils spiked with ReO_4^- ions

Four plant species studied to determine their capacity for rhenium accumulation from soils spiked with ReO_4^- ions (the bioavailable form of Re) were\(^11-13\):

- Mountain-spinach (atriplex hortensis)
- Buckwheat (polygonum fagopyrum)
- Alfalfa (medicago)
- White clover (trifolium repens)

Four pots, each containing 2.5 kg of dry soil seeds of alfalfa, mountain-spinach, buckwheat, or white clover were planted and regularly watered. After two weeks the plant
species grew and developed leaves, and the soil was spiked with 0.3218 g Re as an aqueous KReO₄ solution. The concentration of Re in the soil was 128.72 µg/g soil[12]. Monitoring of bioaccumulated Re in samples of developed vegetation was carried out at different times after spiking of the soil. Plant samples were dried to constant weight under atmospheric conditions. A precise weight of dry plant was incinerated at 480°C, and the rhenium was extracted from the ash using an alkaline solution[14]. Rheinum content in the solution was determined using a highly sensitive catalytic method for rhenium determination with N, N-dimethylthiioxamide, or DMDTO[15].

Test results show that all four plant species are Re hyperaccumulators, the most effective being alfalfa[11-13]. After seven days, Re content in alfalfa growing on soil spiked with ReO₄⁻ ions (CRe = 128.72 g Re/t soil) increased up to 46,586 g Re/t dry alfalfa (4.66% Re) and 294,289 g Re/t ash (29.43% Re), and did not further increase with time. The enrichment factor is 362 for dry mass and 2286 for ash. For the first time, rhenium phytoconcentrate was prepared in laboratory conditions.

White clover also showed very good rhenium accumulation. After 22 days in spiked soil, Re content increased to 35,090 g Re/t dry clover (3.51% Re), and 226,553 g Re/t ash (22.66% Re). The enrichment factor is more than 272 for dry mass and 1760 for ash. By comparison, the richest molybdenum concentrates contain up to 1000-2000 g Re/t concentrate[16]. Moreover, phytoconcentrates are obtained in a natural way (only through watering plants and using their metabolism) with minimum resources, while the ore concentrates are obtained using sophisticated high-cost technologies. The other two plant species showed significantly lower capacities for rhenium bioaccumulation; mountain-spinach (up to 3150 g Re/t dry mass) and buckwheat (up to 9130 g Re/t dry mass[15]).

Re extraction from plant mass

Two simple procedures developed for 100% Re extraction from the plant mass are[17];

- Incineration of dry mass followed by Re extraction from the ash using ammonium hydroxide solution
- Ethanol extraction of Re from raw mass followed by distillation of the ethanol, incineration of the dry residue, and leaching Re from the ash using ammonium hydroxide solution

Re concentration in the leachates was determined using the catalytic DMDTO method[14, 15]. K, Ca, Mg, and Cu concentrations in the leachates were determined using FAAS.

Results showed the alkaline leachate obtained after direct incineration of alfalfa contains 52.79% Re and 47.21% K, Ca, Mg, and Cu (the sum of the main ash elements)[17]. The leachate obtained after ethanol extraction of Re from alfalfa contained 67.4% Re and 32.6% main ash elements[17]. Leachates obtained using the two procedures are not sufficiently purified from the main ash elements, and are not suitable for obtaining pure ammonium perrhenate.

Purification of the Re-containing leachate

The Re species in the alkaline leachate is ReO₄⁻ ions[4, 14], while the main ash elements (K, Ca, Mg, and Cu) are present in the leachate as cations. The usual way to remove cations from solutions is via cation exchange resins[18]. The strongly acidic cation-exchange resin Dowex 50W×8 in H⁺ form was selected[19], and the batch method of sorption was used because of its simplicity. Under laboratory conditions, it was determined that after one hour of dynamic contact between the liquid phase and the resin, the degree of sorption of the cations was about 89%; after two hours, 95%; and after three hours, 99%[12]. Therefore three hours was used in all subsequent experiments. Results showed the leachate obtained after direct incineration of the plant mass and purified by treatment with the cation-exchange resin contains 95.3 % Re and 4.7% main ash elements[12]. The leachate obtained after ethanol extraction of Re from alfalfa and purification contains 98.2 % Re and 1.8 % main ash elements. A simple procedure for purification of the Re-containing leachate from the main ash elements was developed. NH₄ReO₄ is easily obtained from the final solution after alkalization with NH₄OH, preconcentration by evaporation, and crystallization of NH₄ReO₄[19].

Practical application of Re phytomining

A soil sample near the depot of copper concentrate at the Asarel mine was collected. The bioavailable form of Re in the surface environment is the water soluble perrhenate ion (ReO₄⁻), and an aqueous extract from the soil was made to determine Re[11]. The pH of the leaching aqueous solution was 8.5-9.0, which indicates an alkaline soil. Results of analysis using the DMDTO method to determine Re content in the leaching solution[15] showed that CRe is equal to 5µg Re/ g dry soil[11]. In further experiments, one plastic plate with soil sample was planted with alfalfa and regularly watered. Three days after seeding, the alfalfa sprouted and developed small leaves within thirty days. The soil was likely very exhausted and the plant did not get sufficient nutrient ions for its growth. However, the green

### Table 2 — Rhenium Accumulation by Undeveloped Alfalfa Grown on Exhausted Soil(a)

<table>
<thead>
<tr>
<th>Plant species</th>
<th>Sample time after sowing, days</th>
<th>CRe, µg Re/g dry mass(a)</th>
<th>F(b)</th>
<th>CRe, µg Re/g ash(a)</th>
<th>F(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa</td>
<td>10</td>
<td>593</td>
<td>119</td>
<td>2778</td>
<td>556</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>35</td>
<td>1381</td>
<td>276</td>
<td>4869</td>
<td>974</td>
</tr>
</tbody>
</table>

(a) CRe = 5 µg Re/g dry soil. (b) Enrichment factor = CRe in plant/CRe in soil

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mass was harvested at the 10th and 35th day after sowing, dried at 70°C in an oven, and the dry plant mass incinerated at 480°C. Re was extracted from the ash using an alkaline solution, and Re content determined using the DMDTO method\textsuperscript{[14, 15]}. The results are shown in Table 2.

The alfalfa species accumulates extracts and preconcentrates Re from contaminated soil. The Re concentration in alfalfa (4869 μg Re/g ash) growing on the same soil by about 300%\textsuperscript{[2]}. Under-development of alfalfa may be due to the depth of ploughing, the quantity of seed per 1000 m² and depth of sowing, and the quantity of fertilizer, watering, etc.\textsuperscript{[30]}. The authors believe that well-developed alfalfa will accumulate more rhenium.

References
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