



## Phytomining of Re - an Alternative Method for Re Production

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## Phytomining

**Phytomining is: Uptake and preconcentration of bioavailable metal species from the environment into the plant biomass in a natural way.**

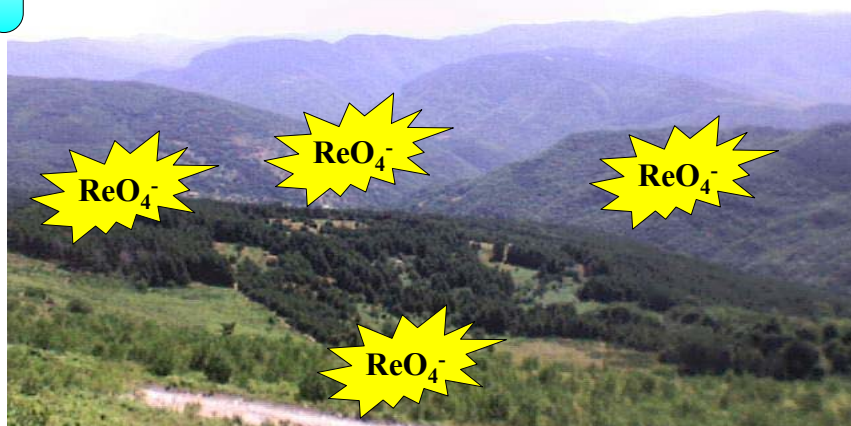
**Main benefit of phytomining is : a less expensive and environmentally friendly method for recovery of dispersed metals from soils and waters, characterized by simplicity of implementation.**

**Enough is to plant the metal containing area with the crop and after plant development, to harvest the green mass and extract the metal from the plant mass, usually by its incineration.**

## Preconditions for Re Phytomining:

1. The unique property of Re to accumulate and concentrate in the green parts of all kinds of plants in a natural way.
2. The plant biosphere in the vicinity of copper mines and around copper processing factories is enriched with rhenium in amounts exceeding many times its natural spread in Earth's crust.

Re is easily accumulated and concentrated as  $\text{ReO}_4^-$  in all green over ground parts of terrestrial plants (more than 98% in leaves)



## Bioaccumulation of Rhenium in algae exceeds its ocean level from 20 to 740 000 times



## Our Approach for Re Phytorecovery from Soils and Waters

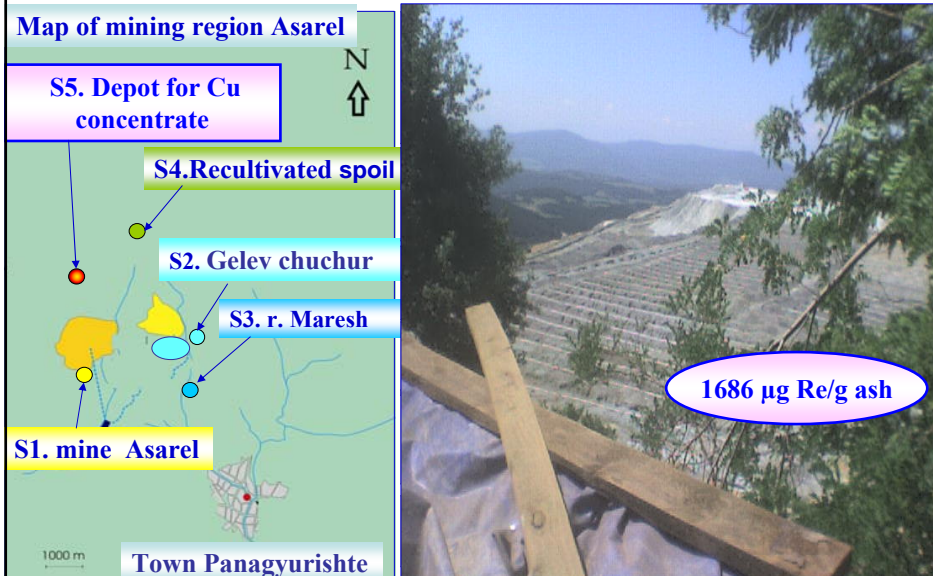
1. To carry out regional investigations on the degree of Re accumulation in various plants from the copper mining region “Asarel”.
2. To find the location with industrial importance of Re concentration in the vegetation ( $C_{\text{Re}} \geq 500 \text{gRe/t ash}$ ).
3. To find the plant species, which hyperaccumulate Rhenium ( $C_{\text{Re}} \geq 1000 \text{gRe/t dry mass}$ ).
4. To develop a simple procedure for Re extraction from the vegetation and for obtaining of  $\text{NH}_4\text{ReO}_4$ .

## Regional investigation on Re distribution in the vegetation of mine “Asarel”

The plant biosphere around mine “Asarel”- Bulgaria is enriched with different amounts of Re exceeding its natural occurrence from hundreds to millions times



## Highest Re Concentrations Found in the Vegetation in Vicinity of Mine “Asarel”



We found the point with industrial importance of Re concentration – acacia leaves, growing close to the depot of oxide Cu concentrate. Tree species are, however, unsuitable for the technological extraction of Re from soils and waters.

For real Re phytomining, a plant hyperaccumulator of Re must be found, which should be:

- a) unpretentious for cultivation;
- b) with great quantity of green mass;
- c) easy for harvesting.

## Conclusions

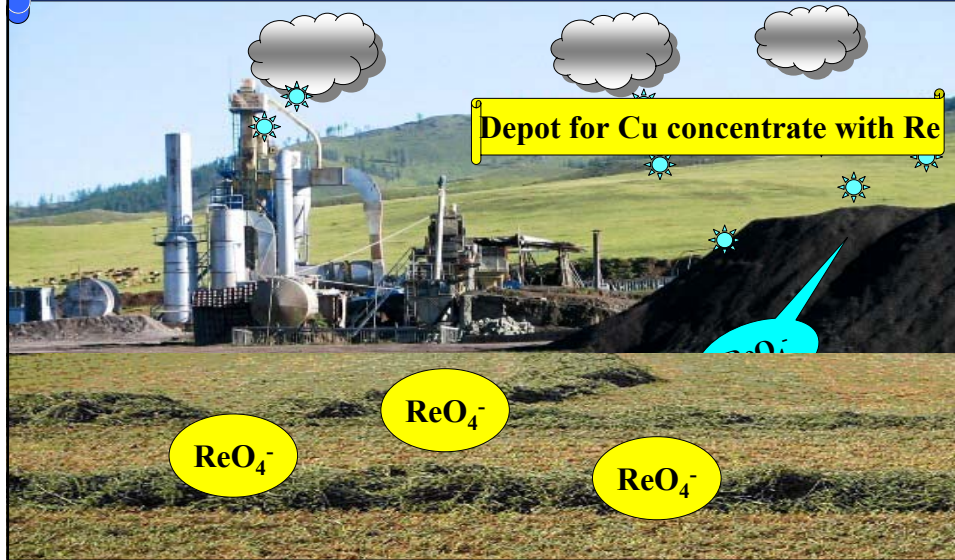
Alfalfa (lucerne) is the best hyperaccumulator of Re and is suitable for real Re phytomining.

We prepared at laboratory conditions a Re

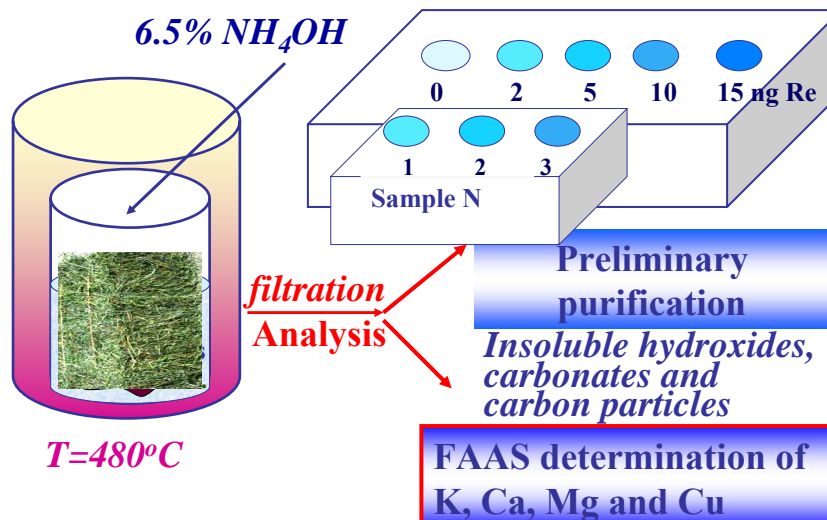
*phytoconcentrate* containing 4.6 % Re in the dry lucerne mass, respectively 29.43% Re in the ash of lucerne.



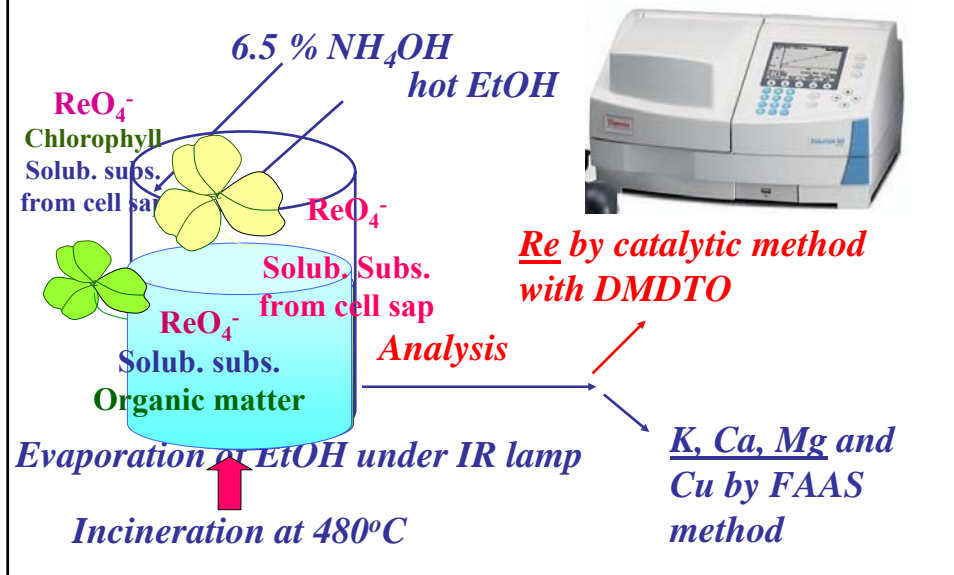
## Harvesting of alfalfa crop



## Methods for Re extraction from vegetation developed by us



## Extraction of Re by hot ethanol from raw plant mass



## Composition of the leaching solutions after Re extraction from the plant mass

By direct incineration:

52.8% Re

47.2% sum of main  
ash elements

By EtOH extraction:

67.3% Re

32.7% sum of main  
ash elements

The leaching solutions are contaminated with  
the main ash elements

Our aim: To achieve additional purification of the  $\text{ReO}_4^-$  containing solutions from cations of the main ash elements such as  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$

## Additional purification of both leaching solutions

The usual manner for the removal of cations from solutions is to use cation exchange resins.

We chose:

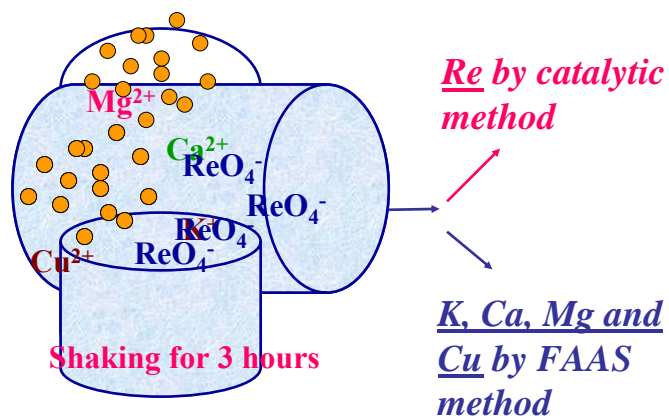
- The strongly acidic cation exchange resin Dowex 50Wx8 in hydrogen ionic form

**Principle of method:**

Sorption of cations of main ash elements on the resin as a result of ion exchange between  $H^+$  in the acidic functional groups of Dowex50Wx8 and cations from the solutions

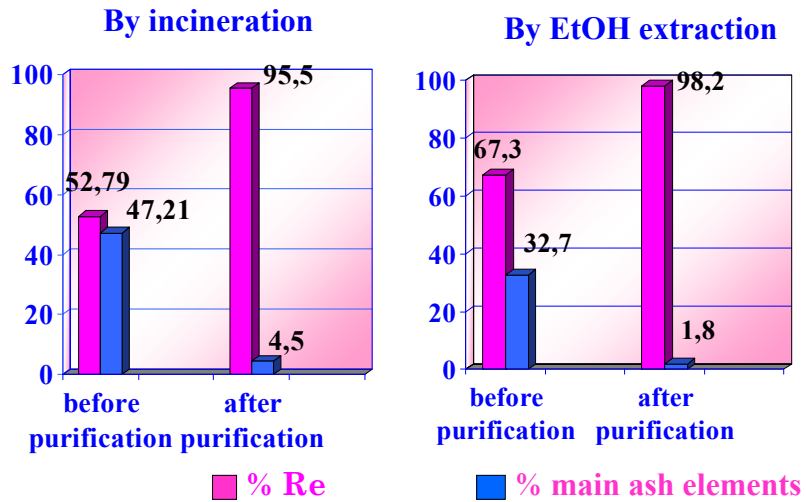
- The batch method because of its simplicity of performance - just shake the solution with resin in a closed vessel

## Purification of leaching solutions with cation exchange resin Dowex50Wx8





## Composition of Re containing leaching solution before and after purification



## Obtaining of $\text{NH}_4\text{ReO}_4$



## Comparison of methods for Re recovery from Phyto and Ore concentrates

<b>Cu and Mo conc.: 40-2000gRe/t</b>	<b>Re Phytoconcentrate: 46 000gRe/t</b>
<b>Pyro and hydrometallurgical Processing of conc. Oxidation of <math>\text{ReS}_2</math> to <math>\text{ReO}_4^-</math>. Catching of volatile Re by scrubbers, electrofilters a.o. Leaching the Re from flu dust and conc. by acids.</b>	<b>Thermal processing of the plant matrix. Direct leaching of Re from ash.</b>
<b>Composition of leaching solutions: <math>10^{-3}</math>-<math>10^{-2}\%</math> Re and macro quantities of Cu, Mo, Fe, Pb, Mn, Co, Si i.e..</b>	<b>Composition of leaching solutions: 53-67% Re and 33-47% impurities as a sum of main ash elements-K, Ca, Mg and Cu.</b>
<b>Separation and concentration of Re by extraction, chromatographic a.o. techniques require costly installations. 65-95% yield of Re</b>	<b>Simple processing of solution by cation exchange resin. Resulting solution -98.2% Re and 1.8% impurities -main ash elements. 100% yield of Re.</b>



## Conclusions

- We developed a low-cost and environmentally friendly technological scheme for real phytorecovery of dispersed Re by alfalfa from the soils of ore dressing regions.
- After obtaining of the Re phytoconcentrate a simple procedure developed by us leads to the production of  $\text{NH}_4\text{ReO}_4$  - the commercial product of Re.

### Acknowledgments:

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