Alternative biohydrometallurgical recovery of metals from sewage sludge, waste incineration residues and similar substances with hyperaccumulating plants

3RD INTERNATIONAL CONFERENCE on Sustainable Solid Waste Management

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Motivation

- More than 90% material import
- Resource scarcity $\Rightarrow$ price $\uparrow$
- Technologies to recover critical raw materials are rare and expensive
- Linear solutions are not sufficient

Source: UNEP Year Book 2011, Emerging issues in our global environment
Introduction

- Hyperaccumulating metalophytes
- Phytomining developed from phytoremediation
- Phytoextraction of metals from substrate
- Harvesting & treating plants to gain “bio-ore”
Phytomining

First suggested by Baker & Brooks in 1989

- Ni extraction & biomass combustion resulted in bio-ore containing 15% Ni
- Fertiliser amendments to increase extraction
- Improving phytoextraction with
  - Increasing metal bioavailability (microorganisms, pH-decrease, chelating agents)
  - Crops themselves (species selection, biotechnology, seed coating)
  - Environmental factors - shortening growth cycle (CO₂, shade)

Phytomining of Ni using Alyssum murale on ultramafic Vertisols in Albania

Source: Guillaume Echevarria, Université de Lorraine, France

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Absolute accumulation on different substrates from pre-trials

**Graph:**
- **Y-axis:** mg/kg DM
- **X-axis:** Different substrates (Dryopteris, Alys sludge, Alys slag, Alys Tr, Pteris, sunfi sludge, sunfi slags, sunfi Tr, Phylolacca, Eichor Tr)
- **Legend:**
  - Nickel
  - Manganese
  - Rubidium
  - Molybdenum
  - Vanadium
  - Strontium
Relative accumulation on sewage sludge from pre-trial

- Dryopteris filix-mas
- Alyssum murale
- Pteris cretica
- Helianthus annus
- Phytolacca americana

- nickel
- manganese
- rubidium
- molybdenum
- vanadium
- strontium
## Overview for sewage sludge

<table>
<thead>
<tr>
<th></th>
<th>Alyssum murale</th>
<th>Helianthus annus</th>
<th>Pteris cretica</th>
<th>Dryopteris filix-mas</th>
<th>Eichhornia crassipes</th>
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<tbody>
<tr>
<td>nickel</td>
<td>✓✓</td>
<td></td>
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<tr>
<td>molybdenum</td>
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<td>manganese</td>
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<td>vanadium</td>
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<td>✓</td>
<td></td>
<td></td>
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</tbody>
</table>

✓✓ high relative accumulation (5x-20x)
✓ moderate relative accumulation (1x-5x)
### Value potential

#### sewage sludge – ashes – incinerator slags

<table>
<thead>
<tr>
<th>element</th>
<th>amount [mg/kg]=[ppm]</th>
<th>price for elements or oxides [€/kg]</th>
<th>value potential [€/t resource]</th>
<th>[€/a]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>sludge</td>
<td>ash</td>
<td>slags</td>
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<tr>
<td>Rb</td>
<td>12.89</td>
<td>30.46</td>
<td>15.77</td>
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<td>Co</td>
<td>3.38</td>
<td>16.7</td>
<td>39.55</td>
<td>€ 20.33</td>
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<tr>
<td>Cr</td>
<td>44.6</td>
<td>169.7</td>
<td>570.5</td>
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<td>Mn</td>
<td>176</td>
<td>736</td>
<td>1653.5</td>
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<td>Mo</td>
<td>3.695</td>
<td>24.05</td>
<td>57.3</td>
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<td>Ni</td>
<td>33.1</td>
<td>140</td>
<td>200.5</td>
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<td>Sb</td>
<td>0.4</td>
<td>43.8</td>
<td>30.3</td>
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<td>V</td>
<td>20.2</td>
<td>72.5</td>
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<td>Zn</td>
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<td>4175</td>
<td>3118</td>
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<td>Ce</td>
<td>7.15</td>
<td>18.9</td>
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<td>Er</td>
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<td>0.514</td>
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<td>0.531</td>
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<td>Ho</td>
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<td>0.162</td>
<td>0.3095</td>
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<td>La</td>
<td>4.23</td>
<td>12.2</td>
<td>28.75</td>
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<tr>
<td>Lu</td>
<td>0.0213</td>
<td>0.0587</td>
<td>0.149</td>
<td>€ 1.887.79</td>
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<td>Nd</td>
<td>2.76</td>
<td>6.73</td>
<td>13.94</td>
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<td>Pr</td>
<td>0.754</td>
<td>1.94</td>
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<td>Sc</td>
<td>1.35</td>
<td>2.84</td>
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<td>Sm</td>
<td>0.534</td>
<td>1.269</td>
<td>2.1955</td>
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<tr>
<td>Tb</td>
<td>0.075</td>
<td>0.167</td>
<td>0.3955</td>
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<tr>
<td>Y</td>
<td>1.96</td>
<td>7.02</td>
<td>15.18</td>
<td>€ 18.27</td>
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</table>

| sum     | € 20.83 | € 52.47 | € 46.62 | € 1.406.135 | € 787.137 | € 6.992.909 |

### Metal content of waste incinerator bottom ash (slags)

### Only critical elements

### Slags have biggest potential

Amount for Vienna:
- Ash: 15.000 t/a (fluidized bed furnace 1-3)
- Sludge: 67.500 t/a from EBS Vienna
- Slags: 150.000 t/a

[www.alchemia-nova.net](http://www.alchemia-nova.net)
Bottom ash is a challenging substrate for plant growth

High pH value (up to 12.5)

High electrical conductivity (2-8 mS/cm)

Low total nitrogen content (< 1 g/kg)

Toxic levels of some heavy metals (total content Cu= 1730-2390 mg/kg, Cr= 140-470 mg/kg; plant available fraction Cu > 2500 µg/kg Cr= 60-580 µg/kg)

Work done by Theresa Rosenkranz from BOKU
Substrate conditioning

First greenhouse trials (Theresa Rosenkranz, BOKU)

- At first treatment with diluted nitric acid to lower pH & increase N
- Leaching with deionized water to decrease salinity
- Amendments: compost (also from MBT), biochar

Field trials on landfill Vienna & further greenhouse trials

- Mixing with compost & 2 months ageing with high surface (reaction with CO\textsubscript{2} from air)
  \(\rightarrow\) pH decrease
Strategies

- Known hyperaccumulators
- High biomass producing plants in favour
- Annual & perennial plants
- Landfill-endemic plants (decided after field collection & analysis)
- Intercropping strategies for rhizosphere interaction
- Aided phytoextraction with EDTA
- Interactions with microorganisms (extraction, selection, inoculation)
Conclusion

- Plants grow also successfully on less amended bottom ash
- Hyperaccumulators did not show expected results so far
- Package of strategies could improve uptake (ageing, EDTA, microorganisms, intercropping)
- Accumulation of some greenhouse trials with aided phytoextraction not yet evaluated
- Field trials just started, results expected this autumn (if goats won’t eat our sprouts)

Source: MA48, municipality of Vienna
Outlook

- Screening of possible (hyper)accumulators for elements of interest also with aided phytoextraction
- Gaining biomass and recovering metals with 5 different methods (biological, physical, chemical) → Phytomining
- Possible strategies to utilise rest of the biomass
- Evaluation of all different methods
- Follow-up projects!
Thank you for your attention!

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