Almadén: Remediation techniques in the largest mercury mining district of the world

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General Index

- Geology and mining
- Metallurgy
- Environmental concerns
- Hazards/risks
- Remediation issues
  - Work done
  - Work to do
Geology

- Location
- Regional geology
- Types of cinnabar deposits
Geology: Location

The Almadén syncline
Geology: Types of Hg deposits

► Two major types:
  - Stratabound
  - Epigenetic
Geology: Types of Hg deposits

- **Stratiform mineralizations: Almadén Type**
  - Disseminated cinnabar (1-7% Hg) in the “Criadero” Quartzite
  - Zonal relationship with the “frailesca” rock
  - Vary scarce pyrite
  - Very variable dimensions: 7.5 Mfl. in Almadén, 350,000 fl. in El Entredicho

*Flask*: commercial unit for mercury trade. 1 fl: 34.5 kg
El Entredicho open pit

5-10% Hg
Geology: Types of Hg deposits

► Stratabound mineralizations: Almadén Mine
  ▪ Active since more than 2,000 years
  ▪ Non-stop mining activity
Almadén mine

- Two branches (*ramas*):
  - Rama Sur: the first in activity, closed from 18 Century to the 80s, active again until May 2002 (final closure)
  - Rama Norte: discovered in 1700, in activity until 1992
Almadén mine

Underground mining: Cut & fill
Geology: Types of Hg deposits

- Epigenetic (discordant) mineralizations: Las Cuevas type
  - Cinnabar in veins and semimassive replacements
  - Cross-cutting the "frailesca" rock
  - Pyrite much more common than in stratiform deposits
  - Minor size - Las Cuevas: 150,000 fl.
Las Cuevas: cinnabar vein filling
Las Cuevas: cinnabar replacement of Frailesca

Up to 30% Hg
Las Cuevas mine

Underground mining, VCR (Vertical Crater Retreat)
Metallurgy

► Roasting: HgS + hot $\rightarrow$ Hg$^0$ + S$^0$

► Evolving methods, with reduction of Hg vapor emission:
  - “Xabecas” furnaces (12 Century - 1646)
  - “Bustamante” furnaces (1646 - 1930)
  - “Idrija” and others furnaces (1930-1957)
  - “Pacific” furnaces, propane fuelled (1954-2005)
Metallurgy

- Xabecas furnaces
- Hand work made by prisoners
Metallurgy

- Aludeles furnaces
Metallurgy

- Pacific furnaces
  - Multilevel system
  - Propane fueled
Environmental concerns

- Mercury cycle
  - In air
  - In soils and mine dumps
  - In water and stream sediments
  - In plants
  - In fauna
Environmental concerns

► Mercury cycle

![Mercury geochemical cycle in the biosphere](image_url)
Environmental concerns

- Mercury in air

Punctual data – Hg: 135,000 ng/m³
Environmental concerns

- Mercury in air: Regional pattern, continuous automobile survey
Environmental concerns

► Mercury in soils

<table>
<thead>
<tr>
<th>Site</th>
<th>N</th>
<th>Hg (ppm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Range</td>
<td>Mean</td>
<td>StDev</td>
</tr>
<tr>
<td>ALM</td>
<td>18</td>
<td>6-8,889</td>
<td>2.573</td>
<td>2.979</td>
</tr>
<tr>
<td>ECH</td>
<td>8</td>
<td>12-132</td>
<td>57.8</td>
<td>33.1</td>
</tr>
<tr>
<td>RD</td>
<td>19</td>
<td>10-188</td>
<td>61.2</td>
<td>55.0</td>
</tr>
<tr>
<td>FIT</td>
<td>22</td>
<td>6-69</td>
<td>22.0</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 1: Mercury concentrations in soils from different sampling sites. ALM: Almadenejos; ECH: Chillón; RD: Rodoviejo; FIT: Phytoremediation site; N: number of data; StDev: Standard deviation.

Environmental concerns

Mercury emission from soils

Hg: 8.650 ng/m³
Environmental concerns

► Mercury in mine dumps

Ore dump
Las Cuevas

Cinnabar
Metallic Hg
Schuetteite
Environmental concerns

- Mercury in mine dumps

Waste dump
El Entredicho

Schuetteite
Environmental concerns

► Mercury in mine dumps

Calcines from Roman times

Hg up to 2,260 µg/g
Environmental concerns

- Mercury emission from mine dumps

Hg: 5,000-50,000 ng/m³
Environmental concerns

- Mercury in **waters and stream sediments**
  - Research in course, with John Gray (USGS) and Mark Hines (Univ. Massachusetts Lowell)
  - Sampling of the main river course (Valdeazogues) and other sites
Environmental concerns

- Valdeazogues river: 9 samples, from upstream the mining area to some 20 km downstream

Hg\textsubscript{W}: 7.61 ng/L  
Hg\textsubscript{SS}: 0.362 µg/g  
Hg\textsubscript{W}: 190 ng/L  
Hg\textsubscript{SS}: 8.22 µg/g
Environmental concerns

Streams from the mining areas to the Valdeazogues river: Azogado stream
- $Hg_w$: 12,500 ng/L
- $Hg_{ss}$: 2,260 µg/g
Environmental concerns

- El Entredicho open pit lake

Hg\textsubscript{w}: 2,800 ng/L
Hg\textsubscript{ss}: 935 µg/g
Environmental concerns

- Mercury in wild plants: several species are very well adapted to soils very rich in mercury

  - Almadenejos metallurgical precinct
  - Marrubium officinalis: up to 16,000 µg/g
  - Soil: up to 1% Hg
Environmental concerns

- Mercury in wild plants: several species are very well adapted to soils very rich in mercury

Las Cuevas
Old mineral dump

Ditrichia graveolens: up to 16,500 µg/g

Soil: up to 2.5% Hg
Environmental concerns

- Mercury in wild plants: hyperacumulators

El Entredicho open pit lake

Typha dominguensis: up to 245,000 µg/g
Environmental concerns

- Mercury in wild plants: hyperaccumulators

Puddles in mine dumps

Polypogon maritimus:
up to 1,500,000 µg/g
Environmental concerns

- Mercury in wild plants: eatable – wild asparagus

Up to 7,000 µg/g
Environmental concerns

- Mercury in fauna: no data

- Domestic pigs in Almadenejos metall. precinct

- Fishing in Castilseras reservoir
Hazards / Risks

► For mine workers
► For local inhabitants
► For trophic chain
► Methylmercury presence
Hazards / Risks

► For mine workers:
  - Working schedule: 8 days a month, 6 hours in underground jobs
  - Health monitoring by the mining company health service: blood and urine
Hazards / Risks

► For local inhabitants:
  ▪ Hg vapor in air over WHO standard (1 µg/m³) in inhabitad areas
Hazards / Risks

► For local inhabitants:
  ▪ Hg vapor concentrations in some buildings

Almadén School of Mines

Hg up to 45,000 ng/m³ in some rooms (old museum)
Hazards / Risks

► For **trophic chain**:
  - Water
  - Fishing
  - Vegetables
Hazards / Risks

► For trophic chain:
  - **Water**: low Hg contents in most natural waters
  - Very low Hg content in drinking water

Hg: 1.78 µg/L
Hazards / Risks

► Drinking water comes from a reservoir away from the mining area

Hg: 9.08 µg/L
Hazards / Risks

► For trophic chain: **Fishing**

- Local people uses to fish in the Valdeazogues river and reservoirs (sport)
- Black Bass (*Micropterus salmoides*), Carp (*Cyprinus carpio*)
- Need to control the Hg and MeHg contents
Hazards / Risks

- For trophic chain: Vegetables
  - Cattle and wild fauna: high risk, since some wild plants contain quite high mercury levels
  - Humans: low mercury contents in agricultural plants (see phytoremediation section)
  - Some wild eatable plants with higher mercury levels
Hazards / Risks

- Methylmercury contents: data on study
  - Natural waters
  - Soils and stream sediments
    - Valdeazogues
    - Azogado stream
    - Entredicho pit lake
  - Calcine heaps
    - Almadenejos furnaces ruins
Remediation issues

► Work done
  ▪ Phytorremediation - phytoextraction
  ▪ Study of crandallitic immobilizator

► Work to do
Phytoextraction

► A collaboration between the E.U.P. Almadén (UCLM), the mining company and CIEMAT
► Trees
► Agricultural plants
► Spontaneous vegetation
Phytoextraction

▶ Trees: *Eucalyptus*

- 5 plots, on soils with Hg contents between tens and hundreds gr Hg/t (ppm)
- 4 years of “activity”
- Resulting on Hg contents in dry matter between 500 and 2.080 ppb
Phytoextraction

► Agricultural plants

- Wheat (*Triticum aestivum*), barley (*Hordeum vulgare*) and lupine (*Lupinus luteus*)
- 15 subplots 10x10 m, 3x plant, 3 fallow land, 3 spontaneous vegetation (2 years)
- 1 plot 100x50 m, barley (2\textsuperscript{nd} year)
- Hg contents in plots: tens of Hg ppm
- Samples of the crops were taken at different growth stages analyzing the Hg loading in the aerial part and in the root separately
Phytoextraction

► Agricultural plants: soils characterization

- PHYSICAL CHARACTERIZATION
  ✓ Granulometry
  ✓ Texture
  ✓ Real and apparent density
  ✓ Moisture

- CHEMICAL CHARACTERIZATION
  ✓ Total mercury
  ✓ pH (H₂O, KCl)
  ✓ Cation Exchange Capacity
  ✓ Organic matter
  ✓ Carbonates, sulfates and nitrates
  ✓ Conductivity

- MERCURY CHARACTERIZATION
  ✓ Mercury speciation: determination of inorganic mercury and methylmercury
  ✓ Sequential extraction: geochemical partitioning of mercury
Phytoextraction

Soils characteristics

GEOCHEMICAL PARTITIONING OF MERCURY

- Residual
- Sulforganic
- Humic
- Fulvic
- Exchangeable
- Water soluble
Phytoextraction

► Soils characteristics

**MERCURY SPECIATION**

- Volatile organomercuric compounds not detected (detection limit = 1 ng g⁻¹)
- Methyl-mercury content lower than 1% of total Hg in all the analyzed samples
## Phytoextraction

### Agricultural plants: results

- **First year (2000-2001):**

<table>
<thead>
<tr>
<th></th>
<th>Straw</th>
<th>Grain</th>
<th>Total (grain+straw)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wheat</strong></td>
<td>0.61475</td>
<td>0.03575</td>
<td>0.47872</td>
</tr>
<tr>
<td><strong>Barley</strong></td>
<td>0.46400</td>
<td>0.05700</td>
<td>0.33873</td>
</tr>
<tr>
<td><strong>Lupine</strong></td>
<td>0.25900</td>
<td>0.04800</td>
<td>0.19550</td>
</tr>
<tr>
<td><strong>Wild veget.</strong></td>
<td>0.32900</td>
<td>--------</td>
<td>0.32900</td>
</tr>
</tbody>
</table>

Mercury content in dry matter (mg/kg)
Phytoextraction

► Agricultural plants, 2\textsuperscript{nd} year

![Diagram showing distribution of mercury in plants vs culture age]
Phytoextraction

➤ Laboratory experiments:
- Study of the mercury availability in soils by means of monitorized lisimeters
- Being carried out by CIEMAT in Madrid
Phytoextraction

► Mercury recovery from biomass

- Biomass combustion in a fluidized bed oven
- Recovery from the effluent gas by means of carbon active filters
- Pyrometallurgy of the Hg-rich carbon active
- To be carried out by CIEMAT + Chemical Engineering Dept., UCLM
Phytoextraction

► Wild plants: already seen
Crandallitic immobilizator

**Lab synthesis of crandallitic compounds**

\[
3\text{Al(OH)}_3 + 2\text{H}_3(\text{PO}_4) + \frac{1}{2}\text{SrCO}_3 + \frac{1}{2}\text{CaCO}_3 \rightarrow \\
\rightarrow \text{Ca}_{0.5}\text{Sr}_{0.5}\text{Al}_3(\text{OH})_6(\text{HPO}_4)(\text{PO}_4) + \text{CO}_2 + 4\text{H}_2\text{O}
\]

- Reaction carried out at 60ºC in 1 dm³ flasks magnetically stirred at 700 rpm under environmental pressure
- Reaction time: 15 days

Crandallitic immobilizator

► Characterization of the product
  ▪ Chemical analysis

<table>
<thead>
<tr>
<th>Composition (% w/w)</th>
<th>Amorphous</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>36.11</td>
<td>51.37</td>
</tr>
<tr>
<td>Al</td>
<td>24.10</td>
<td>18.75</td>
</tr>
<tr>
<td>Sr</td>
<td>13.06</td>
<td>10.83</td>
</tr>
<tr>
<td>P</td>
<td>21.94</td>
<td>14.35</td>
</tr>
<tr>
<td>Ca</td>
<td>4.79</td>
<td>4.70</td>
</tr>
</tbody>
</table>
Crandallitic immobilizator

- Characterization of the product
  - Chemical analysis
  - Grain size
Crandallitic immobilizator

► Characterization of the product
  - Chemical analysis
  - Grain size
  - Scanning Electron Microscopy (SEM)

15 days, 60°C, Room press.

6 months, 200°C, 15 bar
Crandallitic immobilizator

Equilibrium and kinetic studies

- Experimental isotherms for the Hg\(_2^+\)/(Ca\(^{2+}\)-Sr\(^{2+}\)) exchange

<table>
<thead>
<tr>
<th>Solid</th>
<th>(n^-) (meq g(^{-1}))</th>
<th>(K_1)</th>
<th>(s\times10^4) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crandallite</td>
<td>0.93</td>
<td>30.13</td>
<td>7.54</td>
</tr>
</tbody>
</table>

Ion exchange reaction:

\[
2 \text{Ca}_{0.5}\text{Sr}_{0.5}\text{Al}_3\text{(OH)}_6\text{(HPO}_4\text{)(PO}_4\text{)} + 2 \text{Hg}^{2+} \leftrightarrow
\leftrightarrow 2 \text{HgAl}_3\text{(OH)}_6\text{(HPO}_4\text{)(PO}_4\text{)} + \text{Ca}^{2+} + \text{Sr}^{2+}
\]
Crandallitic immobilizator

- Equilibrium and kinetic studies
  - Experimental isotherms
  - Experimental kinetics: equilibrium in $\approx 30$ s

![Graph showing equilibrium and kinetic studies for Crandallitic immobilizator](image)
Crandallitic immobilizator

- Equilibrium and kinetic studies
  - Experimental isotherms
  - Experimental kinetics: Lagergren plot, first order reaction

![Graph showing Lagergren plot with Log qe vs time for different ppm concentrations]

- Lagergren plot, first order reaction

K_{ad} = 8.72 \times 10^{-2} \text{ s}^{-1}

- Crandallitic immobilizator
Crandallitic immobilizator

- **Recovery studies**
  - Thermal treatment: 800°C → 99.9% recovery
  - Chemical treatment: Cl⁻ (10⁻⁴ to 5 10⁻² M) to form soluble HgCl₂⁻²

![Graph showing Hg-crandallite dissolution at optimum pH=2.25]
Work done: Conclusions

► Phytoextraction:
  - Poor results with agricultural plants
  - Some possibilities with wild vegetation

► Crandallitic immobilizator:
  - Good synthesis conditions
  - High Hg$^{2+}$ exchange capacity from mercurial waste waters, similar to that obtained with commercial exchangers such as resins
Work to do

- Relay on National and European founding
- Techniques to apply
  - Immobilizator field application
  - Phytoremediation using wild vegetation
  - Electrodecontamination: Collaboration from the University of Malaga (Spain)
  - Soil and dumps covering to avoid light enhanced mercury vaporization