NATO Challenges of Modern Society

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

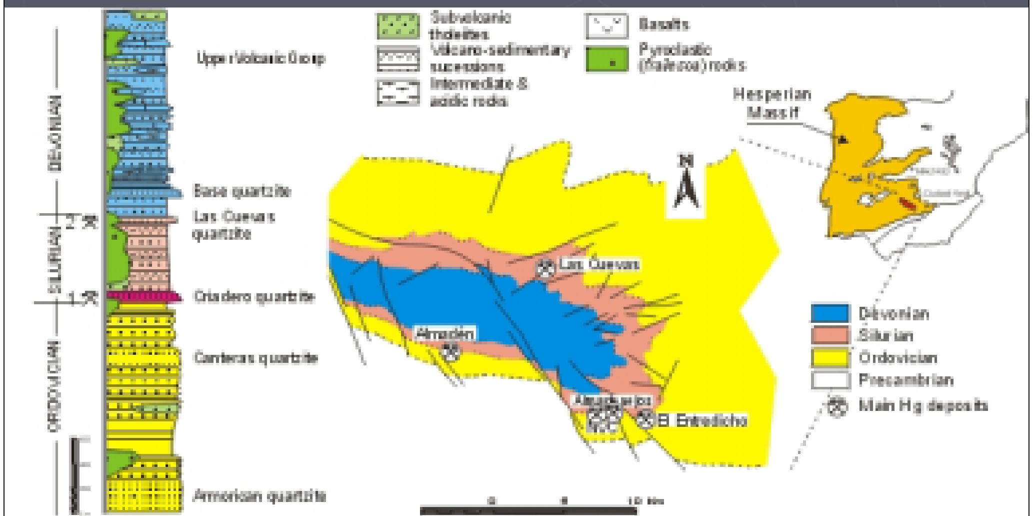
Geology

- Location
- Regional geology
- Types of cinnabar deposits

Geology: Location

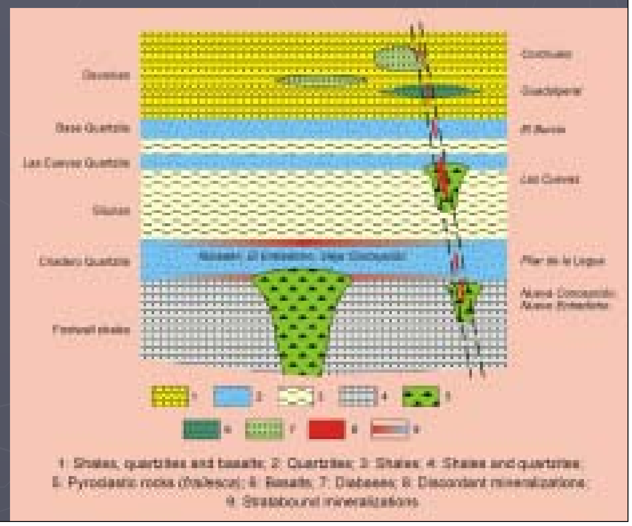
The Almadén syncline

Geology: Regional Geology



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

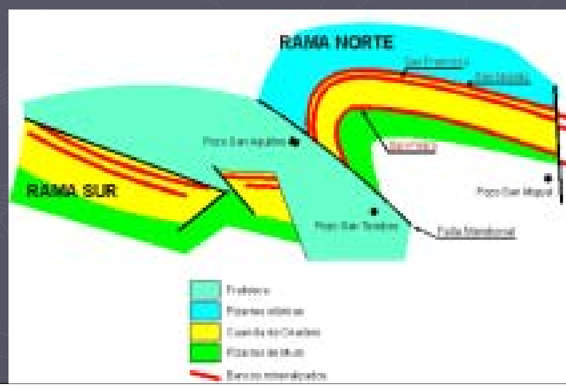
El Entredicho open pit

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

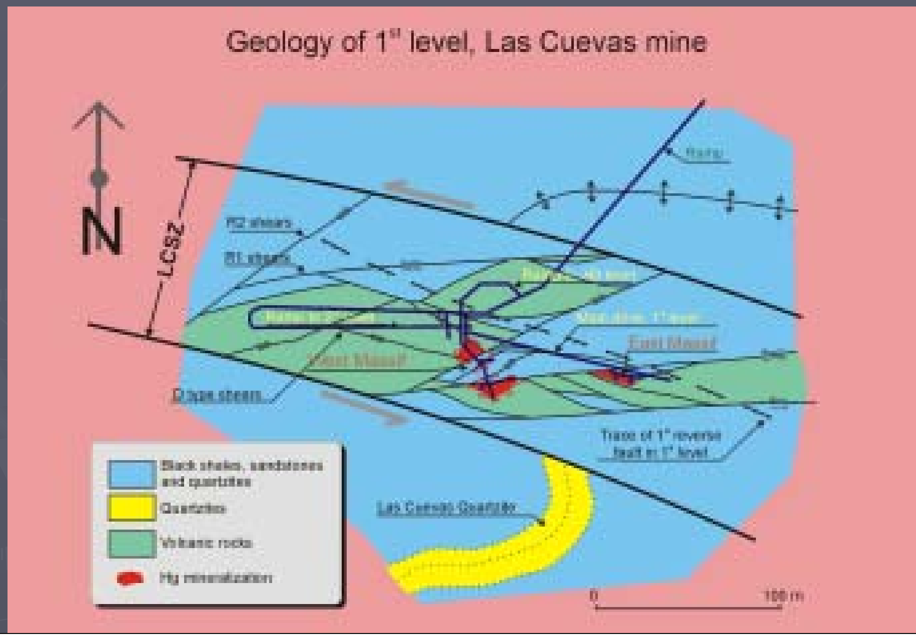
Geology: Types of Hg deposits

- 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



Las Cuevas mine

Underground mining, VCR (Vertical Crater Retreat)

Metallurgy

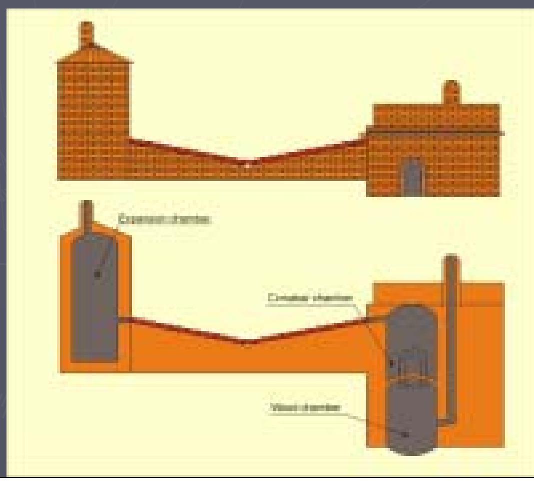
- Roasting: $HgS + hot \rightarrow Hg^0 + S^0$
- Evolving methods, with reduction of Hg vapor emission:
  - "Xabecas" furnaces (12 Century - 1646)
  - "Bustamante" furnaces (1646 - 1930)
  - "Idrija" and others furnaces (1930-1957)
  - "Pacific" furnaces, propane fuelled (1954-2005)

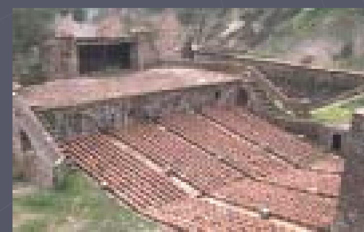
Metallurgy

- Xabecas furnaces
- Hand work made by prisoners

Metallurgy

- Aludeles furnaces





Metallurgy

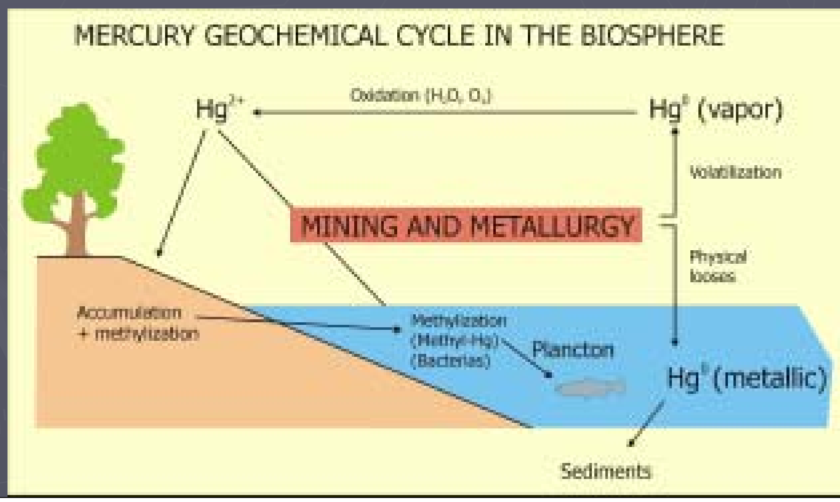
- Pacific furnaces
  - Multilevel system
  - Propane fueled

Environmental concerns

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

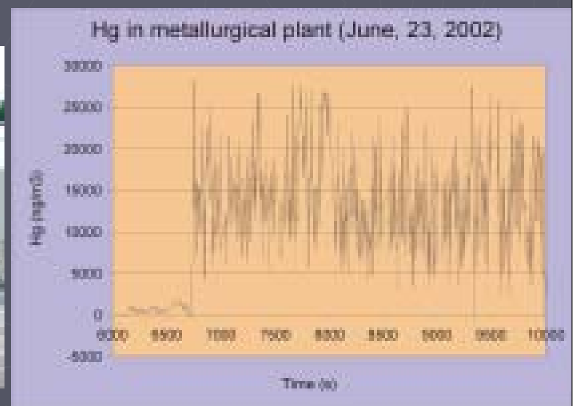
Environmental concerns

- Mercury cycle



Environmental concerns

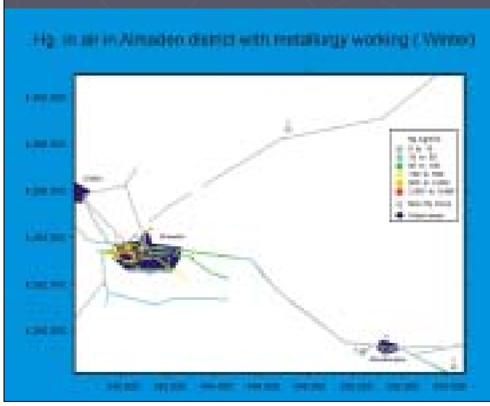
- Mercury in air

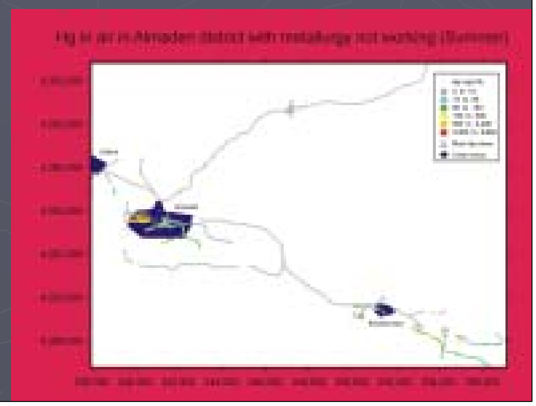


Punctual data – Hg: 135,000 ng/m3

Environmental concerns

- Mercury in air: Regional pattern, continuous automobile survey





Environmental concerns

- Mercury in soils

Site	N	Hg (ppm)		
		Range	Mean	StDev
ALM	18	6-8,889	2,573	2,979
ECH	8	12-132	57.8	33.1
RD	19	10-188	61.2	55.0
FIT	22	6-69	22.0	16.5

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.

Higueras et al. (2003) Journal of Geochemical Exploration, 80: 95-104

Environmental concerns

- Mercury emission from soils

Environmental concerns

- Mercury in mine dumps

Ore dump
Las Cuevas

Environmental concerns

- Mercury in mine dumps

Waste dump
El Entredicho

Environmental concerns

- Mercury in mine dumps

Environmental concerns

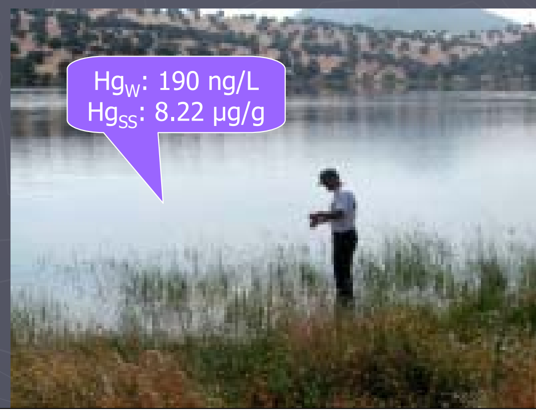
- Mercury emission from mine dumps

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



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

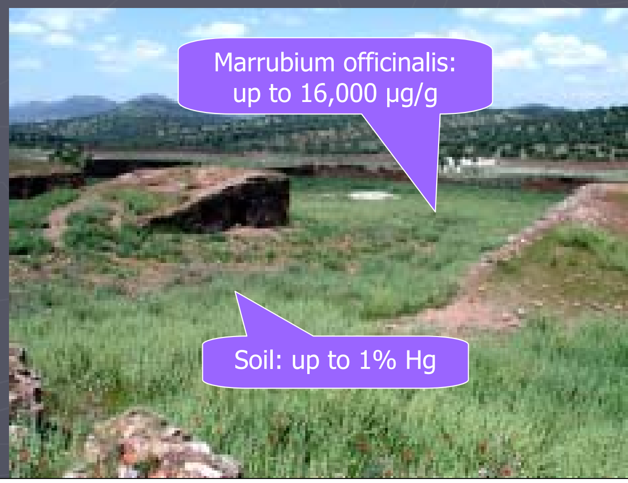
Environmental concerns

- El Entredicho open pit lake

Environmental concerns

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

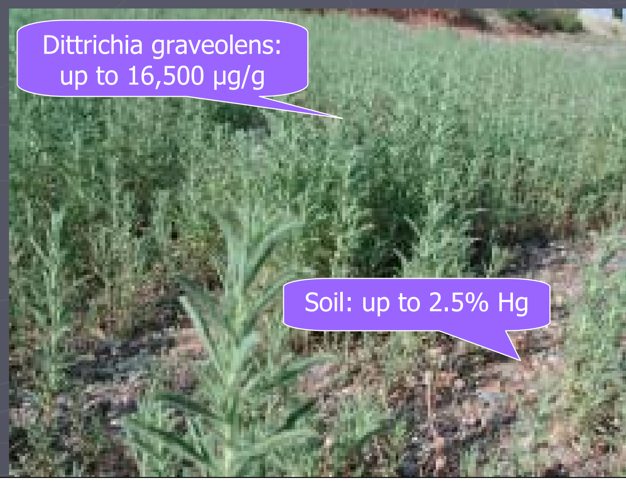
Almadenejos metallurgical precinct



Environmental concerns

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

Las Cuevas
Old mineral dump



Environmental concerns

- Mercury in wild plants: hyperacumulators

El Entredicho
open pit lake

Environmental concerns

- Mercury in wild plants: hyperacumulators

Puddles in mine dumps

Environmental concerns

- Mercury in wild plants: eatable – wild asparragus

Environmental concerns

- Mercury in fauna: no data

Domestic pigs in Almadenejos metall. precinct

Fishing in Castilseras reservoir

Hazards / Risks

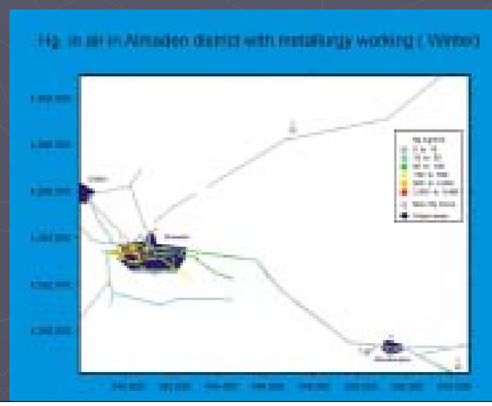
- For mine workers
- For local inhabitants
- For trophic chain
- Methylmercury presence

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/m^3) in inhabitad areas



Hazards / Risks

- For local inhabitants:
  - Hg vapor concentrations in some buildings

Almadén School of Mines

Hazards / Risks

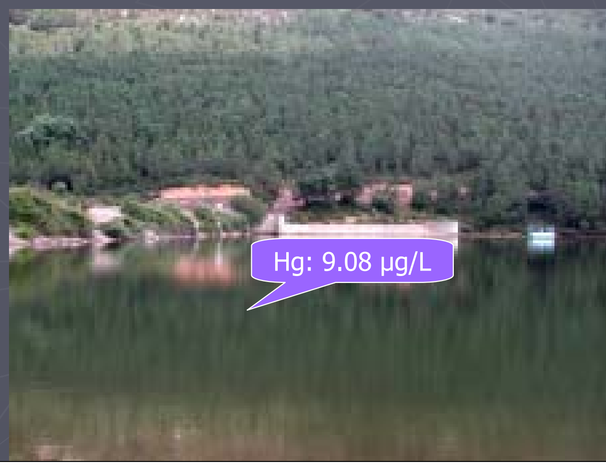
- For trophic chain:
  - Water
  - Fishing
  - Vegetables

Hazards / Risks

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

Hazards / Risks

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



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 (2nd 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

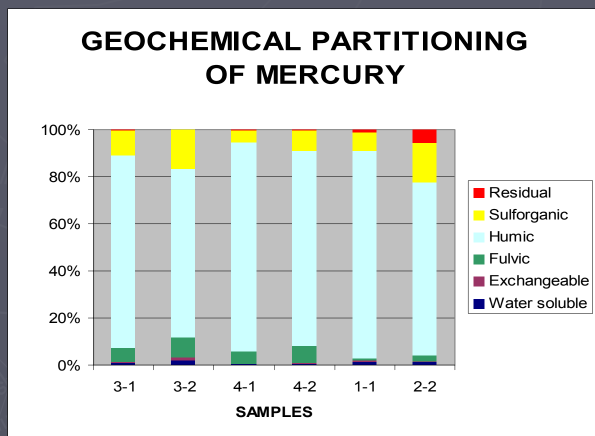
- ✓ Total mercury
- ✓ pH (H_2O, KCl)
- ✓ Cation Exchange Capacity
- ✓ Organic matter
- ✓ Carbonates, sulfates and nitrates
- ✓ Conductivity

- MERCURY CHARACTERIZATION

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

Phytoextraction

- Soils characteristics



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

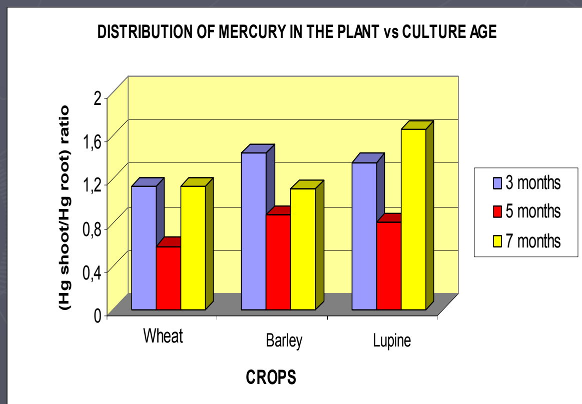
► **Agricultural plants: results**

- First year (2000-2001):

	Straw	Grain	Total (grain+straw)
Wheat	0.61475	0.03575	0.47872
Barley	0.46400	0.05700	0.33873
Lupine	0.25900	0.04800	0.19550
Wild veget.	0.32900	-----------	0.32900
Mercury content in dry matter (mg/kg)			

Phytoextraction

► Agricultural plants, 2nd year



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**

$$3Al(OH)_3 + 2H_3(PO_4) + 1/2SrCO_3 + 1/2CaCO_3 \rightarrow$$
$$\rightarrow Ca_{0.5}Sr_{0.5}Al_3(OH)_6(HPO_4)(PO_4) + CO_2 + 4H_2O$$

- Reaction carried out at 60ºC in 1 dm^3 flasks magnetically stirred at 700 rpm under environmental pressure
- Reaction time: 15 days

Monteagudo et al. (2003) Journal of Chem. Technol. Biotechnol., 78: 399–405

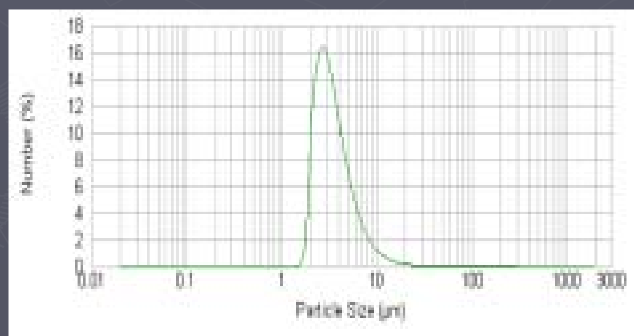
Crandallitic immobilizator

- **Characterization of the product**
  - Chemical analysis

Composition (% w/w)	Amorphous	Crystal
O	36.11	51.37
Al	24.10	18.75
Sr	13.06	10.83
P	21.94	14.35
Ca	4.79	4.70

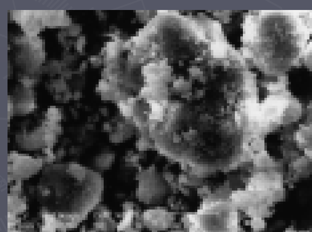
Crandallitic immobilizator

- **Characterization of the product**
  - Chemical analysis
  - Grain size

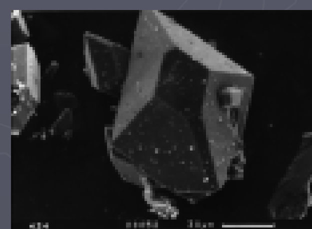


Crandallitic immobilizator

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



15 days, 60ºC, Room press.



6 months, 200ºC, 15 bar

Crandallitic immobilizator

- **Equilibrium and kinetic studies**
  - Experimental isotherms for the $Hg^{2+}/(Ca^{2+}-Sr^{2+})$ exchange

Parameters of the Langmuir equation

Solid	n^{∞} (meq g^{-1})	K_1	s* 10^4 (%)
Crandallite	0,93	30.13	7.54

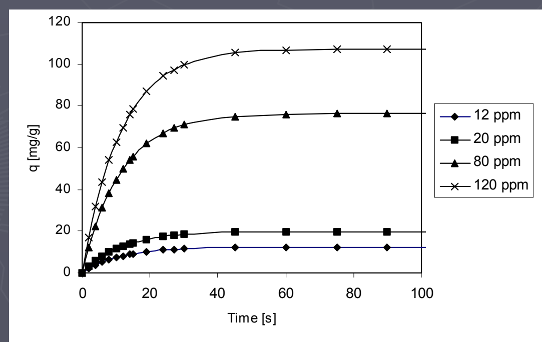
Ion exchange reaction:

$$2\ Ca_{0,5}Sr_{0,5}Al_3(OH)_6(HPO_4)(PO_4) + 2\ Hg^{2+} \leftrightarrow$$

$$\leftrightarrow 2\ HgAl_3(OH)_6(HPO_4)(PO_4) + Ca^{2+} + Sr^{2+}$$

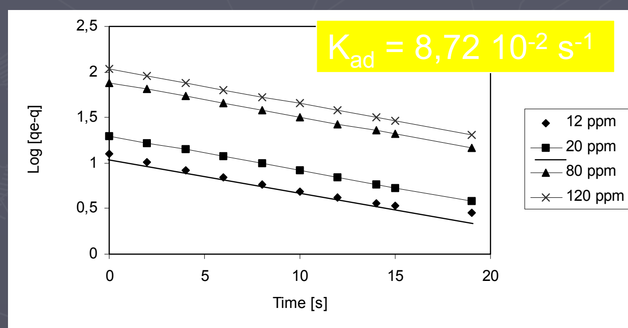
Crandallitic immobilizator

- **Equilibrium and kinetic studies**
  - Experimental isotherms
  - Experimental kinetics: equilibrium in ≈ 30 s



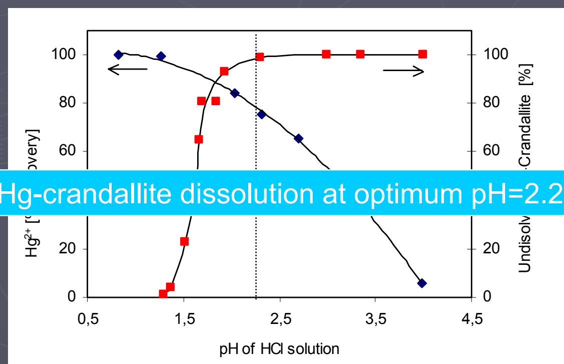
Crandallitic immobilizator

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



Crandallitic immobilizator

- **Recovery studies**
  - Thermal treatment: 800ºC → 99,9% recovery
  - Chemical treatment: Cl^- (10^{-4} to 5 10^{-2} M) to form soluble $HgCl_4^{2-}$



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