

SPANISH TECHNOLOGICAL DEVELOPMENTS ON Hg STABILIZATION AND Hg CONTAINING WASTES

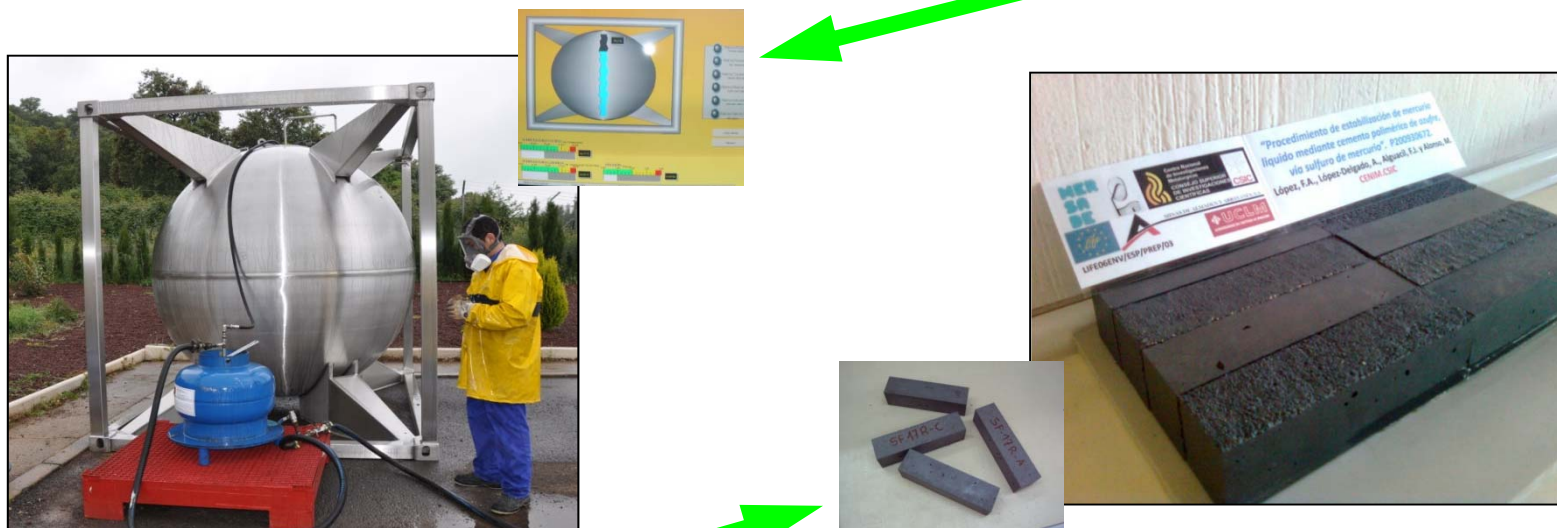
**WORKSHOP ON MERCURY MANAGEMENT AND DECONTAMINATION
IN THE FRAMEWORK OF THE MEDITERRANEAN REGIONAL PLAN ON
MERCURY.**

Almadén, Spain, 12th / 13th December 2012



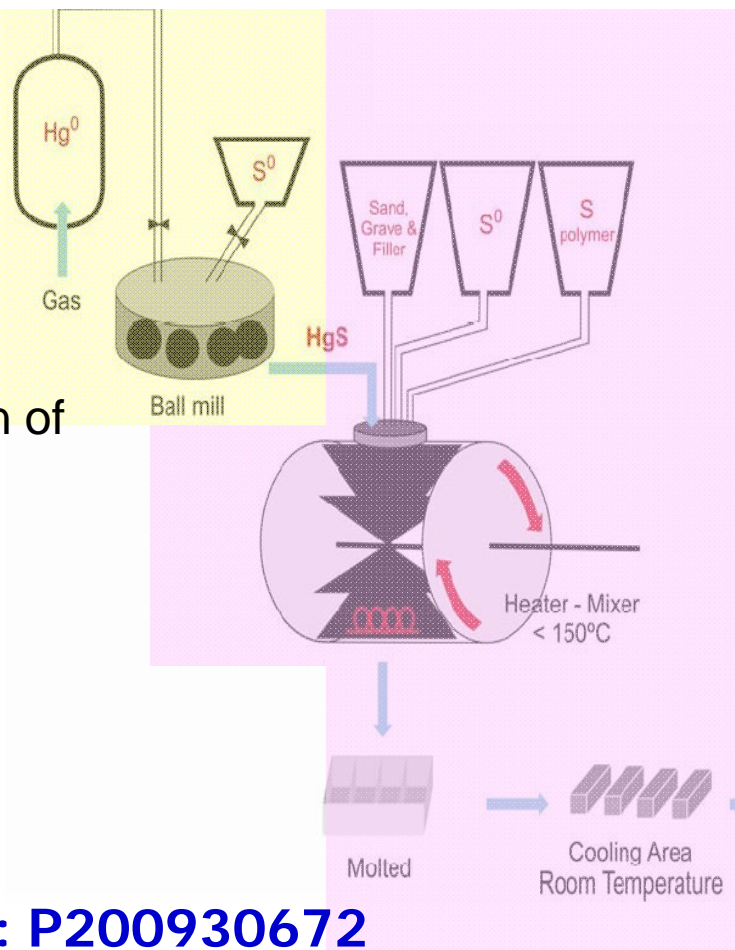
MERSADE Project main tasks (2006-2010):

1. Container for the safe temporary storage of metallic mercury



2. Stabilization / Microencapsulation technique.

Phase 1:
Stabilization of
HgS



Phase 2:
Microencapsulation

Final product

Patent: P200930672

Obtaining mercury sulphide:



Metallic Hg + Elemental sulfur particles (< 60 μm) react in a ball mill to obtain HgS (Cinnabar)

Microencapsulation in a sulphur matrix:



HgS



S



S polymer

HEATER-MIXER (<math><140^{\circ}\text{C}</math>)



POLIMERIC CEMENT OF SULPHUR (Artificial rock)



ADVANTAGES AND GUARANTEES :

- **Inert solid, more resistant than concrete, with low porosity and impermeable.**
- **The MICROENCAPSULATION provides a second and additional barrier for avoiding mercury releases to the environment.**
- **Safer product and easier to be managed: physically and chemically much more stable and environmentally safer.**
- **During the process, 100% of Hg is transformed.**
- **Low energy consumption.**
- **No water consumption, and neither effluents nor wastes are generated.**
- **Ordinary, abundant and affordable reagents.**

- The estimated cost of the stabilization process is around 2,000 €/t of metallic mercury
- The CTNDM has experts to carry out a safe and environmentally sound comprehensive management of mercury (including collection, transport, temporary storage and disposal).
- Facilities for the environmentally sound permanent storage with absolute environmental guarantees already exist in Almaden.
-,



¿ what 's next step ?

EXHAUSTIVE RESEARCH WORKS DONE

HAVE DEMONSTRATED THAT:

- This TECHNOLOGY is fully effective to stabilize and microencapsulate metallic mercury with **whichever degree of purity, no needing previous distillation.**
- This TECHNOLOGY is **directly applicable** to a wide range of mercury containing wastes from diverse industrial processes, **without previous treatment.**
- .

INDUSTRIAL SECTORS AS Hg WASTES PRODUCERS:

- * i. Hg fluorescent dust (FD) from the recycling plants.
- * ii. Hg wastes from the Zn primary production industry.
- * iii. Hg wastes from the Al primary production industry.
- iv. Hg wastes from the Cu primary production industry.
- v. Hg from Gold mining industry.
- vi. Wastes from dental amalgams.
- vii. ... //

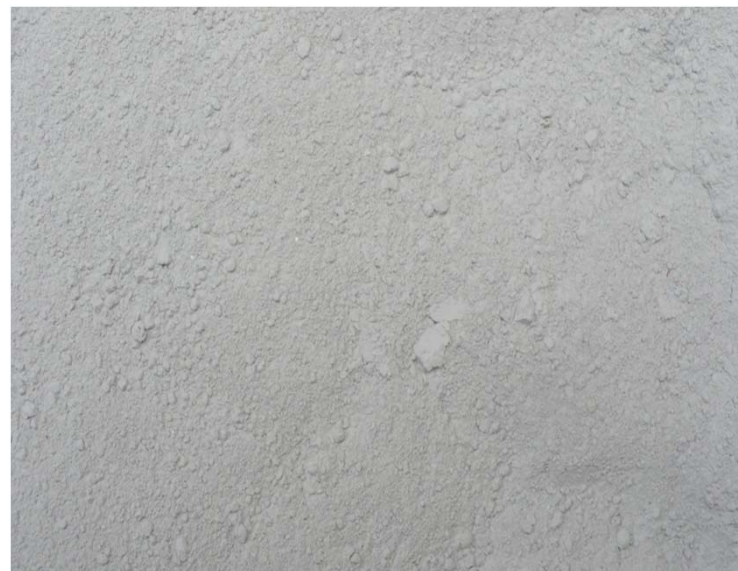
* Works to show now

Providing cooperation:

CTNDM



an Spanish association / recycling plant



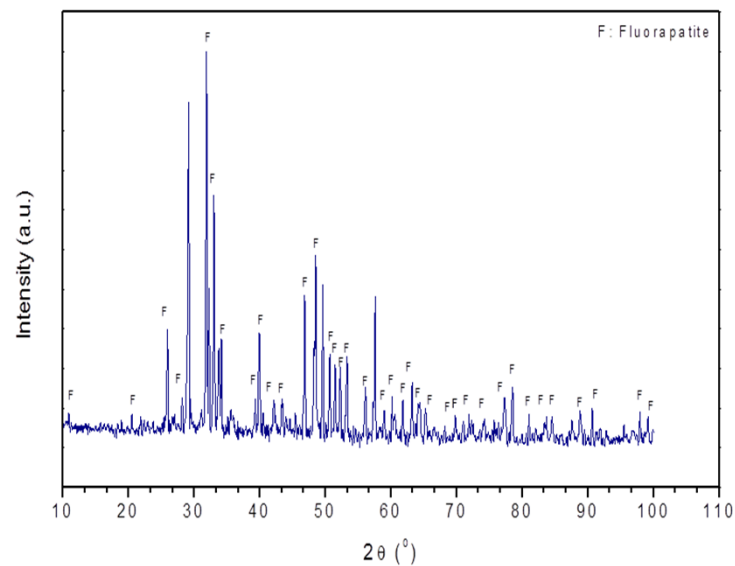
·Appearance of fluorescent dust (FD)

Density: 3.05 gr / cm³

Ø size: < 40 µm

	% weight	error %
CaO	40,67	0,24
P ₂ O ₃	15,93	0,18
SiO ₂	10,28	0,15
Al ₂ O ₃	7,53	0,13
F	3,46	0,26
Na ₂ O	2,65	0,08
MgO	0,83	0,04
HgO	0,03	0,00
Others (SO ₃ , Cl, K ₂ O, MnO, etc)	Up to 99.98	-

Chemical semiquantitative composition by FXR
(in % oxide)



RX diffraction diagram of fluorescent powder



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for Mercury
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Estabilized FD waste (66,5 % w. of waste)

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Providing cooperation:

CTNDM  an Spanish primary **Zn** producer

- Electrolitic Zn production from Zn concentrate ore.
- By oxidation of zinc sulfide in fluidized bed at 950°C.
- Zn & Hg have similar atomic size.
- Pending from origin, Hg content in concentrates ores is <>
- Hg with many others **impurities**: F, Cl, Se, Pb,...are remobilized to the gas phase.

From the wet gas cleaning process, the waste obtained is
a thick, heavy mud with high water content.

Density: 6,15 gr / cm³

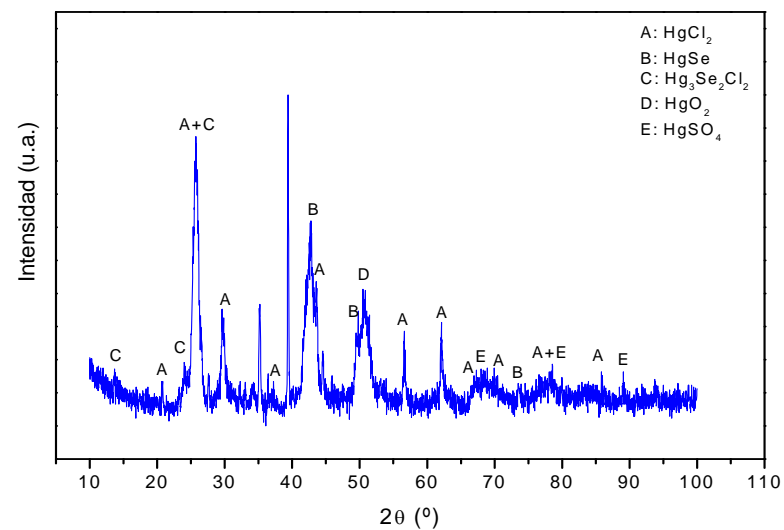
Ø size: < 40 µm

Humidity: 33,2 %

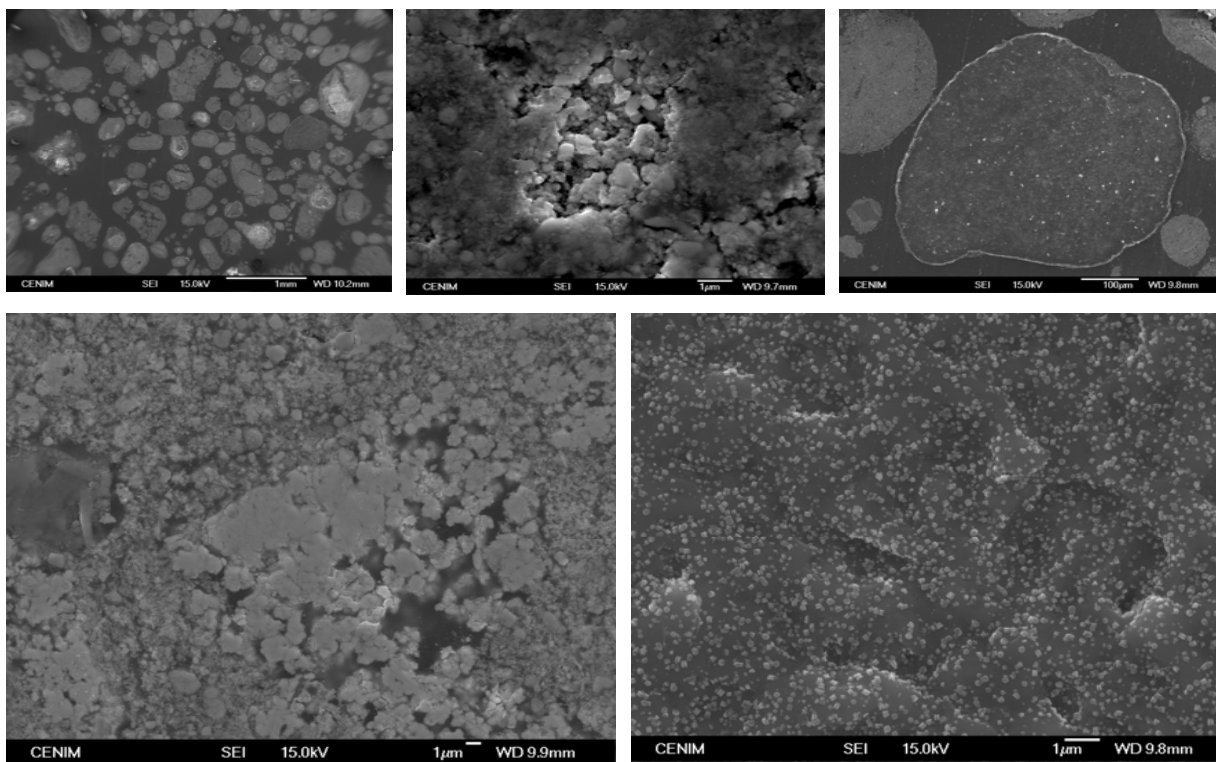


	% peso	error %
HgO	45,60	0,25
SeO ₂	15,79	0,18
Re ₂ O ₇	10,59	3,22
Fe ₂ O ₃	7,85	0,13
SO ₃	5,99	0,12
PbO	5,22	0,11
ZnO	1,83	0,22
SiO ₂	1,54	0,06
Others (Mn,Cu, Br,etc)	4,60	-

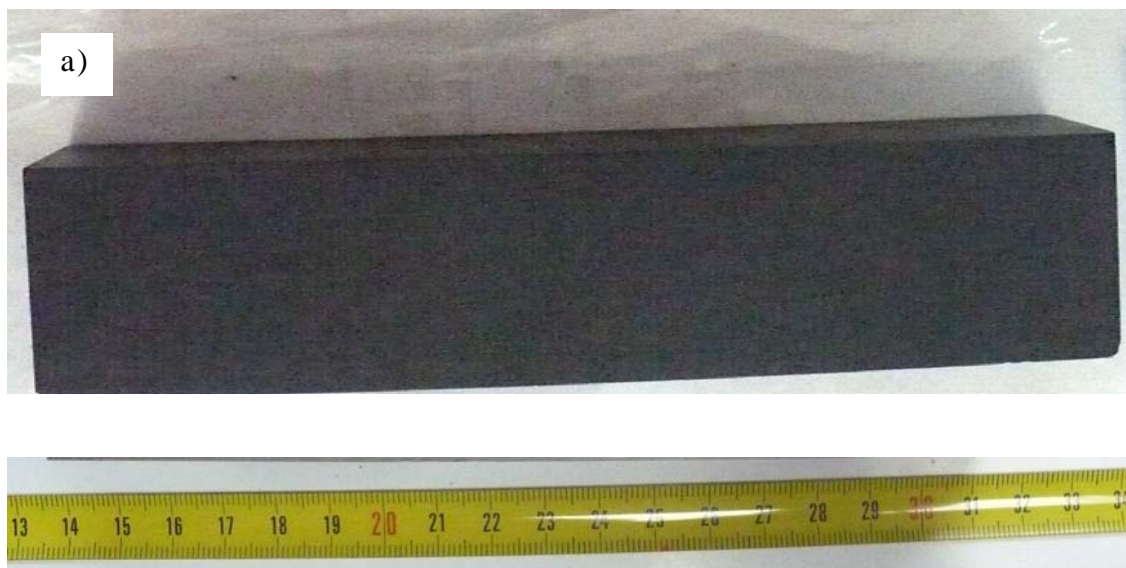
Chemical semiquantitative composition by FXR
(in % oxide)



RX diffraction diagram of zinc waste



• Different SEM pictures of Zn wastes



Estabilized Zn waste (65,2 % w. of waste)

Providing cooperation:

CTNDM  an Spanish Al producer

- Al_2O_3 production from bauxite as first step of Al production. By mixing with caustic soda and increasing T^a .
- Pending from origin, Hg content in bauxite is $\langle \rangle$. (X = 0,11 ppm average)
- Hg vapor in gases from process.
- Hg extracted from gas treatment system and obtained as **metallic mercury (99 to 99,9 %)** by condensation.



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Hg estabilized (65 % Hg)

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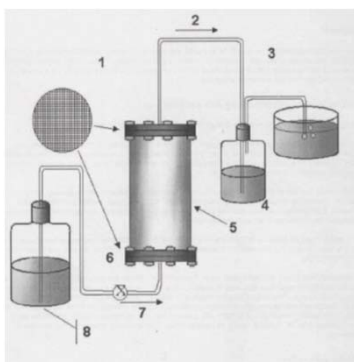
within the current in force **Landfill European
Union Legislation:**

Decision 2003/33/EC

**Leaching limits for Hg as per Standard CEN/TS 14405:2004;
UNE-EN-12457**

European leaching limits values as acceptance criteria:

Leaching columns according to Standard CEN/TS 14405:2004 - (UNE-EN-12457)



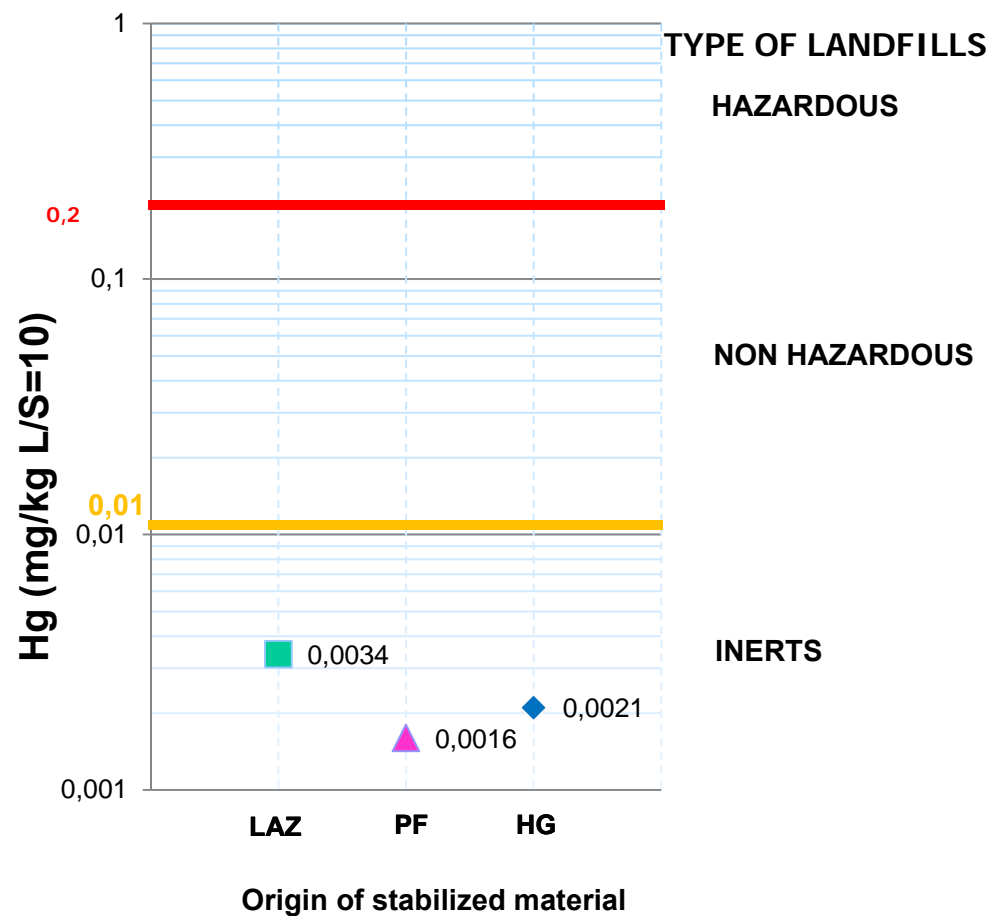
Leaching limits:

Hg for L/S=10

Monolithic waste



Decision 2003/33/EC



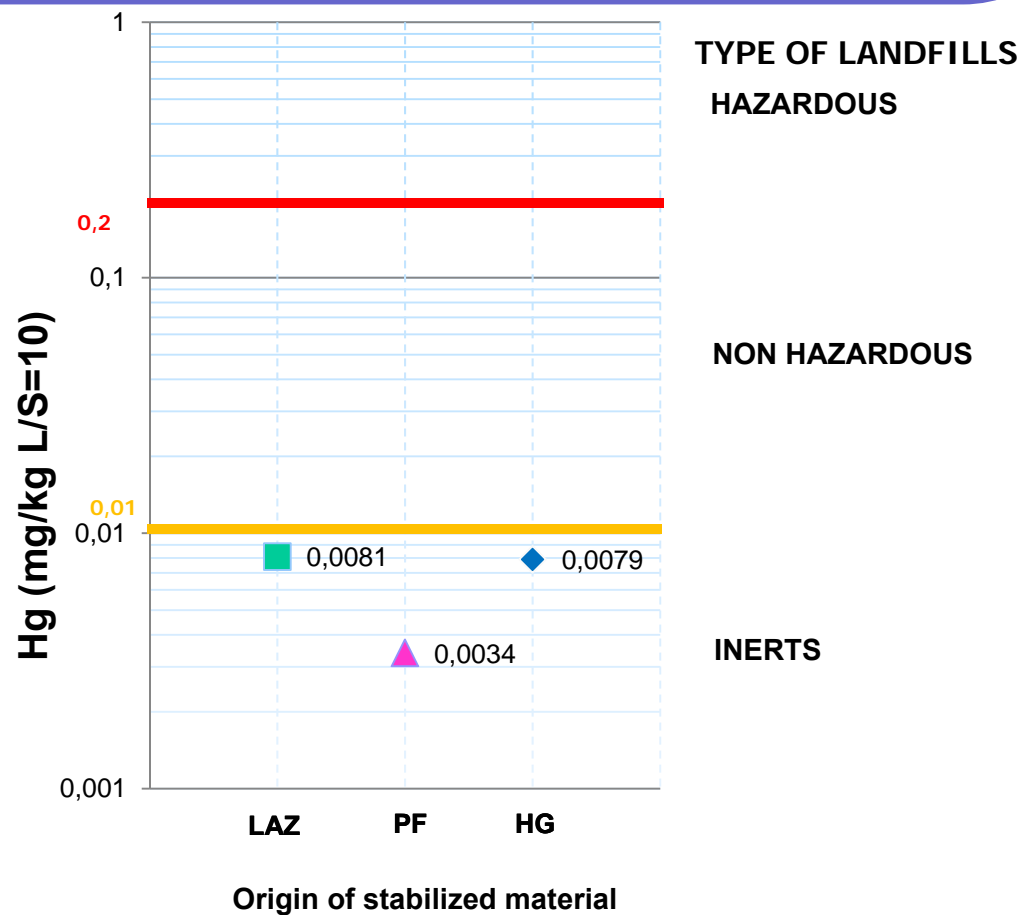
Leaching limits:

Hg for L/S=10

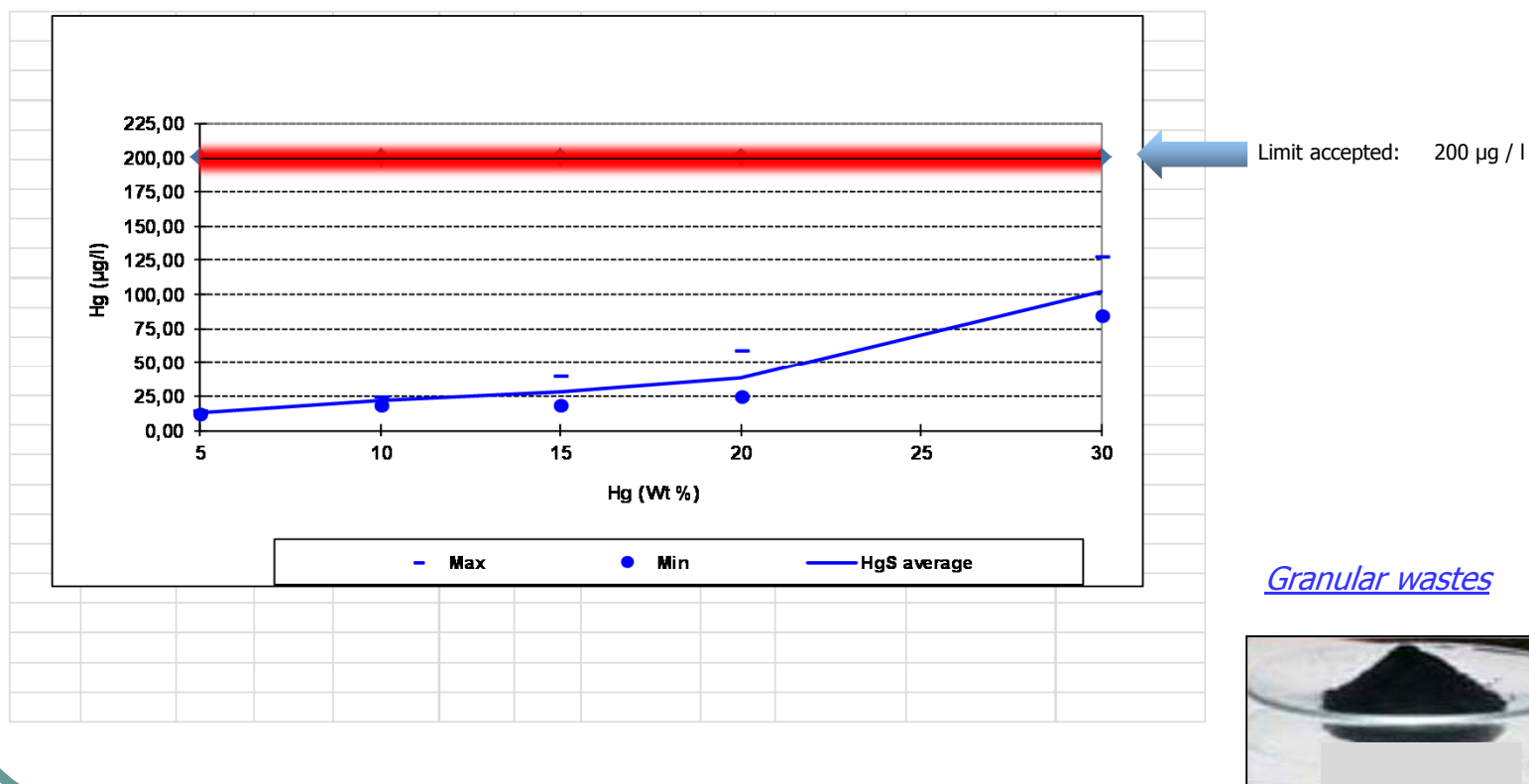
Granular wastes



Decision 2003/33/EC



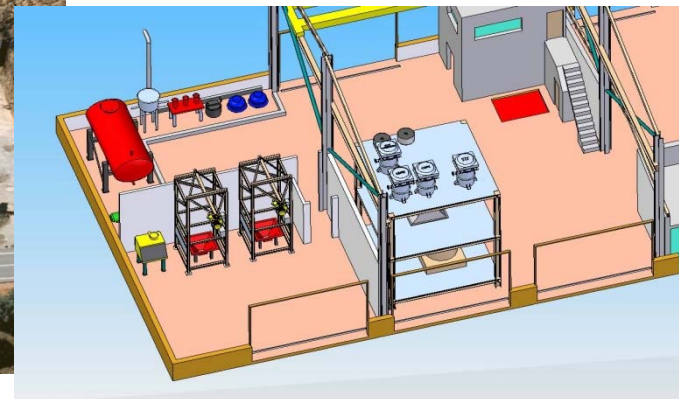
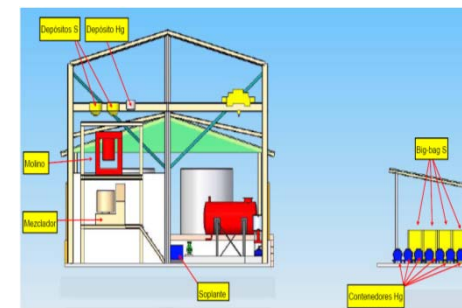
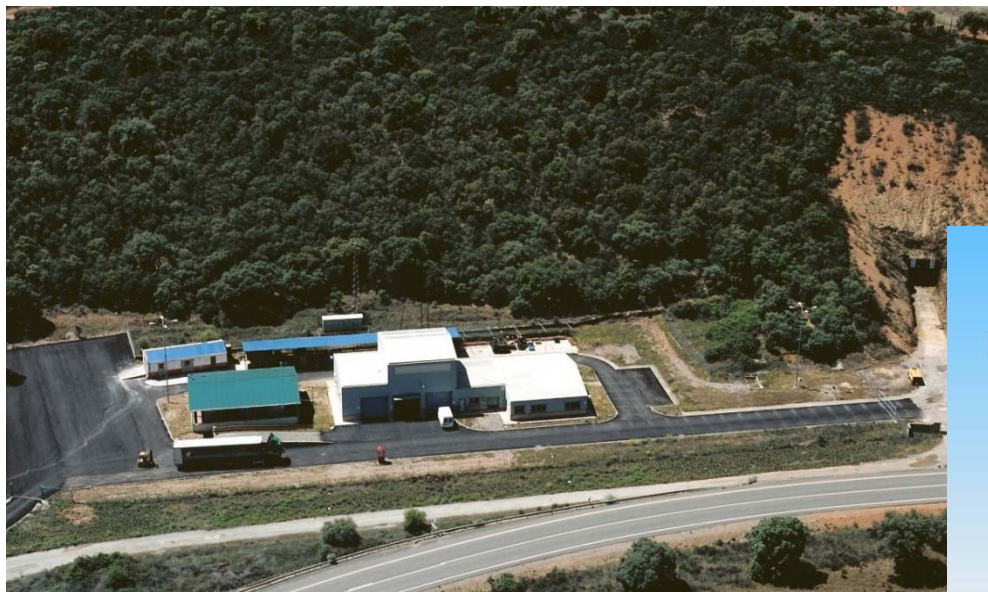
The stabilized metallic Hg also fulfils the TCLP leaching test (USA EPA 1311 on crushed samples):



Steep in progress: **CONSTRUCTION**

“PILOT PLANT OF ESTABILIZATION FOR MERCURY AND MERCURY CONTAINING WASTES.”

- • 2,5 t Hg / day treatment capacity.
- • Treatment of different wastes but same plant.
- • Plants at lower scales for “in situ” applications.





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THANKS FOR YOUR ATTENTION

mramos@ctndm.es

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