SPANISH TECHNOLOGICAL DEVELOPMENTS ON Hg STABILIZATION AND Hg CONTAINING WASTES

WORKSHOP ON MERCURY MANAGEMENT IN THE LATIN AMERICA AND CARIBBEAN REGION

Brasilia, 21st / 22nd May 2012

GOBIERNO DE ESPANA
MINISTERIO DE AGRICULTURA, ALIMENTACIÓN Y MEDIO AMBIENTE

National Technological Center for Mercury Decontamination

National Technological Center for Mercury Decontamination

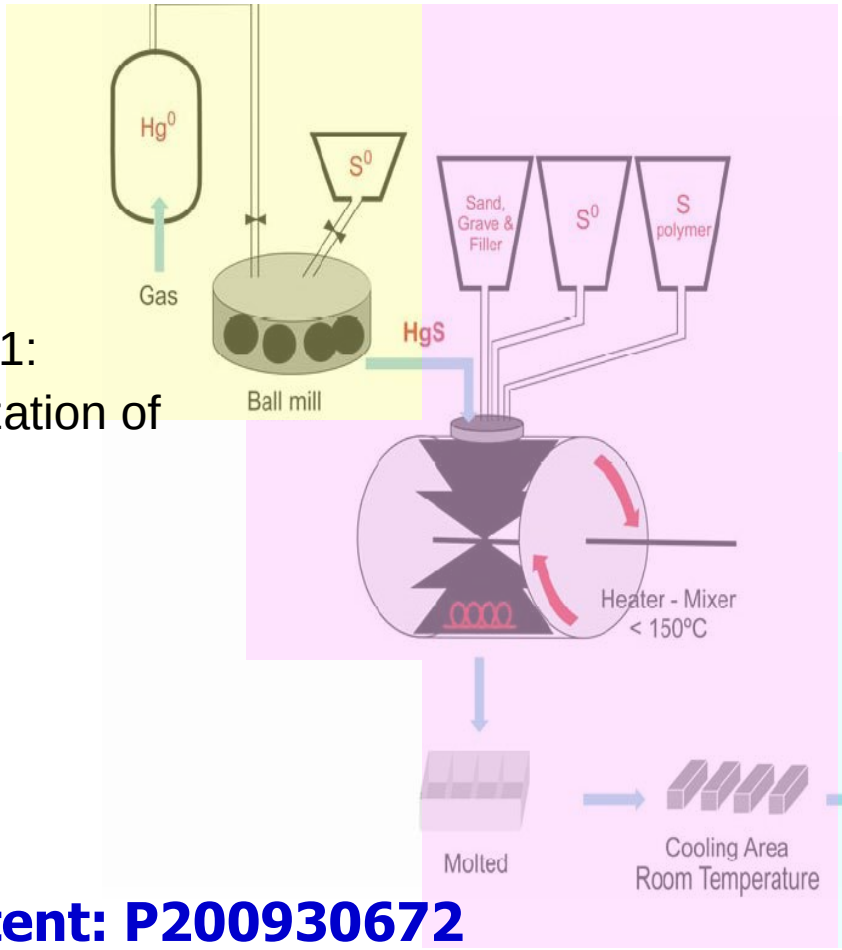
MERSADE Project main tasks (2006-2010):

1. **Container for the safe temporary storage of metallic mercury**

2. **Stabilization / Microencapsulation technique.**

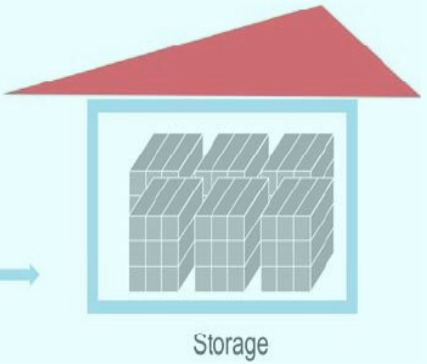
National Technological Center for Mercury Decontamination

Phase 1: Stabilization of HgS



Phase 2: Microencapsulation

Final product



Patent: P200930672

National Technological Center for Mercury Decontamination

Obtaining mercury sulphide:

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

National Technological Center for Mercury Decontamination

Microencapsulation in a sulphur matrix:

HgS S S polymer

HEATER-MIXER (<140ºC)

POLIMERIC CEMENT OF SULPHUR (Artificial rock)

National Technological Center for Mercury Decontamination

ADVANTAGES AND GUARANTEES :

- **Inert solid, more resistant than concrete, with low porosity and impermeable.**
- **No emissions to atmosphere . The final product has 100-150 times lower emissions than mercury sulphide (natural cinnabar ore).**
- **Safer product and easier to handle: its environmentally sound management is easyer, safer and less expensive as well.**
- **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**

National Technological Center for Mercury Decontamination

- **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 ?

National Technological Center for Mercury Decontamination

...from results and keeping as main TARGET:

TO DEVELOP TECHNOLOGICAL SOLUTIONS

FOR MERCURY ISSUES...

National Technological Center for Mercury Decontamination

ACTIVITITES:

- **Application of the stabilization/encapsulation technique to Hg containing wastes**

- **to improve the technique: i.e. non addition of aggregates.**

National Technological Center for Mercury Decontamination

INDUSTRIAL SECTORS AS Hg WASTE PRODUCERS:

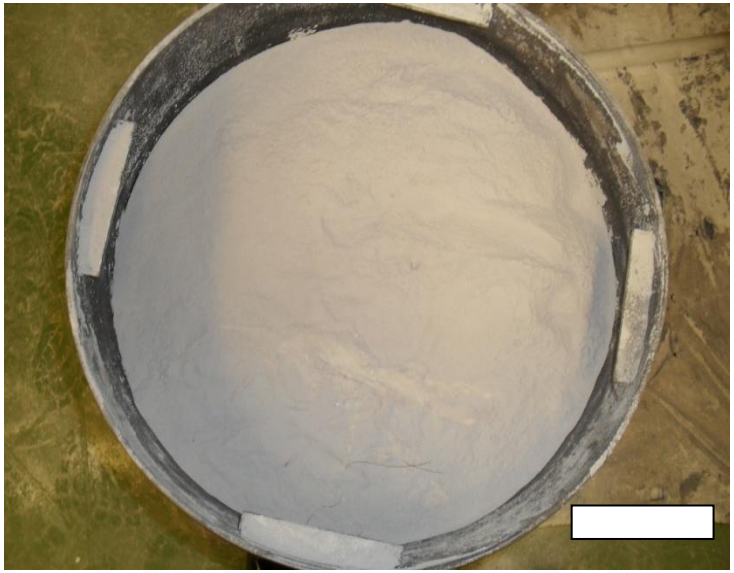
* i. Hg fluorescent dust (FD) from the recycling plants.
* ii. Hg wastes from the Zn primary production industry.
* iii. Hg wastes from the Al primary production industry.
  iv. Hg wastes from the Cu primary production industry.
  v. Hg from Gold mining industry.
  vi. Wastes from dental amalgams.
 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

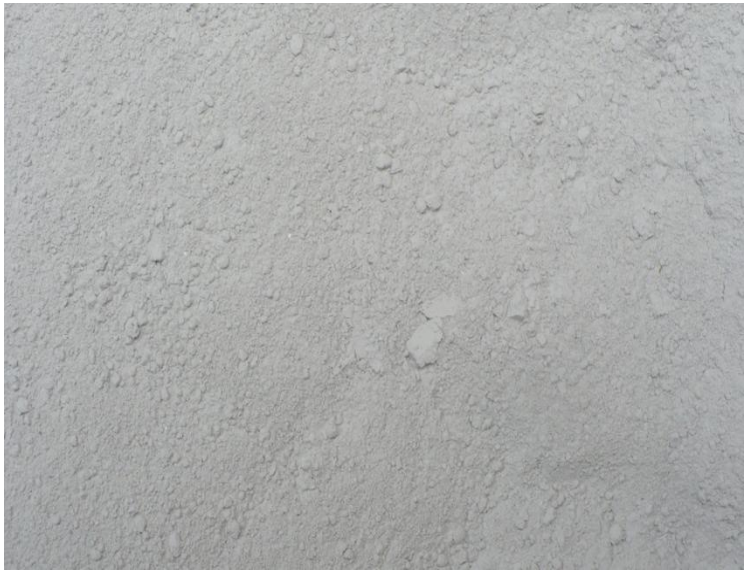
* Works to show now

National Technological Center for Mercury Decontamination

Providing cooperation:

CTNDM ⟷ an Spanish association / recycling plant





- **Appearance of fluorescent dust (FD)**

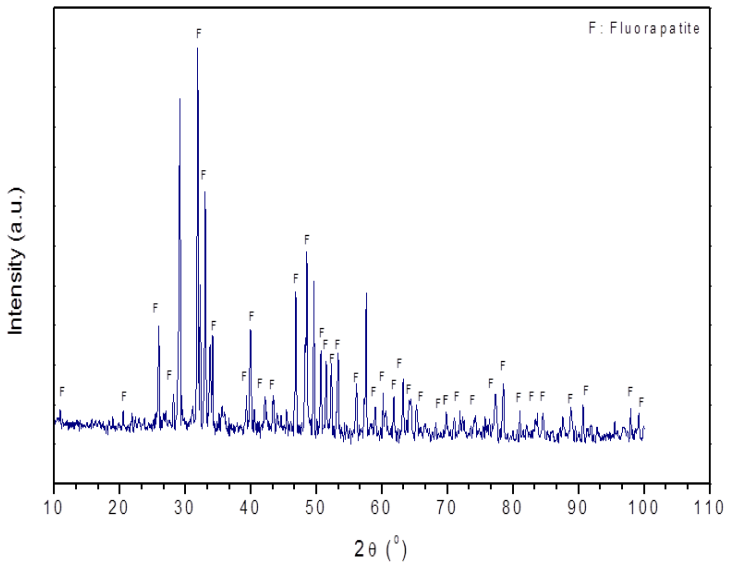
Density: 3.05 gr / cm^3 **Ø size: < 40 µm**

National Technological Center for Mercury Decontamination

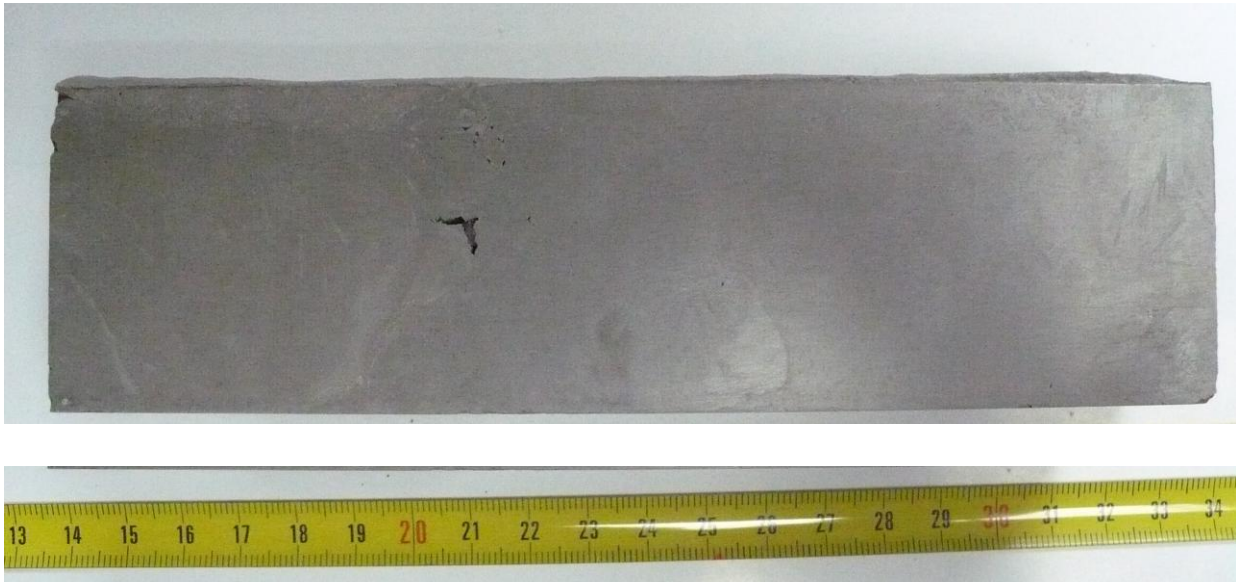
	% weight	error %
CaO	40,67	0,24
P_2O_3	15,93	0,18
SiO_2	10,28	0,15
Al_2O_3	7,53	0,13
F	3,46	0,26
Na_2O	2.65	0,08
MgO	0,83	0,04
HgO	0,03	0,00
Others (SO3, Cl, K2O,MnO,etc)	Up to 99.98	-

Chemical semiquantitative composition by FXR

(in % oxide)



RX diffraction diagram of fluorescent powder



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

National Technological Center for Mercury Decontamination

Providing cooperation:

CTNDM ✚ an Spanish primary **Zn** producer

- Electrolitic Zn production from Zn concentrate ore.
- By oxidation of zinc sulfide in fluidized bed at 950ºC.
- 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.

National Technological Center for Mercury Decontamination

From the wet gas cleaning process, the waste obtained is

a thick, heavy mud with high water content.

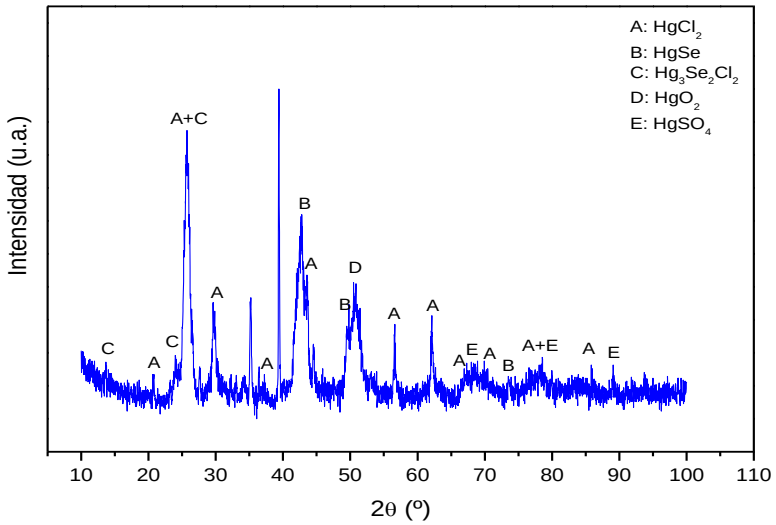
Density: 6,15 gr / cm^3

Ø size: < 40 µm

Humidity: 33,2 %

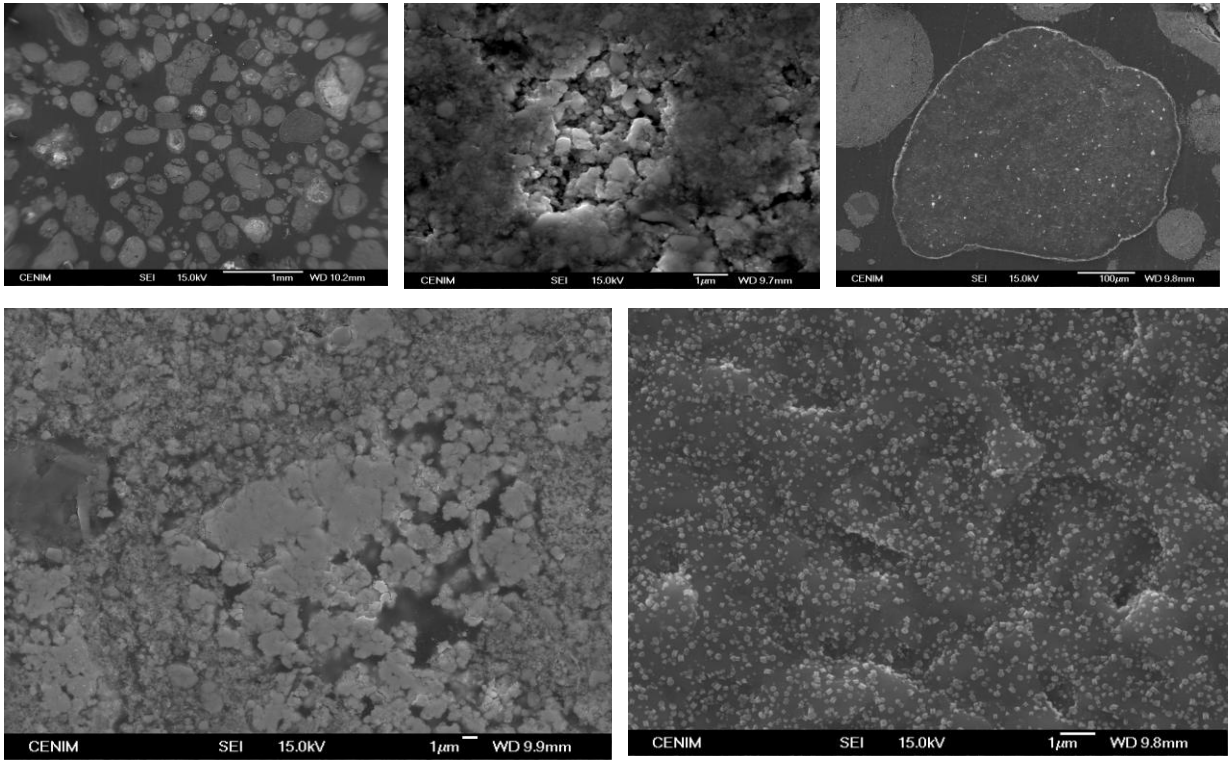
	% peso	error %
HgO	45,60	0,25
SeO_2	15,79	0,18
Re_2O_7	10,59	3,22
Fe_2O_3	7,85	0,13
SO_3	5,99	0,12
PbO	5,22	0,11
ZnO	1,83	0,22
SiO_2	1,54	0,06
Others (Mn,Cu, Br,etc)	4,60	-

Chemical semiquantitative composition by FXR (in % oxide)



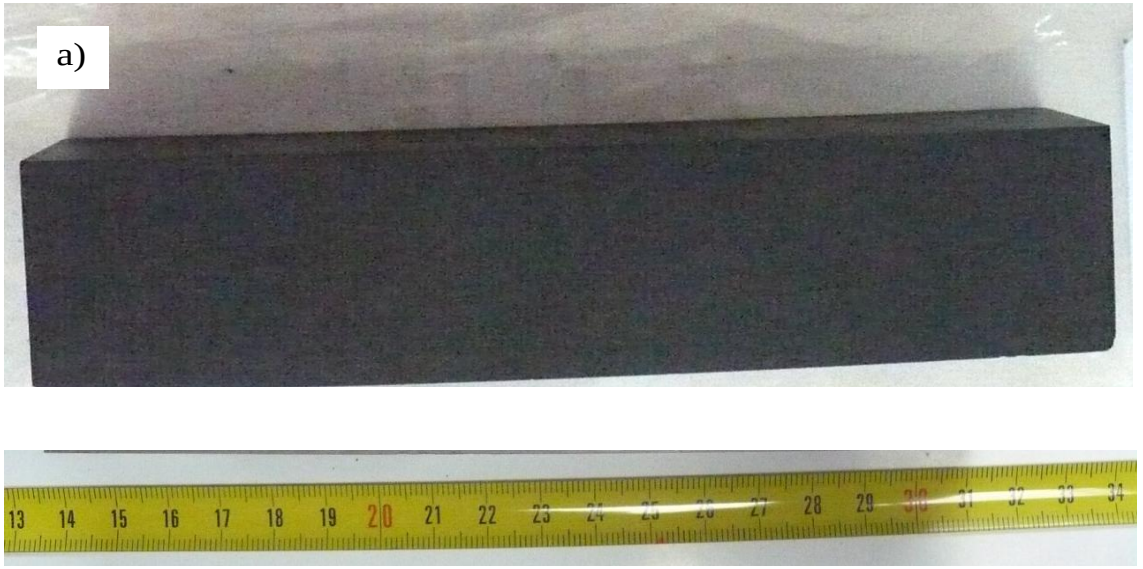
RX diffraction diagram of zinc waste

National Technological Center for Mercury Decontamination



- **Different SEM pictures of Zn wastes**

National Technological Center for Mercury Decontamination



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

National Technological Center for Mercury Decontamination

Providing cooperation:

CTNDM + an Spanish Al producer

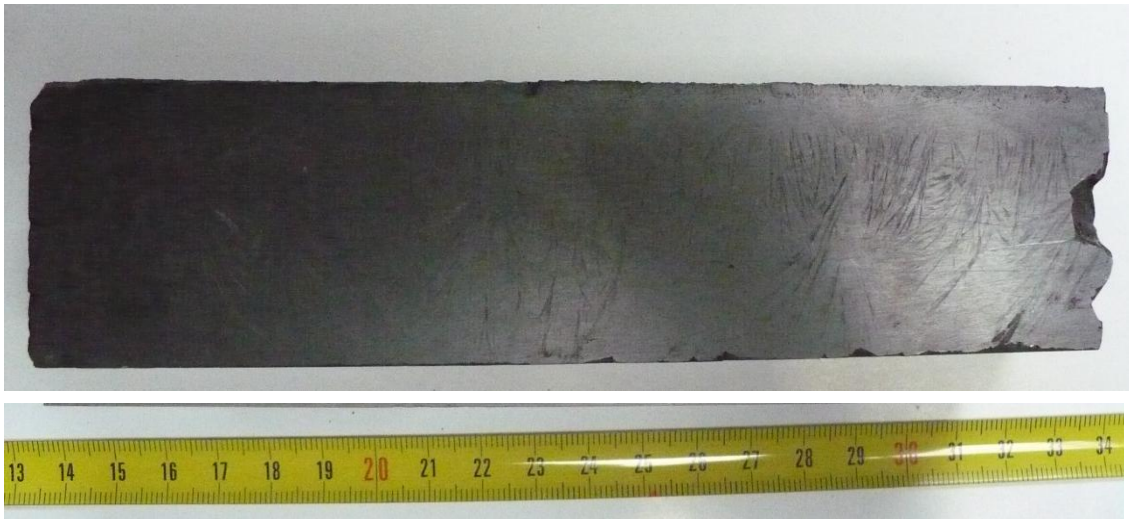
-AL_2O_3 production from bauxite as first steep of Al production. By mixing with caustic soda and increasing T^a.

- Pending from origin, Hg content in bauxite is <>. (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.

National Technological Center for Mercury Decontamination

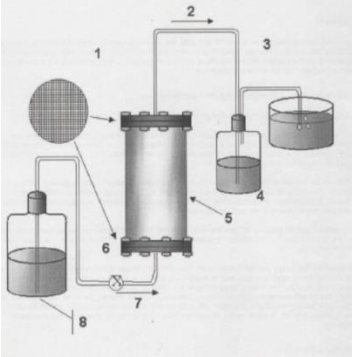


Hg estabilized (65 % Hg)

National Technological Center for Mercury Decontamination

European leaching limits values as acceptance criteria:

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

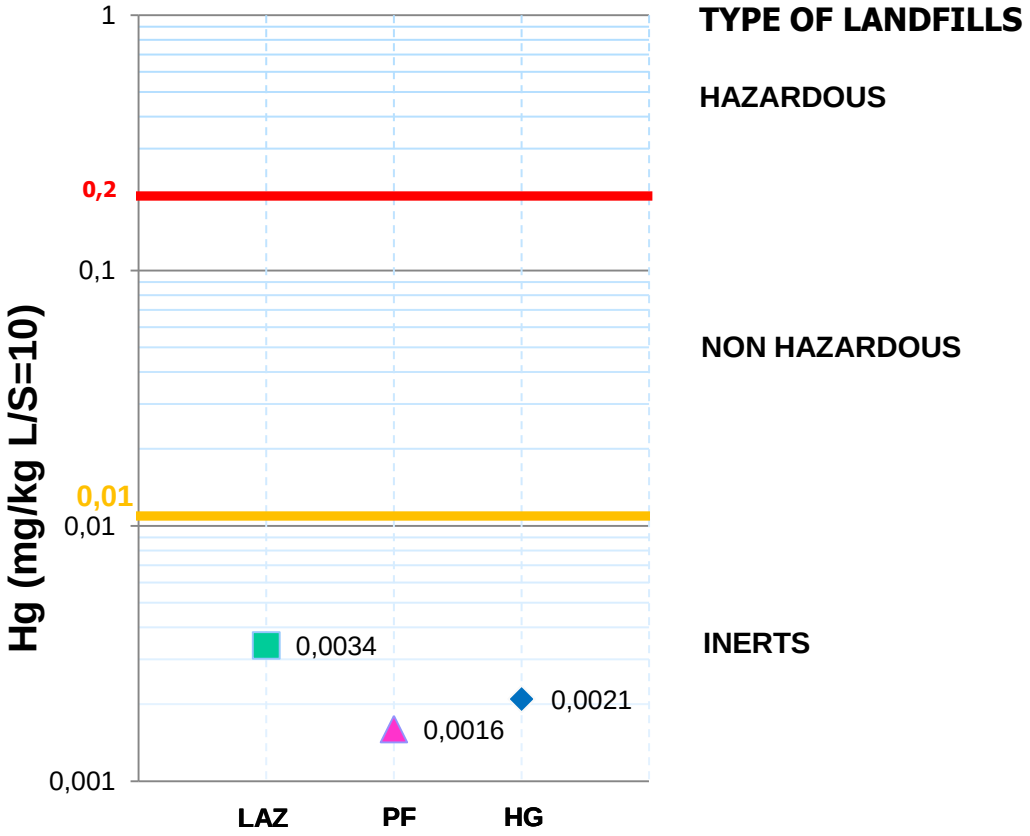


National Technological Center for Mercury Decontamination

Leaching limits:

Hg for L/S=10

Monolithic waste



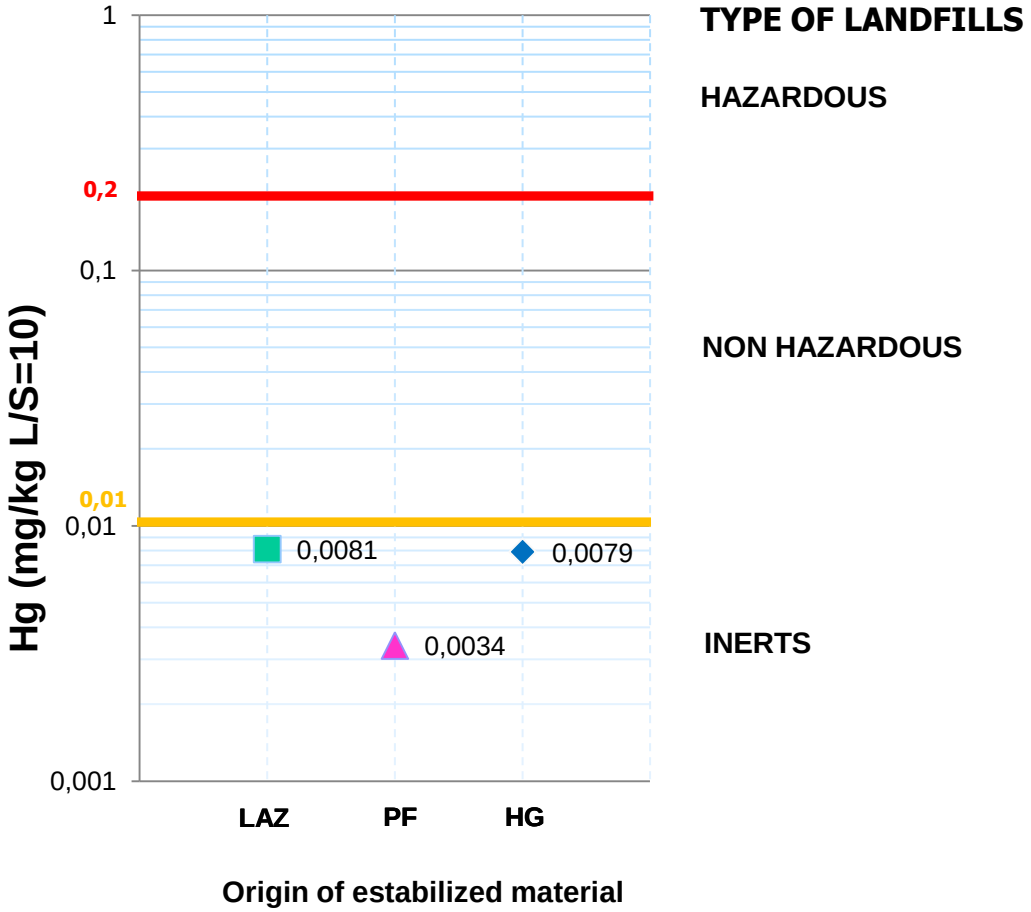
Decision 2003/33/EC

National Technological Center for Mercury Decontamination

Leaching limits:

Hg for L/S=10

Granular wastes



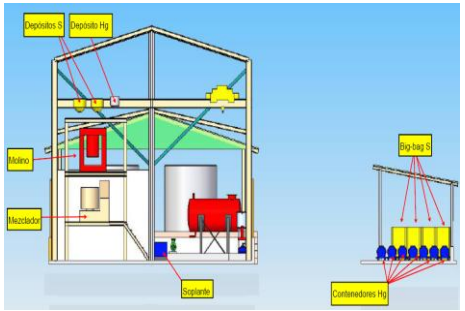
Decision 2003/33/EC

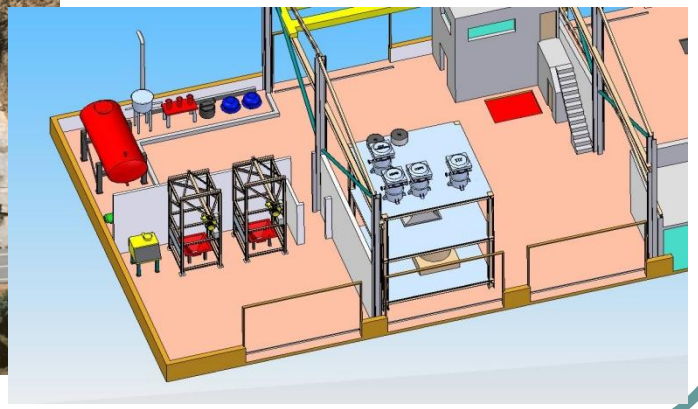
Centro Tecnológico Nacional de Descontaminación del Mercurio

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.**





National Technological Center for Mercury Decontamination

THANK YOU
FOR YOUR ATTENTION

mramos@ctndm.es

Brasilia, 21st / 22nd May 2012