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
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

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:

HEATER-MIXER (<140ºC)

POLIMERIC CEMENT OF SULPHUR (Artificial rock)
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 easier, 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
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?
...from results and keeping as main TARGET:

TO DEVELOP TECHNOLOGICAL SOLUTIONS

FOR MERCURY ISSUES...
ACTIVITITES:

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

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

CTNDM  an Spanish association / recycling plant

Appearance of fluorescent dust (FD)

Density: 3.05 gr / cm³  Ø size: < 40 μm

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### Chemical semiquantitative composition by FXR (in % oxide)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>% weight</th>
<th>error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>40,67</td>
<td>0,24</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>15,93</td>
<td>0,18</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10,28</td>
<td>0,15</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7,53</td>
<td>0,13</td>
</tr>
<tr>
<td>F</td>
<td>3,46</td>
<td>0,26</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2,65</td>
<td>0,08</td>
</tr>
<tr>
<td>MgO</td>
<td>0,83</td>
<td>0,04</td>
</tr>
<tr>
<td>HgO</td>
<td>0,03</td>
<td>0,00</td>
</tr>
<tr>
<td>Others (SO₃, Cl, K₂O, MnO, etc)</td>
<td>Up to 99.98</td>
<td>-</td>
</tr>
</tbody>
</table>

RX diffraction diagram of fluorescent powder
Estabilized FD waste (66.5 % w. of waste)
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.
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 %
<table>
<thead>
<tr>
<th></th>
<th>% peso</th>
<th>error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgO</td>
<td>45,60</td>
<td>0,25</td>
</tr>
<tr>
<td>SeO₂</td>
<td>15,79</td>
<td>0,18</td>
</tr>
<tr>
<td>Re₂O₇</td>
<td>10,59</td>
<td>3,22</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7,85</td>
<td>0,13</td>
</tr>
<tr>
<td>SO₃</td>
<td>5,99</td>
<td>0,12</td>
</tr>
<tr>
<td>PbO</td>
<td>5,22</td>
<td>0,11</td>
</tr>
<tr>
<td>ZnO</td>
<td>1,83</td>
<td>0,22</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1,54</td>
<td>0,06</td>
</tr>
<tr>
<td>Others (Mn,Cu, Br,etc)</td>
<td>4,60</td>
<td>-</td>
</tr>
</tbody>
</table>

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

- AL₂O₃ production from bauxite as first steep of Al production. By mixing with caustic soda and increasing Tª.

- 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.
Hg estabilized (65 % Hg)
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

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Leaching limits:

Hg for L/S=10

Granular wastes

Decision 2003/33/EC

Origin of stabilized material

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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.
THANK YOU
FOR YOUR ATTENTION
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