

Mercury stabilisation

People need raw materials to work with,
and a healthy environment to live in.



DELA
Recycling und Umwelttechnik

**Stabilisation of mercury for final disposal by formation
of mercury sulphide**

Background DELA

Specialist for the treatment of mercury containing wastes

- Operating thermal treatment plants since 1996
 - Rotary Kiln
 - Vacuum Dryer
- Capacity 3000 t/a
- Clients:
 - Chlorine industry
 - Gas exploration sites
 - Chemical industry
 - Wastes:
 - Sludges, Absorbents, Catalysts, Activated Carbons
 - Mercury Purification within EU
 - Business in Europe and Far East



What is HgS ?



The most stable mercury Compound

- Chemical compound composed of Mercury and sulphur
- $\text{Hg}^{2+} + \text{S}^{2-} \rightarrow \text{HgS}$
- Very toxic Hg is transformed into non toxic HgS
- Spontaneous reaction
- Exothermal reaction

HgS identification

- Classified as non hazardous waste
- Most insoluble metallic-sulphide compound


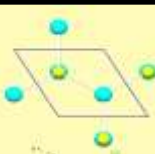



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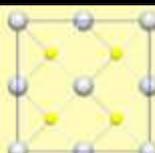
HgS is polymorphic

Crystallizes in 3 polymorphic modifications

3.	γ - HgS HgS _{black}		Hypercinnabar	Crystal structure: hexagonal Wurtzite		
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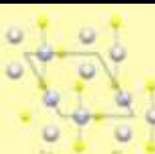
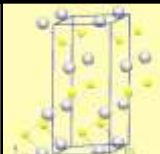
Metastable polymorph for standard temperature and pressure

Stable polymorph for T = 481 - 820 °C

2.	β -HgS HgS _{black}		Metacinnabar	Crystal structure: Cubic zinc-blende		
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Metastable polymorph for standard temperature and pressure

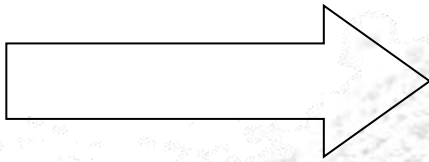
Stable polymorph for T = 345 -481 °C

1.	α - HgS HgS _{red}		Cinnabar	Crystal structure: Trigonal		
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Most stable polymorph for standard temperature and pressure (25° C, 1013 hPa)



Chemical and physical stable modification



α - HgS - HgS_{red} - Cinnabar

- **Crystalline structure**
- **Thermodynamic stability**
- **Tolerable values for leaching behaviour**
- **Final product free of Hg emissions**



DELA stabilisation process



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Bench-scale plant for test runs

- Vacuum technology
- Treatment capacity: 5 kg mercury / test run
- 75 test runs up to now
- Using mercury from DELA, SAKAB and Swedish EPA



Full scale plant

- Vacuum technology
- Volume ca. 600 l /
- Capacity ~ 3 t / d → 1000 t / a
- Operation scheduled for January 2010
- Plant approved by competent authority



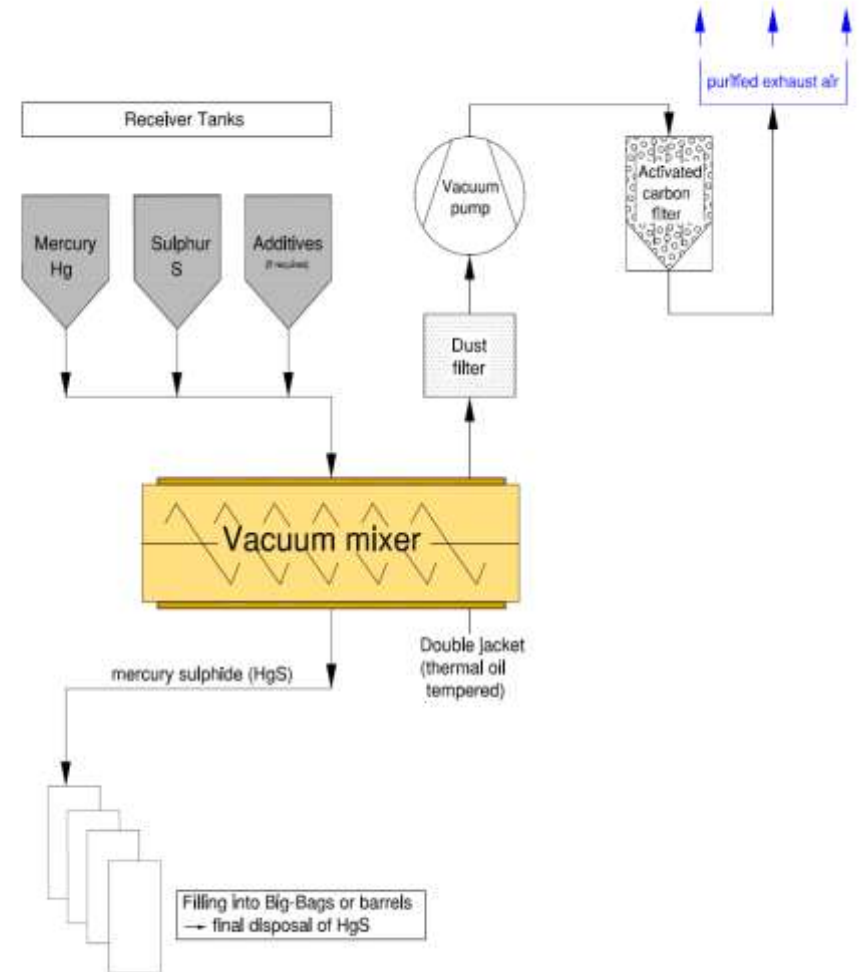
Hg stabilisation process is patent registered by DELA GmbH



DELA stabilisation process

Procedure steps

- Filling receiver tanks
- Pellets can be produced by using additives
- Create inert atmosphere
 - Nitrogen inflow
 - No oxygen
- Setting up vacuum atmosphere
- Total quantity of sulphur required is fed at once
- Defined quantity of mercury added evenly
- Defined mixing time



Vacuum technology

- Mature technology
- No Emissions
- Decrease of boiling point
- Operational safety
- No Oxygen



Test runs Hg stabilisation

- Recipe sulphur and mercury 1:6 ~ stoichiometric ratio [kg]

Influence for final product HgS_{red}

1. Parameter: Temperature [C°]
2. Parameter: Total Mixing time [min]
3. Parameter: Feeding time Hg [min]
4. Parameter: Engine speed [rpm]

- Find the parameter with the optimum outcome for maximum red HgS



Analysis by University Münster, Germany

- **X- ray structure analysis**

- Phase identification
- Crystalline structure
- Lattice parameters

- **Differential Thermo Analysis (DTA)**

- **Thermogravimetric Analysis (TGA)**

Analysis by chemical lab.Terrachem, Germany

- Leaching behaviour Hg [mg/l]

Solid State Chemistry ^{WWU}

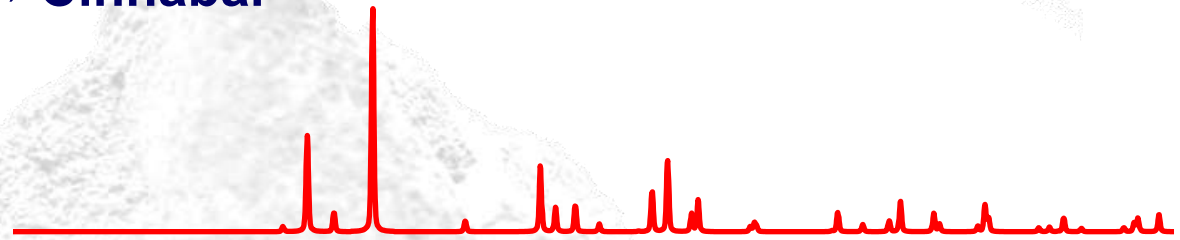
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Westfälische
Wilhelms-Universität
Münster

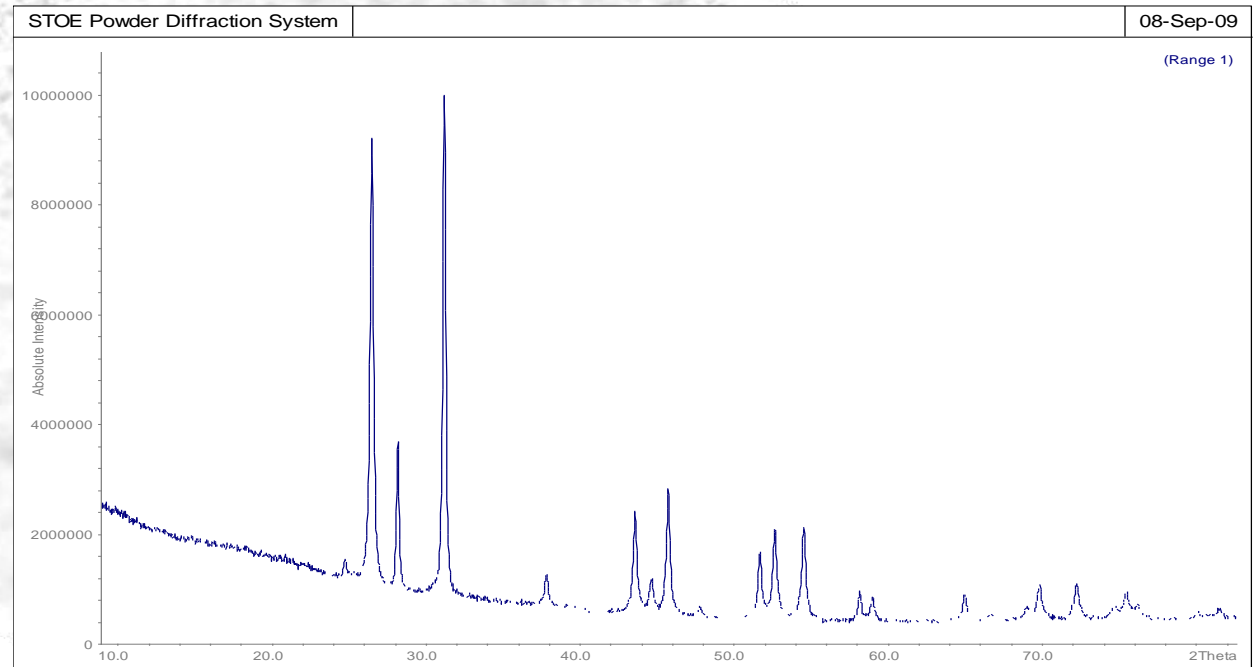




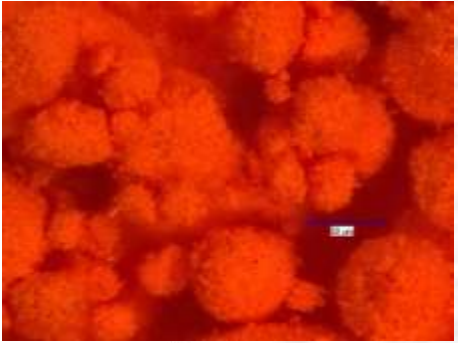

Intensity curve α -HgS \rightarrow Cinnabar



HgS DELA sample

- Product is α -HgS
- 100 % Cinnabar



HgS industrial		HgS DELA GmbH	
	<ul style="list-style-type: none">• Lighter colour: indicates higher proportion of smaller particles		<ul style="list-style-type: none">• Darker red: indicates higher proportion of bigger particles
	<ul style="list-style-type: none">• Generated by sublimation		<ul style="list-style-type: none">• Generated in mechanical process• Temp. increase after mixing

Different compositions of cinnabar:

Colours vary from bright vermillion to dull reddish -black



Lattice parameter DELA α - HgS consistent with existing literature data

Reference data	DELA sample
$a = 414.7 \text{ pm}$; $c = 949 \text{ pm}$	$a = 414.82(9) \text{ pm}$; $c = 949.9(2) \text{ pm}$

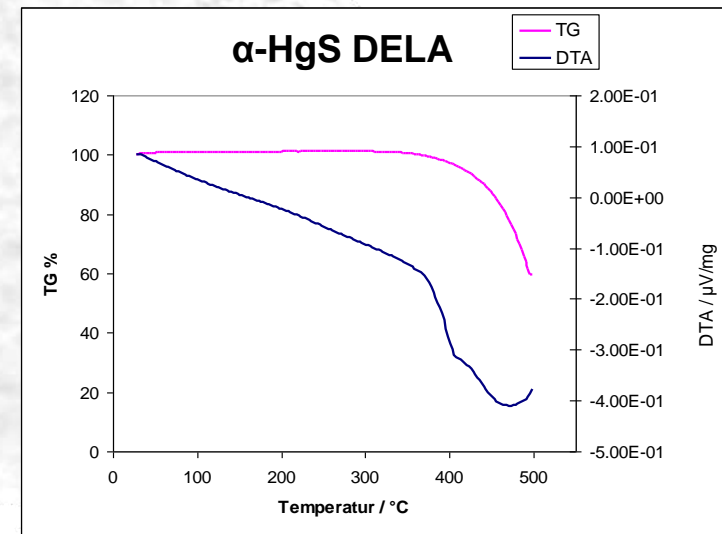
Differential Thermal Analysis (DTA) & Thermogravimetric analysis (TGA)

DTA: Detects phase transition of a substance

TGA: Detects mass loss & thermal information

- Thermodynamic stability of α -HgS

- $T \sim 350^\circ\text{C}$



DELA test samples (Quantity 50 samples)

- Leaching behaviour $HgS_{min} = < 0.001$ [mg/l]
- Leaching behaviour $HgS_{max} = 0.050$ [mg/l]

Average value:

0.009 [mg/l]

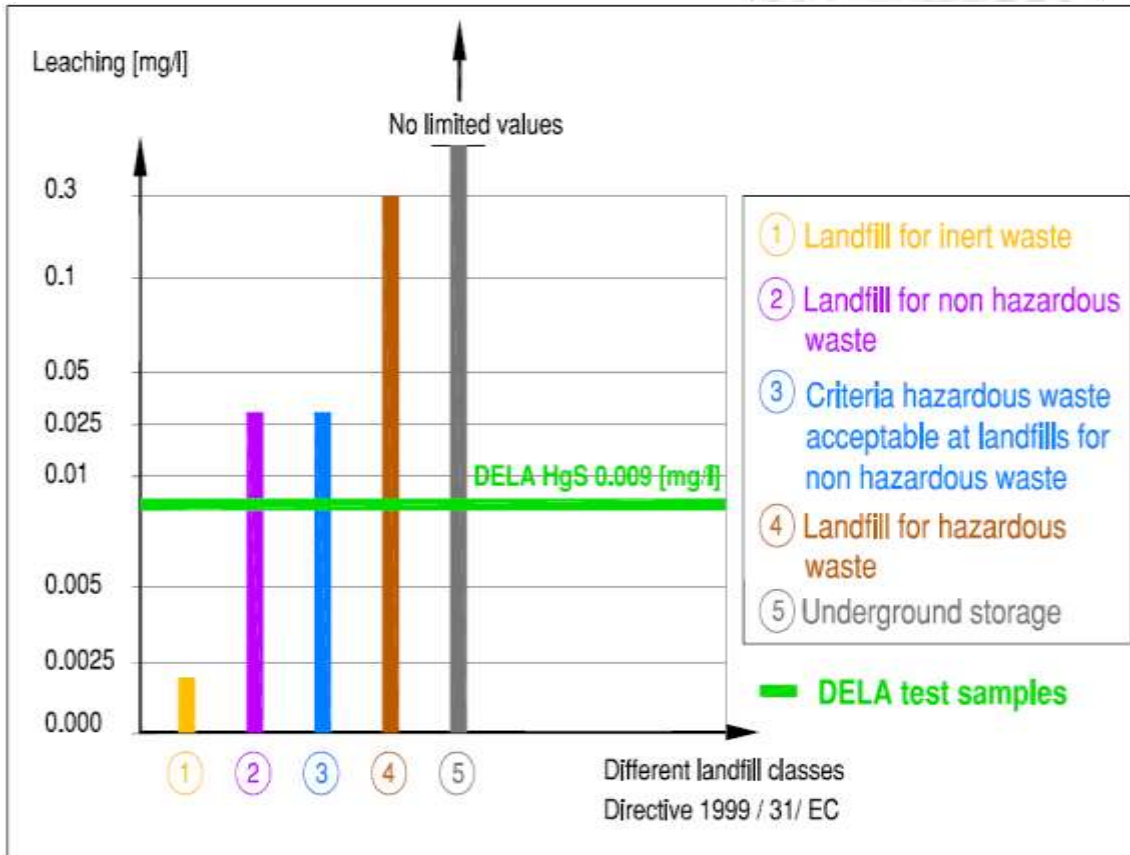
Leaching limit values that apply for different classes of landfills

Criteria for the acceptance of waste for landfills to Directive 1999/31/EC (2003/31/EC)

Section	No.:	Different classes of landfills and criteria for waste acceptance	Waste acceptance criteria
			EN 12457 / 1- 4 Leaching Hg [mg/l]
2.1	1	Landfills for inert waste	0,002
2.2	2	Landfills for non hazardous wastes	0,03
2.3	3	Criteria for hazardous waste acceptable at landfills for non hazardous waste	0,03
2.4	4	Landfills for hazardous waste	0,3
2.5	5	Underground storage	[-] No limited values for leaching



Result



DELA HgS

fulfills disposal criteria for:

- Landfill classes 2 - 5
 - Aboveground landfill
 - Underground storage

Final Disposal not limited to underground storage

→

Above ground disposal feasible!



Mercury vapor analysis



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Chemical analysis University Münster

- No Hg detection in:
 - X - ray structure analysis
 - Light optical microscope photograph

In situ - mercury vapor analysis

- Measurement of Hg vapor in the air



No detection of Hg vapor in any sample !



Conclusion DELA HgS

Crystalline structure



Thermodynamic stability



Good values for leaching behaviour



Final product free of Hg emissions



Project objective

Chemical and physical stable modification





Thank you for your attention !

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