

Evaluation of thermal decomposition and thermal desorption of mercury in soils from the old mining district of Almadén (Spain)

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INTRODUCTION AND OBJECTIVES

The objective of the present work is to study thermal decomposition and thermal desorption of mercury (Hg) in two different soils from the old mercury mining district of Almadén (Spain). One of these soils (S1) was taken from a "dehesa" where natural Mediterranean vegetation is combined with agrosilvopastoral activities. The other soil (S2) was collected from an area where metallurgical processes were carried out in past centuries.



Figure 1. Abandoned metallurgical plant in Almadenejos, Almadén district (R5.5).



Figure 2. "Dehesa de Castilseras", Almadén district (AJ3).

METHODOLOGY

This study examines the Hg thermal decomposition of the study soils. In this way, differential scanning calorimetry (DSC) of them performed under non-isothermal conditions in a N₂ atmosphere. The Friedman method were employed to determine the reaction kinetics (apparent activation energy (E_a) and pre-exponential factor (A)) from the DSC data for Hg desorption.

Moreover, the potential of Hg thermal desorption is evaluated at low, medium and high temperatures in both soils using solar energy. This former experimental work was carried out into a solar furnace (prototype reactor designing to be tested in the Solar Furnace facility SF60 located in Platform Solar from Almería) at different temperatures. A previously dried sample of each original soil was taken and, the following temperature ramp was carried out on each one into the Solar furnace (Bombach, 1994; Navarro, 2009; Windmüller, 1996):

- 60 °C (Potential volatilization of Hg⁰ under field conditions).
- 160 °C (Volatilization of Hg⁰).
- 220 °C (Hg thermal desorption from Hg₂Cl₂ or HgCl₂).
- 280 °C (Hg thermal desorption from OM).
- 360 °C (Hg thermal desorption from HgS).
- 560 °C (Hg thermal desorption from HgO, HgSO₄, pyrite).
- 650 °C (Hg thermal desorption from sphalerita and/or the remained Hg from pyrite and cinnabar).



Figure 3. Solar Furnace: Concentrator and receiver in operation at the focus <http://www.psa.es/webeng/instalaciones/horno.php>

RESULTS AND DISCUSSION

Standard soil parameters

Soil	pH	EC _{ES} (dS cm ⁻¹)	OM (%)	Texture	Total Hg (mg kg ⁻¹)
S1	6.9	1.05	2.8	Sandy loam	34.4 ± 7.2
S2	6.1	3.93	3.7	Sandy loam	10,497 ± 1,564

Table 1. Physicochemical characterization of experimental soils. EC_{SE}: Electrical conductivity of the saturated paste extract; OM: Organic matter.

Thermal decomposition of Hg in the study soils

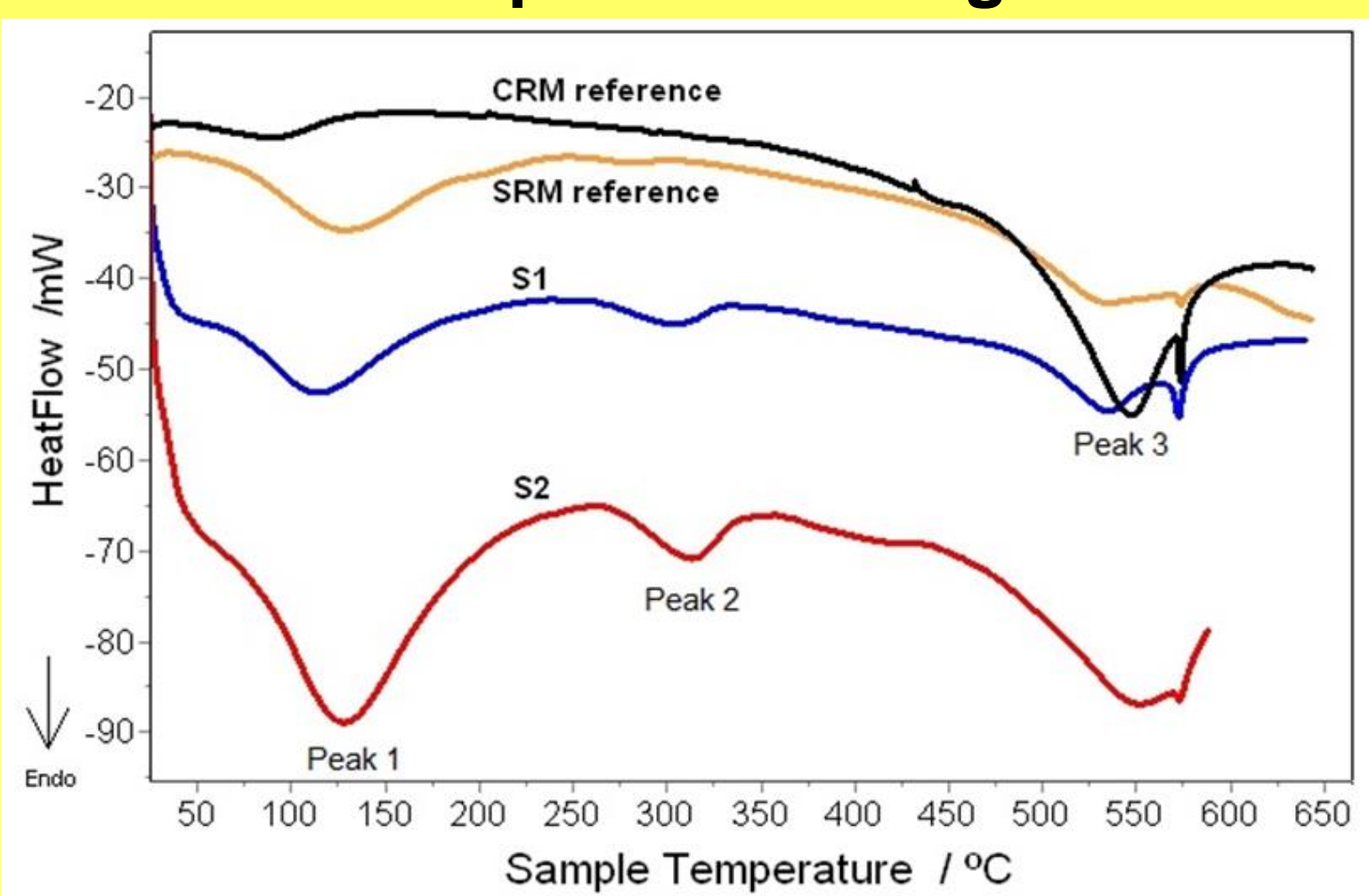


Figure 4. DSC curves of thermal decomposition of the study soils and references materials (Heating rate: 10 °C min⁻¹).

Peak 1: HgCl₂ (s) → Hg(g) + 2Cl(g)

Peak 2: HgS (s) → Hg(g) + S(g)

Peak 3: HgO(s) → Hg(g) + 1/2 O₂(g) (Only "dehesa" (S1))

Table 2. Apparent activation energy (E_a) and pre-exponential factor (A) for S1 and S2 as determined by Friedman method.

Soil	Peak	E _a (kJ/mol)	A (s ⁻¹)
S1	1	44.6	7.7 · 10 ³
	2	138.6	4.7 · 10 ¹⁰
	3	255.2	5.9 · 10 ⁴
S2	1	49.7	1.5 · 10 ⁴
	2	188.7	1.0 · 10 ¹⁵

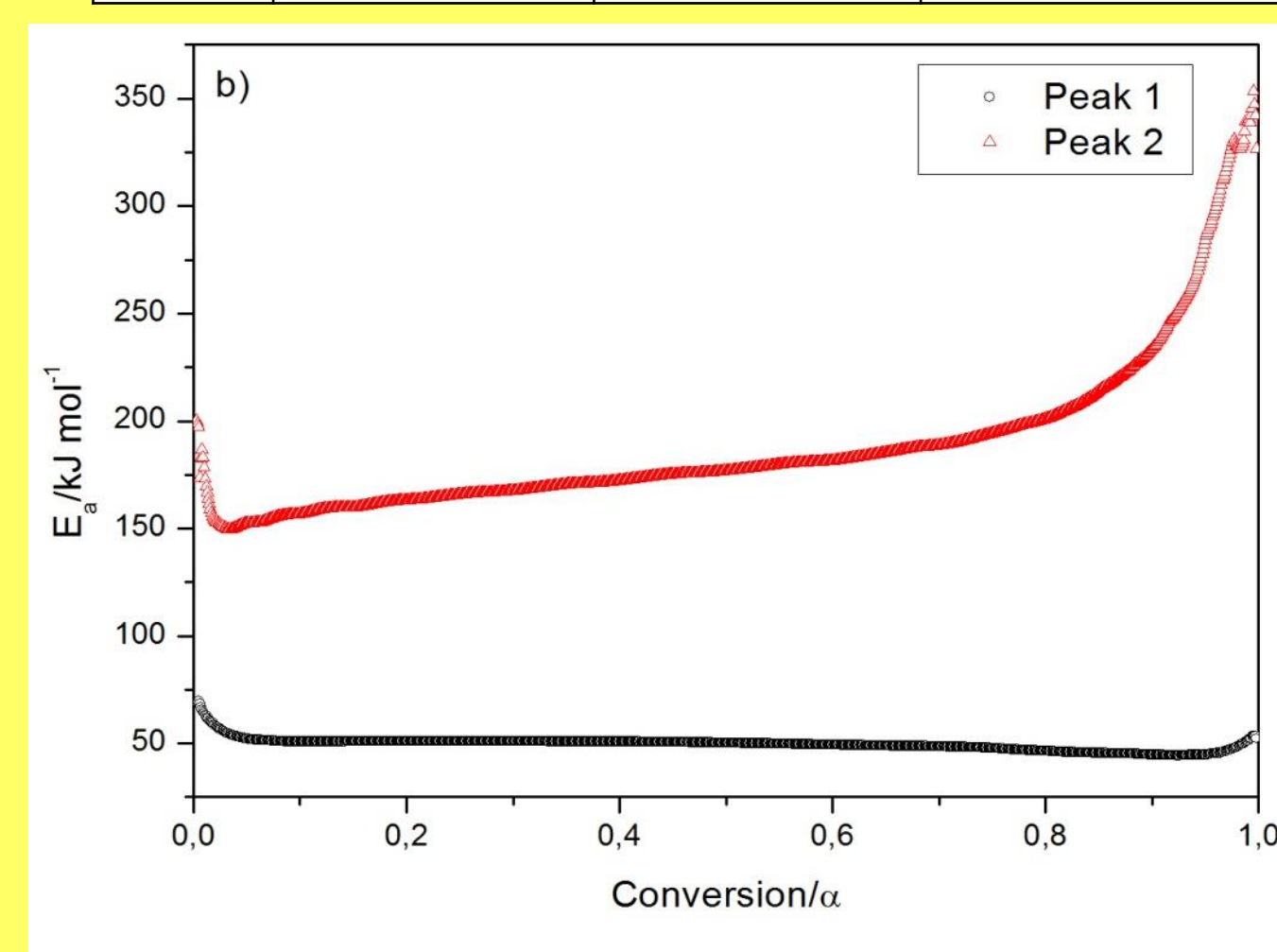
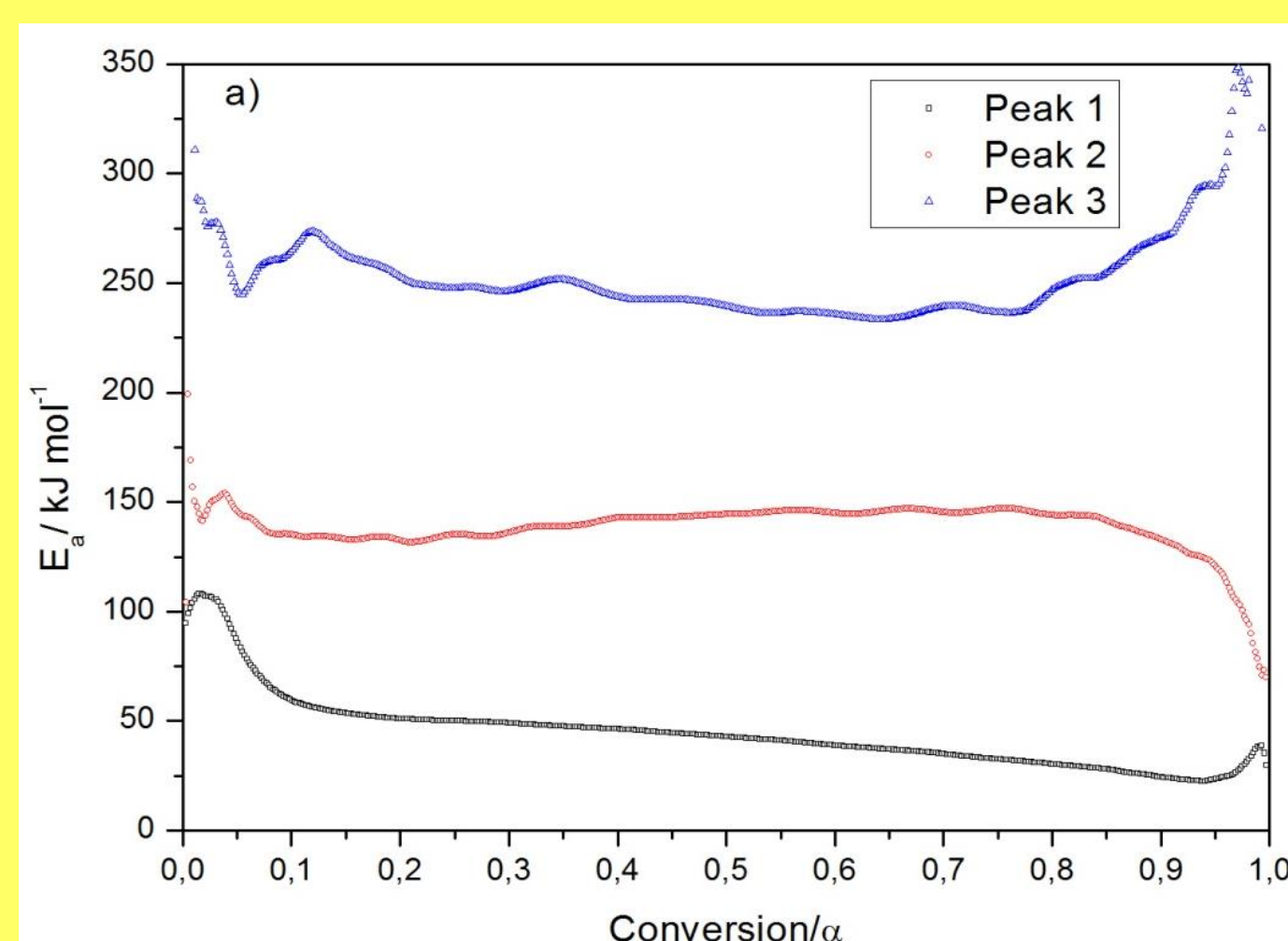


Figure 5.- Apparent activation energy, as determined by the Friedman method for a) Soil S1 and b) Soil S2.

E_a was found to be practically constant in the interval of conversion values (α) 0.1–0.9 for both soils suggesting that the decomposition of Hg compounds is a single-step process. Furthermore, the E_a of each reaction was greater for soil from the old metallurgical plant than for soil from "dehesa", in agreement with the quantity of Hg in each soil.

Thermal desorption of Hg in the study soils

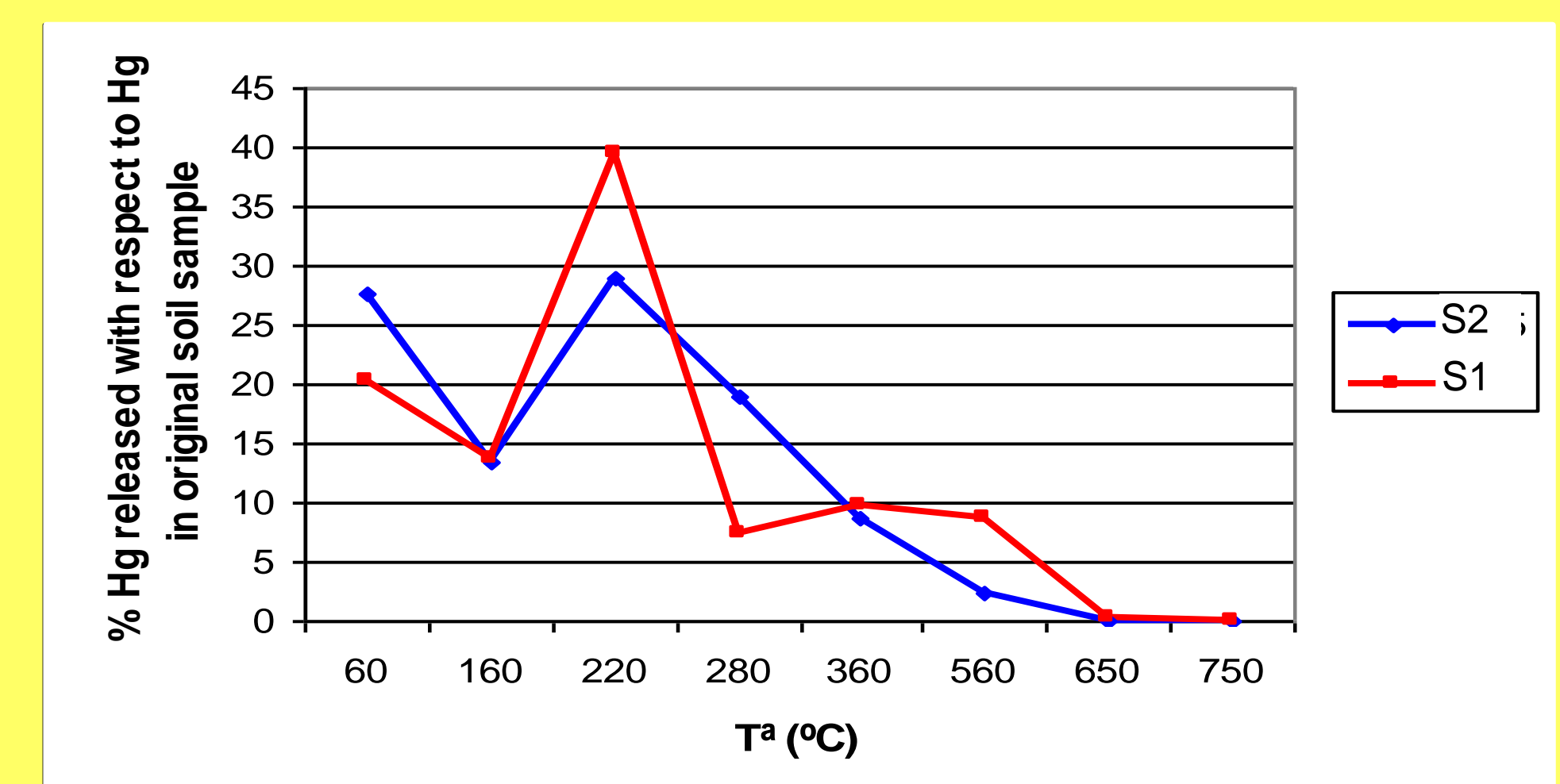


Figure 6. Evolution of % Hg released with respect to Hg concentration in original soil sample along temperature ramp.

- More than 80% of Hg from both original soil samples was released once 280 °C was reached. The most of the remaining Hg (~ 19%) was released in the range between 360 and 560 °C.

- At temperatures lower than 200 °C, Hg released from abandoned Hg metallurgical plant (S2) was the highest because of the direct input of anthropogenic Hg that existed in this site during a long time. In the case of S1 the released Hg⁰ was lower than in the case of S2 because of the Hg⁰ deposited in this site due to the mining influence, has mostly been oxidized to Hg²⁺ and become part of soil compounds. The percentage of Hg released at 280 °C (associated with OM) from S2 was higher than the Hg released from S1 (OM in S2 > OM in S1). Trend is the opposite in the rest of temperatures.

- Regarding the Hg released at temperatures higher than 360 °C, the general trend is that the percentage of released Hg from S1 was almost two times higher than the percentage from S2. This fact implies that Hg from "dehesa" was more strongly joined to soil matrix indicating the more natural character of this soil with respect to soil from abandoned Hg metallurgical plant. Furthermore, it is interesting to point up that the percentage of Hg released at 560 °C (associated to oxides among others) from "dehesa" soil with respect to Hg in original samples is almost four times higher than from the other soil according with results of thermal decomposition.

CONCLUSIONS

- DSC curves of both soils present the same two first peaks which could be showing similar chemical bonds. However, soil from "dehesa" has a third peak that does not appear in the case of soil from old metallurgical plant. Soil from "dehesa" seems to have significantly more HgO than the other soil.
- The results suggest that the decomposition of Hg compounds is a single-step process.
- The results of the Hg released from both soils at different temperatures show that more than 80% of this element was released once 280 °C was reached.
- The analysis of these results confirms the origin of the samples. It shows the natural character of soil from "dehesa" compared to more anthropogenic origin of the soil from the old metallurgical plant.
- These data could be used in order to evaluate the optimum temperature at which a Hg contaminated soil could be considered remediated.

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