HEAVY METALS PARTITIONING DURING THERMAL CONVERSION OF SEWAGE SLUDGE IN A FLUIDIZED BED UNDER CONDITIONS RELEVANT FOR PYROLYSIS AND GASIFICATION

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ABSTRACT: There is a growing concern on the final disposal of urban organic wastes, such as municipal solid waste (MSW) and sewage sludge (SS), since they constitute an available energy and material source currently not efficiently valorized. These wastes become an attractive feedstock provided proper treatment/conversion techniques are applied, dealing with their high load of impurities. The objective of this work was to investigate the partitioning of heavy metals and other relevant species during thermal treatment of sewage sludge in order to properly valorize/dispose this feedstock. Experiments were performed in a fixed-bed and a fluidized-bed reactors under conditions relevant for pyrolysis and gasification.
Keywords: fluidized bed reactor, gasification, pyrolysis, sewage sludge

1 INTRODUCTION

Sewage sludge is a residue from wastewater treatment plants (WWTP), whose production is rapidly increasing with the development of WWTPs in Europe [1]. Currently, landfilling, use as soil amender in agricultural or non-agricultural activities and incineration are the main disposal methods for sewage sludge disposal. However, they are considered unsustainable approaches for sludge management, because of the increase in sludge production and high concentration heavy metals in the sludge [1]. Therefore, it must be disposed of using environmentally and economically sound methods. Previous studies have indicated that heavy metals in sludge could be transferred into soil through landfilling and agriculture utilization, which is potentially hazardous to the food chain [2,3]. The thermal conversion of this solid by pyrolysis, gasification and combustion can be an attractive alternative for the treatment of sewage sludge to reduce its volume and put it into a form suitable for safe disposal.

The objective of the project in which this work is included is to demonstrate the technical feasibility of urban waste valorization by proper thermal treatments, taking into account the undesirable compounds of the material. The first step in this research, summarized in this paper, is to establish the partitioning of the heavy metals during dried sewage sludge granulates under condition relevant for pyrolysis and gasification.

2 MATERIAL AND METHODS

2.1 Sewage Sludge

The sewage sludge (SS) employed was cylindrical with a particle size between 1-2 mm. The SS was characterized previously [4], and a summary is shown in Table I. It presents a high amount of heavy metals, as it will be shown below.

2.2 Experimental set-up and procedure

Experiments have been carried out in two different experimental set-up: a fixed bed reactor (Fig. 1a) and laboratory scale fluidized bed reactor (Fig. 1b). Both reactors were made of stainless steel.

In the fixed-bed reactor, the reactor is placed horizontally and it is surrounded by an electric oven. A batch of sample (35 g for N_2 tests and 10 g for air tests) is put inside the reactor and it is heated to desired temperature. At the end of the test (about 20 min), the sample remaining is collected and weighed to determine the mass loss. The concentration of main heavy metals and carbon were measured for each sample by ICP. A total of 7 tests were performed to study the effect of temperature and atmosphere.

The laboratory-scale fluidized bed reactor has three sections: a preheating zone, a bottom bed and a freeboard. The reactor is surrounded by an electric oven, with two independent heating zones, one for the bottom bed and one for the freeboard. A total of 20 tests were performed to analyze the effect of the temperature, the residence time, the atmosphere, the flux of steam and the addition of HCl in the gas. A fraction of the bottom ashes was collected at the end of the test to measure the concentration in heavy metals.

Table I: Chemical characterization of the SS used [4].

Moisture (%w/w)	8.6
Dry basic (%w/w)	
Ash	43.1
Volatile	51.8
Fixed Carbon	5.1
Dry and ash free basis (%w/w)	
C	51
H	7.3
N	7.9
S	2.05
O	31.8

3 RESULTS AND DISCUSSIONS

Several studies have discussed the fate of heavy metals during SS incineration. Nevertheless, the migration of heavy metals during SS pyrolysis and gasification has not been systematically investigated. Besides, most of previous studies are based on theoretical calculations and focused on the behavior of a few specific heavy metals. However, they have not addressed experimental investigations in a systematic way. This section aims to analyze the behavior of heavy metals under different thermal conditions (temperature, residence time, etc.), comparing with existing works in literature.

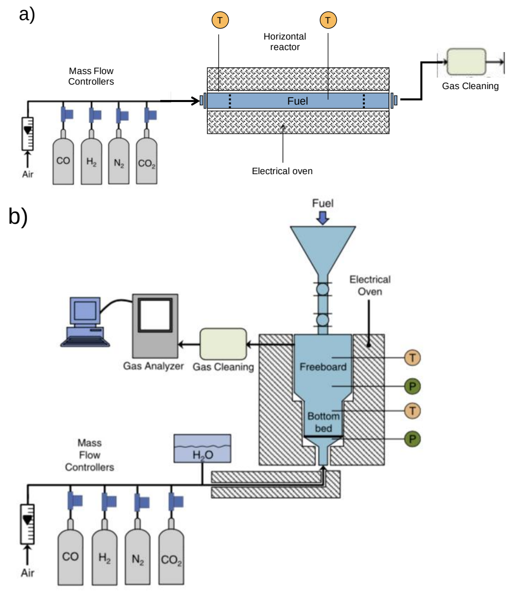

Figure 1: Experimental set-up: a) Fixed bed reactor and b) fluidized-bed reactor

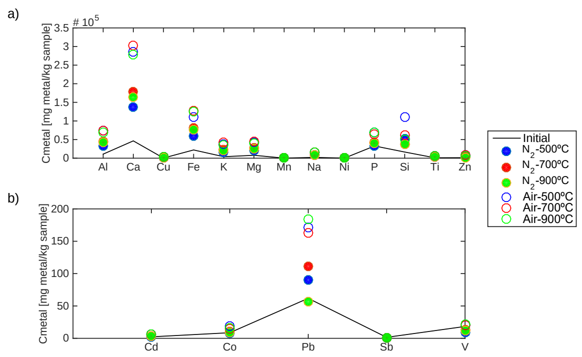

Figure 2: Concentration of heavy metals in the final residue after tests performed in the fixed-bed reactor at different temperatures and gas composition for: a) major elements and b) for minor elements

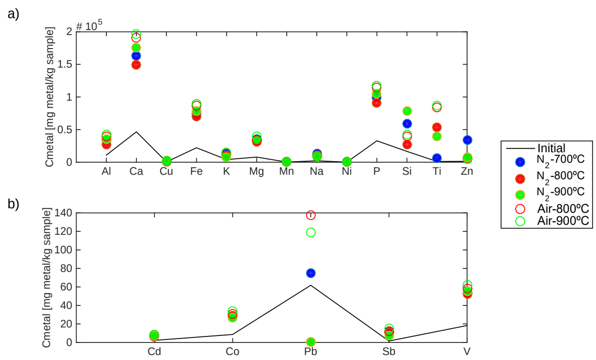

Figure 3: Concentration of heavy metals in the final residue after tests performed in the fluidized-bed at different temperatures and gas composition for: a) major elements and b) for minor elements

Fig. 2 and 3 show the results the concentration of heavy metals at different temperatures and atmospheres in the final residue after tests performed in the fixed-reactor and in the fluidized-bed respectively. Each figure is divided in two groups: major (a) and trace compounds (b) depending on their concentration range. Concentrations of each heavy metal were compared with that in the initial sample.

It was observed that the concentration of heavy metals in the residue (sludge) depends on the experimental conditions and these concentrations are intimately related with the loss of mass and the loss of carbon (Table II) during the process. Hence, the concentration of heavy metals increased versus the initial concentration due to the high loss of mass and metals remained concentrated in the final solid. Similar results were obtained by Dong et al. [5] when studying the partitioning of heavy metals in municipal solid waste in a tubular furnace and by Chang et al [6] during pyrolysis experiments of municipal sludge in a pilot-scale fluidized-bed furnace.

Table I: Percentages of loss of mass and loss of carbon for each experiment performed in the fixed-bed reactor

Atmosphere	T, ºC	% Loss of mass	% Loss of carbon
N_2	500	49.89	65.88
	700	62.37	76.42
	900	64.26	76.70
Air	500	76.00	99.68
	700	76.30	99.93
	900	77.50	99.53

The concentration of heavy metals decreased between 500 and 700 ºC (increasing their volatilization). However, for some elements (as Cd, Fe, Pb or V) using air, the concentration increased between 700 and 900ºC. These trends can be caused by the agglomeration of the samples [6]. Most authors agree with the fact that the increase in temperature favors the metals volatilization, although some metals are more affected than others by this parameter [5, 6].

Experiments using air yielded higher concentrations of most heavy metals in the treated sample (in the form of oxides). The Pb is the metal most affected by the temperature and the use of air, since it forms PbO, which favors the volatilization of Pb. The same effect was observed by Dong et al., [5]. However, some metals, as Cu and Ni was observed to remain in the solid phase [5]. Finally, Cd and Ni retarded their volatilization in air atmosphere because their oxides present higher boiling temperature than the metallic form. This was also observed by Overnberger and Dahl [8].

It was also observed a high loss of mass and carbon during tests with air. Results were also compared by taking the mass of the incoming dried sample introduced in the reactor (Fig. 4) as a basis, clearly showing heavy metals devolatilization during the thermal process (e.g. for Pb).

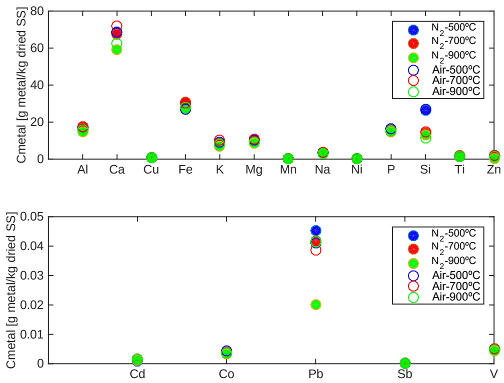

Figure 4: Concentration (mass) of heavy metals in the final residue after tests at different temperatures and atmospheres on the basis kg of dried sample fed in the reactor: a) for major elements and b) for minor elements

Fig. 5 shows the concentration of heavy metals in the final residue at different temperatures and residence times after tests performed in the fluidized bed reactor. It is observed that longer residence time favors the volatilization, moreover, the effect of residence time is most relevant at higher temperatures, also in agreement with Liu et al., [1] and Chang et al., [5].

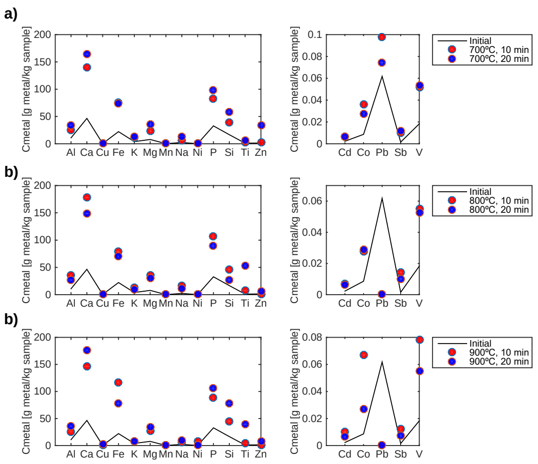

Figure 5: Concentration of heavy metals in the final residue after tests at different temperatures (700ºC (a), 800ºC (b) and 900ºC (c)) and residence times

Finally, Fig. 6 shows the concentration of heavy metals at tests performed with an atmosphere of N_2, at 800ºC and 10 min and, with the same conditions but by introducing 1000 ppm of HCl in the fluidization gas. Most authors have underlined the importance of the presence of Cl in favoring the volatilization of heavy metals and retaining most of the trace metals in the vapor phase while sulfur keeps them in the condensed form [1, 5, 9]. However, the effect is different for each metal. It is observed that the addition of Cl does not affect much the volatilization of Cu, Cd, Pb and Zn, due to the high volatilization degree achieved of these metals without chlorine. This effect would be better observed using the same base for all the compounds, for instance as kg dried SS, but the total sample at the end of the reactor have to be collected (it was not possible in the fluidized-bed tests, in which only a small fraction was sampled from the bed).

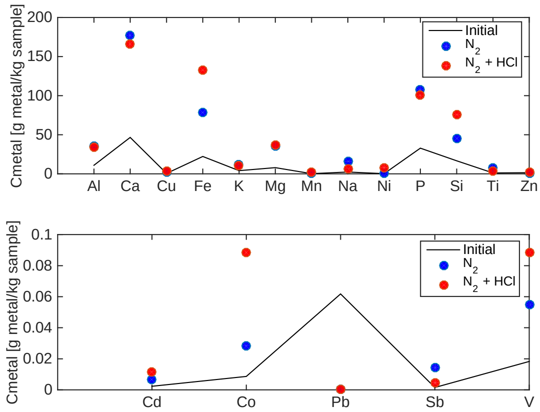

Figure 6: Concentration of heavy metals in the final residue after tests at different temperatures for a gas strema of N_2 an with N_2 doped with 1000 ppm HCl: a) for major elements and b) for minor elements

4 CONCLUSIONS

Thermal conversion tests at different conditions were performed in a fixed-bed reactor and fluidized-bed reactors to establish the partition behavior of major and minor species in dried sewage sludge. The main conclusions are summarized as follow:

- The main differences in the concentration of heavy metals were observed between 700 and 900 ºC.
- Ca, Fe, K, Mg, P, Si and Pb are highly affected by temperature increase, and the final concentration of these metals in the sample (referred to the initial concentration). Therefore, these metals remained concentrated in the final solid, due to the high loss of mass.
- The residence time has a lower impact than temperature; its effect being more significant at high temperature.
- Experiments using air caused higher concentration of almost heavy metals in the final sample. This is because they form oxides with lower volatility than the corresponding metals.
- The addition of HCl affects differently the various metal analysed. Fe, Si, Co and V were the metals more affected, whereas Cu, Cd, Pb and Zn devolatilization did not vary appreciably by HCl addition.

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