Thermal Characteristics of Hyperaccumulator and Fate of Heavy Metals during Thermal Treatment of Sedum plumbizincicola

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Thermal Characteristics of Hyperaccumulator and Fate of Heavy Metals During Thermal Treatment of *Sedum plumbizincicola*

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Thermal treatment is one of the most promising disposal techniques for heavy metal- (HM)-enriched hyperaccumulators. However, the thermal characteristics and fate of HMs during thermal treatment of hyperaccumulator biomass need to be known in detail. A horizontal tube furnace was used to analyze the disposal process of hyperaccumulator biomass derived from a phyto-extracted field in which the soil was moderately contaminated with heavy metals. Different operational conditions regarding temperature and gas composition were tested. A thermo-dynamic analysis by advanced system for process engineering was performed to predict HM speciation during thermal disposal and SEM-EDS, XRD and sequential chemical extraction were used to characterize the heavy metals. The recovery of Zn, Pb and Cd in bottom ash decreased with increasing temperature but recovery increased in the fly ash. Recovery of Zn, Pb and Cd fluctuated with increasing air flow rate and the metal recovery rates were higher in the fly ash than the bottom ash. Most Cl, S, Fe, Al and SiO_2 were found as alkali oxides, SO_2, $Fe_2(SO_4)_3$, iron oxide, $Ca_3Al_2O_6$, K_2SiO_3 and SiO_2 instead of reacting with HMs. Thus, the HMs were found to occur as the pure metals and their oxides during the combustion process and as the sulfides during the reducing process.

Keywords: hyperaccumulators, heavy metals, thermal disposal, thermodynamic analysis

Introduction

Phytoextraction using hyperaccumulators is considered to be an efficient and low cost technology to remove heavy metals from contaminated soils (Lasat 2002). *S. plumbizincicola*, a zinc- and cadmium-hyperaccumulator, has considerable capacity to phytoextract Zn and Cd (Jiang *et al.* 2010; Wu *et al.* 2013a) and has been demonstrated to successfully remediate Zn- and Cd-contaminated soils.

It was reported (Wu *et al.* 2013b; Jiang *et al.* 2010; Wu *et al.* 2006) that *S. plumbizincicola* could produce large biomass containing several thousands of mg Zn /kg and hundreds of mg Cd /kg would be produced by hyperaccumulator plants grown at the phytoremediation site in Zhejiang province, east China.

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The safe and economical disposal of the harvested biomass to avoid secondary environmental pollution is therefore a challenging problem. Incineration is generally recommended rather than other general disposal methods for contaminated biomass such as composting, compaction, incineration, ashing, pyrolysis, direct disposal, and liquid extraction (Sas-Nowosielska *et al.* 2004). Incineration is a feasible and economically acceptable method that offers the advantage of >90% reduction of the waste volume and destruction of organic compounds (near complete). On the other hand, the metal species contained in the waste are not destroyed during high temperature incineration, but instead condense to form metallic particles during the cooling of the flue gas.

Previous studies have indicated that the volatilization rate of heavy metals from waste incinerators is a complex function of the incinerator operating conditions such as temperature, gas composition and residence time (Jakob *et al.* 1996; Knacke *et al.* 1991; Brunner *et al.* 1986). Heavy metals evaporate more or less independently of temperature and concentrate in the solid residues (bottom ash and fly ash) in incinerators or as airborne aerosols exiting the stack (Zhang *et al.* 2008a). For example, Cd is a volatile heavy metal that is concentrated in

fly ash (Lars *et al.* 2003) but nearly 1/3 of Pb and Zn are distributed in the fly ash and 2/3 in the bottom ash (Zhang *et al.* 2008b; Abanades *et al.* 2002). In a burning waste load some regions may be locally oxygen-depleted (reducing conditions) and it is therefore necessary to determine the effect of the oxygen content on the incineration process. Most heavy metals can form sulfate salts in the presence of sulfur at temperatures below 700°C (Chen *et al.* 1998).

The volatilization rate of heavy metals from waste incinerators depends on the composition of the hyperaccumulators and the physico-chemical properties of the metals and their compounds (chlorine, sulphur, or alumino-silicates). Sulfur present in the biomass may interact with heavy metals such as Cd during incineration and will affect their emissions. Sulfur can, in principle, delay heavy metal volatilization when the incineration temperature is below 800°C (Verhulst *et al.* 1996). Chlorides can significantly enhance metal volatilization through the formation of metal chlorides, thereby increasing toxic heavy metal emissions (Wang *et al.* 1999). SiO_2- and Al_2O_3-containing minerals can function as sorbents stabilizing heavy metals as condensed phase solids (Zhang *et al.* 2008; Wu *et al.* 2013).

The objective of this study was to quantify experimentally the impact of temperature, air excess ratio and compounds (chlorine, sulphur, or alumino-silicates) in *S. plumbicizincola* on the partitioning of heavy metals under simulated incineration conditions and to understand their speciation from thermodynamic calculations. The partitioning of HMs was thermo-dynamically predicted in a well-defined system whose composition corresponds to that during the incineration of hyperaccumulator biomass. The equilibrium calculations focused on the influences of the operating temperature, air excess ratio and compounds (chlorine, sulphur, or alumino-silicates) in the combustion residues and flow gas on heavy metal speciation. The thermodynamic calculations focused on the influence of the operating temperature in the range 350–1950°C and the oxygen contents in the combustion gas. The theoretical thermodynamic results were compared with several analytical results, related either to the HM distribution among bottom ash, fly ash and flue gas from different temperatures and air flow rates or to the chemical species in these samples from tubular furnace reactor experiments. The study focused on Zn, Cd and Pb but the behaviors of other elements found in *S. plumbizincicola* such as S, Al, Ca, Cu, Cr and Fe were also briefly studied.

Materials and Methodology

Materials

S. plumbizincicola was grown at a moderately polluted farmland site in the suburbs of Fuyang city, Zhejiang province, east China. The biomass was collected to carry out the combustion tests in a horizontal quartz tube. The proximate and ultimate analysis of *S. plumbizincicola* is given in Table 1. Large amounts of organically bound fuel-nitrogen, volatile matter and ash were observed in the biomass and high concentra-

Table 1. Proximate and ultimate analysis of *S. plumbizincicola*

Proximate analysis		Ultimate analysis	
Ash (ad%)	16.6	C (%)	37.5
Volatilecarbon (ad%)	66.2	H (%)	5.5
Fixed carbon (ad%)	13.6	N (%)	2.2
Moisture (ad%)	3.6	S (%)	0.2
		O (%)	38.0
		Calorific value (J g^{-1})	15620

tions of Cd and Zn but low concentrations of sulfur occurred in the biomass.

Experimental Facility and Sampling

The experimental facility includes two high pressure gas sources (O_2, N_2), a flow control valves and a meter, a horizontal quartz tube with a surrounding electrically heated furnace, and a flue gas absorption device (Figure 1). The horizontal quartz tube has an inner diameter of 45 mm, a length of 1000 mm of which 400 mm is in the temperature controlled reaction zone heated and controlled by the electrical furnace from 100 to 1100°C. For each experiment all the flue gas was sampled. The absorption device was based on US EPA Method 29. A fiber-glass filter was plugged in the joint between the quartz tube and the absorption bottle to avoid blocking the flue gas flow in the exhaust tube and sampled as fly ash. Test conditions for the thermal treatment experiments included the type of reacting atmosphere, reaction temperature, and reaction time, and are listed in Table 2. About 3 g of *S. plumbizincicola* powder was placed in a dried and weighted quartz boat and transferred to the center of the quartz tube which was pre-heated to the desired temperature and was purged with N_2 in advance for about 10 min. The gas flow was introduced into the quartz tube at the start of the experiments. After each experiment the absorption bottles with 5% HNO_3 + 10% H_2O_2 solution were removed and replaced by another set of bottles to dispose of the exhaust gas. At the same time the heating source was cut off. After the tube furnace had cooled sufficiently the bottom ash was taken out
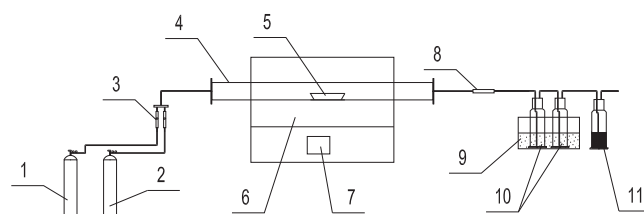

Fig. 1. Schematic diagram of the setup of the horizontal tube furnace NB: 1, high-pressure O_2; 2,high-pressure N_2; 3, flow meter; 4, horizontal quartz tube; 5, quartz boat; 6, electrically heated furnace; 7, temperature controller; 8, Fiber-glass Filter 9, iced-water bath; 10, absorption solution 1 (5% HNO_3 + 10% H_2O_2); 11, silica gel.

Table 2. Elemental Composition of *S. plumbizincicola* (mg kg^{-1})

Element	Concentration
Zn	2793 ± 46
Cd	77.5 ± 0.5
Pb	69.4 ± 2.2
Cu	12.7 ± 0.1
Cr	44.4 ± 3.4
Fe	2049 ± 39
Na	130 ± 0
K	7986 ± 9
Al	847 ± 40
Ca	46472 ± 4704
Cl	4414 ± 465
SiO$_2$	950

carefully, allowed to cool to room temperature, weighed, and sealed in a sampling bag.

Analysis of Heavy Metals

Solid samples such as fly ash and bottom ash were digested with a solution of HNO$_3$, HClO$_4$ and HF (3: 2: 1 HNO$_3$: HClO$_4$: HF by volume) for determination of Cd, Zn, and Pb. The concentrations of Zn and Pb were determined by flame atomic absorption spectrophotometry (Varian SpectrAA 220FS). Cd concentration was determined by a Varian SpectrAA 220Z spectrophotometer using a graphite furnace.

Equipment and Method in TG-DTG Experiment

A TG-DTG (Setaram Setsys Evolution 16) analyzer was used to study the evolution of weight and of volatile matter of *S. plumbizincicola* during pyrolysis and combustion. Approximately 10 mg of the sample was used in this study. It was crushed to powder finer than 0.2 mm. Room temperature to 800°C was set as the temperature range and the heating rate was set at 10°C min^{-1}. Nitrogen was used as the inert gas during pyrolysis and air was used during combustion.

Thermodynamic Simulations by Advanced System for Process Engineering (ASPEN)

Combustion of *S. plumbizincicola* constitutes a multi-component and multi-phase system. To identify the dominant
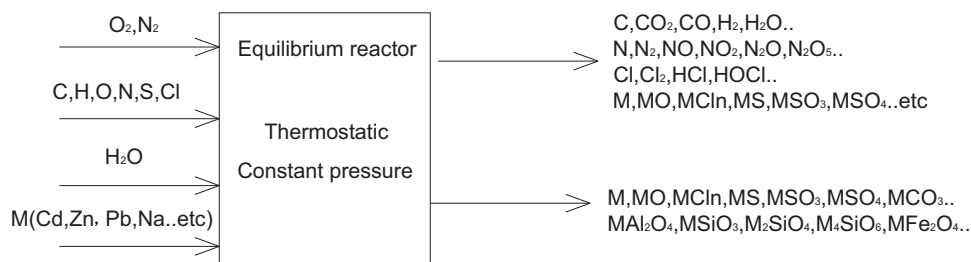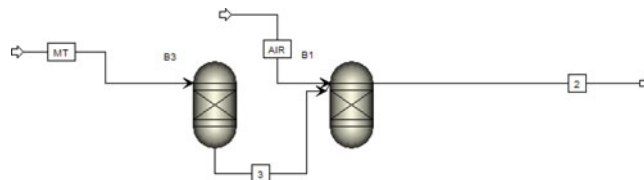
Fig. 3. *S. plumbizincicola* incineration process flowsheet (B1: Rgibbs block; B3: Ryield block; MT: stream for *S. plumbinzincicola*; AIR: stream for air; 3: stream between B3 and B1; 2: output stream).

species of each element, the principle of minimizing the total Gibbs free energy of the system was used to calculate the thermodynamic equilibrium. The final equilibrium state is obtained by determining all possible species that can be derived from the elements of the input system. The analysis serves to determine the major metallic species and to predict the possible chemical interactions between the HMs and the matrix components (Figure 2).

The process flow-sheet consists of two blocks (Ryield and Rgibbs) and 4 streams (Figure 3). MT stream (*S. plumbizincicola*) pyrolysed in the Ryield block and then incineration in the RGibbs block. The flow rate of biomass set as 20 kg h^{-1} and the air excess ratio set at 1.2.

Chemical Extraction Series

The operating conditions of each step are described in Table 3. Steps 3 and 4 respectively determine the "easily reducible" and the "moderately reducible" phases as defined by Kersten and Förstner (Kersten *et al.* 1994). A boric acid attack to dissolve possible fluoride precipitates and to eliminate the HF excess supplemented the last extraction step. To respect fixed pH procedures, HNO$_3$ was added during steps 1 and 2 to the pH of the solution. The solid-to-extractant ratio was 1 g 10 ml^{-1} for all steps.

Results and Discussion

TG-DTG Studies on Sedum plumbizincicola

The TG and DTG curves of *S. plumbizincicola* in pyrolysis and combustion conditions are displayed in Figure 4. The pyrolysis process of the sample was subdivided into three steps. In the first step moisture evaporated when the temperature was <170°C and about 3.56% of moisture evaporated from

Fig. 2. Thermodynamic equilibrium calculations of Incineration (M: Heavy metals and Alkali metal in Table 2).

Table 3. Procedure of chemical extraction series

| Step	Reagent	Conditions
Water soluble	De-ionised water (DW)	20°C, 3 h, pH7,continuous agitation
Acid soluble	0.5 M CH_3COOH_2 +0.1 M $Ca(NO_3)_2$	20°C, 3 h, pH5,continuous agitation
Easily reducible	0.175 M $(NH_4)_2C_2O_4$ + 0.1 M $H_2C_2O_4$	95°C, 3h,variable agitation, without light
Moderately reducible	0.1 M Na_2EDTA + 0.3 M $NH_2OH.HCl$	95°C, 24 h,variable agitation
Residual	10 mL HCl 36% + 5 mL HNO_3 69% +2.5mL HF 40% + 2.5mL DW	150°C, 48–72 h,continuous agitation

S. plumbizincicola. The second step, fast decomposition, occurred from 170 to 400°C. Hemicelluloses and cellulose crack in this state. *S. plumbizincicola* peaked at 301°C. About 49.8% of weight of *S. plumbizincicola* lost was found during this stage. The third step, the further cracking of fixed carbon, took place from 400°C to the end of the experiment. The weight loss of the sample during the whole pyrolysis process was 81.2%. In addition to pyrolysis, the combustion process of the sample was divided into three stages. In the first step, from room temperature to 185°C, about 10.8% of the moisture evaporated from *S. plumbizincicola*. The second step, from 185°C to 400°C, was fast decomposition and similar to the pyrolysis process. About 49.0% of the weight of *S. plumbizincicola* was lost during this stage. Before 400°C pyrolysis and combustion processes have similar DTG curves which indicates that the presence of oxygen did not accelerate the weight loss of the sample at low temperature. The third step, the combustion of fixed carbon, occurred from 400 to 697°C. It was observed in the figure that the weight loss during combustion was even greater than during pyrolysis during this stage and therefore oxidation of inorganic constituents of the sample might occur during combustion. The total weight loss of *S. plumbizincicola*

during combustion was 82.7%. The combustion behavior of *S. plumbizincicola* was similar to that of other types of biomass. Both reached a peak at around 300°C and only combustion of carbon residues occurred after 400°C.

In conclusion, the weight loss performance of *S. plumbizincicola* was similar in pyrolysis and combustion conditions at low temperature. However, at high temperature the presence of oxygen favored the weight loss of the residue. It was best to maintain the temperature over 700°C with excess air supply for the thermal disposal of *S. plumbizincicola*.

Impact of Temperature on Transportation of HMs During the Incineration of S. plumbizincicola *and Equilibrium Distribution of HMs Simulated by ASPEN*

Temperature significantly impacted the volatilization of the HMs. Higher temperatures can enhance vaporization by raising the vapor pressure of HMs and enhance their rates of diffusion (Syc *et al.* 2012; Sun *et al.* 2004; Liu *et al.* 2010).
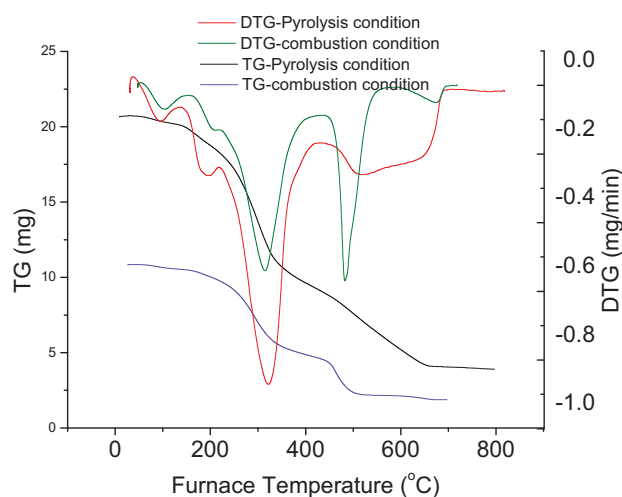
Fig. 4. TG/DTG of *S. plumbizincicola*.
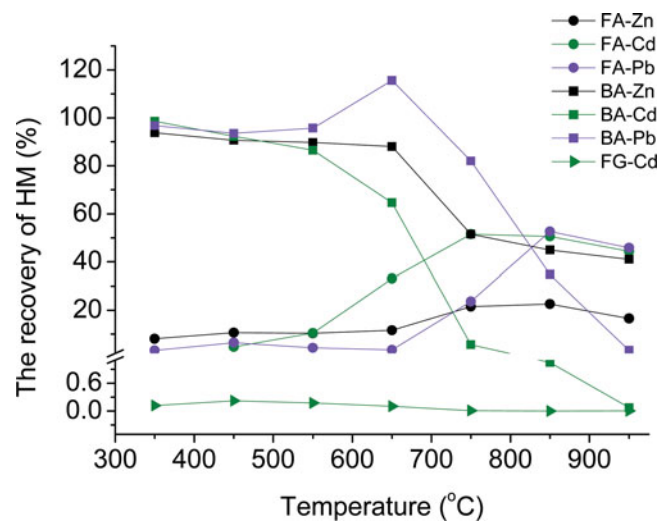
Fig. 5. Impact of temperature on transportation of heavy metals during incineration of *S. plumbizincicola* (FA represents fly ash and BA represents bottom ash).
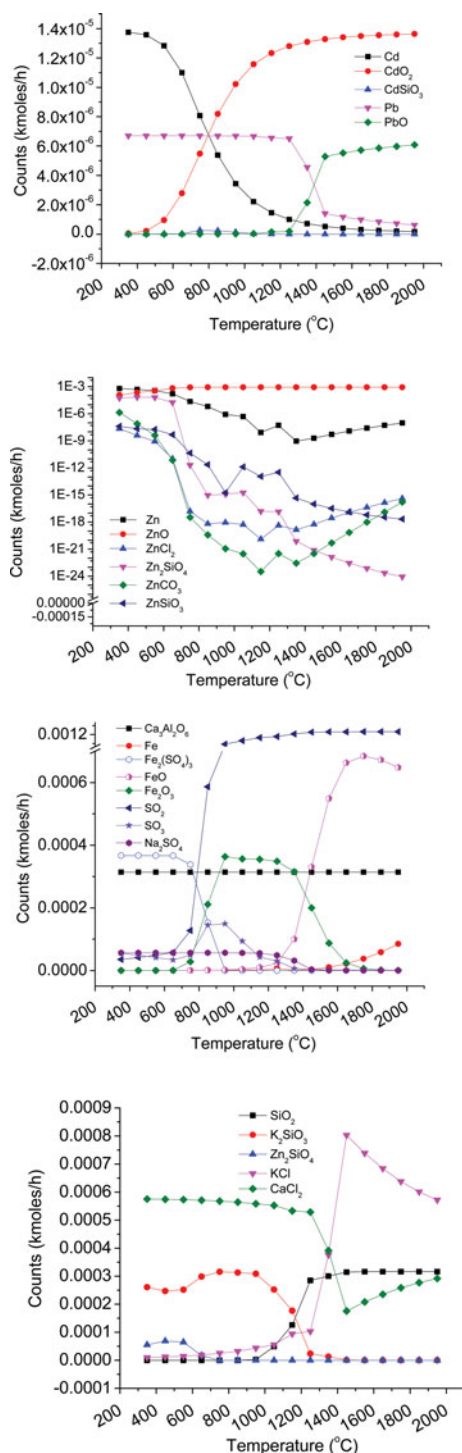
Fig. 6. Equilibrium distribution of HMs versus temperature of *S. plumbizincicola* simulated by Aspen.

The recovery rates of heavy metals ware depicted in Figure 5. The recoveries of Zn, Cd and Pb decreased with the elevated temperatures in the bottom ash and increased in the fly ash, thus following the volatilization behavior of HMs during incineration. HMs initially vaporize in the flame and the resultant metallic vapors then undergo homogeneous nucleation to form an ultra-fine aerosol (Vogg 1987; Chun *et al.* 1996). In

the post incineration region the flue gas cools rapidly and the condensed aerosol of HMs and their oxides grows continuously by heterogeneous coagulation in the fly ash, so that little of the HMs was found in the flow gas. Therefore, as Figure 5 shows, the recovery of Cd from flue gas was 0.015–0.05% and Zn and Pb were undetectable in the flow gas. The partitioning of HMs during the combustion process varies significantly with the element type. More of the Zn was captured in the bottom ash than the fly ash but more Cd and Pb were found in the fly ash than the bottom ash when temperatures were > 750°C and 850°C, respectively.

The equilibrium distributions of HMs simulated by AS-PEN in the temperature range of 350–1950°C for a typical air excess ratio a = 1.2 is shown in Figure 6. Chlorine, sulphur, iron, aluminum and silicates were reported as important compounds in the vapor of heavy metals and were also studied. As Figure 6 shows, most of the S, Fe, Al and SiO_2 were found as $CaCl_2$, KCl, SO_2, $Fe_2(SO_4)_3$, Fe_2O_3, FeO, $Ca_3Al_2O_6$, K_2SiO_3 and SiO_2 during the combustion process instead of reacting with HMs. Therefore, Zn was found as Zn ($< 550°C$) and ZnO ($\geq 650°C$). Small amounts of Zn_2SiO_4, $ZnSiO_3$ and $ZnCO_3$ were found when the temperature was $< 650°C$ and decreased with increasing temperature. Cd was found as Cd and CdO. At low temperatures ($< 750°C$) $CdSiO_3$ can be found and decreases with increasing temperature. Pb was the major species at low temperatures ($< 750°C$); at higher temperatures PbO was the dominant species. Therefore most of the Zn, Cd and Pb were exited as pure metals and their oxides during the combustion of *S. plumbizincicola*.

The Impact of Air Flow Rate on Transportation of Heavy Metals during the Incineration of S. plumbizincicola *and* Equilibrium Distribution of HMs Simulated by ASPEN

The air flow rate is an important parameter controlling the combustion process (Frandsen *et al.* 1994). The conventional mass burn systems require 20–100% excess air over the stoichiometric value (Tillman *et al.* 1989), resulting in a typical incinerator in which the mean combustion atmosphere is oxidizing. Nevertheless, reducing conditions may exist around
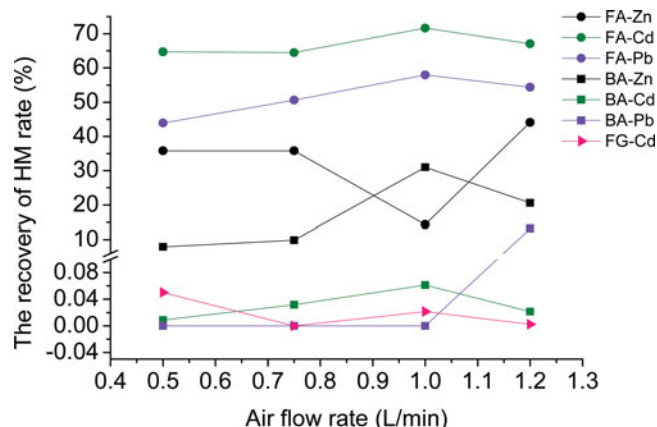

Fig. 7. Impact of air flow rate on transportation of heavy metal during incineration of *S. plumbizincicola*.
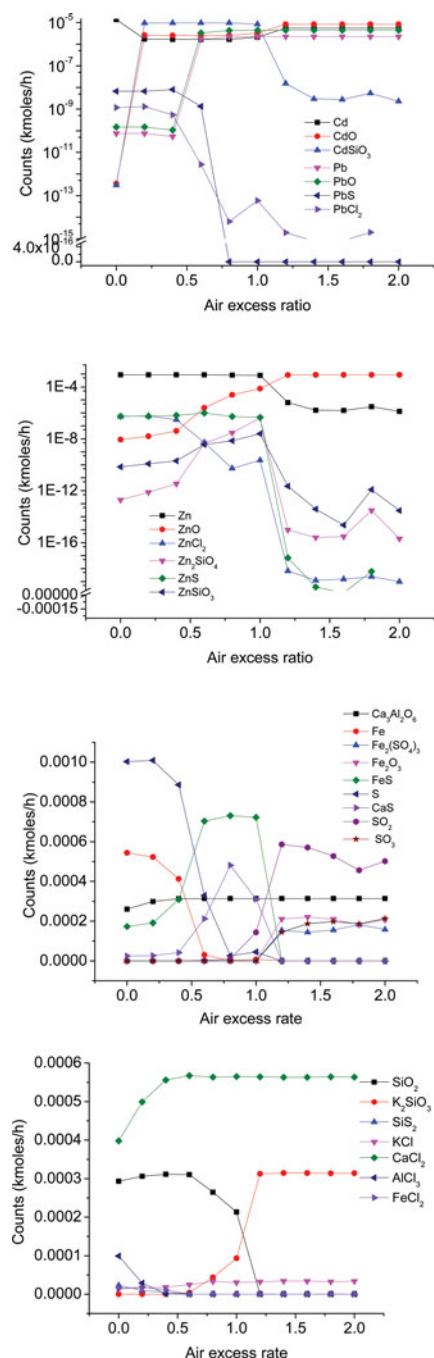
Fig. 8. Equilibrium distribution of HMs versus air excess ratio of *S. plumbizincicola* simulated by Aspen.

and inside burning particles in the combustion zone even if the air supply is above the theoretical value. The influence of the total air flow rate (characterized by the air excess ratio) was studied at $850°C$ and both reducing and oxidizing conditions were considered by varying air flow rate between 0.5 and 1.2 L min^{-1}. The Zn, Cd and Pb results are displayed in Fig. 7. For Cd and Pb the recovery rates from fly ash were higher than from bottom ash. This indicates that at higher temperatures ($> 850°C$) both the oxidizing atmosphere and reducing conditions favor the transfer of HMs such as Cd, Pb, and Zn to the

fly ash phase as observed previously in municipal solid waste incineration (Belevi and Langmeier 2000).

Figure 8 shows the equilibrium distributions of different HMs in air excess ratio range 0.2–2 for a typical temperature of $850°C$. Unlike oxidizing conditions, sulphur compounds are the most important in the vapor of heavy metals in reducing conditions. As the Figure 8b shows Zn was alternatively found as Zn, ZnO and ZnS when a < 0.6, and only ZnO was found when a > 0.6. Cd and CdS were found in reducing conditions (a < 1), while CdO and Cd were found when a > 0.2. Pb and PbS were the dominant species when a < 1 and the mass of PbO increased with increasing air excess ratio. There were low concentrations of Cl in *S. plumbizincicola* (Table 2) and $PbCl_2$ and $ZnCl_2$ were formed when a < 0.4 and a < 1, respectively. However, most of the Zn, Cd and Pb were exited as Zn, ZnO, ZnS, Cd, CdS, Pb, and PbS under reducing conditions.

Characterization of Bottom Ash of S. plumbizincicola *at* $850°C$

The morphologies of bottom ash at $850°C$ were analyzed in order to identify crystalline phases formed as the ash deposits grow and the visual SEM results of bottom ash at $850°C$ are shown in Figure 9. As illustrated in Figure 9, the size of ash was divergent and the divergences in ash particle sizes might be the result of a different diameter biomass. The deposited ash particles were mainly spherical in the bottom ash and irregularly shaped (elongated, needle-shaped or plate-like) in the initial deposition layer. Furthermore, part of the attached sub-micrometer ash particles on the surfaces of large ash particles also have some propensity to stick at high temperatures and play a role as "adhesives" to bond some large particles together (Fig. 9c and 9d), forming larger ones (Friedlander *et al.* 2000).

Analysis of major elements at typical points has been performed using EDS. The major elements of 'point a' in Figure 10 were O, K, Al, C, Si, and Na with a small quantity of P, Fe, Zn and Cd. In Figure 11 the main elements of 'point b' were also C, O, Na, Al, K and Si; meanwhile, the minor elements such as Mg, P, Cl, Ca, Fe, Cu and Zn, Cd could not be detected. Al and Si at 'point a' were 4.73 and 2.57 times higher than that of 'point b'; 0.66% and 0.04% of Zn and Cd were found at 'point a', while 0.05% and 0% were found at 'point b'. This finding may due to the form of alumino-silicates and silicates of Cd and Zn oxides (Figure 6).

The Powdered XRD Patterns of Fly Ash or Bottom Ash

The powdered XRD patterns of fly ash or bottom ash are shown in Figure 12. S, Al_2O_3 and SiO_2 were reported as sorbent materials to control the heavy metals and thus their chemical compounds were studied in this study. Under combustion conditions crystalline phases of Zn at $850°C$ were found as ZnO and $Zn(OH)_2$. Crystalline phases of Cd were found as CdO and $CaO_{0.67}Cd_{0.33}CO_3$. At $650°C$, $ZnSO_3(H_2O)_2$ and $Cd(H_2PO_2)_2$ and were found, and crystalline phases of Pb were not found. In pyrolysis conditions crystalline phases of Cd, Zn and Pb were found as CdS, ZnS and $Pb_2P_2O_7$.
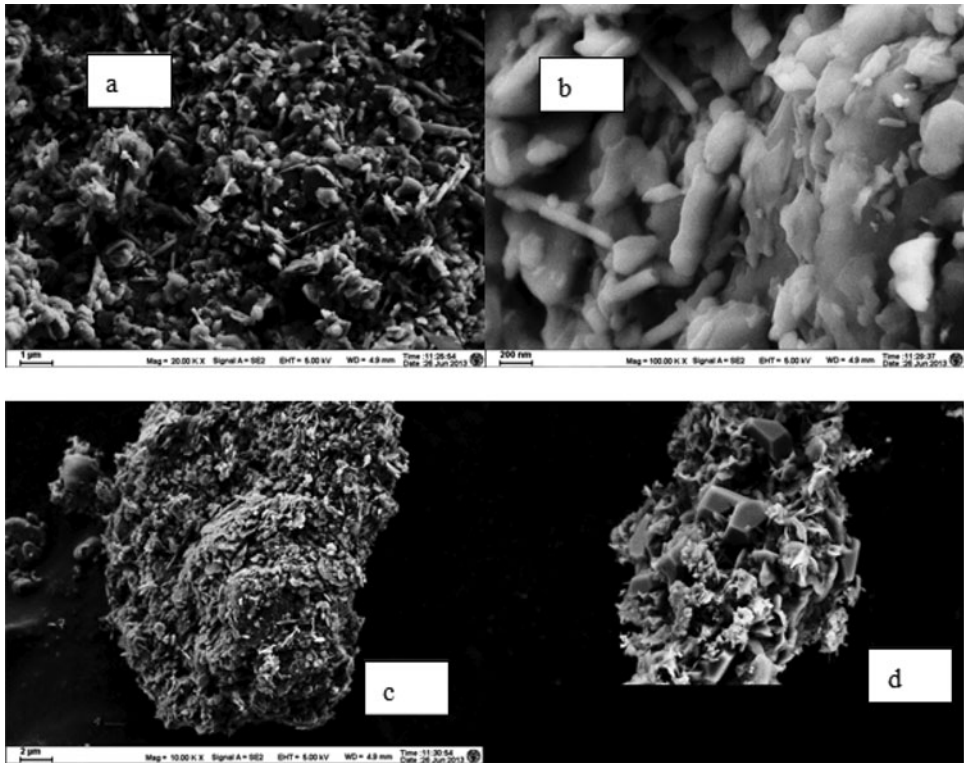
Fig. 9. SEM for the bottom ash of *S. plumbizincicola* at 850°C.

The Sequential Extractions of Fly Ash and Bottom Ash

Figure 13 shows that the sequential extractions revealed that Zn in both bottom ash and fly ash had weak mobility. Most of the Zn was found in the 'moderately reducible fraction' in the fly ash and the 'residual fraction' in the bottom ash and as previously reported the metals would be together with those associated with silicates, alumino-silicates, crystalline pure metals or as crystalline oxides (Abanades *et al.* 2002). In contrast, Cd and Pb were mainly in easily leachable phases (soluble in water or ion-exchangeable) in fly ash and more of the Cd and Pb were

leached out with increasing temperature which indicates that they may be present as their carbonates, free metals or as amorphous oxides. Cd and PbO are low boiling point compounds which may vaporize to the flue gas and react with Cl_2, CO_2 and SO_3 to form chlorides, carbonates, sulfates or free metals. More Cd and Pb were leached in water at 350°C because lower combustion temperatures may result in higher contents of trace metals leachable from the ash (Wu *et al.* 1980). Moreover, the matrix-elements iron and manganese oxide-forms of Cd, Pb and Zn were leached to a much lesser extent by
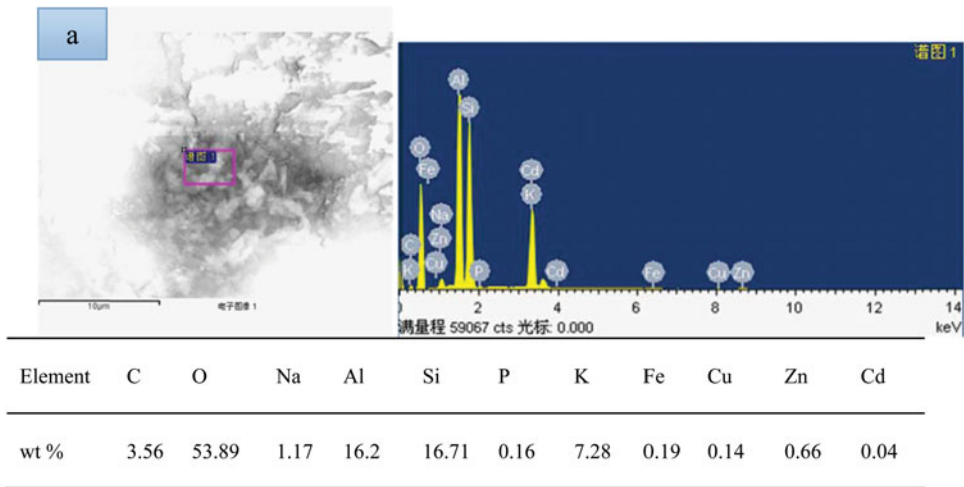

Element	C	O	Na	Al	Si	P	K	Fe	Cu	Zn	Cd
wt %	3.56	53.89	1.17	16.2	16.71	0.16	7.28	0.19	0.14	0.66	0.04

Fig. 10. SEM-EDS data for the bottom ash of *S. plumbizincicola* at 850°C.

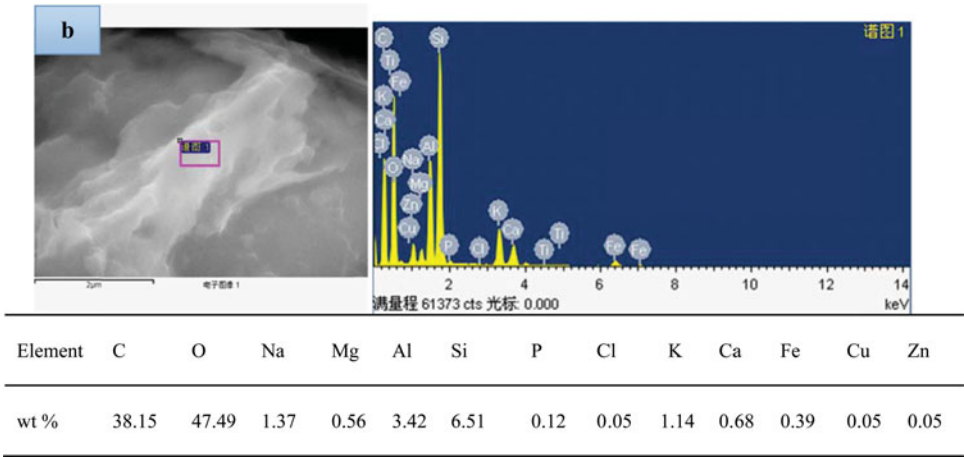**Fig. 11.** SEM-EDS data for the bottom ash of *S. plumbizincicola* at 850°C.

0.175 M $(NH_4)_2C_2O_4$ and 0.1 M $H_2C_2O_4$ (easily reducible fraction).

As Figure 14 shows, the sequential extractions of Cd and Pb in bottom ash showed a weaker mobility during the pyrolysis conditions than combustion. In contrast, Zn was mainly in easily leachable phases during the pyrolysis conditions, which indicates that Zn may be present as the carbonate, iron and manganese oxide-form or as free metal.

Notice that easily leachable metallic compounds such as chlorides were not detected with XRD since they were eliminated with water when polishing the samples. The combina-

tion of the results from the three methods used indicates that the most probable chemical forms of lead under combustion conditions were the pure metal, its oxide in both the fly ash and bottom ash. For Cd and Zn, possible components were the pure metals, their oxides, and also their sulphates, carbonates and silicate compounds at low temperature. Under anoxia conditions the most probable chemical forms of lead and Cd were their oxides or other complex compounds in both fly ash and bottom ash. For Zn, possible components were its oxide and also its sulphate.
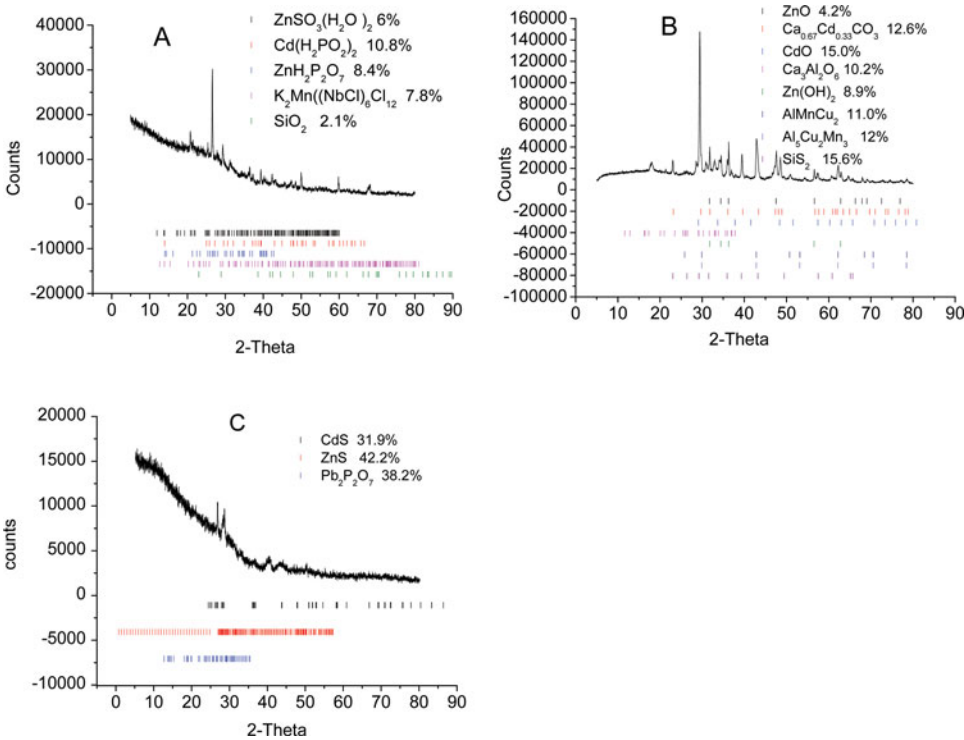

Fig. 12. Powdered XRD patterns of fly ash and bottom ash X-ray diffraction traces for $2\theta = 13–90°$ CuKα radiation. Vertical bars in various colors refer to the 2θ positions of the X-ray reflections for the 8 crystalline phases. A, fly ash of combustion at 650°C; B, fly ash of combustion at 850°C; C, bottom ash of pyrolysis at 850°C).
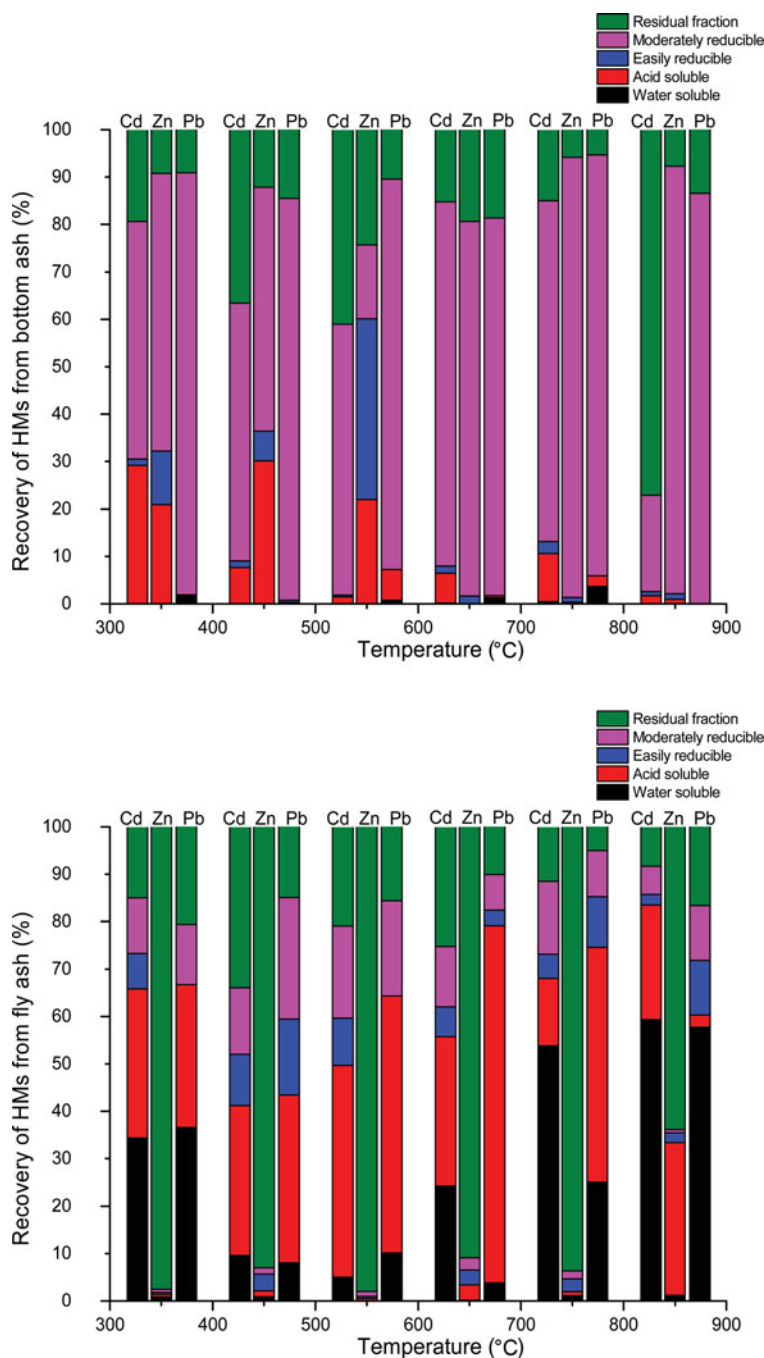
Fig. 13. Results of sequential chemical extraction of Cd, Zn and Pb versus temperature.

The comparison between the results of the characterization and of the thermodynamic calculations indicate the following:

1. Under combustion conditions the experimental data agreed well with predictions for the three metals zinc, lead and cadmium. In particular, residues characterization did not show the chlorides because most Cl was found as KCl; Previously predicted pure metals and their oxides. Carbonates and sulphates were possible speciations of Pb and Cd with respect to sequential extraction in the fly ash, although thermodynamic calculations never predicted Pb at inciner-

ation temperatures. Their formation may occur at low temperature according to the thermodynamics (Verhulst *et al.* 1996);

2. Under anoxia conditions predictions for the three metals were the pure metals and their sulphates which agreed well with the experimental data for Zn and Pb but the thermodynamic calculations for Cd did not show the sulphate.

In addition, note that more complex speciation, in particular ternary oxides, was not taken into account in the thermodynamic calculations because of the lack of data, although
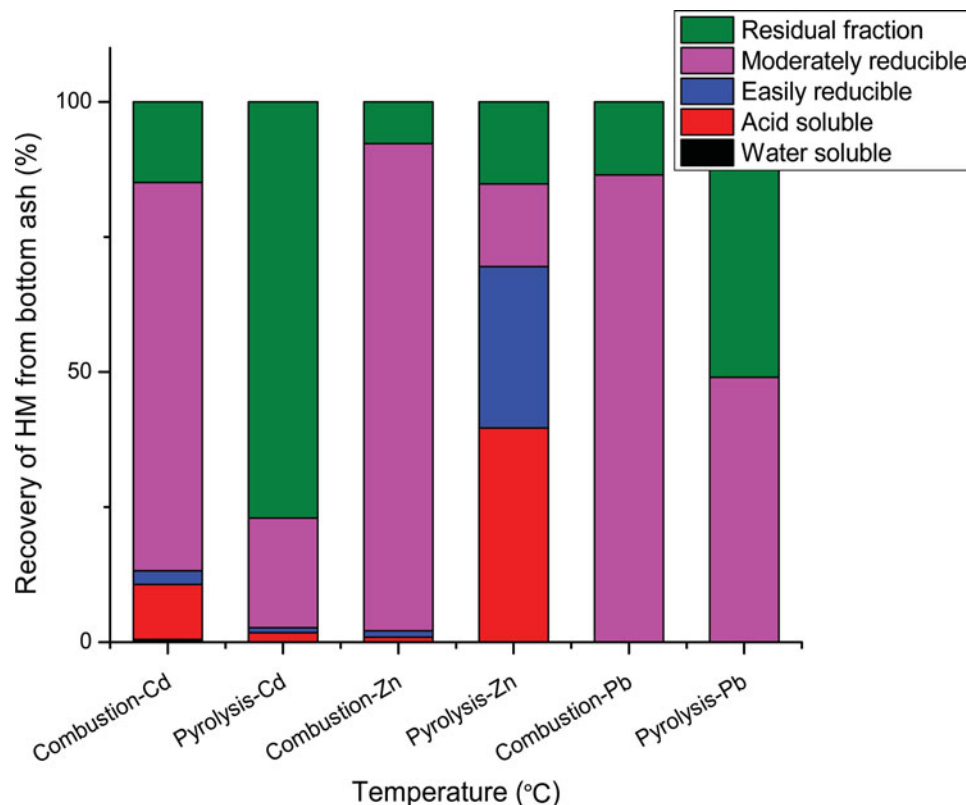
Fig. 14. Sequential chemical extraction of Cd, Zn and Pb versus oxygen content.

their existence has been pointed out in the residues (Griepink *et al.* 1987).

Conclusions

In this study the weight loss performances of *S. plumbizincicola* were similar in pyrolysis and combustion conditions at low temperature. However, at high temperature the presence of oxygen favored the weight loss of the residue. It was best to maintain temperatures > 700°C with excess air supplied in the thermal disposal of *S. plumbizincicola*.

According to the experimental results the recoveries of Zn, Cd and Pb mainly decreased with increasing temperatures in the bottom ash and fly ash, and elemental sulfur and sulfide increased the retention of HMs on the bottom ash through formation of sulfides under the local reducing environment in the furnace. In contrast, the presence of sulfur in the forms of Na_2SO_3 and Na_2SO_4 had little effect on HM volatilization. Chlorine compounds did not increase HM volatilization and partitioning on the fly ash during incineration because most of the chlorine was found to be present as KCl. The equilibrium calculation results also suggest that SiO_2- and Al_2O_3-containing materials were found as K_2SiO_3, Na_2SiO_3 and $Ca_3Al_2O_6$, instead function as sorbents stabilizing HMs as condensed phase solids. Thus, most of the HMs were found as pure metals and their oxides. Comparison of equilibrium calculation results with those from exper-

imental investigation shows that this approach gives a good qualitative view of HM behavior during hyperaccumulator incineration.

More than 99% of Cd, Pb, and Zn enriched in fly and/or bottom ash fractions after the thermal disposal can be captured by air pollution control devices. Thermal disposal of *S. plumbizincicola* might allow the achievement of a sustainable, environmentally safe, and friendly production of energy from HM-polluted land.

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