



Leaching of major and trace elements from paper–plastic gasification chars: An experimental and modelling study

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H I G H L I G H T S

- Biomass gasification chars are good sorbents for mercury capture.
- Similar results were found in an experimental and a modelling study of leaching.
- Char samples could be acceptable at landfills as non-hazardous waste.
- Sorption on the solid surfaces of the char is negligible at alkaline pH values.
- Complexation involving dissolved organic matter plays an important role at higher pH values.

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The control of soluble metal species in the sub-product leachate generated in electricity production processes is of great concern from an environmental and health point of view. Unlike fly ash, the leaching behaviour of char materials has received little attention. Yet, these solids are captured together with fly ashes in the particle control devices of power plants and are emitted in the same way as by-products. The present study was carried out using two char samples: (i) a raw char and (ii) the same type of char employed in a previous study so that it could serve as a sorbent for mercury species in gas phase. The char samples were by-products (residues) that had been generated during the gasification of plastic and paper waste. The leachates were analyzed for the following elements: Al, Ca, Si, Mg, Ba, Cu, Ni, Pb, Zn, Mo and Hg. In addition, geochemical modelling of the leaching test results was employed to identify the underlying chemical processes that led to the release of toxic elements. The results showed that at alkaline pH values, sorption on the solid surfaces of the char was negligible due to the inorganic complexation of cations in the solution. When the char was used as mercury sorbent slight changes occurred on the reactive surface resulting in the modification of the binding of some elements. As the pH increased, complexation with dissolved organic matter played a more important role in the case of some elements such as Cu because of the greater concentration of dissolved organic matter in solution.

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1. Introduction

The impact of anthropogenic sources of metals and ions upon the environment and health cannot be evaluated solely by measuring the total concentration of individual elements. It is also necessary to evaluate their mobility which is heavily dependent on their chemical form and the type of binding. This has led a number of researchers to study the dissolution behaviour of elements from the sub-products of coal combustion processes and municipal solid waste incinerators that are dumped at disposal sites [1–3].

A considerable amount of solid waste is generated in coal-fired power plants [4,5] in addition to gases (CO₂, NO_x, SO_x) and direct particulate matter emissions to the atmosphere. The accumulation of such wastes often has a negative impact on industrial soils and disposal sites and subsequently on rivers and streams through the infiltration of leachates containing toxic elements.

It is well known that the leachability of toxic trace elements is closely related to the concentration in the solid residues, mode of occurrence, other ions and adsorption, the conditions of the thermal process, the role of sorption/desorption, the redox conditions and, most important of all, on the pH. Trace element mobility in water is particularly pH-dependent [6,7]. Several studies have been focused on the leaching behaviour of toxic elements from fly- and bottom ashes [1,3,8–10], and although it has been established that

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the leaching of major elements from fly ashes is controlled by solubility, the leaching of trace elements cannot be modelled solely on the basis of this factor [7,11]. For instance, Warren and Dudas [12] have suggested that adsorption and co-precipitation, especially on secondary minerals, may also affect the partitioning of trace elements between the fly ash and the leachate.

Injection of carbon materials prior to the particulate control devices (PCD) or after the PCD using a secondary PCD seems to be a promising method of controlling trace elements in gas phase [13]. However, the drawback of these materials in the plant will be in the PCDs, where they will be captured together with the fly ashes. Consequently the collection of data on the leaching behaviour of these carbon materials when used as sorbents will be also essential for controlling their behaviour in future applications or during their disposal. There is, above all, a lack of knowledge on the dissolution of major and trace elements in residues such as the chars generated in gasification processes [14,15].

Gasification has emerged as a clean and effective way to produce gas from biomass and is considered a promising technology for producing chemicals and energy from renewable sources. Char is basically a partly converted fuel which escapes from the gasification reaction. This residue, generated during a thermal conversion process, may contain different elements, depending on the type of material burned. Some of these elements are necessary for the health of humans in minute amounts (micronutrients like Co, Cu, Cr, Mn, Ni, Zn), although an excess could be harmful. Some elements are carcinogenic or toxic and may affect the central nervous system (Mn, Hg, Pb, As), the kidneys and liver (Hg, Pb, Cd, Cu) or skin, bones and teeth (Ni, Cd, Cu, Cr) [16,17]. In most cases, in order to assess the potential health hazard of such elements or the toxicity of the element itself, it is necessary to consider its solubility in a given media and the speciation.

The goal of this work is to understand the leaching of major (Al, Ca, Si and Mg) and trace elements (Ba, Cu, Ni, Pb, Zn and Mo) from paper–plastic gasification chars, over a wide range of pHs using a geochemical speciation model. This topic has received little attention to date. The study focuses not only on the concentration of toxic elements but also on identifying those processes most likely to control the leaching of each element.

2. Experimental

Two chars obtained from the gasification of paper and plastic waste (PW, PW-Hg) were used for the leaching study. The chars were obtained from a circulating fluidized bed (CFB) gasifier pilot gasification plant of 500 kWth (called BIVKIN) at the Energy Research Centre of the Netherlands (ECN) in Petten. The char was characterized in a previous work [14]. The char taken directly from the gasifier was labelled PW. The same char after being used as a mercury sorbent at laboratory scale in a simulated coal combustion flue gas (5% O₂, 1300 mg Nm⁻³ SO₂, 500 mg Nm⁻³ NO₂, 20.3 mg Nm⁻³ HCl, 120 µg m⁻³ Hg) was labelled PW-Hg.

Leaching experiments were carried out as prescribed by the European standards for the pH-static leaching test CEN/TS14997 [18] of PW char and char PW-Hg was subjected to a concise and simplified version of this test [19]. The pH-static test requires that the pH be controlled at pre-selected values over the entire testing period (pH2–12) (PW) by continuous measurement and the automatic addition of acid or base in such a way that equilibrium is approached at the end of the procedure (48 h). While the recommended method provides a full characteristic behaviour curve for materials available in quantities >100 g, a version based on three analysis leaching points was used in the simplified test, for materials available in smaller volumes, as in the case of the PW-Hg char. The pH dependence tests belong to the category of “Basic

characterization” developed by European Standardization Organization (CEN/TC 292) for the analysis of the leaching behaviour of waste materials. In accordance with this technical specification, individual sub-samples of PW and PW-Hg were leached at a liquid to solid ratio (L/S) of 10 L/kg for 48 h in acid-cleaned 300 mL PTFE vessels. Each suspension was adjusted to a specific pH by adding 5 M HNO₃, 5 M NaOH and 1 M NaOH and the pH was kept constant throughout the duration of the experiment. The suspensions were continuously stirred with a magnetic stirrer and kept at 20 °C. After the equilibration period, the suspensions were centrifuged and then filtered (0.45 µm) in order to separate the liquid phase from the solid phase. The filtrates were acidified with supra-pure HNO₃ and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). A carbon analyzer (Shimadzu TOC 5000a) was used to determine the dissolved organic carbon (DOC) concentration in the non-acidified eluates.

The analytical leaching data formed a good basis for investigating the underlying leaching mechanism by means of mechanistic geochemical modelling. The modelling was done by using the ORCHESTRA (Objects Representing CHEmical Speciation and TRANsport models) software [20,21] within the LeachXSTM database/expert system, where chemical speciation models can be implemented and combined to calculate chemical speciation and mass transport processes in complex matrices. The dissolution and precipitation reactions of minerals in ORCHESTRA were calculated on the basis of an extended MINTEQA2 thermodynamic database [22].

3. Results and discussion

The measured concentrations and model predictions of the major and trace elements, i.e., Al, Ca, Si, Mg, Ba, Cu, Ni, Pb, Zn and Mo are shown as a function of pH in Figs. 1 and 2 for PW char specimen. It should be noted that the concentrations of the elements in the eluates from all the leaching tests were below the limits established for the landfilling of inert waste as stipulated in Annex II of the European Landfill Directive (2003/33/EC) [23].

The partitioning between the dissolved and particulate phases was calculated using a mechanistic modelling approach that took into account the major, minor and trace elements, and the reactive surfaces of iron, aluminium and organic matter (dissolved and particulate) (Figs. 3 and 4). Geochemical modelling of the leaching test results was used to identify the underlying chemical processes leading to the release of contaminants. The most relevant geochemical processes and parameters took into consideration in the ORCHESTRA program were [24]:

1. Dissolution and precipitation reactions of minerals on the basis of an extended MINTEQA2 thermodynamic database. The potential solubility controlling minerals were selected on the basis of the saturation indices (the calculated logarithm saturation indices were sought relatively close to zero) and on the curve shapes predicted by the model in accordance with the data from the concentrations vs. pH graphs (Figs. 1–2).
2. Binding to solid and dissolved organic matter. Sorption to dissolved (DOC) and particulate organic matter (POM) was modelled using the NICA–Donnan model approach [25]. The total reactive organic matter (OM) comprises the reactive particulate organic matter (POM) and the reactive dissolved organic matter (DOC). Both DOC and POM were represented by “generic” humic acid (HA) in the model.
3. Sorption to reactive iron- and aluminium (hydr)-oxide surfaces. The Generalized Two Layer Model (GTLTM) of Dzombak and Morel [26] was used to model the surface complexation and surface precipitation of ions to Hydrated Ferric Oxide (HFO), amorphous

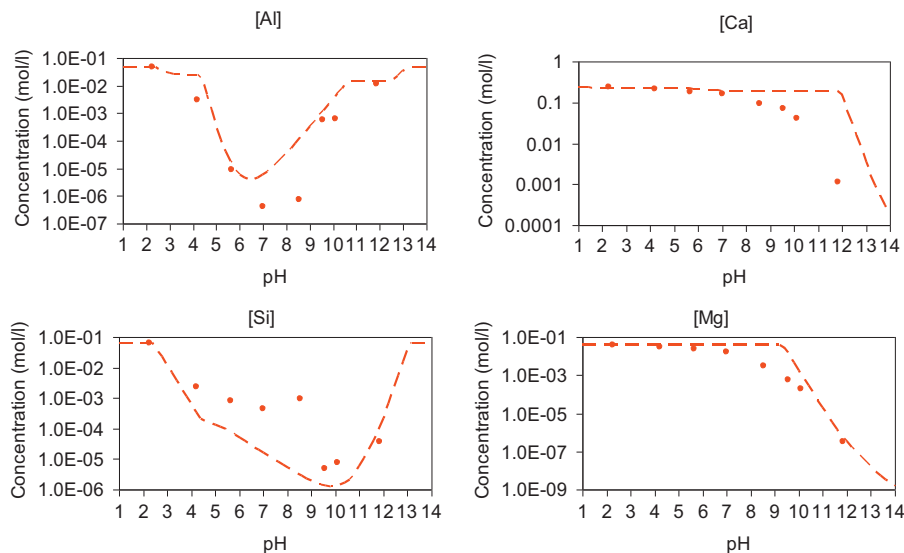


Fig. 1. Leached concentrations of major elements (Al, Ca, Si and Mg) as a function of the pH after 48 h (red circles) together with the model predictions (red curves) for the PW char (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

Al (hydr-)oxides and crystalline Fe. The surface precipitation model (SPM) is an integral part of the GTLM. It was used in order to provide an accurate description of the elements which would not be possible if only GTLM were employed, as has been shown in previous studies on Zn [8].

4. Sorption to clay surfaces. Following Weng et al. [27], non-specific sorption to permanently charged clay surfaces was simulated using a Donnan model assuming a charge density of 0.25 eq/kg and a fixed Donnan volume of 1 L/kg . These may be considered as average values for illitic clay minerals [28].

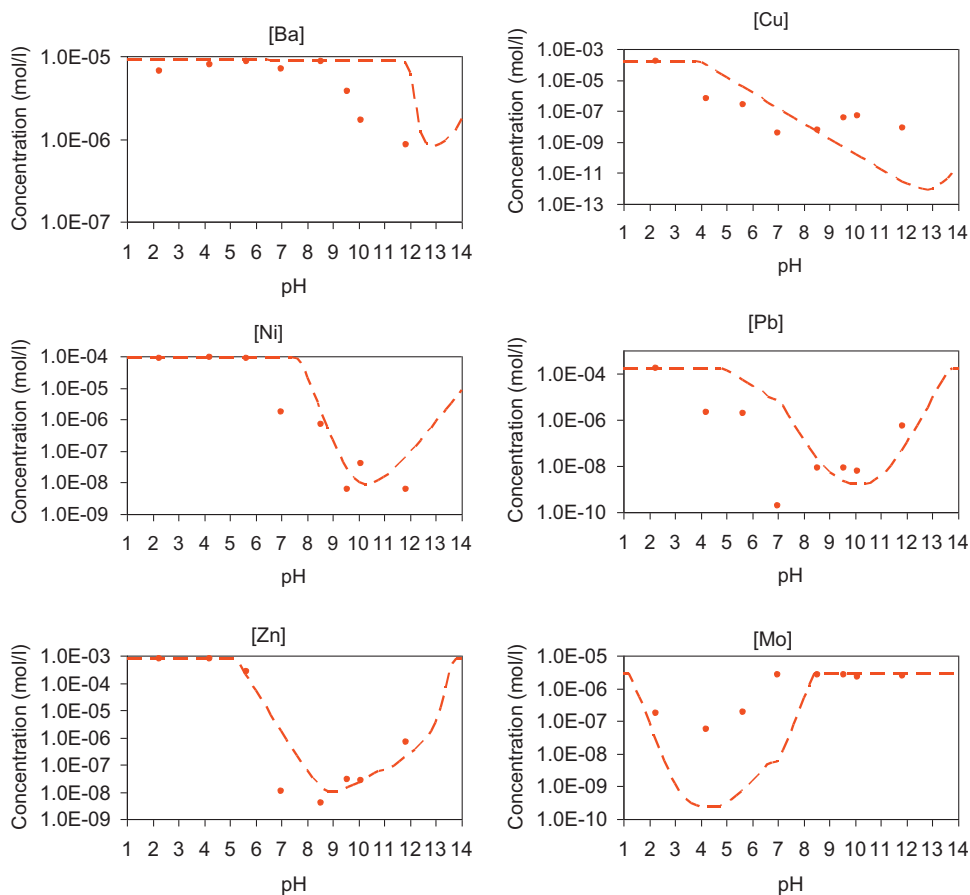


Fig. 2. Leached concentrations of trace elements (Ba, Cu, Ni, Pb, Zn and Mo) as a function of the pH after 48 h (red circles) together with the model predictions (red curves) for the PW char (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

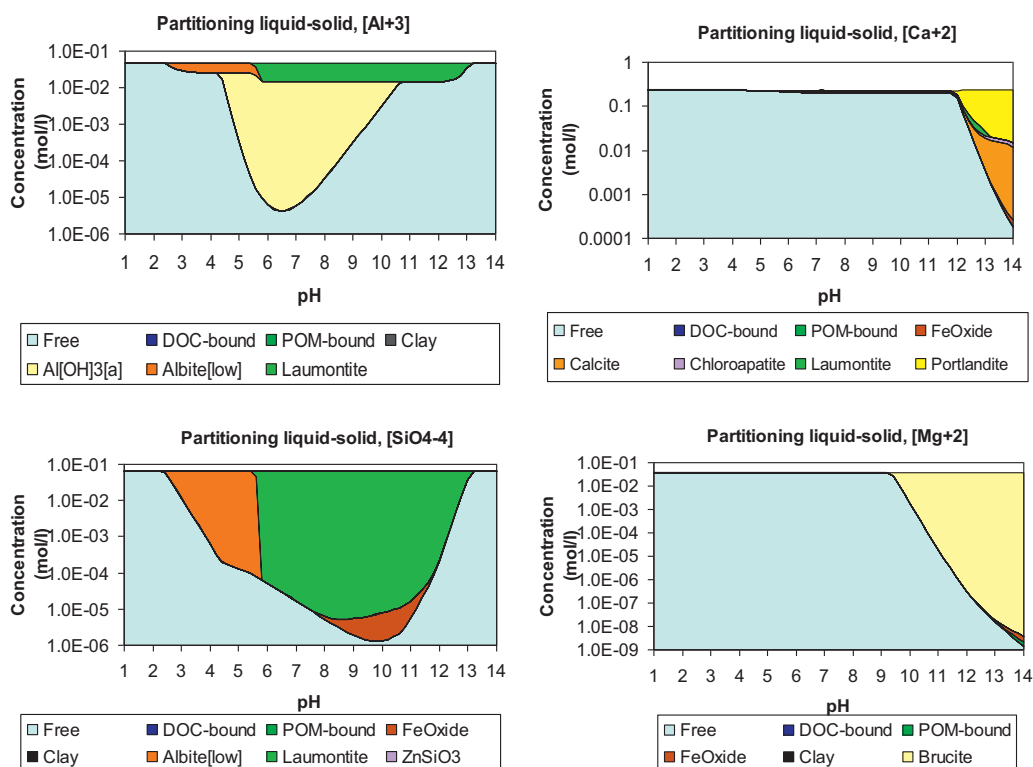


Fig. 3. Calculation of the distribution of the major elements (Al, Ca, Si and Mg) among the different surfaces, expressed in mol/L (POM = particulate organic matter; DOC = dissolved organic matter; Free = free ions (Me^{n+})) in PW char.

5. The pH and the redox potential (pe) according to $\text{pH} + \text{pe} = 6$, in simulation of a moderately reducing environment. Other values were also tested (e.g. $\text{pH} + \text{pe} = 10$) that it is common for combustion residues, although the best predictions were obtained using the value of 6. The model calculates the speciation of all elements simultaneously at fixed pH values (Figs. 1–5).
6. Available concentrations of the elements studied for leaching, i.e., the maximum leachable amount of elements at the lowest pH for cations and at the highest pH for the oxy-anions. It was assumed that cations/anions are fully desorbed from Fe and Al (hydr-)oxide surfaces and that the solubility controlling mineral phases are largely dissolved under these conditions. These values were used as first estimates of the concentrations of active major and trace elements in the mineral dissolution/precipitation and sorption processes.

It was found that the major components Al, Ca and Si (the elemental composition of the char samples has been presented in a previous work [14]) play a main role in governing the pH and the buffering capacity of the leachate [2,3]. Therefore, an accurate prediction of these components is crucial for predicting the pH using geochemical modelling. Al and Si display V-shaped pH-dependent leaching curves, whereas Ca and Mg reveal no variation in their leachable concentrations up to pH 7, at which point they start to decrease (Fig. 1). It should be noted that, although model predictions for major and trace elements are accurate to within approximately one or two orders of magnitude (considering the whole pH range), the biggest differences are observed at around the natural pH of the sample ($\sim \text{pH } 9$) (Figs. 1 and 2). The model predictions for Ba and Mo (which is very soluble at a high pH, as can be seen in Fig. 2) were respectively over- and underestimated compared to the experimental measurements. In the case of Cu the leached concentrations were predicted reasonably well. However, the concentrations were underestimated at pH values higher than 8.

By means of the model it was possible to assess the relative importance of the different reactive surfaces of the char sample as a function of its pH (Figs. 3 and 4). Although the model descriptions are not satisfactory in all cases, they do provide a valuable indication of the relative importance of each type of surface considered by the model. In general, the highest contribution to speciation in the char sample is provided by the species in the solution phase. The contribution of organic matter, non-specific adsorption to clay surfaces and the contribution of iron and aluminium (hydr)oxides is minor and only in the case of iron oxide is there a significant binding for Si at pH 8–11 and for Pb at pH 5–11 (Figs. 3 and 4).

The speciation in solution phase can be subdivided into organic complexes, inorganic complexes and free metals (Me^{2+}). The free Me^{2+} ions appear to be the predominant species for most metals below pH 4, and these are the main species for Ca, Ba and Mg below pH 10. In the case of Mo the free MoO_4^{4-} form is the main species at pH > 8. The inorganic species are abundant at neutral and basic pH, most of the elements showing a V-shaped curve with the exception, as already mentioned, of Ca and Mg. This suggests that at low pH values heavy metal sorption to variable charged surfaces is generally weaker than at neutral and basic pH values, due to competition for surface sites by protons and to repulsive charge effects.

Though it is valuable to gain insight into the mechanisms of leaching of (toxic) metals from char, the main aim of this study was to evaluate the differences between fresh char (PW) and the same char after it had been used as a sorbent for mercury in a simulated coal combustion atmosphere (PW-Hg). This should shed light onto the binding mechanism for mercury, as chars from the gasification of paper and plastic waste proved to be good sorbents for mercury retention at laboratory scale in a previous work [14]. Furthermore, it is important to ascertain the environmental risks posed by a char previously used as a mercury sorbent before it can be safely stored outdoors or landfilled. Therefore, in addition to Al, Ca, Si, Mg, Ba, Cu, Ni, Pb, Zn and Mo, the possibility of the leaching of Hg from char PW-Hg was also assessed.

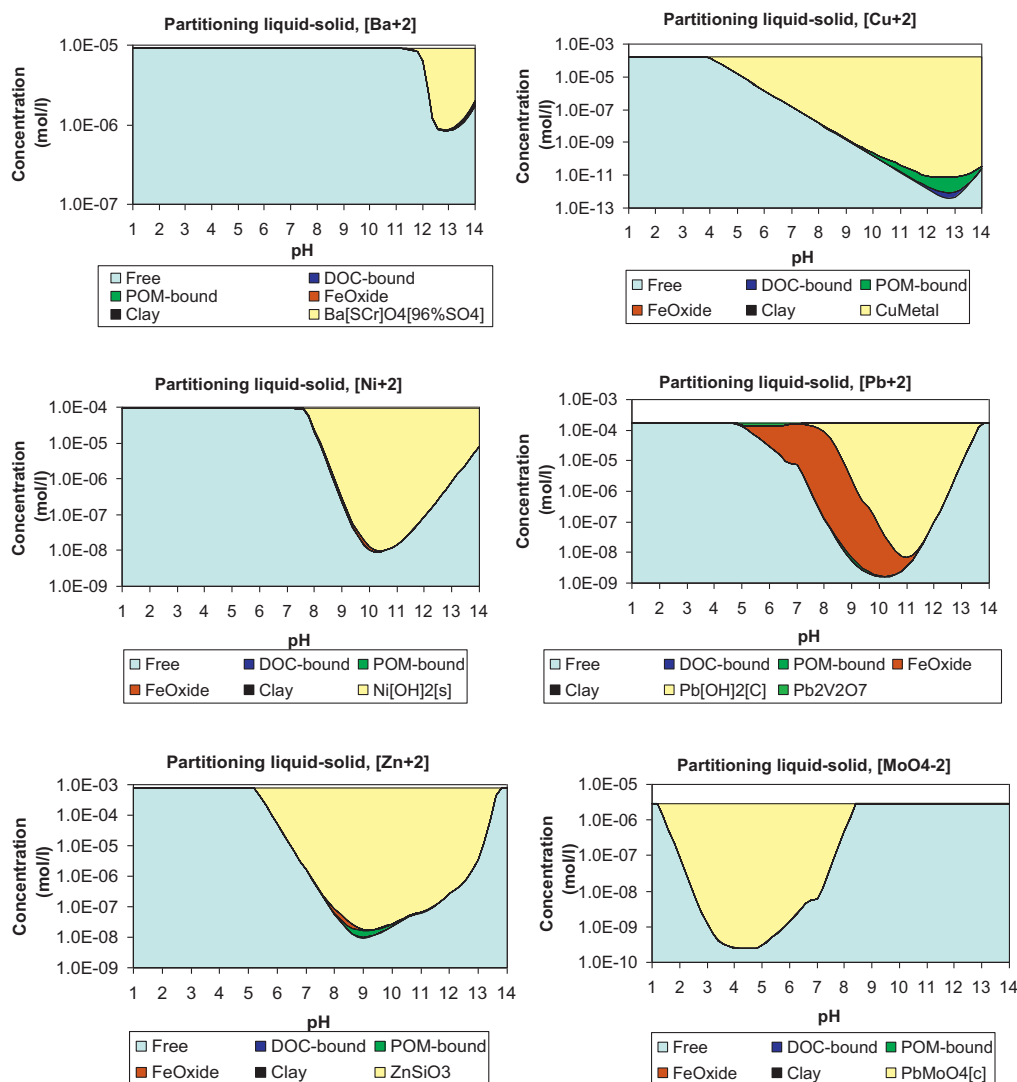


Fig. 4. Calculation of the distribution of trace elements (Ba, Cu, Ni, Pb, Zn and Mo) among the different surfaces, expressed in mol/L (POM = particulate organic matter; DOC = dissolved organic matter; Free = free ions (Me^{n+})) in PW char.

The first difference between the raw PW and PW-Hg was to be found in their pHs – pH 9 and pH 5.5, respectively – as might be expected when a char has been subjected to a combustion atmosphere containing acid gases. Leaching experiments with PW-Hg were carried out at pH 2, 7 and 12. As in the case of PW, PW-Hg fulfils safety requirements for disposal at landfills sites. The leachable Hg at all the pHs was <1 ppb. Although it was not possible to confirm the precise speciation of the adsorbed mercury species from the modelling programme, it was found that most of the mercury present on the surface of the chars was in an oxidized form. The solubility of metallic species was observed to vary only slightly over the range of pHs used in the test. The presence of metallic forms within the char itself was imposed in the modelling since the gasification conditions might cause the reduction of the metals and their transformation into a metallic form. In fact, the model predicts the leached concentration of Cu under the assumption that metallic Cu is present from pH 4 for the PW char and over almost the entire pH interval for the PW-Hg char (Figs. 2–5).

Overall, no significant differences emerged from the pH-concentration diagrams. The behaviours provided by the experimental measurements and the model predictions of the elements for the PW and PW-Hg char specimens were similar. However, some differences can be appreciated in the diagrams that

represent liquid–solid partitioning for Ca, Si, Ba, Cu, Pb and Zn (Fig. 5). The highest contribution to speciation in the PW-Hg char was again the species in the dissolved phase at low pH. In the case of Ca, after exposure of the char to a combustion atmosphere the main mineral present was calcite which, unlike PW, may occur at low pH (Figs. 3 and 5). This result is consistent with the X-ray diffraction (XRD) analysis results of a previous work [14] which also identified calcite as the main species present in both PW and PW-Hg. With respect to Si, the V-shaped curve is similar in both PW and PW-Hg and Si leaching seems to be controlled by solubility of mineral phases. Si was found in the form of aluminosilicaceous minerals in both PW and PW-Hg, mainly as laumontite (zeolite group) in PW (Fig. 3) and albite (feldspar group) in PW-Hg (Fig. 5). Although the organic matter plays only a minor role as the reactive surface in the solid phase (POM) compared to the overall adsorption, the adsorption of the trace elements Ba, Cu, Pb and Zn in PW-Hg (Fig. 5) was greater than in PW (Fig. 4) at neutral and basic pHs and over almost the entire pH range in the case of Cu. The binding of Cu to DOC contributed significantly to the complexation reaction in solution at neutral and high pH values in PW-Hg. This mechanism did not occur in PW (Figs. 4 and 5) and is explained by the absence (<1 ppm) of DOC in this material.

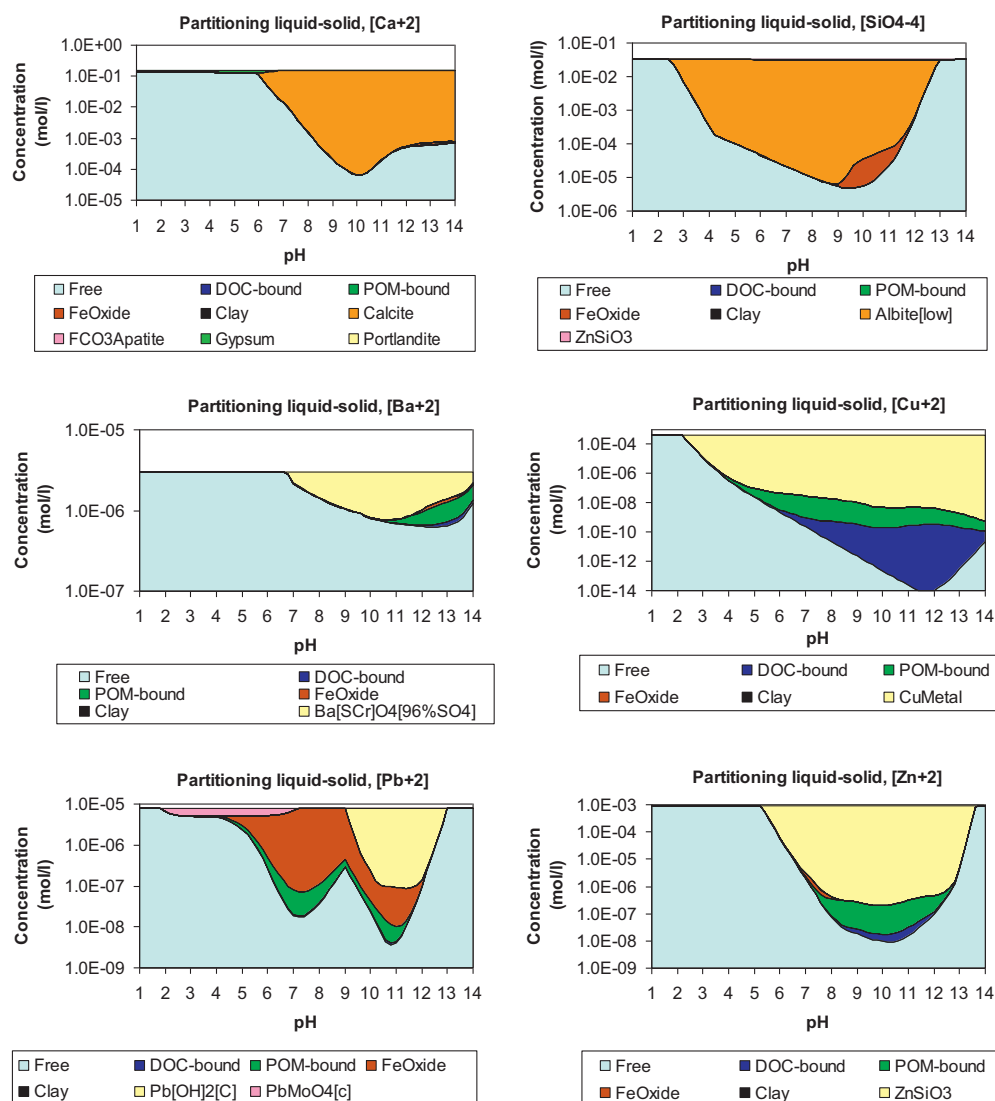


Fig. 5. Calculation of the distribution of major and trace elements (Ca, Si, Ba, Cu, Pb and Zn) among the different surfaces, expressed in mol/L (POM = particulate organic matter; DOC = dissolved organic matter; Free = free ions (Me^{n+})) in PW-Hg.

4. Conclusion

The char obtained from mixed plastic and paper residue gasification and the same char used as mercury sorbent in a simulated flue gas of coal combustion showed that the leachable concentrations of regulated elements were below the values established as a limit for the disposal of inert waste on landfill sites by the European Landfill Directive (2003/33/EC). The pH leaching experiments and the modelling programme used in this study has led to a better understanding of the leaching of major and trace elements from chars obtained from the gasification of paper–plastic waste. In general, at alkaline pH values, sorption to the solid surfaces was negligible due mainly to the positive charge of these surfaces leading to inorganic complexes of the cations in solution. When the char was used as a mercury sorbent slight changes occurred on the reactive surface. The natural pH of the material dropped from around 9.5 to 5.5. This change resulted in a modification of the binding (strength) of some elements. At higher pH values, complexation involving dissolved organic matter played an important role in the case of Cu because of the increased DOC concentration in solution. In the case of Zn, a higher contribution of POM-bound was observed in the 8–12 pH range. This effect should be taken into account when considering reuse and disposal options for this material.

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