QUALIFICATION METHOD AND RISK MANAGEMENT IN CASE OF WASTE INCINERATION FLY ASH BY PLASMA PROCESSES

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Abstract

Incineration is often considered as the most efficient process for urban waste destruction. If it is a rather clean technique, it is often suspected to be the source of severe pollutions such as metal pollution or dioxin and furan emissions. In order to reduce hazardous emissions, various operating furnace parameters can be controlled, like the gas residence time, the flame temperature and the excess air flow rate, among others. According to European regulations, incineration fly ash corresponds to class 1 disposal landfills, which demonstrates that it is considered as a toxic waste. We have developed two kinds of technical one-line analysis in order to make a qualification of the fly ash composition. The main objective is to determine the degree of toxicity for their manipulation and their stocking.

1. Introduction

The last European regulations for heavy metal and chloroorganics content in fly ash are correlated with the specific characteristics of the fine particles collected by the electrostatic filter in the out gases of the burning system of the domestic or industrial wastes. The main properties of these particles of less than 1 μm of diameter are their high content in chlorine species (including metallic and organochlorine species) which are able to rich 20% w/w.

We have developed two kinds of technical on-line analysis: plasma induced by laser pulse (TRELIBS) in order to qualify in less than 106 the chemical composition in the elements with a sensibility of 106 g/g. This technique permits to vaporize a part of the powder and by optical emission analysis, we are able to identify the atomic emission lines, the qualification of the elements and their quantification.

For the chloroorganic species, we have developed a plasma fluidized bed reactor at low-pressure in order to identify by mass spectrometry the organic functions which are able to desorb, and the nature of chlorine species such as phosgene and chlorohydrocarbons compounds.

The final purpose of these analyses is to determine by soxhlet method of extraction and GC/MS analysis the dioxins content in the fly ash.
2. Analysis of fly ash by TRELIBS

During these last fifteen years, the technique of Time Resolved Laser Induced Breakdown Spectroscopy (TRELIBS) has become an established method for real time analysis of surfaces, liquids and gases as well. Focusing powerful laser pulse on a surface produces the vaporization of a small amount of the sample, then induces, near the focal region of the lens, a high temperature plasma. By using spectral time resolved plasma emissions, the element composition of the material can be determined (fig. 1).

![Experimental set-up of TRELIBS analysis](image)

**Fig. 1: Experimental set-up of TRELIBS analysis [1].**

The main advantage of this method is that, without complex chemical preparations, it especially provides direct analysis of solids. Only optical access to the sample is required, and sample contamination-induced risks are minimal. The aim is the detection and identification of the main heteroatoms (fluorine, chlorine, and sulfur...) (fig. 2) and atomic elements such as Si, Ca, Al, Cr, Mg, Pb, Fe... in fly ash at very weak concentration (10^{-6} g/g) [1].

![Spectral resolution and choice of atomic emission lines: chlorine and carbon examples](image)

**Fig.2a: Spectral resolution and choice of atomic emission lines: chlorine and carbon examples**

![Time evolution of emission intensities](image)

**Fig.2b: Time evolution of emission intensities**
Fig. 3: Identification of atomic elements from fly ash.
The Ni atomic line at 361.939 nm is overlapped by the Fe line at 361.876 nm.

Fig. 4: Scanning Electron Microscopy analysis of fly ash
(Heterogeneous system, 50< particles size <500μm, specific area measured: 5.45 m²/g)

These results show that a porous matrix, where the main elements are the silicon, the alumina, and the calcium, presented in silicea (SiO₂), alumina (Al₂O₃) and calcite (CaO) forms, and chlorides establish fly ash (Fig. 3 and 4). One will also note the strong content in chlorine, this one not being only under shape NaCl and KCl, but also in the form of metal chlorides, chloroorganic compounds such as polychlorobenzenes.

Being much more loaded in metals than clinkers, fly ashes contain important concentrations in volatile metals (lead, zinc, cadmium) associated to strong contents in chlorides and sulfates.

3. Study of organic compounds desorption from fly ash by mass spectrometry

The identification of the organic compounds trapped in a solid matrix represents an important information for the knowledge of the fly ash toxicity notably during their manipulation and their stocking. It can be made by means of a chemical protocol constituted by a solid/liquid extraction of the compounds, followed by purification (separation of the chemical classes) and of an analysis by GC/MS. This protocol needs time for extraction and analysis, this one being included between 4 and 28 o’clock. The plasma process developed can be substituted itself for the classic technique of extraction, with for essential advantage a time of analysis of few seconds.
The experimental device includes five main elements, namely the gases feed, the RF plasma source, the fluidized bed reactor in order to mix the particles with the plasma gases, the system of analysis spectrometric and the system of gases sampling (fig.5) [2].

Fig. 5: Experimental device of chloroorganics compounds desorption analysis trapped in fly ash’s matrix.

The reactor is constituted by a glass tube of 0.04 m of external diameter (0.036 m of internal diameter) on a length 0.3 m. The plasma is created by a radio frequency 13.56 MHz generator through a capacitive coupling. The analysis of the chlorinated species trapped in the mineral matrix of the fly ash is made by an on-line mass spectrometry through a capillary. The sensibility is 1 ppm, and corresponds so to the environmental standards current.

The use of a non-equilibrium plasma for fly ash treatment provides a specific reactivity where electron impact is the initiation step of the overall reaction without any thermal energy requirements.

The on-line analyses by mass spectrometry allow us to qualify the different chlorinated and non-chlorinated desorbed compounds: analyses show the presence of chlorinated aromatic hydrocarbons in ashes, these compounds being the precursors of dioxins [3].

<table>
<thead>
<tr>
<th>Identified molecules</th>
<th>Alkanes</th>
<th>Aromatic compounds</th>
<th>Polychlorobenzenes</th>
<th>Others species</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetylene (C₂H₂)</td>
<td>Benzene (C₆H₆)</td>
<td>C₆H₅Cl</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Ethane (C₂H₆)</td>
<td>Toluene (C₇H₈)</td>
<td>C₆H₄Cl₂</td>
<td>HCl</td>
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<tr>
<td></td>
<td>Alkanes C₄ to C₁₃</td>
<td>Phenol (C₆H₅OH)</td>
<td>C₆H₅CH₃</td>
<td>Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₆H₅CH₂OH</td>
<td></td>
</tr>
</tbody>
</table>

Tab.1: Identification of the organic compounds trapped in fly ash.
This list is not exhaustive: it does not reflect completely the nature of all the organic compounds trapped in fly ash. The process of organic compounds desorption leads to split up the complex molecules having a strong chemical bond with the mineral matrix. The role of transition metals on the stability of the species, even on the secondary reactions of fragmentation during the impact of the molecules of the plasma allows to approach the content in trapped organic chains, or part of molecules.

The introduction of hydrogen in the plasma during the treatment of fly ash sample reduces the percentage of aromatic chlorinated compounds and enhances the percentage on HCl, Cl and the other aromatic compounds in the exhaust gas (fig. 6).

![Mass spectra of organic compounds analysis contained in fly ash (desorption under Ar/H₂ plasma, fly ash m = 0.7 g; Pw = 100 W; P = 100 Pa; Argon = 284 ml/min; H₂ = 24 ml/min).](image)

Under electron impact, radicals such as C²⁺, C₆H₄⁺... are formed. When hydrogen is added, the radical H⁺ reacts with the above radical forming HCl, C₆H₆... Thus, the recombination between chlorine and the aromatic skeleton is limited, also limiting the formation of undesired toxicics.

This study shows the existence of chemical reactions between the excited species produced from the plasma (H₂⁺, H⁺, O₂⁺, O⁺, CH⁺, CH₂⁺, Ar...) and the molecules desorbed from the mineral matrix of fly ash during the plasma treatment through the chemical analysis of the gaseous effluent. This protocol has been validated using thoroughly characterised standard fly ash in order to evidence the chlorine desorption process [2].

4. Solid/liquid extraction of organic compounds from fly ash: qualification of dioxins

Techniques used to identify the volatile organic compounds (VOC) always collide in even difficulties. VOC are often present in weak quantity in complex mixtures. Given the complexity of fly ash and their weak contents in VOC, it is necessary to proceed to a preparation of samples before analysis [4,5].
The first stage consists of a solid/liquid extraction of the semi-volatile molecules, often called the soluble organic fraction (SOF) [3].

This fraction so obtained by soxhlet technique is then cleansed to eliminate any interference due to the important number of present sorts, then injected in a GC/MS apparatus, which the sensibility is 1 ppb.

So, it is necessary to note that fly ash contains a content of dioxins (fig.7) of the order of 90 µg/kg, that is 90 pg/g. Dioxins measurements were carried out after the US EPA 1613 protocol [6].

5. Conclusion

The physico-chemical qualification of fly ash's matrix requires to go beyond the measure of its atomic composition by knowing how to approach the nature of the trapped molecular sorts and in particular the chloroorganic compounds, precursors of dioxins.

TRELIBS analyses permit to define the main heteroatoms and atomic elements at very weak concentration. So, the mineral particles of fly ash consist of a matrix of aluminosilicates where VOC, mineral chlorides and heavy metals are adsorbed. The complexity and the nature of their composition brings rightly to define the modes of adsorption of the various sorts, chemical-sorption and physical-sorption, two different processes which often lead to chemical modifications of molecules.

The organic chemical inventory of these ashes has been determined by two different protocols following the standards, the one appealing to a solid/liquid extraction of the organic phase of fly ash and in an analysis GC/MS, the other one by a low-pressure plasma process coupled with a spectrometer of mass.

The list of the various identified compounds is not exhaustive but allows to put in evidence the nature of the present families, the main clauses of which are alkanes, chlorobenzenes, polycyclic aromatic hydrocarbons, phenols and sulphurated compounds. Let us note that dioxins are also a part of these materials, that requires particular capacities for their manipulation and their stocking.

Acknowledgment

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