Behaviour of Micropollutants
in Sludge Incineration

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Summary

The management of sewage sludge in an economically and environmentally acceptable manner is one of the critical issues facing the society today, due to the large production deriving from the installation of extended sewerage and advanced wastewater treatments, to the problems of contamination from industrial effluents and to the stricter guidelines imposed for disposal. Decreasing landfills availability and increasing difficulties for sludge utilisation in agriculture make nowadays sewage sludge incineration attractive, especially for large plants where possibilities for energy recovery can render this disposal option further competitive.

The Italian National Research Council (CNR) - Water Research Institute (IRSA) has undertaken a research project to test the technical, economical and environmental feasibility of sludge incineration. In this paper, the results of tests carried out by a pilot plant, equipped with fluidised and rotary drum furnaces, are presented. The partitioning of heavy metals among the different phases of the incineration process was studied considering a thermodynamic model. In addition, lab investigations to assess the effects of chlorinated compounds and process failure modes on organic emissions were performed.

INTRODUCTION

In incineration processes, inorganic (heavy metals) and organic (PAH, PCDDs, PCDFs) micropollutants can be produced and emitted together with particulate and carbon and nitrogen oxides (CO, NO x). The presence of organic chlorine in sewage sludge is generally negligible, so the problem of appearance of dioxins and furans is of minor importance with respect to the incineration of municipal solid wastes. Metals are instead present in sewage sludge at noticeable concentrations and they can be transferred to the gaseous phase depending on their volatility, on the presence of

other species and on conditions inside the furnace (temperature, oxygen concentration).

The CNR-IRSA is carrying out a research to assess the conditions favouring the appearance of contaminants in the emissions from sludge incineration and the harmfulness of ashes. Other aim of the research project is to verify the environmental feasibility of hazardous sludge incineration.

The research activities were carried out by an incineration pilot plant and by laboratory equipment.

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EXPERIMENTAL

Pilot plant

The pilot plant is located in Bari (Southern Italy) in the area of one of the two municipal sewage treatment works serving the town. Main units are dryer, two incineration furnaces (completely circulated fluidised bed and rotary kiln which can operate in co- or counter-current mode), afterburning chamber, heat recovery system and flue gas cleaning system (bag filter and wet scrubber). The throughput of the plant is about 250 kg/h of sewage sludge at 20% solids concentration (60% volatile) or 160 kg/h of dried sludge at 75% solids. The two furnaces can operate alternatively, being in common all the other facilities. The pilot plant is equipped with analytical instrumentation for continuous gas monitoring in different sections: (a) oxygen (exhaust gas from the furnace), (b) oxygen, carbon monoxide and dioxide and total hydrocarbons (exhaust gas from the afterburning chamber), (c) oxygen, particulate, NO_x, SO_2 and HCl (exhaust gas in the stack). Sampling points of exhaust gases in five different sections of the plant allow the other organic and inorganic micropollutants to be monitored.

The main equipment characteristics of the plant are shown in Table 1 and the process scheme in Figure 1.

The behaviour of sewage and hazardous sludge during combustion was studied with particular reference to hazardous compounds emissions and to the optimal conditions for minimising fuel consumption and exhaust gas production (excess air, temperature in the afterburning chamber, cake concentration before incineration).

Investigations were performed using sewage sludge either alone or spiked with hazardous compounds; in particular, a Surrogate Organic Mixture (SOM) consisting of 55% of tetrachloroethylene (C_2Cl_4), 25% of chlorobenzene (C_6H_5Cl) and 20% of toluene ($C_6H_5CH_3$) as a solvent was used to simulate a typical hazardous sludge.

Laboratory
Organic micropollutants

The laboratory equipment employed in the present investigation is the system for thermal diagnostic studies (STDS), a highly versatile thermal simulation unit with interchangeable components. The system is composed of four integrated sub-assemblies: a control console, a thermal reaction compartment, a cryogenic trapping gas chromatograph (GC) and a mass selective detector (MS). The system set up is shown in Figure 2. In the console sub-assembly the controls of gas flow rates, gas composition, pressures and residence time are located. The thermal reaction compartment is a modified GC equipped with a pyroprobe as injector (simulating the first incineration step) and a high temperature furnace that allocates an interchangeable quartz reactor (simulating the after-burning step). The pyroprobe is connected via a 3 mm i.d. silicon steel tube to the quartz tubular reactor and then, by another silicon steel tube, to a capillary GC column located in GC that is interfaced, through a transfer line heated to 300℃, with a MS equipped with an electron impact ion source. During the thermal experiments the GC analytical column was kept at -60℃ in order to cryofocus the evolved organic compounds into a small band. After completion of the thermal experiment, the compounds trapped at the top of the GC column, after purging and pressurising the column with helium, were separated by raising the oven temperature to 300℃ at a rate of 15℃/min. Electron impact mass spectra, at an electron energy of 70 eV, were recorded by scanning the quadrupole from mass 35 to 550 Dalton at 1.4 scan/s. The background-subtracted mass spectra were matched against those of NIST mass spectra library.

Heavy metals

The behaviour of heavy metals during sludge incineration was studied by comparing the metal content among feed sludge, bottom ash, and fly ash. In addition, the elemental composition of the feed sludge, as well as the morphological and struc-

Table 1 Equipment main characteristics of the demonstration incineration plant

| Operating unit	Parameter	Value
Toxic waste storage unit	volume, m^3	15
Dewatered sludge storage unit	volume, m^3	15
Sludge indirect dryer	surface, m^2	30
	water evaporation capacity, kg/h	440
	internal diameter, mm	590
Fluidised bed furnace	height, m	9.6
	heat capacity, kcal/h	800,000
Cyclone	internal diameter, mm	1,000
Rotary kiln furnace	internal diameter, mm	1,200
	length, m	6
Afterburning chamber	internal diameter, mm	1,200
	height, m	5.3
Heat recovery section	exchange capacity, kcal/h	360,000
Air preheater	exchange capacity, kcal/h	60,000
	air flow rate, Nm^3/h	1,500
	oil flow rate, kg/h	21,000
Bag filter	surface, m^2	90
Gas washing column	gas flow rate, Nm^3/h	4,000
	diameter, mm	1,100
	height, m	12
	gas flow rate, Nm^3/h	4,000
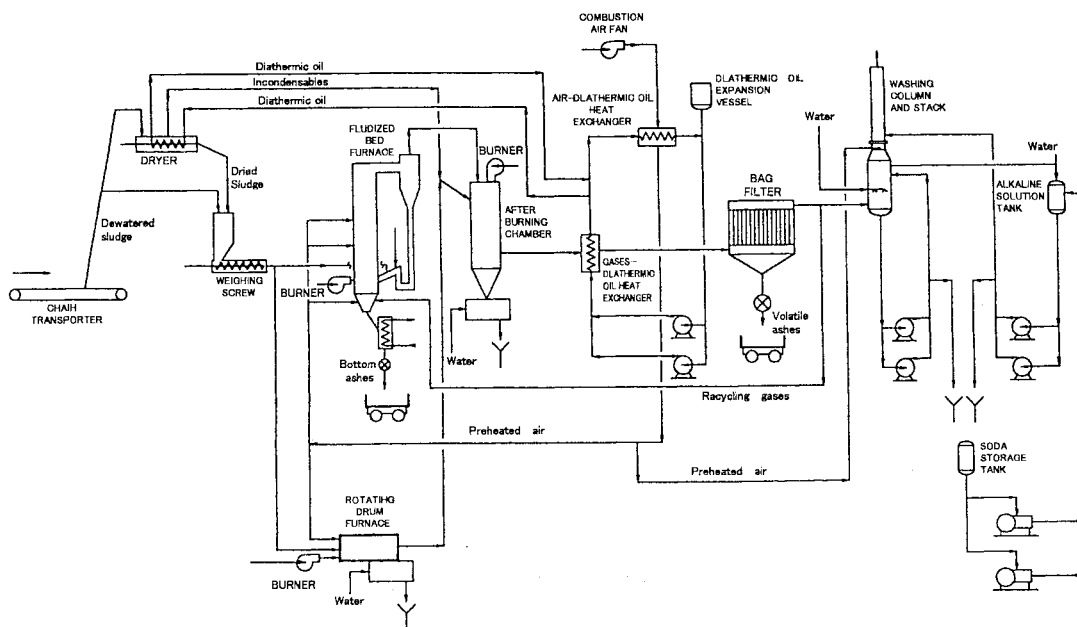
Fig. 1 Process scheme of the pilot plant

tural properties of bottom and fly ash were deter-
mined.

During each pilot plant test, after reaching steady
state conditions, grab samples of feed sludge and
ash from every solid stream was collected three
times per day. For each sampling point, the three
grab samples were blended in one daily sample,
that was subsequently dried and finely ground in
a ball mill.

Solids content of the feed sludge, as well as loss
on ignition and fixed fractions, were measured com-
paring constant weights at 105 and 550℃. As for
the major sludge elements, the analysis of C, H,
N, S, and O was performed using a Carlo Erba
Nitrogen Analyser NA1500 in two different layouts:
1) simultaneous determination of N, C, H, and S by
oxidation with excess oxygen or 2) oxygen deter-
mination by pyrolysis. As for the chlorine content
of the feed sludge, only the fraction of soluble
chloride was determined by performing an aqueous
extraction on the dried sludge and measuring
extracted chloride with ion chromatography
analysis.

To determine the metal content of feed sludge and
ash samples, three aliquots of the finely powdered
sample were digested in a microwave digestion sys-
tem (Spectroprep, CEM) with a mixture of con-
centrated HNO_3, HCl, and HF. The metal content
of the digestion mixture was analysed with atomic
absorption spectroscopy and inductively coupled
plasma emission spectrometry.

The morphological properties of ash samples were
determined by scanning electron microscopy
(SEM). Backscattered images were taken with a
Philips XL30 microscope, at 15 kV accelerating
voltage and 1500x-2500x magnification range.
X-ray maps were obtained with the same micro-
scope equipped with an energy dispersive X-ray
fluorescence (EDXRF) spectrometer. The structural
properties were determined from X-ray diffraction
patterns obtained on a Siemens D500 diffrac-
tometer and peak identification was performed using
JCPDS database.

The experimental results obtained in this work were
contrasted with a simple thermodynamic model
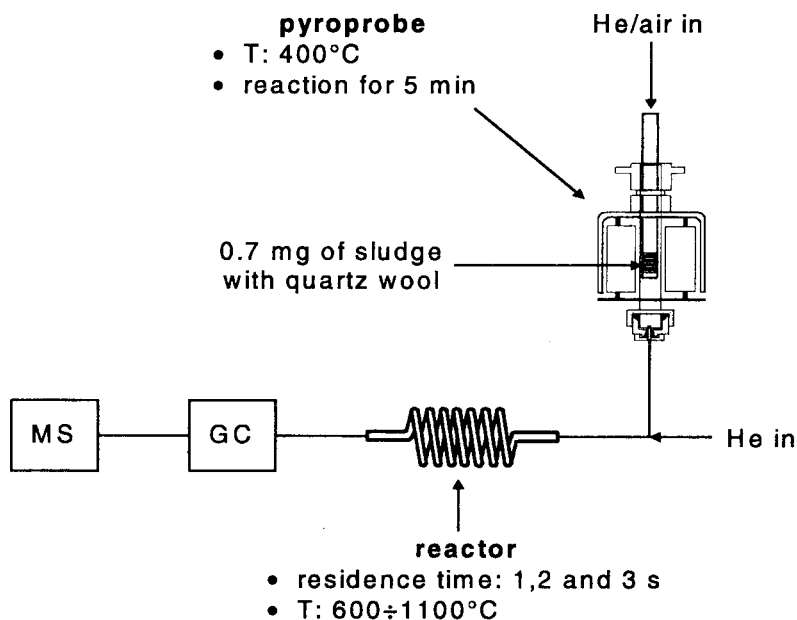predicting the equilibrium speciation inside the com-

Fig. 2 STDS instrumental set-up for lab-scale combustion tests

bustion chamber[1,2,3]. The model assumes that all elements of the input streams (air, sludge, and fuel) are intimately mixed in the combustion chamber, where thermodynamic equilibrium conditions are reached. Combining the constraints of mass conservation and free energy minimisation, the model provides a set of equations that can be solved to determine equilibrium composition of the given chemical system at the set temperature and pressure conditions. In order to compute equilibrium composition, the HSC computer code was used[4]. The model chemical system included 13 elements (C, H, N, S, O, Cl, Cd, Cr, Cu, Mn, Ni, Pb, Zn) representing the input streams of fuel, air, and sludge. As for the fixed solids fraction of the sludge, in this preliminary work only the above seven selected heavy metals were considered in the model. Chlorine was also considered in the model system for its potential effect on metal vaporisation. The thermochemical database of the HSC software included 432 chemical species (both in gaseous or condensed phase) that may form by reacting the 13 elements considered. Out of those 432 species, only 342 are stable at the temperature range (600-1000℃), atmospheric pressure and oxidising conditions considered in the model.

PILOT PLANT RESULTS

Three tests were carried out with the fluidised bed furnace (FBF) and two with the rotary drum furnace (RKF). The operating conditions were the following:

1. incineration by FBF of dewatered sludge and afterburning of exhaust gases at 950℃;
2. incineration by FBF of dewatered sludge spiked with SOM and afterburning of exhaust gases at 1,200℃;
3. incineration by FBF of dried sludge and afterburning of exhaust gases at 950℃,
4. incineration by RKF, in co-current mode, of dried sludge and afterburning of exhaust gases at 950℃,
5. incineration by RKF, in counter-current mode, of dewatered sludge and afterburning of exhaust gases at 950℃.

Other process variables are reported in Table 2.

The performance of the plant resulted generally satisfactory. In particular, the plant fulfilled the standards of Italian legislation for the afterburning furnace and for the emissions at stack (Table 3) also for test no.2 where the Cl input was at 5% of fed sludge, thus evidencing a satisfactory HCl abatement.

However, in spite of the fulfilment of legislation standards, a few operating problems were ob-

Table 2　Process variables of demonstrative tests

Test no.	Feed sludge		Loss on ignition	Dried sludge to the furnace	Toxic mixture flow rate	Air to furnace	Methane to the furnace	Methane to the afterburning chamber	Exhaust gas from the afterburning chamber	Exhaust gas to the washing column
	(kg/h)	(%)	(% of DS)	(kg/h)	(kg/h)	(Nm³/h)	(Nm³/h)	(Nm³/h)	(Nm³/h)	(Nm³/h)
1	268	20.64	67.8	-	-	372.9	68	32.2	2,505	4,250
2	172.5	18.73	71.7	-	23.66	501.5	40.9	37.9	1,834	3,178
3	553.8	18.99 (90.26*)	66.9	116.51	-	446.6	-	30.2	1,740	2,129
4	580	18.85 (94.89*)	67.9	115.21	-	315.5	22.3	32	2,096	2,330
5	250	18.22	67.9	-	-	298.9	79.35	23.4	2,487	4,704

*concentration after thermal drying

Table 3 Stack emissions for the different test runs (at reference O_2 concentration of 11%)

Parameter	Test					Italian limits
	1	2	3	4	5	
Temperature (°C)	51	73.4	58	43	53	-
Flow rate (Nm³/h)	5,900	4,338	4,574	6,533	6,633	-
Moisture (g/Nm³)	54.6	26.7	24	30.6	37	-
Oxygen (% volume)	16.6	16.5	17.0	17.2	17.6	-
SO_x (mg/Nm³)	<0.1	61.5	57.6	0.5	0.13	300
NO_x (mg/Nm³)	98	95.2	127.8	78	289	500
CO (mg/Nm³)	8.5	49.1	49.4	5.7	22.9	100
HCl (mg/Nm³)	1.6	2.75	0.6	2.2	2.9	100
HF (mg/Nm³)	0.24	0.11	<0.06	1.2	2.3	4
TOC (mg/Nm³)	ND	0.59	3.0	ND	0.7	20
Particulate (mg/Nm³)	2.3	2.9	2.2	0.14	10	100
Cd (µg/Nm³)	0.2	0.039	0.16	<0.2	<0.2	200
Hg (µg/Nm³)	0.2	0.057	<2.2	0.2	<0.1	200
Cr (µg/Nm³)	1.2	0.061	0.43	<0.1	<0.6	-
Pb (µg/Nm³)	<0.7	0.85	1.2	<0.7	1.3	5,000
Cu (µg/Nm³)	2.3	0.95	1.6	0.7	1.3	5,000
Zn (µg/Nm³)	14.9	12.9	57.6	0.8	27.1	
As (µg/Nm³)	<0.2	<0.05	<0.05	<0.2	<0.2	1,000
PCDD (ng/Nm³)	-	<2.7	<0.5	-	-	
PCDF (ng/Nm³)	-	<6.5	0.75	-	-	
PAH (µg/Nm³)	-	0.402	0.124	-	-	100

served. In particular, clogging of dryer at solids concentration around 60%, clogging of the gas sampling system in the afterburning chamber operating at 1,200°C, need of frequent maintenance and calibration of control instrumentation, slag formation in the rotary kiln furnace when in co-current operation were observed.

LABORATORY INVESTIGATIONS

Organic micropollutants

Different tests were carried out using the STDS to compare the thermal degradation chromatograms of sewage sludge with those of sludge spiked with different chlorinated hydrocarbons.

Sludge in the experimental tests was the same used for pilot tests. It was dried at 105°C for 7 h, then grounded and sieved at 100 μ m. Parallel tests were also carried out with sludge spiked with the same surrogate organic mixture (SOM) used in pilot tests, in order to obtain a sludge containing 5% of organic chlorine as total weight. In a typical STDS experiment, 0.7 mg of hazardous sludge sample was placed onto a quartz capillary tube (1.5 mm i.d.,

15 mm length) and held in place by quartz wool at both ends. The quartz tube was inserted into the quartz probe which was, in turn, inserted into the pyroprobe, held at 400°C, for first thermal degradation step. The reaction in the pyroprobe was carried out under controlled oxygen rich atmosphere by feeding a variable helium/air mixture (total flow = 2.66 mL/min) through the quartz probe. Two different conditions of oxygen excess were used being respectively 30 and 160% more of the stoichiometric oxygen theoretically required for the sludge combustion. To quantitatively describe the different reaction condition of oxygen excess atmosphere the ratio Φ has been used, defined as $\Phi = O_2$ available for combustion/stoichiometric O_2. The oxygen available for combustion can be calculated knowing respectively the sludge reaction time (5 min) and the air flow rates that were, respectively, 0.66 ($\Phi = 1.3$) and 1.32 mL/min ($\Phi = 2.6$). The organic compounds formed during the first incineration step were then swept into the other reactor and subjected to high temperature (500-1100°C) for a fixed residence time (1, 2 and 3 s) obtained by properly setting the helium flow

rate at the reactor inlet. The thermal reaction products were then transferred into the cryogenic trapping GC chamber where they were focused on a capillary GC column, separated by a temperature ramp, and identified by MS.

In order to compare the thermal stability of Principal Organic Hazardous Constituents (POHCs), the afterburning temperatures required for 99% destruction (T_{99}) were used. Table 4 reports the T_{99} found for the POHCs spiked onto the sludge with, as a reference, the T_{99} of the same compounds during thermal degradation in absence of sludge. The results show that residence time has no influence on T_{99} while, in general, Φ has a positive effect on POHCs thermal degradation, i.e. the higher the Φ value the lower T_{99}. Comparing the T_{99} with and without the presence of sludge, it seems that the presence of sludge makes toluene thermally more stable. This is a direct consequence of toluene reformation at elevated temperatures by decomposition of sludge matrix. Its concentration, in fact, starting from 600℃ increases with the afterburning temperature, reaches a peak at 700℃ and then decreases. Such a toluene production could be explained by the formation of stable benzyl radicals that in turn can recombine with hydrogen atoms, possibly present in high concentration. Conversely the behaviour of choloro-benzene resulted to be independent of reaction atmosphere and also of the presence of sludge. Results for chloro-benzene were different form those obtained in absence of sludge by Graham et al[5]. who found that the higher in oxygen is the reaction atmosphere the faster the degradation. This could be explained taking into account that chlorobenzene may be formed as PIC in chlorinated wastes[6]. The thermal degradation of tetrachloro-ethelene resulted to be improved both by the sludge presence and, for experiments carried out with sludge, by increasing Φ. The former result of sludge matrix positive effect could be explained taking into account that sludge thermal decomposition produces a variety of reactive radicals that, in turn, can increase the number of possible reaction for tetrachloroethelene thermal decomposition. As far as thermal reaction products are concerned, experimental results showed that the majority of organic emissions from hazardous sludge thermal experiments resulted from decomposition of

Table 4 T_{99} of investigated POHCs in presence and absence of sludge

Compound	with sludge[a]		without sludge[b]
	$\Phi=1.3$	$\Phi=2.6$	$\Phi=1$
Toluene	950	850	750
Chlorobenzene	800	800	800
Tetrachloroethelene	800	750	850

a: residence time=1, 2 and 3 s;
b: residence time=2 s

sludge biomass itself (Figure 3), while the spiked hazardous compound gave a minor contribution to Products of Incomplete Combustion (PICs) formation. Such a contribution is only due to the PICs that are also formed when the spiked organic mixture is allowed to thermally react, under the same conditions, without the sludge presence. The maximum number of PICs (over 70 compounds) was detected at 600℃. At this afterburning temperature the number and intensities of PICs were independent of both residence time and Φ. This could be explained considering that, under these conditions, the thermal failure mode is the controlling factor and the employment of efficient conditions of residence time and oxygen rich atmosphere are not effective in minimising PICs production.

As reported in Table 5, at the afterburning temperature of 600 and 700℃, among the PICs detected, many long-chain carboxylic acids, alkanes, aldehydes and aromatic compounds are generated by thermal decomposition of biological material present into the sludge. It also appeared that at afterburning temperature of 700℃ the number of compounds produced was the same obtained in tests at 600℃, with the only difference that the intensities for most of them were lower. It was also

observed that at 700℃, both residence time and Φ had no influence on PICs production. When the afterburning temperature was above 700℃ the number of PICs decreased drastically in the whole range of experimental conditions. In these conditions it was found that the oxygen excess atmosphere has a strong influence on PICs emitted as shown in the chromatograms of Figure 3. The chromatograms a, b and c clearly evidence that at Φ = 1.3 and at an afterburning temperature of 600℃, corresponding to the afterburning thermal failure mode, a large number of compounds are emitted with also an overwhelming organic matrix as background. The same chromatograms show that,

at Φ = 1.3, a number of PICs, mainly aromatic compounds such as benzene, toluene, benzonitrile and other polycyclic aromatic hydrocarbons (PAHs), are still detected even though afterburning temperature is raised up to 1100℃.

This PICs persistence at such a high temperature could be explained by assuming that, with the conditions of residence time and Φ employed, pyrolysis pockets are formed. The pyrolysis pockets are formed because, due to mild conditions of oxygen excess (Φ = 1.3) during the reaction in the pyroprobe, the sludge sample does not react uniformly but with flash volatilisation. When a sludge flash volatilisation occurs, it could need more

Table 5   Major thermal decomposition products detected in laboratory tests.

Compound	Temperature (°C)											
	600	700	800				900		1000		1100	
			Φ				Φ		Φ		Φ	
	a	a	1.3^a	2.6^b	2.6^c	2.6^d	1.3^a	2.6^a	1.3^a	2.6^a	1.3^a	2.6^a
CO_2	x	x	x	x	x	x	x	x	x	x	x	x
SO_2	x	x	x	x	x	x	x	x	x	x	x	x
alkanes (C_3-C_8)	x	x	x	x	x	x						
alkenes (C_3-C_{18})	xxx	xx	xx	x	x							
alkynes (C_3-C_8)	x	x	xx	x	x		x		x		x	
aliphatic ketones (C_3-C_6)	xx	x										
aliphatic aldehydes	xxx	xx	x									
aromatic aldehydes	xx	xx	xx	x	x							
organic acids (C_2-C_{16})	xxx	xx	x	x								
aliphatic nitriles	xx	x	x				x		x		x	
aromatic nitriles	xx	xx	xxx	xx	xx		xx		x		x	
furans	xx	x	x	x	x		x		x			
pyrroles	x	x	x									
pyridines	xx	x	x				x					
toluene	xx	xxx	xx	x	x		x		x		x	
tetrachloroethene	x	x										
chlorobenzene	xxx	xx	x	x	x							
benzene	x	xx	xx	xx	x		xx		xxx		xxx	
alkyl-benzenes	xx	x	x				x		x		x	
phenols	xx	x										
PAHs	x	xx	xx	xx	x		xx		xxx		xx	

a: residence time=1, 2 and 3s;   b: residence time =1s;
c: residence time =2s;   d: residence time =3s;
GC-MS peak area counts: xxx: $> 10^7$; $10^7 >$ xx $> 10^5$; x: $< 10^5$.

of the instantaneous available oxygen to react completely and this situation gives rise to the formation of pyrolysis pockets that are responsible for the formation of PICs which then escape the pyroprobe region. The same occurs into the reactor for the afterburning step where extra air is not fed. Therefore even a temperature as high as 1100℃ is not able to destroy all of them and a number of aromatic compounds are emitted.

The formation of aromatic compounds could be explained taking into account that, under pyrolytic conditions, hydrogen atoms are the reactive radicals predominant in the system. Thus the pyrolytic degradation of aliphatic compounds produces a number of radicals that act as building blocks and give rise to the formation of benzene and polynuclear aromatics. Furthermore, the above considerations could also explain the negligible influence of residence time found for all the experiments at Φ =1.3: in fact when the formation of pyrolysis pockets occurs the mixing failure mode controls PICs formation and even the highest residence time is not able to decrease PICs emission.

Experiments carried out at Φ =2.6 and 800℃ showed a different trend. The PICs number resulted lower than that obtained at Φ =1.3, under the same conditions of residence time, while the residence time showed a strong influence on PICs emitted: in fact, at residence time = 1 s the PICs detected were the same as at Φ =1.3 but with lower intensities, at residence time = 2 s their number was remarkably reduced and at residence time = 3 s they almost disappeared. It is evident from these results that the temporal failure mode may control PICs emission when properly operative conditions of afterburning temperature and oxygen rich atmosphere are met. It follows that the influence of residence time is limited to a small range of afterburning temperature and Φ conditions. Fig. 3d depicts a typical STDS chromatogram obtained at an afterburning temperature of 900℃ and Φ =2. 6 for all the residence times. It is evident that such an afterburning temperature is sufficient to thermally destroy all PICs formed in the pyroprobe

region when proper conditions of oxygen excess are employed. Thus, the comparison of chromatograms c and d of Fig. 3 indicates that, when enough oxygen is available for afterburning, the presence of reactive oxygenated species is achieved: this results in an increased rate of oxidation toward thermodynamic completion reducing the number of radical building blocks which give rise, by radical- radical recombination or radical addition, to the formation of polynuclear aromatics.

Heavy metals behaviour
Sludge and ash characterisation
The content of heavy, toxic metals in the sewage sludge used in this work is summarised in Table 6 and compared with the values reported in the literature. The comparison shows that the metal content of the sewage sludge used for the demonstrative tests is typically in the lower part of the ranges of literature values, suggesting that the sludge under study is mainly of domestic origin, with low contribution from industrial discharges. This work was focused on the behaviour of seven selected metals (Cd, Cr, Cu, Mn, Ni, Pb, and Zn) in the preliminary pilot plant tests carried out using rotary kiln furnace (tests no. 4 and 5).

Table 7 compares the composition of the sludge fed in the above incineration tests. Apart from the sharply different water content shown in Table 2, the two sludge samples seem to have a substantially similar composition in terms of volatile and fixed solids and in terms of major elements. Acidifying dried sludge samples prior to C analysis it was found that the amount of carbon is almost entirely (96-98%) organic carbon, which increases to about 55% if referred to volatile solids. This value is close to the expected carbon percentage of the biological material, that is typically represented with the formula $C_5H_7O_2N$ (WEF, 1992). As for the content of heavy metals, concentrations typically decrease in the order Zn, Cu, Pb, Cr, Mn, Ni, Cd. For each individual metal, however, significantly different concentrations are found in the two sludge samples. The chlorine content

Table 6   Metal content in sewage sludges (mg/kg on dry solids)

Element	This work	Literature data	
		Concentration range	Typical value
As	1.1 - 1.8	0.3-20	2
Cd	3.3 - 10	1-50	5
Cr	112 - 404	40-1500	200
Cu	250 - 500	160 - 1600	400
Hg	1.1 - 3.1	1-12	3
Mn	94 - 127	240 - 600	150
Ni	13.3 - 54	20 - 240	50
Pb	136 - 193	80 - 850	300
Zn	1183 - 2162	900-4200	1600

reported in Table 7 for test 5 was measured through an aqueous extraction on the dried sludge sample, and therefore represents total inorganic chloride. In this preliminary work no attempt was made to analyse total (organic and inorganic) chlorine content. Literature data suggest, however, that the organic chlorine content of sewage sludge is negligible[7].

Micrographs of bottom ash and fly ash samples are compared in Figure 4. Randomly aggregated particles of the bottom ash sample do not present any predominance of well defined geometrical form. In contrast, in the bag filter ash sample spherical particles are intermingled with sintered agglomerations and platelet particles, in accordance with morphologies observed in fly ash samples from coal burning and municipal solid waste incinerators[8, 9, 10]. In fact, the bulk of fly ash material is typically constituted of spherical particles that are formed through the condensation of molten droplets of aluminosilica glass (Reardon EJ, 1997). Intermixed with the glassy, spherical material, crystalline outcroppings mainly composed of $CaSO_4$, NaCl, KCl have been identified in fly ash samples (Ontiveros JL, 1989; Furuya K, 1987). Accordingly, the preliminary EDXRF results of this work suggests that the spherical particles shown in Figure 4 (sample b) are mainly composed of silicon and aluminium. In addition, $CaSO_4$ has been identified as major component of the crystalline frac-

tion of the bag filter ash sample.

Metal partitioning

In Table 8 the metal content of the feed sludge is compared with the metal content of the relevant incineration residues. The table also reports the concentrations of metals on inert basis which corresponds to the expected concentrations in all the solid residues if the metal evenly partitions among the different solid streams (i.e. there is no metal volatilisation in the combustion chamber). According to their behaviour during incineration, the seven metals of concern may be sorted in two groups. A first group of metals (Ni, Mn, Cr and Cu) do not show a significant enrichment in the finer fraction of the solid residues. The content of these four metals is approximately equal in all the solid streams and close to the expected concentration when vaporisation is not considered. A second group of metals (Zn, Pb and Cd) presents increasing concentrations from bottom to filter ash. In the bottom ash these metals are diluted with respect to the "expected concentration", suggesting metal loss from the combustion chamber through vaporisation.

The subsequent condensation yields enrichment in the fly ash by one or two order of magnitude with respect to concentrations in the bottom ash. These general considerations seem to be valid for both tests reported in Table 8, suggesting that metal

Abundance

a Reactor temperature:600°C, ϕ=1.3

Abundance

b Reactor temperature: 800°C, ϕ=1.3

Abundance

c Reactor temperature: 1100°C, ϕ=1.3

Naphthalene

benzen $C_{12}H_8$

$C_{14}H_1$

$C_{16}H_1$

$C_{18}H_1$

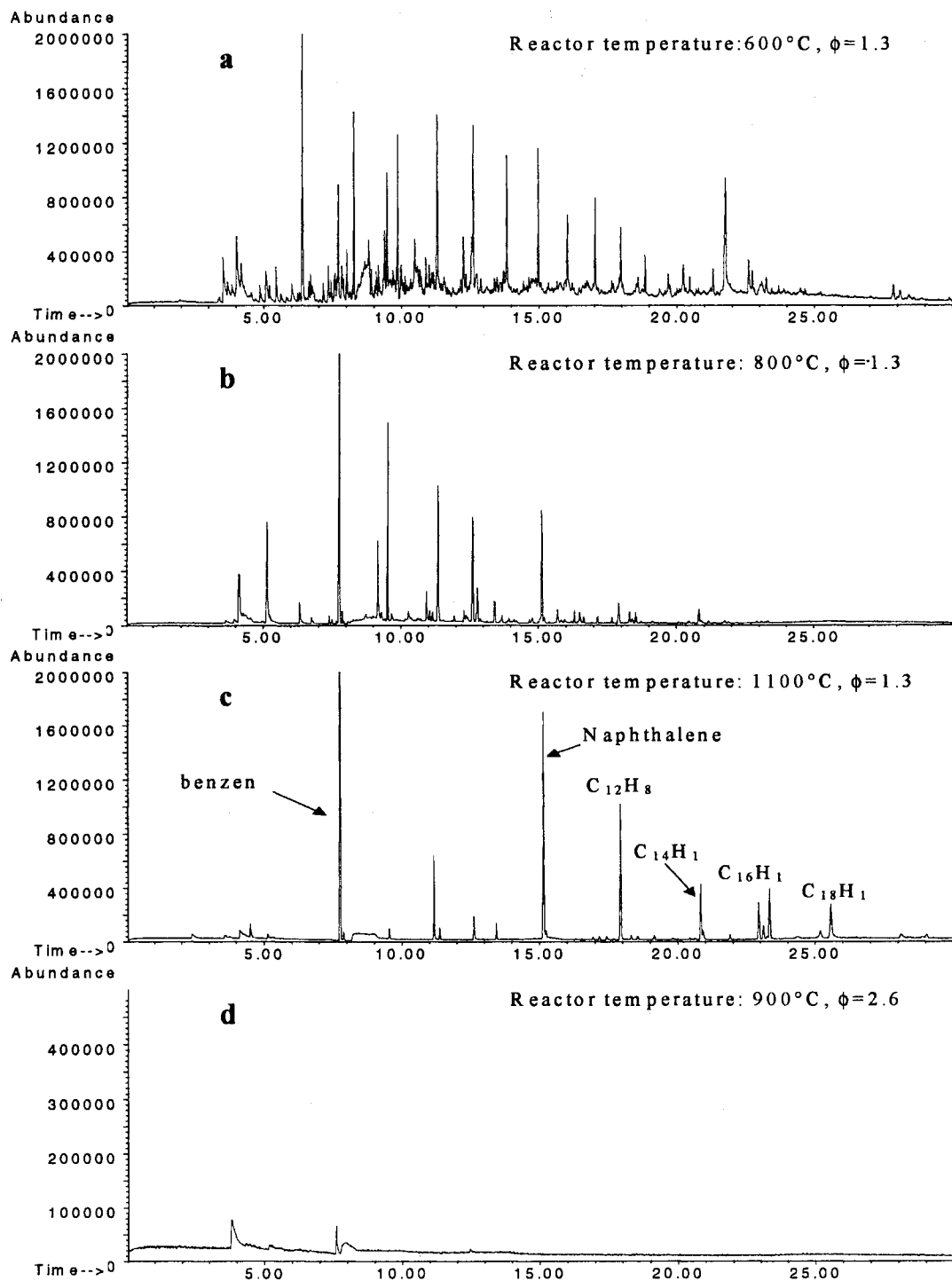**Abundance**

d Reactor temperature: 900°C, ϕ=2.6

Fig. 3 STDS-GC chromatograms of hazardous sludge obtained with residence time=2s.

Table 7 Composition of the feed sludge (referred to dry matter).

	Test 4	Test 5		Test 4	Test 5
Proximate analysis (%)					
Loss on ignition	67.9	69.8			
Fixed solids	32.1	30.2			
Major elements (%)			*Heavy metals (mg/kg)*		
C	38.2	39.3	Cd	3.7	3.7
H	5.1	5.3	Cr	115	95
N	4.3	4.7	Cu	474	248
O	23.4	23.6	Mn	102	91.2
S	0.6	0.6	Ni	39.4	19.2
P	1.4	1.6	Pb	151	127
Ca	5.4	6.1	Zn	2089	1363
Si	2.4	2.7			
Al	2.2	2.6			
Fe	0.6	0.6			
Mg	0.5	0.5			
Na	0.3	0.3			
K	0.2	0.2	Inorganic chlorine (mg/kg)		1822

behaviour is not significantly affected by the feeding conditions (sludge water content, co-current vs. counter-current feeding).

To check whether the metal behaviour shown above may be explained and predicted by metal speciation in the combustion chamber assuming equilibrium conditions, the HSC computer model was run with the input data representing the chemical composition of the feed (air + fuel + sludge) of test 5. Figure 5 shows that manganese, nickel and chromium are predicted to predominantly partition in condensed oxide phases in the combustion chamber, in agreement with the results of Table 8.

Regarding copper behaviour, around 900°C a small, yet significant amount of metal is predicted to volatilise as CuCl(g). These model predictions may explain the ambiguous experimental behaviour of copper reported in Table 8, even though a rigorous comparison of model predictions between test 4 and test 5 is hampered by the lack of chlorine input data in Test 4.

Figure 6 depicts the predicted speciation of the three metals (Cd, Pb and Zn) that showed clear enrichment in tests 4 and 5 (Table 8). Consistent with the experimental behaviour, at 900°C both cadmium and lead are predicted to volatilise in substantial amount. The main gaseous species are $Cd_{(g)}$, $CdCl_{2(g)}$, $PbO_{(g)}$, $PbCl_{(g)}$ and $PbCl_{2(g)}$. On the contrary, Figure 6 shows a clear discrepancy between the predicted zinc speciation and the metal behaviour reported in Table 8. On the basis of HSC thermochemical database, the concentration of gaseous zinc species ($Zn_{(g)}$, $ZnCl_{(g)}$, $ZnCl_{2(g)}$ and $ZnO_{(g)}$) in the combustion chamber is negligible with respect to solid ZnO concentration even at very high temperatures.

The discrepancy about zinc behaviour might be explained recalling that the model assumes a homogeneous reactor, whereas inhomogeneities in the rotary kiln incinerator may induce locally reducing conditions even in the presence of excess air. Unlike the other metals considered in this work,
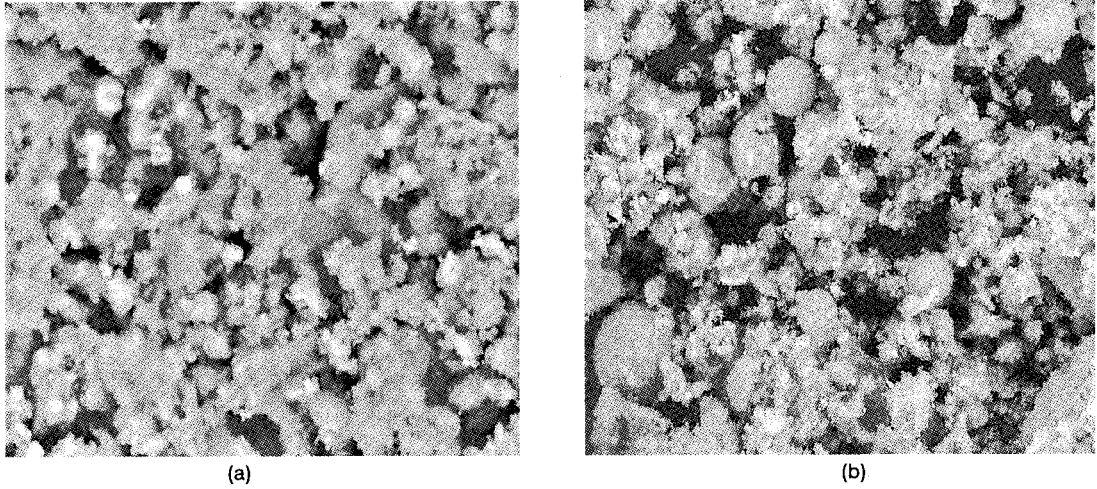
(a)　　　　　　　　　　　　　　　　　　(b)

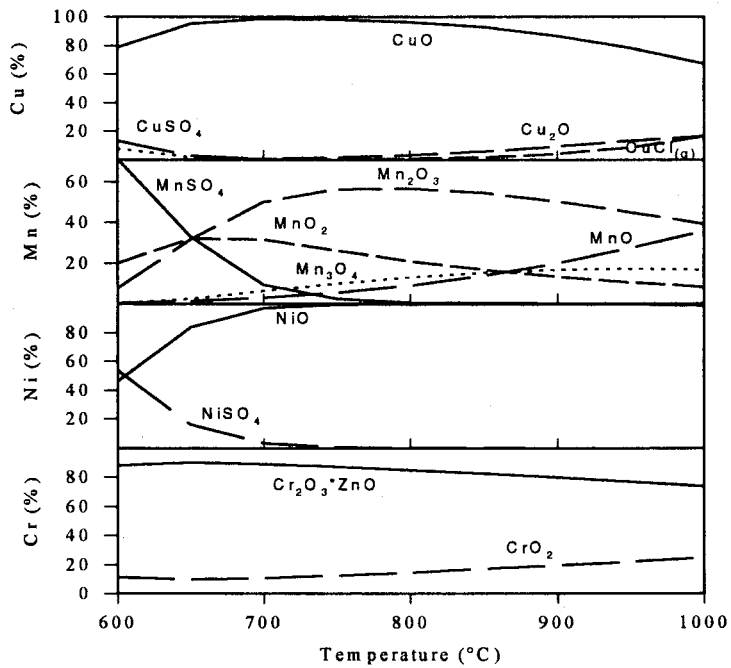Fig. 4   SEM micrographs of bottom ash (a) and bag filter ash (b) samples from test 5.

Fig. 5   Predicted effect of temperature on Cu, Mn, Ni, and Cr speciation
in the combustion chamber during test 5.

Table 8   Metal concentrations (mean ± standard deviation, mg/kg) in feed sludge and in solid residues of rotary kiln incineration tests (test 4 and test 5).

test 4

Metal	Feed sludge	Sludge metal concentration referred to fixed solids	bottom ash	Measured in heat exchanger. ash	filter ash
Ni	39.4 ± 7	123	100 ± 14	109 ± 4	111 ± 5
Mn	102 ± 6	318	341 ± 8	293 ± 4	291 ± 5
Cr	115 ± 4	358	319 ± 10	360 ± 14	337 ± 9
Cu	474 ± 11	1,477	1,402 ± 126	1,565 ± 31	2,004 ± 96
Zn	2,089 ± 69	6,508	2,549 ± 46	13,114 ± 887	28,133 ± 1,705
Pb	151± 7	470	156 ± 9	1,098 ± 14	1,662 ± 83
Cd	3.7 ± 1	11.5	<1	33.3 ± 1	35.4 ± 3

test 5

Metal	Feed sludge	Sludge metal concentration referred to fixed solids	bottom ash	Measured in cyclone ash	filter ash
Ni	19.2 ± 4	64	97.4 ± 5	82.6 ± 11	85.9 ± 2.4
Mn	91.2 ± 5	302	301 ± 14	302 ± 8	253 ± 6
Cr	94.7 ± 5	314	400 ± 15	405 ± 13	389 ± 10
Cu	248 ± 18	821	835 ± 88	525 ± 22	891 ± 29
Zn	1,363 ± 69	4513	1,784 ± 78	4,918 ± 97	32,503 ± 2,891
Pb	127 ± 2	421	32.7 ± 4	497 ± 15	6,707 ± 150
Cd	3.7 ± 2	12.3	2.8 ± 0.3	24.6 ± 3	429 ± 12

zinc speciation in the combustion chamber is greatly affected by the redox conditions. At 900°C, for example, the thermodynamic model predicts (Figure 7) the predominance of the reduced gaseous species $Zn_{(g)}$ over solid oxide when the oxygen input to the model system is decreased. On the basis of these considerations locally reducing conditions, due to inhomogeneities in the rotary kiln incinerator, may satisfactorily explain the observed discrepancies. Similar considerations have been also reported by Verhulst et al. to explain zinc behaviour in municipal incineration furnaces[11]

CONCLUSIONS

The pilot tests evidenced that the standards at the stack can be met: detected concentrations for different parameters (heavy metals and organic mic-

ropollutants) were generally of three order of magnitude lower than limit values. Some operational problems were however evidenced, particularly with regard to the feeding system, possible clogging of the dryer and slag formation in the rotary kiln furnace when in co-current operation.

The partition of seven metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn) was monitored in the two tests using the rotary kiln furnace. The experimental results show two distinctive metal behaviours, that are independent of sludge water content and of flow conditions (co-current vs. counter-current). A first group of metals (Cr, Cu, Mn, Ni) evenly partition between bottom residue and fly ash. In contrast, the remaining three metals (Cd, Pb, Zn) show enrichment in the fly ash by one or two order of magnitude with respect to concentrations in the bottom ash. A comparison between experimental results
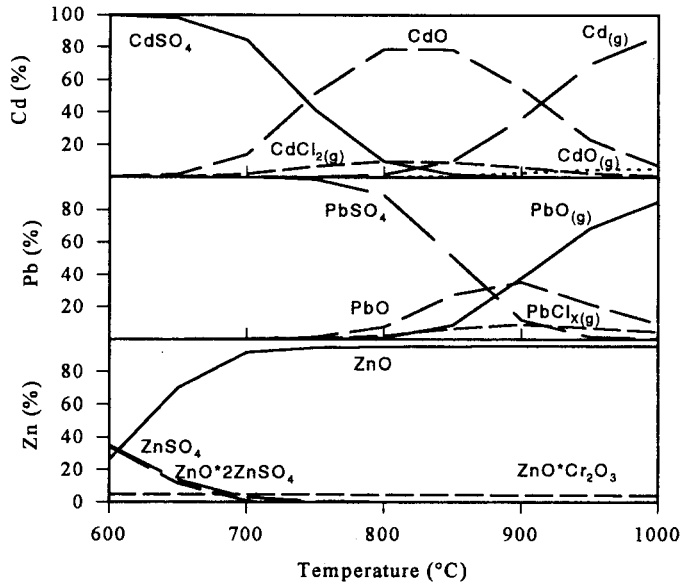
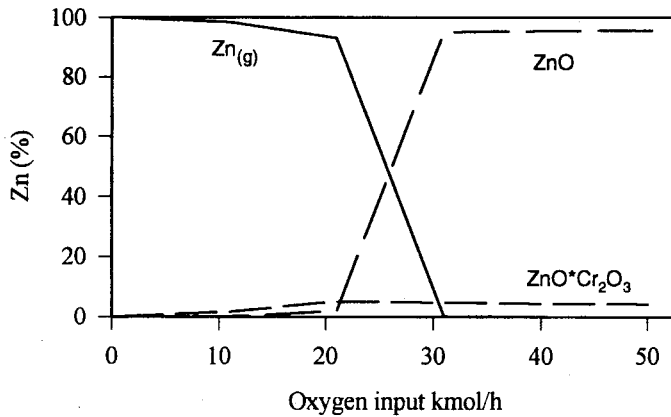Fig. 6　Predicted effect of temperature on Cd, Pb, and Zn speciation in the combustion chamber during test 5.

Fig. 7　Predicted effect of redox conditions (oxygen input) on Zn speciation at 900℃.

and model predictions, based on the assumption of equilibrium conditions in the combustion chamber, suggests that the thermodynamic model may satisfactorily predict the behaviour of "non volatile" metals like Cr, Cu, Mn, Ni, as well as the behaviour of "volatile" Cd and Pb. In contrast, the experimental zinc enrichment is not explained by the thermodynamic model, where perfect mixing in the combustion chamber is assumed. A reasonable explanation of the clear discrepancy about zinc behaviour may be the hypothesis that inhomogeneities in the rotary kiln incinerator likely induce locally reducing conditions, even in the presence of large excess air. The thermodynamic model predicts that in such reducing conditions zinc volatilises as Zn (g). The results of this work suggest that calculation of thermodynamic equilibria may help understanding metals behaviour during

incineration. The practical validity of model predictions, however, may be limited by the simplifying assumptions of the thermodynamic model.

Results of lab-scale investigation carried out to study the influence of several process variables simulating failure modes (thermal, temporal and fuel-oxidant mixing) on the PICs formation during hazardous sludge incineration mainly indicate that:

- at an afterburning temperature of 600℃ a large number of compounds are formed and no effects of both oxygen excess and afterburning residence time are observed. By increasing the afterburning temperature, the number of PICs emitted decreases;

- the influence of oxygen excess becomes evident when the afterburning temperature is higher than 700℃. In fact, at $\Phi = 1.3$ (30% excess oxygen) some PICs, including benzene, benzonitrile and naphthalene, are detected even at 1100℃ while at $\Phi = 2.6$ no organic compounds are detected at 900℃;

- the effect of residence time is detectable at an afterburning temperature of about 800℃ and $\Phi = 2.6$.

On the basis of the results obtained it is possible to assess that lab-scale incineration evaluations can be used to obtain information for reducing toxic organic emissions in full-scale incinerators. Above considerations allow to conclude that the operating conditions of a full scale plant for hazardous sludges incineration should be based on afterburning temperatures higher than 900℃ and the establishment of an oxidant atmosphere with at least 150% of excess oxygen. If the afterburning temperature decreases to 800℃ the residence time remarkably influences the plant performance: a residence time of at least 3 s is then needed to guarantee disappearance of PICs in the emissions.

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