



Case study

Partitioning characteristics of targeted heavy metals in IZAYDAS hazardous waste incinerator

Mithat Bakoglu, Aykan Karademir*, Savas Ayberk

Department of Environmental Engineering, University of Kocaeli, Kocaeli, Turkey

Received 12 January 2002; received in revised form 24 December 2002; accepted 29 December 2002

Abstract

Partitioning of eight targeted heavy metals (Cr, Mn, Cu, Pb, Sn, Co, Ni and Zn) was carried out during five trial burns in Izmit hazardous and clinical waste incinerator (IZAYDAS). Metal contents of the original wastes and their concentration in the bottom ash (BA), fly ash (FA), filter cake (FC) and flue gas were determined. Partitioning behavior of metals during the two-stage incineration was evaluated with respect to physico-chemical properties of feed waste and metals, and the operational conditions. Results suggest that combustion temperatures and retention times are the dominant parameters determining the volatility of metals in the first combustion chamber. Targeted metals were generally partitioned in the rank of bottom ash, filter cake, fly ash and flue gas. High filter cake/fly ash ratios showed that high temperatures in the second stage increase both the formation of gaseous metallic compounds and the enrichment of metals in fine particles. Since ESP could not be effective in removing fine particles and volatilized metallic compounds, the necessity of an additional system that would remove heavy metals efficiently was emphasized for the modern incinerators.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Incineration; Hazardous wastes; Heavy metals; ESP; Wet scrubbers

1. Introduction

Although the incineration technology has been used for the disposal of municipal and hazardous (industrial or clinical) wastes for a long time in the world, it is rather a new topic for Turkey. The first, and for the present, the only incinerator in Turkey is Izmit hazardous and clinical waste incinerator (IZAYDAS) which was built in Izmit, the most industrialized area of Turkey. IZAYDAS incinerator was built by Lurgi GmbH, Germany in Solaklar Village, Izmit and started to operate in December 1997. At this time, some strict legislative controls had been introduced by the European Commission due to the environmental risks

* Corresponding author.

caused by the incinerators and the public concern over emissions of pollutants such as particles, heavy metals, acid gases, and especially dioxins. These strict legislative controls and emission limits have been adopted by Turkish Ministry of Environment.

This study aims to evaluate the partitioning of eight targeted heavy metals (Cr, Mn, Cu, Pb, Sn, Co, Ni and Zn) into flue gas, filter cake (FC), fly ash (FA) and bottom ash (BA) by presenting the results obtained during five trial burns conducted at different dates in 2000. These tests have been carried out in the plant since it started operating, as a legal requirement for licensing by the ministry. The main objective was to determine and assess the emissions (especially PCDD/F and heavy metal releases to atmosphere) of the plant, but detailed analyses of wastes and solid residues were also performed to observe the fate of metals, halogens, etc. in the incinerator.

Since the partitioning of heavy metals in the incinerator systems depends on the combustion conditions like temperature, retention time, etc. as well as some physico-chemical properties of heavy metals, similarities and differences in the behavior of heavy metals in pilot and real incinerator studies have a great importance both in predicting the behavior of metals and in designing incinerator systems.

2. Information about the plant

Schematic diagram of the plant is shown in Fig. 1. The capacity of the plant is 35,000 tonnes per year. It has a two-stage combustion system consisting of a rotary kiln and a vertical shaft. Industrial and clinical wastes in solid and liquid forms are combusted in the plant. The dimensions of the rotary kiln are 12 m in length and 4.2 m in diameter, with combustion temperatures in the range of 950–1050 °C (set point is 1000 °C) and a retention time of 2–2.5 h for solids. The slag produced in rotary kiln is taken to an ash quench chamber to contact with water for 10 min, and then it is transferred to landfill site by a bunker after sampling. The second stage combustion occurs in the vertical shaft with 12 m height and 4.1 m diameter. This unit serves as a post-combustion chamber, equipped with independent burners and fans, ensuring complete destruction of hazardous organic compounds. The gases produced in rotary kiln, vapors of ash quench chamber and some liquid wastes are incinerated in this vertical shaft, with a retention time of about 2 s at 1150–1250 °C (set point is 1100 °C). Air pollution control system consists of an electrostatic precipitator (ESP) and two-stage venturi scrubber. An additional activated carbon unit for the removal of organic gases, especially dioxins and furans was built, but it was not in the operation during the tests.

Stack gases leaving the ESP enter the first stage venturi scrubber. In the scrubber, HCl, HF and heavy metals together with the fine particulate matter escaping ESP are removed in the acidic environment (pH range is between 1 and 2). A two-stage pulverization washing is used here and the utilization rate of the washwater is 170 m³/h. Then the flue gases enter the second stage wet scrubber in which the gas comes into contact with the lime solution again to remove SO₂, organic gases and any remaining pollutants. Flue gases pass through two washing steps in two different levels and 500 m³/h washwater is used in each step. The wastewaters from the scrubbers are treated chemically by coagulation–flocculation–sedimentation processes.

The solid residuals generated by the incinerator are classified in three parts: (i) bottom ash representing the mixture of slag of rotary kiln and bottom ashes of vertical furnace; (ii) fly

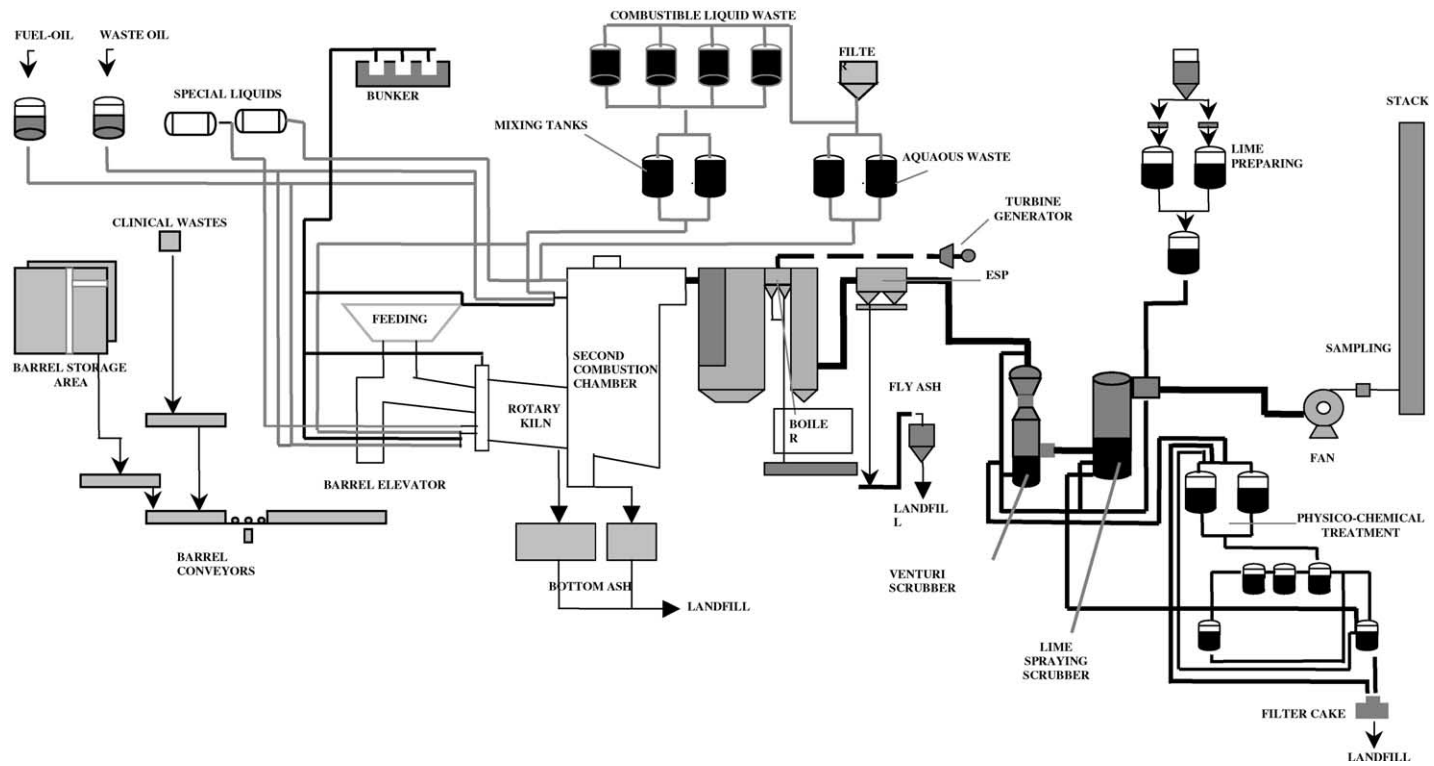


Fig. 1. IZAYDAS incinerator process flow scheme.

ash containing the particles collected from electrofiltration of flue gas and the particles accumulated in boiler; and (iii) filter cakes, which are produced by the chemical treatment of the wastewaters from both scrubbers. Since the incineration of most wastes takes place in rotary kiln, almost all of the bottom ash is comprised of the slag of rotary kiln. Metals removed in two-stage scrubbers are both in gas form (as vaporized organometallic compounds, metal chlorides, etc.) and in solid form, as bound on ultrafine particles escaping ESP.

These solid residues are, in general, heterogeneous materials resulting from complex processes occurring during the incineration and the raw gas treatment. ESP ashes contain original fuel materials that have been mechanically transferred into the flue gas as well as condensate species found on the surfaces of fly ash particles, which result from the condensation of volatile species during the cooling phase of the flue gas inside the boiler. Filter cakes or wet scrubber residues contain salts from the neutralization of acid gases, mercury-bearing compounds, and other volatile-rich metal compounds depending on the particle slip of the filter. Since fine particles that mainly pass the filter are enriched in volatile metals, filter cakes determine the efficiency of the process, and are therefore important to characterize.

3. Experimental methods

Metals were analyzed in bottom ash, fly ash, filter cake and flue gas. Analyses in bottom ash, fly ash and filter cake were made by inductively coupled plasma atomic emission spectroscopy (ICP/AES) (Spectra) at IZAYDAS Laboratory after acidic digestion based on the analytical method of DIN 38406-E22 and expressed on weight basis (weight of metal to total dry weight of sample). Samples of bottom ash, fly ash and filter cake were taken according to TS 12090 and ICS 13.03.10. For each group, a sample of 2 kg was taken, dried for 24 h at 105 °C and homogenized by mixing. Then 3 g samples of each group were digested with 50 ml HNO₃:HCl mixture at 3:1 by volume for 24 h before ICP/AES analysis.

Flue gas was sampled according to US EPA MM5 method. Sampling train included a stainless steel probe, three impinger solutions of 100 ml 0.1 M HNO₃ (submerged in an ice bath), silica gel and an isokinetic sampler (ZAMBELLI 6000 PLUS). A flue gas volume of 2 Nm³ was taken in 3–4 h in each test. Samples were analyzed directly by ICP/AES and results were expressed as mg/Nm³ (11% O₂).

Analysis of waste composition was made in IZAYDAS Laboratory. Samples from solid wastes were taken according to TS 12090 and ICS 13.03.10, while samples of liquid wastes (special liquid wastes, waste oils, etc.) were taken according to TS-ISO 5667-5–10. Metals were analyzed in the same manner for each waste type. Chloride, sulfur, fluoride, iodide, bromide and phosphorus were analyzed by ion chromatography based on DIN EN ISO 10304-2 method.

4. Results and discussion

Partitioning behavior of metals mainly depends on combustion temperatures, but S/Cl content of wastes, other operational conditions and physico-chemical properties of heavy

metals and compounds formed during combustion could have a significant role. Therefore, the results of the performance tests should be evaluated separately by taking into account the characteristics of wastes and operational conditions in each test with respect to reaching general results.

4.1. Waste composition

A general summary of waste properties, amounts, combustion temperatures and flue gas compositions in tests are shown in [Table 1](#). Industrial wastes are various solid wastes coming from different industries and fed to rotary kiln by bunker. Their calorific values lie between 12,000 and 17,000 kJ/kg. Clinical wastes include wastes in tablet or powdered forms and their plastic packages, with calorific values between 11,000 and 16,000 kJ/kg. Other wastes represent certain industrial solid and liquid wastes fed in barrels. Their calorific values change according to type of waste, from about 1000 kJ/kg for emulsion oil in Test 4 to about 35,000 kJ/kg for waste thinner in Test 1. Waste oil fed to vertical furnace serves as auxiliary fuel, according to its calorific value that could be sometimes as high as 40,000 kJ/kg based on the quality and water content of the oil.

4.2. Partitioning of metals

Partitioning of metals was examined by measuring the metal contents in bottom ash, fly ash, filter cake and flue gas. Fate and behavior of metals during combustion processes were examined in many research studies [1–20]. Additionally, a number of simulation studies have been performed by using the thermodynamic models based on the minimization of the Gibbs' free energy for a system [7,10,14,20–23]. These models enable the prediction of potential metal reactions and the existing phases as a function of process variables such as temperature, contents of chlorine and other reactants in the system. Wichmann et al. [24] presents a detailed review of many metal-partitioning investigations based on model simulations and pilot-scale and real incinerator studies. The studies showed that combustion temperature is the major parameter determining the metal volatility, although there might be a number of other factors having significant effects in waste incinerators. Therefore, incineration tests were classified based on the main factors affecting metal partitioning (see [Table 2](#)).

The classification in [Table 2](#) was made according to average values for comparison of metal behaviors in the tests. Retention time was accepted as a function of waste amount fed to the rotary kiln. [Table 3](#) shows the results for metals in flue gas, bottom ash, filter cake and fly ash. Moisture contents of the residuals ranged between 30.5 and 35.0% for filter cake, 1.5 and 8.9% for fly ash, and 28.0 and 37.7% for bottom ash. Mass balance calculations for metals (input being the wastes and output being the sum of flue gas, filter cake, fly ash and bottom ash) showed a good and acceptable confirmation for the reliability of the results. Output/input ratio was between 0.73 and 1.29 in Test 1; 0.72 and 1.29 in Test 2; 1.04 and 1.13 in Test 3, 1.02 and 1.27 in Test 4 and 0.95 and 1.01 in Test 5. Metal concentrations in the flue gas were ranged between 0 and 0.04 mg/Nm³, which were too below the metal emission limit of 0.5 mg/Nm³ in Turkey. In partitioning of the metals, the portion emitted to the atmosphere by flue gas did not exceed 0.4% for all metals studied in all tests. The

Table 1
Waste properties, operational conditions and flue gas compositions in the tests

	Test 1	Test 2	Test 3	Test 4	Test 5	Average
Waste types						
Solids to rotary kiln (kg per day)						
Industrial wastes	30910	39634	13527	20621	43630	
Clinical wastes	5774	163	621	–	5807	
Other	–	3666	1547	2268	2998	
Liquids to rotary kiln (kg per day)						
Industrial liquids	1750	1826	2957	1048	4255	
Liquids to vertical furnace (kg per day)						
Waste oil	10563	20662	7732	7000	11005	
Total	48997	65951	26384	30937	67695	47993
Average combustion temperatures (°C)						
Rotary kiln	990	923	916	969	1109	981
Vertical furnace	1069	959	1073	1041	1116	1052
Flue gas composition ^a						
Flow rate (Nm ³ /h)	20350	24500	10100	14900	27000	19370
O ₂ (%)	8.05	7.16	7.72	7.35	9.93	8.04
CO ₂ (%)	6.97	6.85	7.13	7.20	7.27	7.08
CO (mg/Nm ³)	0.79	0.77	0.81	0.83	0.60	0.76
SO ₂ (mg/Nm ³)	0.33	0.91	1.40	0.89	1.17	0.94
NO ₂ (mg/Nm ³)	123.1	111.7	135.4	127.2	146.0	128.7
Particles (mg/Nm ³)	1.05	1.27	1.12	1.03	0.79	1.05
Moisture (%)	18.9	17.8	18.3	19.1	17.5	18.3
Chemical composition of wastes (% w/w) ^b						
Moisture	32.7	34.9	36.1	36.8	31.2	34.3
Cl	0.18	1.58	0.31	0.43	3.14	1.127
S	0.11	0.49	0.81	0.18	0.66	0.448
Cr	0.011	0.010	0.024	0.022	0.028	0.019
Mn	0.032	0.050	0.062	0.056	0.032	0.046
Cu	0.212	0.175	0.320	0.080	0.263	0.210
Ni	0.114	0.125	0.181	0.045	0.177	0.128
Pb	0.023	0.033	0.095	0.024	0.055	0.046
Sn	0.010	0.006	0.015	0.010	0.015	0.012
Co	0.010	0.012	0.028	0.012	0.018	0.016
Zn	0.820	0.720	0.621	0.446	0.823	0.686

^a Average of on-line measurements during the sampling.

^b On dry basis.

Table 2
Classification of incineration tests

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5
First stage temperature	Moderate	Low	Low	Moderate	High
Second stage temperature	Moderate	Low	Moderate	Moderate	High
Retention time	Moderate	Short	Long	Long	Short
Cl content	Low	High	Low	Low	High
S content	Low	Moderate	High	Low	High

Table 3
Metal contents of filter cake, fly ash and bottom ash in tests

	Test 1	Test 2	Test 3	Test 4	Test 5	Average
Filter cake (kg per day)	8820	4987	8800	9460	9440	8301
Fly ash (kg per day)	1126	1517	606	711	1556	1103
Bottom ash (kg per day)	15990	28016	5998	7535	14313	14370
Metal concentration (% w/w)						
Cr						
FC	0.051	0.025	0.039	0.042	0.062	0.044
FA	0.023	0.024	0.042	0.048	0.020	0.031
BA	0.003	0.017	0.045	0.027	0.087	0.036
Mn						
FC	0.080	0.099	0.103	0.083	0.145	0.102
FA	0.029	0.036	0.034	0.024	0.026	0.030
BA	0.050	0.066	0.112	0.119	0.053	0.080
Cu						
FC	0.552	0.502	0.397	0.089	0.829	0.473
FA	0.520	0.320	0.321	0.748	0.568	0.495
BA	0.301	0.317	0.746	0.113	0.596	0.415
Ni						
FC	0.239	0.310	0.196	0.065	0.603	0.283
FA	0.165	0.178	0.117	0.321	0.124	0.181
BA	0.200	0.225	0.460	0.066	0.417	0.274
Pb						
FC	0.028	0.050	0.098	0.005	0.197	0.076
FA	0.610	0.562	0.420	0.472	0.398	0.492
BA	0.009	0.041	0.220	0.045	0.076	0.078
Sn						
FC	0.015	0.015	0.010	0.010	0.018	0.014
FA	0.065	0.075	0.018	0.045	0.046	0.050
BA	0.017	0.009	0.048	0.023	0.049	0.029
Co						
FC	0.032	0.020	0.052	0.032	0.032	0.033
FA	0.018	0.018	0.011	0.022	0.028	0.019
BA	0.010	0.023	0.052	0.012	0.072	0.034
Zn						
FC	0.421	0.325	0.530	0.245	0.242	0.352
FA	0.520	0.785	0.385	0.420	0.895	0.601
BA	2.220	1.550	1.847	1.452	3.495	2.113

metal with the highest emitted fraction was Sn with an average of 0.22%. Emitted fraction of metals was neglected in partitioning studies.

Since waste characteristics and operational conditions were different, partitioning of metals in each test could be different. As shown in Table 2, the most similar tests with respect to waste characteristics and operational conditions were Tests 1 and 4. Figs. 2 and 3 show the partitioning of metals in bottom ash, fly ash and filter cakes in these tests.

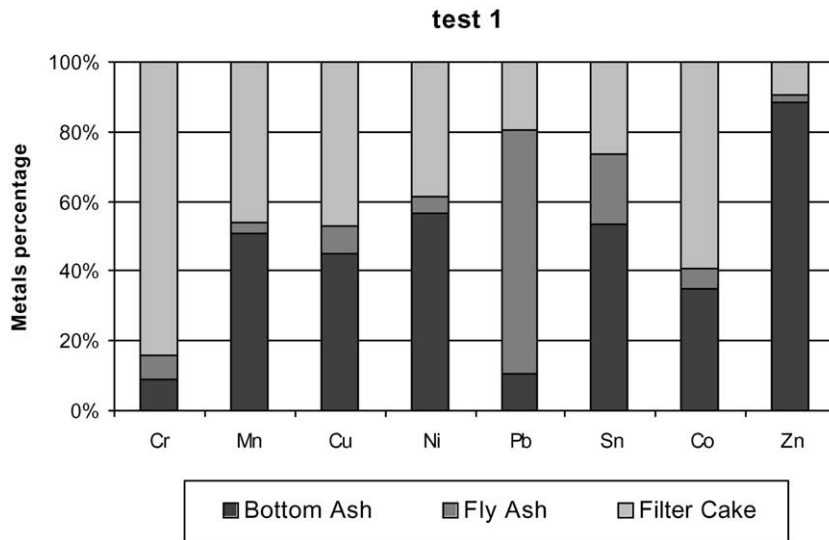


Fig. 2. Distribution/partition of metals in Test 1.

Figs. 2 and 3 show that metals demonstrated similar distribution between bottom ash, fly ash and filter cakes in similar tests, although percentages of residuals were different for some metals (especially Cr, Pb and Ni). Accepting fly ash and filter cake fractions as volatile, volatilization ratio of Cr and Pb was higher in Test 1, while that of Cu, Ni and Co

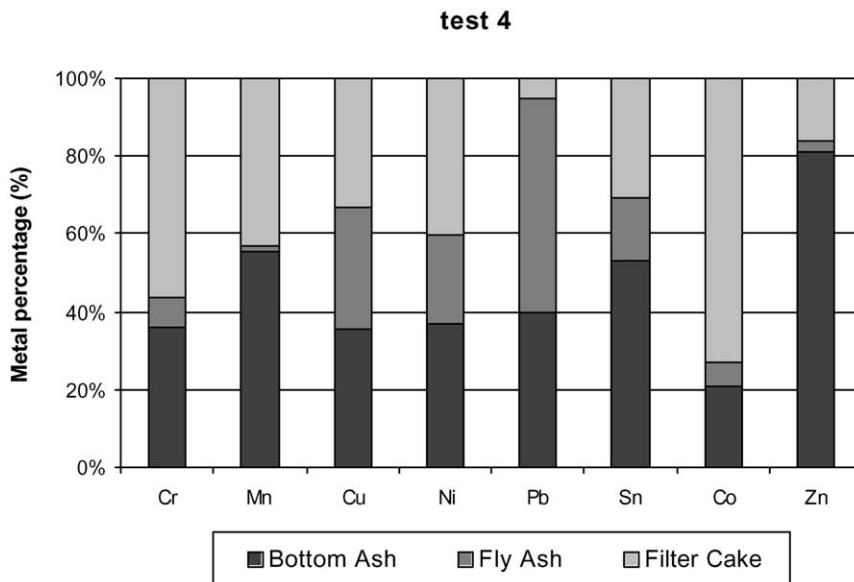


Fig. 3. Distribution/partition of metals in Test 4.

was higher in Test 4. Average distributions of these eight metals between bottom ash, fly ash and filter cakes in Tests 1 and 4 were very close: 44, 15 and 41% for Test 1 and 45, 18 and 37% for Test 4, respectively, leading to almost equal average volatilization ratios (56 and 55%). However, the waste amount in Test 1 was about 1.5 times more than the waste in Test 4 (Table 1), which could cause less volatilization of metals due to the retention time. This was possibly caused by the differences in waste types in tests. In Test 1 the wastes other than bunker were clinical wastes and waste thinner with high calorific values between 10,000 and 35,000 kJ/kg, while the wastes in Test 4 were contaminated iron sheet barrels and emulsion oil with calorific values about 1000 kJ/kg. Distribution of heavy metals in other tests was somewhat different due to the differences in temperature, retention time, etc. whose effects are evaluated below.

4.3. Effect of kiln temperature on metal partitioning

Since the extent of evaporation of the metals and metal compounds in the furnace is directly related to combustion temperature, it is the key parameter for metal partitioning in incinerators. Highly volatile metals such as mercury and cadmium start to volatilize at the temperatures as low as 200 °C. It is believed that operating temperature in an incinerator should be higher than 850 °C to minimize dioxin formation [1,3,6,25–27]. However such high temperatures increase volatilization of hazardous metals and lead to adverse environmental effects. PCDD/F emission rates of IZAYDAS and their relationship with the combustion temperatures were reported by Bakoglu et al. [28].

Having similar properties, Tests 2 and 5 could be used to compare temperature effects on partitioning (see Table 2). Metal distribution in bottom ash, fly ash and filter cakes in these tests is shown in Figs. 4 and 5.

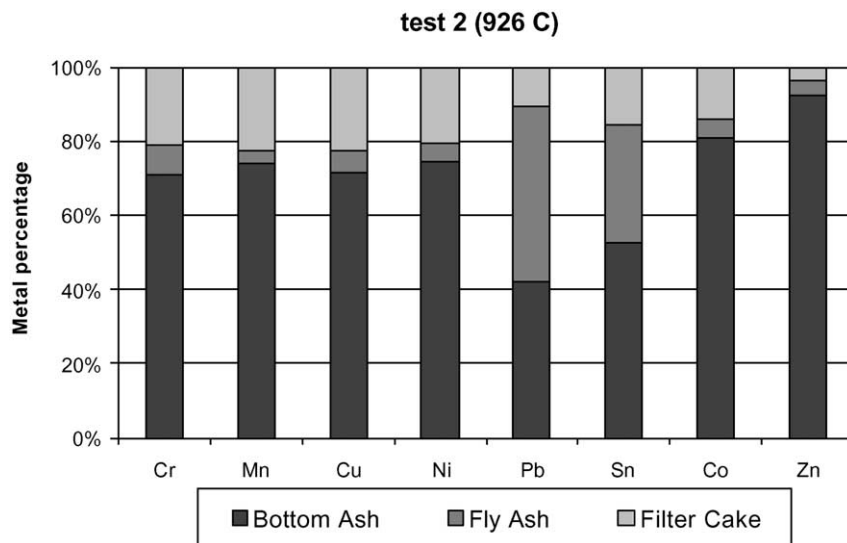


Fig. 4. Distribution/partition of metals in Test 2.

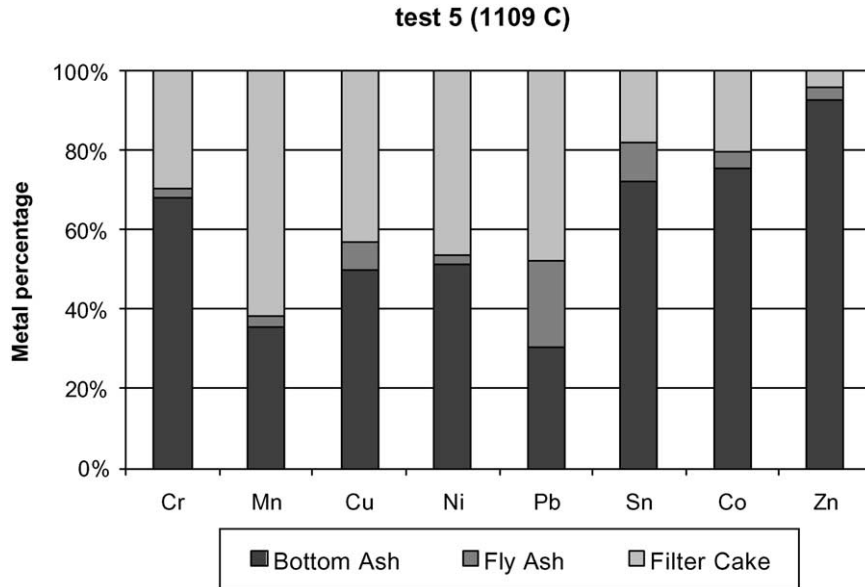


Fig. 5. Distribution/partition of metals in Test 5.

Results indicate that lower kiln temperatures in Test 2 caused all the metals except Pb, the most volatile one, to be retained mostly in bottom ash, leading to an average volatilization ratio of 30%, the least value observed in the tests. Bottom ash fraction of Pb in Test 2 was 42%, and it represents the highest bottom ash percentage for Pb. Similarity of partition behavior of all metals other than Pb in Test 2 confirms the conclusion of Corella and Toledo [4], stating the predominance of operational conditions on the fate or partitioning of the metals for a given test. In Test 5, 41% of the metals was transferred into combustion flue gas. Since Cl content was high in both of the tests, increased volatilities of metals (especially Pb, Cu and Zn) at elevated temperatures through the low-boiling point chlorides could be expected. Temperature effect is obvious for Pb, Cu, Mn and Ni with volatilities 1.5–2 times higher than those of Test 2, while other metals except Sn showed no significant changes in partitioning behavior.

4.4. Effect of retention time on metal partitioning

Another operational parameter affecting the fate of metals is retention time of the wastes in combustion zone. By taking it as a function of waste quantity fed to the rotary kiln, two low-temperature tests with different waste loadings, Tests 2 and 3, could be compared to determine retention time effects. Another reason for choosing these tests in spite of differences in waste Cl content was the similarities in types and heating properties of the wastes used in the tests. Rotary kiln temperatures were almost the same, while the waste feed in Test 2 was as high as 2.5 times the waste feed in Test 3. Metal partitioning in Test 3 is shown in Fig. 6.

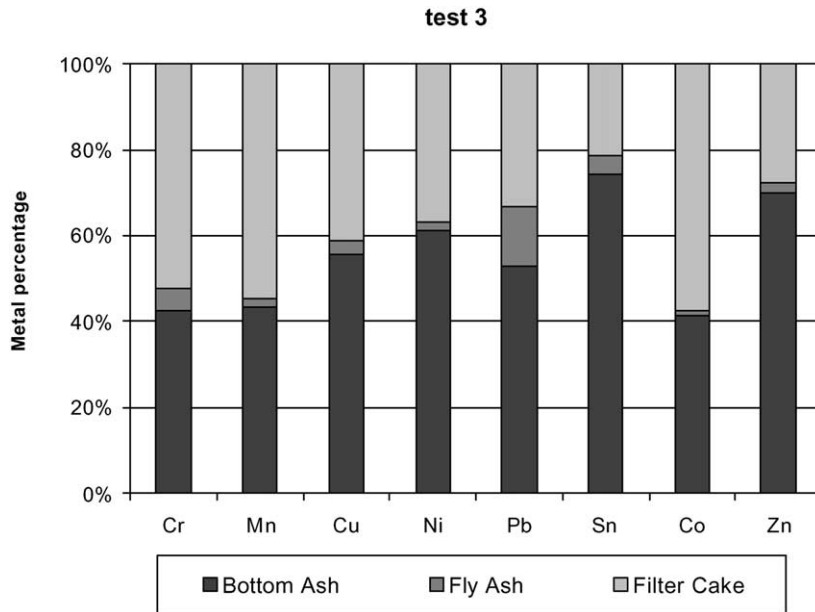


Fig. 6. Distribution/partition of metals in Test 3.

A comparison between Figs. 4 and 6 gives the effect of retention time on partitioning. All the metals other than Pb and Sn showed higher volatilities in Test 3, leading to an average volatilization ratio of 45%, as compared to 30% in Test 2. Another comparison could be made between Test 4 with moderate kiln temperature and long residence time and Test 6 with high temperature and short residence time. Although kiln temperature and waste Cl content was higher in Test 6, 41% of metals was transferred into flue gas, while this ratio was 55% in Test 4. Therefore, it could be said that the higher the amount of waste, the larger the fraction of metal that is retained in bottom ash.

4.5. Effect of waste Cl and S content on metal partitioning

Heavy metals react with other elements such as O₂, Cl and S to form different compounds (oxides, chlorides, sulfates) at high temperatures during incineration process. Phases and possible secondary reactions of these compounds could have a significant role on metal partitioning. The presence of waste-derived Cl enhances volatilization by formation of metal chlorides that are typically more volatile than metal oxides, and therefore increases toxic metallic emissions. Chloride formation in an incineration system depends on many factors: Cl/metal ratio, temperature, affinity of metal to Cl, presence of hydrogen, carbon, sodium, etc. [5,6,10,14,16,18,22,24]. Sulfur, on the other hand, reduces the volatilization by formation of stable metal sulfates that displace the chlorides and oxides at low temperatures; while volatile sulfides may appear at high temperatures, particularly under reducing conditions [6,10,18,22,24].

In IZAYDAS tests, effects of Cl and S were not apparent due to the predominance of physical factors including temperature and retention time. Two high-Cl tests (Tests 2 and 5) showed lower metal volatilization rates as compared to other low-Cl tests, as a result of higher feed rates. Test 4 had the same average metal volatility rate with Test 1 with similar temperature but higher waste feed; although Cl and S contents of the waste feed in Test 4 were 2.5 and 1.5 times higher than those in Test 1, respectively. These results suggest that kiln temperature and retention time prevail over waste Cl/S content in determining metal volatilization in IZAYDAS. Moreover, volatilization rates of metals are in contradiction with thermo-chemical estimates of simulation models. In Test 6, for example, elevated metal volatilities would be expected due to the highest Cl/metal ratios (on molar basis) and kiln temperatures in the tests; however, they showed lower values than those in low-Cl tests. The main explanation of this discrepancy is that the pre-conditions of these equilibrium models (complete mixing of reactants, unlimited residence time, etc.) are not reached in reality [24]. Reactor configuration is another reason, since rotary kiln is a highly heterogeneous environment causing incomplete mixing and local differences in temperature and reagent concentrations [10,18]. Difficulties related with the incineration of solid wastes (poor mixing, requirement of long residence times for complete combustion, etc.) should also be considered. Since solid wastes contain most of the metals, penetration of the outside temperature into the furthest point inside the solid, i.e. the center, could take longer times than the theoretical ones, leading metals to be retained in bottom ash, even if the physical and chemical conditions are suitable for volatilization. Therefore, the part of metals retained in bottom ash is usually larger than that estimated by models or found in pilot-scale tests with artificial wastes. The presence of other elements with affinity to chlorine (H, Na, Mg, K, Ca, Ba, Al, Si, Fe, etc.) has an effect also, by decreasing available Cl for formation of volatile metal chlorides [5,10,12,14,16,20,24]. A study on Cl-distribution in residues of IZAYDAS [29] shows that 65–95% of the waste Cl is retained in bottom ash, indicating much less free Cl in the system.

4.6. Average distribution of metals in residues

Fig. 7 shows the average metal distribution of targeted heavy metals in the tests. As shown in Fig. 7, metals are retained mostly in bottom ash, with the exception of Cr and Pb. Larger bottom ash fractions as compared to fractions of other residues have commonly been observed for majority of the metals except for some volatile metals such as mercury, cadmium, and to some extent, lead and zinc, particularly in solid waste incineration studies [1,5,6,12,14,20].

The distribution of metals in APCE residues is directly related to the particulate removal by APCE, since most metals eventually end up in the particulate phase by condensation/nucleation processes during the flue gas cooling prior to APCE [1,3,4,18,20,21]. Previous studies showed that metals tend to be concentrated in finer fractions [12,21,24,30,31]. Wichmann et al. [24] states that both heterogeneous condensation and reaction processes of metal species taking place on the surface of particle result in an enrichment of metals in the fine particles, while homogeneous condensation (nucleation) enables the formation of new particles $< 1 \mu\text{m}$ from the gas phase. Electrofiltration removes larger fly ash

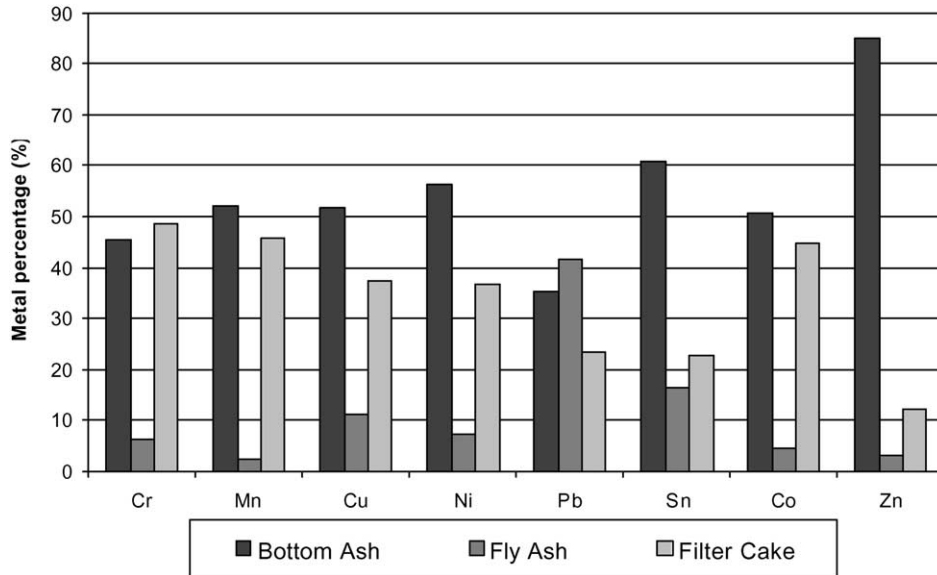


Fig. 7. Average distribution/partition of metals in tests.

particles but is less efficient for vapor and finer particles. Additionally, it is likely that some of the fine and ultrafine particles escaped ESP remained aerosolized in the flue gas. Since fine particles that mainly pass the filter are enriched in volatile metals and removed by wet scrubbers, filter cakes determine the efficiency of process and are therefore important to characterize.

All metals other than Pb showed much less ESP ash fractions (ranging between 2.4 and 16.2%) as compared to filter cake fractions (see Fig. 7). This suggests that metals at the exit of second stage vertical shaft are generally in gaseous forms or bounded to the finer particles that could not be removed by ESP, confirming the enrichment of metals in fine and ultrafine particulate fractions. Such high enrichment in fine particles could be related with two-stage combustion system of the plant. Niessen [2] reported that staged combustion systems exhibit the fine particle enrichment process. The particles dragged by gas flow are exposed to a second combustion process and, since the temperatures are higher in second stage, further vaporization of the metals by the effect of temperature (decreasing the adsorption of heavy metals on particles [16]), and breaking of large particles to finer ones could be expected. Therefore, as the temperature in the second stage increases, vaporization of metal species (on the particles coming from first stage) and subsequently, metal enrichment in ultrafine particles by condensation processes during gas cooling increases too. For example, the tests with higher second stage combustion temperatures (Tests 3 and 5) produced higher filter cake/fly ash ratios on average for all metals. Consequently, we suggest that the second combustion stage with temperatures above 1000 °C together with the metal enrichment processes is the reason of high metal fractions in filter cake representing metal removal by wet scrubbers. On the other hand, some metals (Pb, Cu, Ni and Cr) had the highest filter cake/fly

ash ratios in high-Cl Test 5. Pb and Cu have been reported to show high affinity to Cl, while this is not valid for Ni and Cr [5,22,24]. Although there are some model predictions showing significant Ni volatilization at high-Cl input at temperatures about 1000 °C (in the form of gaseous NiCl and NiCl₂), experimental studies did not comply with these predictions [10]. Similarly, theoretical equilibrium calculations of Ljung and Nordin [22] predicted that significant amount of gaseous Cr hydroxides and oxohydroxides may form in the temperature above 500 °C, which did not supported by case studies too. However, Zn is known to be medium volatile metal and Zn volatilization increases as Cl input increases [10,24], but no clear effect of Cl on filter cake/fly ash ratios of Zn was observed. This can be explained by high Zn concentrations and retention of most of Cl in bottom ash [29], which leads to lower Cl/Zn ratios and consequently minimizes the effect of Cl on Zn. Verhulst et al. [10] states that there could be some difficulties in complete volatilization of Zn due to its presence in larger quantities in feed waste and stable metal oxides. On molar basis, Cl/Zn ratio ranged between 0.4 and 7.0, and considering that available Cl (that was not retained in bottom ash) never exceeded 35% in IZAYDAS [29], these ratios should be lowered further. However, Chen and Wey [7] stated that formation of gaseous ZnCl₂ increases after Cl/Zn ratio of 5 at 750–1000 °C. This means that most of Zn in the incinerator is found as its elemental form or in the forms of complex oxides, sulfates, etc. all of which are in solid or condensed forms up to temperatures higher than 1000 °C. The studies on the chemistry and mineralogy of the bottom ash and fly ash confirmed the dominance of these compounds [11,12]. Therefore, we suggest that high Zn concentrations in the wastes reduced Zn volatilization during incineration. It was enriched in filter cake, in accordance with the study of Forestier and Libourel [12].

Another comparison between the fractions of fly ash, filter cake and flue gas, which was accepted as negligible, shows that metal removal through APCE takes place in wet scrubbers mostly, indicating the high efficiency of scrubbers in collecting submicron particles and also for gaseous metal compounds. The effect of lime slurry should be concerned here, because some previous studies have shown that scrubbing of the flue gas with lime slurry after the ESP is effective in removing over 99% of most heavy metals [1]. Overall metal removal rates over 99% in IZAYDAS agreed with these studies. On average, wet scrubbers removed 76% of metals in the flue gas. Fig. 8 shows the percentage ratios of elements between fly ash and filter cakes, as a reflection of the partitioning of the metals between particulate and gaseous hosts. The ranking in Fig. 8 demonstrates the removal efficiencies of wet scrubbers for each metal. The distribution of metals between fly ash and filter cake differs from the results of Forestier and Libourel [12] for Pb, Co, Ni and Cr, probably due to the higher metal enrichment in finer particulates promoted by second combustion chamber.

In incinerators combusting hazardous wastes of various industries and clinical wastes, high temperatures are desirable for the complete destruction of organic matter to minimize the formation of toxic organics (dioxins, furans, etc.) during incineration, but they also enhances the metal volatility, resulting in an increase in the release of volatile metallic compounds, which could be also toxic, to the atmosphere. Therefore, from the public health point of view an efficient metal removal system is indispensable in incinerators. Toxicity of these compounds also increases the importance of further studies on the chemical behavior of metals during incineration.

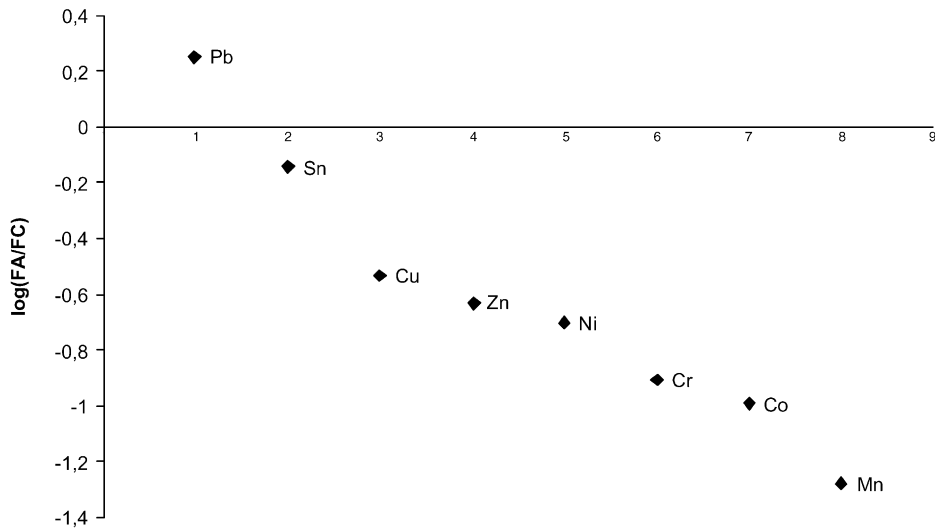


Fig. 8. Distribution of metals between fly ash and filter cakes on average percentage basis.

5. Conclusions

1. In IZAYDAS incinerator, metals are generally partitioned with the rank of bottom ash, filter cake and fly ash. Pb showed the highest fly ash fraction, while Cr has the highest filter cake and Zn has the highest bottom ash fractions.
2. Filter cake fractions between 25 and 50% indicated that metals generally showed high volatilities as compared to literature data. These were attributed to the effect of second stage incineration and high temperatures applied in this stage.
3. Incineration temperatures and retention time are the dominant parameters in metal partitioning. In the first stage, i.e. the rotary kiln, bottom ash fractions of the metals decreases as the temperature and retention time increase.
4. Filter cake fractions representing the volatile part of the metals are related with the combustion temperature in the second stage, i.e. vertical furnace, and retention time. Increasing the temperature and retention time results in an increase in partitioning to filter cake.
5. High-Cl input did not affect the metal volatilization noticeably due to the dominant effects of physical parameters. But it might increase the partitioning to filter cake in the second stage combustion, particularly for the metals with high-Cl affinity like Pb and Cu.
6. Zn showed the least volatility among the metals concerned, although it is known as a medium-volatile metal with a significant affinity to Cl. This was explained by high Zn content in the waste feed, which caused lower Cl/Zn ratios (between 0.4 and 7.0).
7. Low fly ash fractions together with the relatively high filter cake fractions suggested that a higher portion of the metals in the flue gas is in the form of gaseous species or is bound to finer particles that could not be removed by ESP. Concerning possible toxicity

of volatile metallic compounds, an additional removal system other than that for particle removal is necessary to control metal emissions successfully.

Acknowledgements

Literature survey was conducted at the University of Newcastle upon Tyne, in the scope of a Turkish Scientific and Technical Research Institution (TUBITAK)–NATO fellowship program. Authors thank to TUBITAK and NATO for the financial support. Special thanks to Prof. G.K. Anderson (Head of Environmental Engineering Department, University of Newcastle upon Tyne) for his close interest. We also thank IZAYDAS Laboratory for numerous analyses, and Tony Flapjack for revision of the paper.

References

- [1] P.T. Williams, Pollutants from incineration: an overview. Waste incineration and the environment, in: R.E. Hester, R.M. Harrison (Eds.), *Issues in Environmental Science and Technology*, 2, Royal Society of Chemistry, Thomas Graham House, Science Park, Cambridge, UK, 1994 (ISBN: 0-85404-205-9).
- [2] W.R. Niessen, *Combustion and Incineration Processes Applications in Environmental Engineering*, second ed., Marcel-Dekker, New York, NY, 1995 (ISBN: 0-8247-9267-X).
- [3] L.A. Ruth, Energy from municipal solid waste: a comparison with coal combustion technology, *Prog. Energy Combust. Sci.* 24 (1998) 545–564.
- [4] J. Corella, J.M. Toledo, Incineration of doped sludges in fluidized bed. Fate and partitioning of six targeted heavy metals. I. Pilot plant used and results, *J. Hazard. Mater.* B80 (2000) 81–105.
- [5] K.S. Wang, K.Y. Chiang, C.C. Tsai, C.J. Sun, C.C. Tsai, K.L. Lin, The effects of FeCl_3 on the distribution of heavy metals Cd, Cu, Cr and Zn in a simulated multimetal incineration system, *Environ. Int.* 26 (2001) 257–263.
- [6] F.-S. Zhang, S.-i. Yamasaki, M. Nanzyo, K. Kimura, Evaluation of cadmium and other metal losses from various municipal wastes during incineration disposal, *Environ. Pollut.* 115 (2001) 253–260.
- [7] J.-C. Chen, M.-Y. Wey, The effect of operating conditions on the capture of metals with limestone during incineration, *Environ. Int.* 22 (6) (1996) 743–752.
- [8] F. Hasselriis, A. Licata, Analysis of heavy metal emission data from municipal waste combustion, *J. Hazard. Mater.* 47 (1996) 77–102.
- [9] K. Nakamura, S. Kinoshita, H. Takatsuki, The origin and behavior of lead, cadmium and antimony in MSW incinerator, *Waste Manage.* 16 (5/6) (1996) 509–517.
- [10] D. Verhulst, A. Buekens, P.J. Spencer, G. Eriksson, Thermodynamic behavior of metal chlorides and sulfates under the conditions of incineration furnaces, *Environ. Sci. Technol.* 30 (1996) 50–56.
- [11] K.-Y. Chiang, K.-S. Wang, F.-L. Lin, W.-T. Chu, Chloride effects on the speciation and partitioning of heavy metal during municipal solid waste incineration process, *Sci. Total Environ.* 203 (1997) 129–140.
- [12] L. Forestier, G. Libourel, Characterization of flue gas residues from municipal solid waste combustors, *Environ. Sci. Technol.* 32 (1998) 2250–2256.
- [13] C. Holbert, J.S. Lighty, Trace metals behavior during the thermal treatment of paper-mill sludge, *Waste Manage.* 18 (1998) 423–431.
- [14] G. Trouvé, A. Kauffmann, L. Delfosse, Comparative thermodynamic and experimental study of some heavy metal behaviors during automotive shredder residues incineration, *Waste Manage.* 18 (1998) 301–307.
- [15] M.-C. Wei, M.-Y. Wey, J.-H. Hwang, J.-C. Chen, Stability of heavy metals in bottom ash and fly ash under various incinerating conditions, *J. Hazard. Mater.* 57 (1998) 145–154.
- [16] M.-Y. Wey, L.-J. Yu, S.-I. Jou, The influence of heavy metals on the formation of organics and HCl during incineration of PVC-containing waste, *J. Hazard. Mater.* 60 (1998) 259–270.

- [17] K.-S. Wang, K.-Y. Chiang, S.-M. Lin, C.-C. Tsai, C.-J. Sun, Effects of chlorides on emissions of toxic compounds in waste incineration: study on partitioning characteristics of heavy metal, *Chemosphere* 38 (1999) 1835–1849.
- [18] G. Mininni, C.M. Braguglia, D. Marani, Partitioning of Cr, Cu, Pb and Zn in sewage sludge incineration by rotary kiln and fluidized bed furnaces, *Water Sci. Technol.* 41 (8) (2000) 61–68.
- [19] M. Wobst, H. Wichmann, M. Bahadir, Distribution behavior of heavy metals investigated in a laboratory-scale incinerator, *Chemosphere* 44 (2001) 981–987.
- [20] S.S. Thipse, E.L. Dreizin, Metal partitioning in products of incineration of municipal solid waste, *Chemosphere* 46 (2002) 837–849.
- [21] S.K. Durlak, P. Biswas, J. Shi, Equilibrium analysis of the affect of temperature, moisture and sodium content on heavy metal emissions from municipal solid waste incinerators, *J. Hazard. Mater.* 56 (1997) 1–20.
- [22] A. Ljung, A. Nordin, Theoretical feasibility for ecological biomass ash recirculation: chemical equilibrium behavior of nutrient elements and heavy metals during combustion, *Environ. Sci. Technol.* 31 (1997) 2499–2503.
- [23] J.-C. Chen, M.-Y. Wey, J.-L. Su, Two-stage simulation of the major heavy metal species under various incineration conditions, *Environ. Int.* 24 (4) (1998) 451–466.
- [24] H. Wichmann, R. Sprenger, M. Wobst, M. Bahadir, Combustion induced transport of heavy metals in the gas phase—a review, *Fresenius Environ. Bull.* 9 (2000) 72–125.
- [25] M.-B. Chang, Y.-T. Chung, Dioxin contents in fly ashes of MSW incineration in Taiwan, *Chemosphere* 36 (1998) 1959–1968.
- [26] T. van Remmen, Evaluation of the available air pollution control technologies for achievement of the MACT requirements in the newly implemented new source performance standards (NSPS) and emission guidelines (EG) for hospital and medical/infectious waste incinerators, *Waste Manage.* 18 (1998) 393–402.
- [27] K.-J. Shin, Y.-S. Chang, Characterization of polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls and heavy metals in fly ash produced from Korean municipal solid waste incinerators, *Chemosphere* 38 (11) (1999) 2655–2666.
- [28] M. Bakoglu, A. Karademir, S. Ayberk, The Evaluation of PCDD/F Emissions of IZAYDAS Incinerator, in: *Proceedings of ISWA 2002*, vol. 5, Istanbul, Turkey, 2002, pp. 2535–2542.
- [29] S. Cetin, S. Veli, S. Ayberk, An investigation of halogens in İzmit hazardous and clinical waste incinerator, unpublished data.
- [30] J.M. Chimenos, M. Segarra, M.A. Fernandez, F. Espiell, Characterization of the bottom ash in municipal solid waste incinerator, *J. Hazard. Mater.* A64 (1999) 211–222.
- [31] M.B. Chang, C.K. Huang, H.T. Wu, J.J. Lin, S.H. Chang, Characteristics of heavy metals on particles with different sizes from municipal solid waste incineration, *J. Hazard. Mater.* A79 (2000) 229–239.