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Hazardous waste characterization among various thermal processes in South Korea: A comparative analysis

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ABSTRACT

Ministry of Environment, Republic of Korea (South Korea) is in progress of converting its current hazardous waste classification system to harmonize it with the international standard and to set-up the regulatory standards for toxic substances present in the hazardous waste. In the present work, the concentrations along with the trend of 13 heavy metals, F^-, CN^- and 19 PAH present in the hazardous waste generated among various thermal processes (11 processes) in South Korea were analyzed along with their leaching characteristics. In all thermal processes, the median concentrations of Cu (3.58–209,000 mg/kg), Ni (BDL–1560 mg/kg), Pb (7.22–5132.25 mg/kg) and Zn (83.02–31419 mg/kg) were comparatively higher than the other heavy metals. Iron & Steel thermal process showed the highest median value of the heavy metals Cd (14.76 mg/kg), Cr (166.15 mg/kg) and Hg (2.38 mg/kg). Low molecular weight PAH (BDL–37.59 mg/kg) was predominant in sludge & filter cake samples present in most of the thermal processes. Comparatively flue gas dust present in most of the thermal processing units resulted in the higher leaching of the heavy metals.

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1. Introduction

Hazardous waste is defined as a waste possessing one or more of the hazardous properties such as explosive; oxidizing; highly flammable; flammable; irritant; harmful; toxic; carcinogenic; corrosive; infectious; toxic for reproduction; mutagenic; releases toxic gas in contact with water, air or an acid; sentitizing; ecotoxic; capable of yielding another substance which possesses any of the above characteristics after disposal [1].

In South Korea (Republic of Korea), hazardous waste is controlled under the Waste Management Act and it is termed as "designated waste" [2]. Due to the rapid industrial growth in South Korea, the generation of the hazardous waste is increasing continuously [3]. The total generation of hazardous waste in 2010 was 3,463,240 t/year, which was an increase of 9.9% compared to the year 2005 [4].

The current hazardous waste coding system in South Korea is small [5] comparing to European hazardous waste list [1] and US hazardous waste list [6]. It needs to be further subdivided in order to harmonize it with OECD waste list [7] or with the other international coding system. Thus Ministry of Environment is in progress of converting the current classification system to harmonize it with the European hazardous waste list and to set up the regulation standards for inorganic and organic components present in the hazardous waste. To achieve this objective, the study of the detailed characterization of each form of hazardous waste belonging to each source/processes along with their leaching characteristics is needed.

A thermal process is one among the processes which contribute significantly towards generation of hazardous wastes and creation of substantial environmental pollution. Typically, 300–400 kg

Abbreviations: 1-Mnap, 1-methyl naphthalene; 2-Mnap, 2-methyl naphthalene; 3-MChl, 3-methylcholanthrene; Acne, acenaphthene; AcNy, acenapthylene; AlM, aluminium thermal metallurgy; An, anthracene; BaA, benzo(a)anthracene; BaP, benzo(a)pyrene; BbF, benzo(b)fluoranthene; BghiP, benzo(g,h,i)perylene; BkF, benzo(k)fluoranthene; Cer, manufacture of ceramic goods; Chr, crysene; CuM, copper thermal metallurgy; DBahA, dibenzo(a,h)anthracene; Fecas, casting of ferrous pieces; FGD, flue-gas dust; Fl, fluorene; FLA, fluoranthene; G, manufacture of glass and glass products; HMW-PAH, high molecular weight PAH; IP, indeno[1,2,3-c,d]pyrene; IS, iron and steel industry; LMW-PAH, low molecular weight PAH; Nap, naphthalene; NFe, other non-ferrous thermal metallurgy; NFecas, casting of non-ferrous pieces; P, power stations; PbM, lead thermal metallurgy; Phe, phenanthrene; Py, pyrene; S&F, sludges & filter cakes collected from gas treatment equipments; SW, solid waste from gas treatment equipments; T-PAH, total PAHs; ZnM, zinc thermal metallurgy.

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of slag is produced when 1 t pig iron (hot metal) in blast furnace route is produced. Similarly, the red mud generated in alumina/aluminum production is about 1–1.5 times the alumina extracted by the Bayer process and 4 times of aluminum produced by electrolytic smelting [8,9]. Thus the objective of the present work is to study the detailed characterization, leaching characteristics and possible relationship among the hazardous waste generated among thermal process involved various sectors.

In this paper we discussed about the 13 heavy metals, F^-, CN^- and 19 PAH present in the hazardous waste generated among various thermal processing units in South Korea and their leaching characteristics. It covers 11 sectors such as iron & steel (IS), aluminum thermal metallurgy (AlM), lead thermal metallurgy (PbM), zinc thermal metallurgy (ZnM), copper thermal metallurgy (CuM), other non-ferrous thermal metallurgy (NFe), casting of ferrous pieces (Fecas), casting of non-ferrous pieces (NFecas), power sector (P), glass (G) and ceramic goods (Cer) manufacturing sector. To the best of our knowledge, this may be the first study to report different heavy metals and PAH present in the hazardous waste of various thermal processing units in South Korea.

2. Materials and methods

2.1. Sampling procedure

Thermal process units for sampling were selected based on its production capacity, raw material, production process, waste treatment methods, the nature and mainly quantity of hazardous waste generated. Real time statistical data on production, collection, transportation, and treatment of designated (hazardous) waste were obtained from the "All Baro" system, which is the name of web-based Korean e-manifest system [10]. Sampling was carried out between the months of March to October 2011. In total, 95 waste samples were collected from 11 types of thermal processes. The nature (Form) of waste collected from each process was according to the hazardous waste listed in EWC code 10 [1]. Table 1 provides the details of the sampling size, thermal processing units sampled with major raw materials and end products along with the process temperature. Planning and execution of the sampling procedure are detailed in the supplementary material. Table S1 (Supplementary material) provides the details of the industry process, type of waste collected and their hazardous properties as per Annex III of Council Directive 2008/98/EC [1]. Collected samples were manually crushed and sieved through a 5 mm sieve to homogenize.

2.2. Analytical procedure

The methodology used to measure the concentration of the pollutants present in the hazardous waste is presented in Table 2. Standard solutions were purchased from PlasmaCAL and if required, diluted using distilled deionized water.

2.3. Leaching procedure

Leaching test was carried out using the Korean standard official method ES 06150 [11]. The leachate solution of pH 5.8–6.3 (adjusted with HCl) was used; the ratio of the sample to leachate volume was 1:10 (w:v); the leaching time was 6 h and agitated horizontally with 200 RPM. The leachate was pre-treated (if required) and filtered through 1 μm glass fiber filter [12].

2.4. Statistical analysis

Descriptive statistics and correlation analysis were applied to evaluate the analytical data using SPSS software (version 18). Principal component analysis (PCA) was performed with Varimax rotation with Kaiser Normalization in the study. Square Euclidian distances of standardized median values (*Z* scores) were used for cluster analysis (CA) by applying the Ward's method.

3. Results and discussion

3.1. Heavy metals distribution in the waste

The multiple box and whisker plots for the distribution of thirteen heavy metals along with F^- and CN^- concentrations among the eleven thermal processes waste are shown in Fig. 1. The normality of the data for each heavy metals in each process were checked with the skewness and kurtosis as well as Shapiro–Wilk test. Shapiro–Wilk test is more suitable for the sample size less than 50 [13]. The non-normal data were transferred logarithmically to ensure normal distribution. Most of the heavy metals showed a wide variation in their concentrations, and the highest medians were shown by Cu (3.58–209,000 mg/kg), Ni (BDL–1560 mg/kg), Pb (7.22–5132.25 mg/kg) and Zn (83.02–31,419 mg/kg) (Supplementary material Table S2).

The distribution of the heavy metals in the waste of each thermal process depends on the various factors such as process temperature [14], the type and removal efficiency of the waste gas treatment equipments, boiling point and vapor pressure of the heavy metals [15], solubility and reactivity of the metals. In the thermal processes, the metal compounds with lower boiling point are more easily vaporized [15,16] whereas higher boiling point metals remain as solid waste [17]. Sometimes, heavy metals with low boiling points may react with other elements such as oxygen, chlorine, sulfur etc. to form high boiling point species which remain as waste and vice versa [18,19].

Iron & Steel thermal process (IS) wastes showed the highest median value for the heavy metals Cd (14.76 mg/kg), Cr (166.15 mg/kg) and Hg (2.38 mg/kg) (supplementary material Table S2). IS mostly uses iron/steel scrap as the raw material which contains Cd and Hg as contaminants, thus it becomes an important source of release of these metals. Cd which evaporates during the process ends up in flue gas cleaning residues due to its tendency to adhere to particles [20].

The concentration of Hg (BDL–22.79 mg/kg) present in IS waste was much greater than any other thermal processes (Fig. 1). Hg is easily captured by wet scrubbers and particle control systems [21–24] and ends up mainly in the filter cake from the flue gas cleaning system [20]. The average Hg removal efficiency of the existing APCDs in Korea was reported to be 23–92% [25]. The mercury concentrations in the various solid wastes from five capital steel companies in Japan had been reported to be BDL–28,500 μg/kg by Fukuda et al. [26].

ZnM waste presented a relatively high median concentration of Cd (3.34 mg/kg), Sb (23 mg/kg) and Pb (5132.25 mg/kg) apart from Zn (1772.37 mg/kg) (Supplementary material Table S2). Pb is a co-product and cadmium is a byproduct of the zinc production [27]. Agrawal et al. [8] presented the summary of the waste generated in zinc plants located in India, which clearly reflected the high percentage of Zn (1.26–30), Pb (0.6–10), Cd (0.02–14) and Cu (0.02–50). Ettler et al. [28] reported the range of Pb and Zn as 235,900–305,175 and 4195–4993 mg/kg in the solid wastes of a Pb metallurgy. However, in our study we observed the range as 26,331–1,446,194 mg Pb/kg and 849–32,386 mg Zn/kg.

Compared to all the heavy metals, the median concentration of Zn (83.02–31,419 mg/kg) was much greater in almost all the thermal metallurgies (supplementary material Table S2). It has been observed that the median concentration of Zn present in CuM waste (31,419 mg/kg) was much greater than the ZnM waste

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