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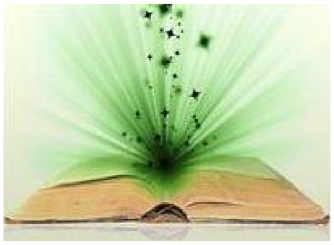

Assessment of Heavy Metals in Solid Waste Used for Electricity Generation during Pre & Post Combustion in Different Seasons

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ABSTRACT

Solid waste contains heavy metals, after combustion in waste to energy facilities is collected in fly and bottom ash, small quantity is being discharged from stack as flue gases. This study reviews the characteristics and presence of heavy metals in the solid waste used in the electricity generation units. The samples of solid waste are collected before and after combustion process to study the concentration of heavy metal presences. The range of trace metal emissions from a single waste-to-energy (WTE) facility over a period of three seasons is compared with individual tests by selected parameters indicating that the waste composition and the combustion technology employed contribute to the variability of metals and particulate emissions. Analysis of heavy metals like chromium, cadmium, mercury, arsenic, cobalt, copper, nickel, zinc, manganese, vanadium and lead is being carried out by using ICP-AES technique, the heavy metals like As and Hg in raw material and ash remains stable in pre & post combustions in contrast, the Pb, Zn and Cu tended to increase, which likely enhanced their release potential during combustion.

Keywords: Combustion, Municipal solid waste (MSW), Heavy metals

INTRODUCTION

The rapid urbanization, industrialization and increasing economic syndrome produce colossal of the solid waste, which is usually classified as municipal, industrial and biomedical waste, has been a problem in the past, has become a serious threat and herculean task in recent years and the situation is going to be a conundrum in coming years. Municipal solid waste (MSW) contains manufactured and natural materials, including paper, plastics, textiles, food wastes, yard wastes, and other organic materials, as well as inorganic materials such as glass, metals dirt and miscellaneous other components. Almost all of these components contain some quantity of the heavy metals which are categorized as toxic at certain concentrations like lead, cadmium, chromium, mercury and nickel [1]. As all the kinds of solid waste components are gathered into a landfill site and later the heavy metals in them are converged and become a new artificial sink. Therefore, the knowledge of the heavy metal contents in solid waste components and the origin of these levels are prior objectives. It is also crucial for policy making orientated at reducing heavy metal inputs to surrounding environment.

Rapid economic growth by industrialization of the developing countries in Asia has created serious problems of waste disposal due to uncontrolled and unmonitored urbanization [2]. The problem is further aggravated by the lack of financial as well human resources trained in SWM practices in the sphere of collection, transportation, processing and final disposal. Whereas aspects like recycle, reuse and recovery of the solid waste is grossly demand and supply driven or disorganized in most cases. In this scenario, the responsible persons or agencies concerned with the public health and environment protection face the crisis of ineffective MSWM.[3] Waste-To-Energy ("WTE") facilities employ a form of recycling, involving the use of solid waste as a fuel to produce steam which in turn is used to produce electricity. Nowadays, solid waste incineration plants tend to be among the most expensive solid waste management options, and they require highly skilled personnel and careful maintenance. Incineration is an efficient way to reduce the waste volume and demand for landfill space. Here during the combustion process the total volume of solid waste is reduced by 90 per cent, resulting in an ash generation of nearly 10 per cent by volume and 30 per cent by weight. In most modern WTE facilities, refuse is combusted at temperatures approaching 1800 to 2500^0 F. At this temperature, most organic materials in the solid waste are reduced to base elements such as carbon, oxygen and nitrogen. Whereas, inorganic materials such as iron, aluminium, calcium, sodium and silicates make up the major components of ash residue, along with much smaller weight fractions of heavy metals such as Pb, Cd and Zn which are regulated due to their relative toxicity and potential threat to the environment. In particular, incineration of waste containing heavy metals and so on should be avoided to maintain a suitable slag quality before energy can be recovered for heat or power consumption. Hence there is a dire necessity for monitoring the slag quality before it is used. Most of the heavy metals in untreated ash are not soluble, but are present as insoluble. Some of the environmental benefits of combusting solid waste are volume reduction, converting large amounts of solid waste material into smaller volumes, is a basic environmental protection practice that has been used for thousands of years. Many federal solid waste regulations are based on this premise and it has been a preferred solid waste management option for more than a century. Combusting municipal solid waste and converting it into energy has three basic purposes. First and foremost, the high temperatures accomplish sterilization and deny food and habitat to disease vectors such as rats and flies. Secondly, volume reduction is successfully accomplished. And thirdly, useful energy is captured. The present work focused on heavy metal analysis in solid waste samples which were collected during the pre and post combustion process[4,5].

Yu-Yang Long, Dong-Sheng Shen studied the MSW components which are complicated and significantly different. Components of PL(plastic), PA (paper), AS (ash) and KW (kitchen waste) have high universality in MSW and accounted for 55.1–95.5% in each MSW sample. These four components are also the main heavy metal sources of MSW, which accounted for 76.3% and

82.3% contribution of the Cu and Zn contents respectively. The contents of Cu and Zn in the gross MSW sample were 41.2–1643.7 mg $.kg^{-1}$ and 109.3–1077.9 mg $.kg^{-1}$ respectively, which on different degree exceeded the set standard for "environmental quality standard for soil" (Cu, 100 $mg.kg^{-1}$; Zn, 400 $mg.kg^{-1}$) of China and have high potential of environmental risk. The heavy metal contents in the gross MSW do not have significant spatial variation but has high seasonal variation, significantly higher in summer than winter ($P < 0.01$). Much more attention should be paid on the MSW management in summer to avoid heavy metal pollution[6].

P. Flyhammar studied heavy metal transformation in municipal solid waste and come to conclusion that the available and reactive heavy metal binding forms are changed under anoxic conditions in a MSW deposit. Assuming that the fractionation patterns of the fresh MSW show the dissolution of exposed lattice structures and surface forms which are stable under toxic conditions, the fractionation patterns of the de- graded waste imply the importance of other solid phases. The accumulation of heavy metals in phases which are stable under anoxic conditions creates reservoirs of heavy metals which may be mobilized under changing conditions. The results indicate that potentially available and reactive phases containing heavy metals constitute only a few percent of the total content of heavy metals such as Pb, Cr, Ni and Cd, while the percentage for Cu and Zn are expected to be higher [7].

Dong-Qing Zhang, Hua Zhang, Chang-Lin Wu, Li-Ming Shao, Pin-Jing He studied that Bio-drying significantly increased the LHV (lower heating value) of Municipal solid waste (MSW) and decreased its water content. Organics degradation led to the concentration of heavy metals in MSW during bio-drying and the increasing amounts of heavy metals per kg of bio-dried MSW transferred into combustion flue gas, especially in the Aerobic treatment which obtained the greatest organics degradation and least leachate production. Nevertheless, bio-drying and metal speciation had little effect on the transfer and partitioning of As and Hg during combustion due to their volatility, and their partitioning ratios in flue gas remained constant. In contrast, those of Pb, Zn, and Cu tended to increase during bio-drying, contributing to their speciation variation (Pb–OMB, Zn–FeMnOX, Cu–OMB, and Cu– FeMnOX) in OFMSW during bio-drying. This would further affect their transfer and partitioning behavior during combustion. Aerobic and Combined 1 showed the largest and the least increase of metal transfer respectively [8].

Kuen-Sheng Wang studied the heavy metal content of the physical component of municipal solid waste in Taiwan and heavy metal partitioning between flue gases, fly ash and bottom ash after burning. The results indicate that the heavy metal in the noncombustible components of the MSW (i.e. glass, metals, dirt, and ashes) are 20-100 times the amounts in the combustibles for the targeted heavy metals Pb, Cd, Cr, Cu and Zn. The mass burning of local MSW, partitions more than 80 percent of the refractory volatile Cu and Cr to the bottom ash. The medium volatile Pb and Zn are found to be approximately equally partitioned between the bottom ash and the fly ash. However, highly volatile Cd is partitioned more than 70 percent to the fly ash. The results suggest that the source separation of noncombustible components including glass, metals, dirt and ashes from the local MSW may be an effective means and an urgent and utmost priority for the reduction of the partitioning of heavy metals to the incineration discharges. By removing these inert substances the heavy metal discharge from the incineration process can be comparatively reduced to less than 5 percent of the amount generated by mass burning [9].

Tawach Prechthai studied the leaching potential of heavy metals contaminate in the dumpsite was determined through solid waste characterization, sequential extraction analysis, TCLP test and leachate quality analysis. The concentrations of heavy metals in the waste were in the following order: Zn > Cu > Mn > Cr > Pb > Ni > Cd > Hg. In the case of mobility potential, Zn, Cu and Mn showed relatively high mobility potential compared to other metals. From the TCLP test the leaching potential of carbonate bound Mn, Zn and Cd when the pH level of dumpsite is decreased was proved. On the other hand, the heavy metal concentration in the actual leachate was different from that of the leachate from boreholes and from the results for the mobility potential based on different forms. The leachate quality analysis showed heterogeneity of solid waste age and the methanogenic condition in dumpsite. The possible dissolution of carbonate bound metals is expected to be low from the pH values determined for solid waste and leachate. The presence of optimum moisture content in the waste has influenced the degradation rate generating organic acid. This has enhanced the concentration of heavy metal especially Cu, Cr and Ni in leachate runoff.

Although the concentration of all the metals except for Cr in the runoff leachate was below the effluent standards, potential of these metals to be toxic to the plant species were revealed from the toxicity test. Therefore, the focus on the removal of heavy metals from the leachate in the present condition is necessary [10].

The main objective of the study is to investigate the most conventional heavy metals such as As, Cd, Co, Hg, Ni, Pb, Sb, Se, Sn, Ti and V which are present with extensive distribution in many kinds of solid waste components by using ICP-AES technique. The present investigation aims to provide reference information on solid waste management and heavy metal pollution control.

MATERIALS AND METHODS

Waste Sampling : The procedure for waste sampling has been followed considering guidelines from Manual on Municipal Solid Waste Management, Government of India, Ministry of Urban Development; Central Public Health and Environmental Engineering Organization (CPHEEO) Waste samples have been prepared from the freshly arrived waste at the SWDS. Samples have been collected from 10 selected incoming vehicles (identified tipper trucks carrying waste from representative generation sources using quartering & coning method). An approximate of 8 – 10 kg of sample is prepared from one or more such representative vehicle. The sample is then sorted and segregate into desired parameters for waste composition as per IPCC1 guidelines namely; Food Waste, Wood & Wood Products, Paper and Cardboard, Textiles, Park & Garden Yard, Glass, Plastic, Metal, other Inert Matter.

Quartering and coning method: The technique involves pouring the sample into a conical shape, and then dividing into quarters; the two quarters separated on opposite to one another are discarded, while the other two are combined and constitute the reduced sample. The sample process is continued until an appropriate sample size is prepared. Analysis was made with respect to the sample left behind.

Proximate and ultimate analysis of solid waste

Determination of moisture, volatile matter, ash and fixed carbon in solid waste comprises its proximate analysis.

Determination of moisture content: Loss in weight of solid waste caused by heating of weighed quantity of the sample for an hour at 105°C is the moisture content in the solid waste. A known amount of finely powered sample is kept in a silica crucible and heated in a muffle furnace at 105-110°C for an hour. Thereafter the crucible is taken out, cooled in desiccators and weighed. The process of heating, cooling and weighing is repeated a number of times till constant weight of sample (anhydrous) is achieved. The percentage of moisture is given by

$$\text{\% moisture in sample} = \frac{\text{loss in weight of sample}}{\text{Weight of sample initially taken}} \text{ X100}$$

Determination of volatile matter in sample : It is the loss in weight of moisture free powered solid waste when heated in a crucible fitted with cover in a muffle furnace at 950°C for 7 minutes.

$$\text{\% volatiles in sample} = \frac{\text{loss in weight of moisture free sample}}{\text{Weight of moisture free sample}} \text{ X 100}$$

Determination of ash in sample : It is the weight of residue obtained after burning a weighed quantity of sample in an open crucible (i.e., presence of air) at 750°C in a muffle furnace till a constant weight is achieved.

$$\text{\% ash in sample} = \frac{\text{weight of residue ash formed}}{\text{weight of sample initially taken}} \text{ X 100}$$

Determination of fixed carbon : It is determined indirectly by deducting the sum total of moisture, volatile matter and ash percentage from 100.

% fixed carbon in sample = 100 – (% moisture + % volatile matter + % ash)

Ultimate analysis of solid sample

Determination of total carbon, hydrogen, nitrogen, oxygen and sulphur percentage in solid waste comprises its ultimate analysis.

Determination of carbon and hydrogen in solid waste: A known amount of sample is burnt in a current of dry oxygen thereby converting C and H of coal into CO_2 ($C + O_2 = CO_2$) and H_2O ($H+½O_2= H_2O$) respectively. The products of combustion (CO_2 and H_2O) are passed over weighed tubes of anhydrous calcium chloride and potassium hydroxide which absorb H_2O and CO_2 respectively. The increase in the $CaCl_2$ tube represents the weight of water (H_2O) formed while increase in the weight of KOH tube represents the weight of CO_2 formed.

% of Hydrogen (H) and carbon (C) in solid waste can be calculated as below

Let, x = weight of solid waste sample taken
y = increase in the weight of $CaCl_2$ tube
z= increase in the weight of KOH tube

Therefore, the amount of carbon in the coal sample = 12/44 X z since 44 grams of CO_2 is produced from 12 grms of carbon and 32 grms of oxygen.

Determination of Nitrogen in Solid Sample: Nitrogen estimation in solid sample is done by Kjeldahal's method. A known weight of powered sample is heated with concentrated sulphuric acid in presence of potassium sulphate and copper sulphate in long necked flash (called Kjeldahal's flask) thereby converting nitrogen of coal to ammonium sulphate. When clear solution is obtained (i.e., when whole nitrogen is converted into ammonium sulphate) it is treated with 50% NaOH solution. The ammonia thus formed is distilled over and absorbed in a known quantity of standard sulphuric acid solution. The volume of unused sulphuric acid is then determined by titrating against standard acid solution. Thus, the amount of acid neutralized by liberated ammonia (from the sample) is determined.

$$\% \text{ of nitrogen in solid sample} = \frac{\text{volume of acid used X normality}}{\text{Weight of sample taken}} \text{ X } 1.4$$

Since, $(NH_4)_2 SO_4 + 2NaOH = Na_2SO_4 + 2NH_4OH$

One litre of 0.1N H_2SO_4 consumed is equivalent to 0.1 gm mole of ammonia or 1.4 gm of nitrogen.

Volume of acid used = $V_1 - V_2$

Where V_1 = volume of H_2SO_4 neutralized in blank, c.c.

V_2 = volume of H_2SO_4 neutralized in determination, c.c

Determination of Sulphur in solid sample: A known quantity of solid sample is burnt completely in bomb calorimeter in a current of oxygen. Ash, thus obtained contains sulphur of the sample as sulphate which is extracted with dilute hydrochloric acid and extract is treated with barium chloride solution to precipitate the sulphate as barium sulphate

$$S \xrightarrow{O_2} SO_4 = \xrightarrow{BaCl_2} BaSO_4$$

The precipitate of $BaSO_4$ is filtered, washed, dried and weighed from which the sulphur in solid sample can be computed as follows:

32 grams of Sulphur in the solid sample will give 233 grams $BaSO_4$

If, x = weight of solid sample taken

y= weight of $BaSO_4$ precipitate formed

then, amount of sulphur in sample = 32y / 233 = 0.1374 y

So % of sulphur in sample = 0.1374y/x X 100

Alternative method for sulphur determination: A known quantity of coal is heated with Eschka mixture (which consists of 2 parts of MgO and 1 part of anhydrous Na_2CO_3) at 800°C. the sulphate formed is precipitated as $BaSO_4$ (by treating with $BaCl_2$) and it is weighed as done in previous method of sulphur determination.

% of sulphur in sample = 0.1374 y/x X 100

Where x=weight of coal sample taken

y= weight of $BaSO_4$ precipitate formed

Determination of Oxygen in solid sample : It is deduced indirectly as follows:

% oxygen in solid sample = 100 – (% of C + H + N+ S+ ash)

ANALYSIS OF HEAVY METALS USING ICP-AES

Sample Preparation Procedure

Wet Digestion Procedure : Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned to minimize the potential of cross-contamination. For each Digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

For the digestion of samples for analysis by AAS or ICP, add 10 ml of 1:1 HNO_3 & 10 ml of 1:1 HCl mix the slurry, and cover with a watch glass or vapour recovery device. Heat the sample to 95◦C ± 5◦C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 ml of concentrated HNO_3 , replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 ml of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapour recovery system, either allows the solution to evaporate to approximately 5 ml without boiling or heat at 95◦C ± 5◦C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

After the sample has cooled, add 2 ml of water and 3 ml of 30% H_2O_2. Cover the vessel with a watch glass or vapour recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cools the vessel. Continue to add 30% H_2O_2in 1-ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total of 10 ml 30% H_2O_2 .

Cover the sample with a ribbed watch glass or vapour recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 ml or heat at 95◦C ± 5◦C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times. Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95◦C ± 5◦C in 6 minutes and remain at 95◦C ± 5◦C without boiling for 10 minutes.

After cooling, dilute to 100 ml with water. Particulates in the digestate should be removed by filtration, or by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by ICP-AES.

Steps of analysis in ICP-AES : The main steps in analyzing samples by ICP-AES are described below:

The elements to be determined are selected. Solutions of samples are prepared using the conventional techniques of quantitative chemical analysis. A set of calibrating solutions is prepared. Each solution contains accurately known concentrations of the analyte elements, and the range of concentrations for each element in the set is chosen to include the expected concentration of that element in the sample solutions. The calibrating solutions and sample solutions are sprayed into the plasma and the intensities of appropriate emission lines are recorded. Calibration graphs (‘analytical working curves’) are prepared for each element from the emission intensities of the calibrating solutions. The concentrations of the elements in each sample solution are determined from the calibration graphs. The concentrations in the original sample are then calculated from the measured concentrations of the elements in the sample solution and the known dilution factor.

Automated spectrometers, with computers and programmable sample changers, are generally used. This can make steps 4 to 6 automatic, greatly simplifying the task of the operator and increasing the speed of analysis.

Sample Introduction : For most analyses the liquid sample is pumped into a pneumatic nebulizer, where it is converted to a fine aerosol by a stream of argon. After passing through a spray chamber to remove unfavourably large droplets, the aerosol enters the plasma through the inner, or injector, tube of the plasma torch. Sample introduction will be covered in more detail in a subsequent chapter.

Plasma Torch : The plasma is formed in a fused-silica torch consisting of three concentric tubes. The main argon stream (the plasma gas) is introduced tangentially between the intermediate tube and the outer tube. This confines the plasma and helps prevent the torch from overheating. A plasma is initiated by a brief spark discharge into this gas stream. In the induction coil region electrons from the spark provide a path for energy transfer between the coil and the argon, and self-sustaining plasma is quickly established. Energy is transferred into the plasma most effectively in the outer regions of the plasma, nearest the coil. As a result, the lower part of the plasma assumes a ‘doughnut’ shape.

The argon stream carrying the sample aerosol, emerging from the innermost tube, passes into the central ‘hole’ in the base of the plasma and forms a distinctive axial channel through the plasma. An intermediate gas flow, provided in the space between the inner tube and the intermediate tube, is useful in stabilizing the plasma under certain circumstances, such as when the analytical solutions contain organic solvents. A small flow of oxygen added to the argon intermediate gas is particularly useful in eliminating the problems of plasma instability, carbon build-up and spectral interference that can otherwise occur in the analysis of organic solutions.

Radio Frequency Supply : The basic circuit for a RF generator is simple, consisting of a capacitor and inductor in either a series or parallel configuration. This is called a ‘tank circuit’ and is tuned to resonate at the desired operating frequency. Radio-frequency generators are grouped into two categories, depending on whether the resonant circuit acts as an amplifier or as an oscillator. In modern practice, the power stability of both types of generator can be controlled to better than 0.1%. Operating frequencies are commonly either 27.12 MHz or 40.68 MHz, which are frequencies set aside in most countries for industrial use. The higher frequency is increasingly preferred for ICP-AES, because the plasma is less disturbed by the introduction of different materials into the central channel.

Optical Spectrometer : ICP-AES instruments detect and measure many analytical lines simultaneously, while others operate sequentially. Simultaneous instruments use some type of polychromator, with a detector for each analytical wavelength. These instruments are capable of impressive speed, but they are limited to measurements at pre-selected lines that are usually rather difficult to change. Simultaneous instruments are best suited for laboratories needing to determine the same set of elements routinely in the same sorts of samples. An optimized set of analytical wavelengths can then be chosen to suit both the elements and the samples. Sequential instruments offer complete freedom of choice in the selection of wavelengths, at the expense of speed of measurement. Sequential ICP-AES instruments are also generally smaller and less costly. Because of the benefits in cost, size and versatility, fast sequential spectrometers have become the more widely used optical spectrometers in ICP-AES.

Detector and Readout System : Of last, the photometric detectors in ICP-AES are almost universally photomultiplier tubes. They show extremely high photometric sensitivity while at the same time the dark current (the current generated while the device is in total darkness) is very low. The maximum usable current is usually about 100 million times the dark current. There is much more interest in applying the new generation of solid state optical detectors in ICP-AES.

RESULTS AND DISCUSSION

Proximate analysis of MSW and RDF : The proximate analysis of municipal solid waste collected and after processing to Reduce Derived Fluff (RDF) is presented in table I, which is self explanatory of itself.

Table I

Sl. No.	**Characteristics**	**Values**	**Fresh MSW**	**RDF**
1	Moisture content	%	18.96	21.24
2	Volatile matter	%	48.18	46.05
3	Ash content	%	16.28	15.49
4	Fixed carbon	%	16.58	17.22
5	GCV	Kcal/kg	1488	1562
6	C:N ratio	--	38:1.2	37:1.4

Physical Characteristics of Municipal Solid Waste : The physical characteristics of municipal solid waste are presented in the table II. Municipal solid waste is processed in the processing unit and it is reduced into small portion known as Reduce derived fluff (RDF).

Table II Physical Characteristics of municipal Solid Waste

Reduce Derived Fluff		
Sl. No.	**Characteristics**	**Values (%)**
1	Moisture content	2.40
2	Volatile matter	76.23
3	Ash content	1.92
4	Fixed carbon	19.45
5	GCV	2352.00 (kcal/kg)
6	PH	5.26
7	Carbon	61.50
8	Hydrogen	3.90

9	Sulphur	0.50
10	Oxygen	32.14
11	Mineral matter	1.96

The table presents that the gross calorific value (GCV) is 2352 kcal/kg which implies that it increases the heating capacity of the fuel to use in the combustion process, followed by volatile matter is 76.23%, carbon is 61.50%, oxygen is 32.14% and fixed carbon is 19.45% giving boost for the burning process. The moisture content is 2.40% implying more heating capacity. The pH is acidic at 5.26% indicating the acidic nature of solid waste. The remaining units have lower concentrations but innocuous and act as catalyst.

Physical Characteristics of Fly Ash : The physical characteristics of fly ash generated after combustion process are shown in table 3 where it is observed that after the burning of solid waste the moisture content, volatile matter, carbon, hydrogen, oxygen decreases implying the reduction of re-burning capacity. The increase in pH showing the solid waste after combustion turns to alkaline.

Table III Physical Characteristics of Fly Ash generated after Combustion

Sl. No.	Characteristics	Values (%)
1	Moisture content	2.26
2	Volatile matter	0.62
3	Ash content	93.62
4	Fixed carbon	3.50
5	GCV	82.00 (kcal./kg)
6	pH	9.52
7	Carbon	2.62
8	Hydrogen	0.54
9	Sulphur	0.04
10	Oxygen	1.06
11	Mineral matter	95.74

Gross Calorific Value of the waste : GCV of all the material available in the sample municipal solid waste is analysed before and after processing the waste to Reduce Derived Fluff (RDF) which contains textile, plastic and plastic products, pulp paper and cardboard, Food Waste, Metal, other Inert Matter. The gross calorific values of the each and every material present municipal solid waste presented in the table IV:

Table IV Gross Calorific Values of the each and every material present in municipal Solid waste (MSW) in Kcal/kg

Sl.No.	Sample particulars	Result of fresh MSW	Result of RDF
1	Textile	1720	1482
2	Plastic and plastic products	1448	1213
3	pulp, paper and cardboard	2960	3546
4	Wood and wood products	2244	1944
5	Food, food waste, beverages and tobacco	926	784
6	Glass, metal and other inert matter	402	424
7	Garden yard and park waste, straw, packing waste etc	1262	1388
8	Rubber	1324	1510
9	Thermocol	2782	2274

The major components of fresh municipal solid waste are pulp, paper and cardboard (2960kcal/kg), thermocol (2782 kcal/kg), Wood and wood products(2244 kcal/kg), textile(1720 kcal/kg), Plastic and plastic products(1448 kcal/kg) and rubber(1324 kcal/kg). The concentration of other components is very low compared to the above components.

Heavy Metals

Summer Season : The concentration of heavy metals during pre and post combustion in summer has been estimated and presented in the table V.

Table V Heavy Metals during Pre and Post combustion in Summer (values in ppm)

Sl.No.	Heavy Metals	Pre- combustion MSW	Post-combustion MSW
1	Cadmium	3.8	29.7
2	Cobalt	1.2	9.7
3	Chromium	4.9	52.4
4	Copper	16.2	164.2
5	Arsenic	3.5	0.9
6	Manganese	19.6	72.4
7	Nickel	8.9	42.4
8	Lead	18.7	96.4
9	Zinc	19.4	132.6
10	Mercury	<0.1	<0.1
11	Vanadium	12.6	64.9

The table shows that the concentration of heavy metals during pre combustion in summer was very low and highest concentration is observed in manganese at 19.6 ppm, zinc at 19.4 ppm, lead at 18.7 ppm, copper at 16.2 ppm and vanadium at 12.6 ppm. The concentration of other elements is rather low. In post combustion the concentrations of the elements enriched due to some of the reasons like, various materials present in the municipal solid waste in the area selected for the study, implementing proper source segregation of waste before processing to RDF. The zinc concentration abnormally increased from 19.4 ppm in pre combustion to 132.6 ppm in post combustion, copper from 16.2 ppm to 164.2 ppm, lead from 18.7 ppm to 96.4 ppm, manganese from 19.6 ppm to 72.4 ppm. The concentration of majority the elements has been increased. On the contrary, the concentration of arsenic decreased from 3.5 ppm in precombustion to 0.9 ppm in post combustion whereas the concentration of mercury did change but static at < 0.1 ppm.

Winter Season : The concentration of heavy metals during pre and post combustion in winter has been estimated and presented in the table VI.

Table VI Heavy Metals during Pre and Post combustion in Winter (values in ppm)

Sl.No.	Heavy Metals	Pre-combustion MSW	Post-combustion MSW
1	Cadmium	2.8	26.8
2	Cobalt	<0.1	<0.1
3	Chromium	3.9	42.8
4	Copper	11.9	126.4
5	Arsenic	3.2	0.5
6	Manganese	14.8	49.4
7	Nickel	7.2	40.1
8	Lead	13.9	90.9
9	Zinc	12.6	98.3
10	Mercury	<0.1	<0.1
11	Vanadium	7.1	34.8

The table shows that the concentration of heavy metals during pre combustion in winter was very low and highest concentration is observed in manganese at 14.8 ppm, lead at 13.9 ppm, zinc at 12.6 ppm, copper at 11.9 ppm, nickel at 7.2 ppm and vanadium at 7.1 ppm. The concentration of other elements is rather low. In post combustion the concentrations of the elements enriched due to presence of moisture content in the solid waste which can be eliminated by proper solar drying of the waste before processing and using it to generate electricity. The copper concentration abnormally increased from 11.9 ppm in pre combustion to 126.4 ppm in post combustion, zinc from 12.6 ppm to 98.3 ppm, lead from 13.9 ppm to 90.9 ppm, manganese from 14.8 ppm to 49.4 ppm. The concentration of majority the elements has been increased. On the contrary, the concentration of arsenic decreased from 3.5 ppm in precombustion to 0.5 ppm in post combustion whereas the concentration of cobalt and mercury did change but static at < 0.1 ppm.

Monsoon Season : The concentration of heavy metals during pre and post combustion in monsoon has been estimated and presented in the table VII.

Table VII Heavy Metals during Pre and Post combustion in Monsoon (values in ppm)

Sl.No.	Heavy Metals	Pre-combustion MSW	Post combustion MSW
1	Cadmium	1.9	17.168
2	Cobalt	<0.1	<0.1
3	Chromium	2.8	35.3
4	Copper	8.6	111.6
5	Arsenic	2.6	0.8
6	Manganese	18.5	65.9
7	Nickel	9.04	36.8
8	Lead	11.1	87.2
9	Zinc	9.6	80.4
10	Mercury	<0.1	<0.1
11	Vanadium	8.2	42.8

The table shows that the concentration of heavy metals during pre combustion in monsoon was very low and highest concentration is observed in manganese at 18.5 ppm, lead at 11.1 ppm, zinc at 9.04 ppm, nickel at 9.04 ppm copper at 8.6 ppm and vanadium at 8.2 ppm. The concentration of other elements is rather low. In post combustion the concentrations of the elements enriched due to the presence of water content in the waste which may lead to leaching of the metals for which proper steps needs to be taken for processing the waste and utilizing in the power plant in monsoon season like proper drying process should be implemented before processing the waste to RDF and see that using the same in power plant does not contain moisture while transferring it from the processing unit, proper storage of waste needs to be checked, proper collection and storage of ash should also be taken care as if ash left in the rain it may lead to ground water contamination. The copper concentration abnormally increased from 8.6 ppm in pre combustion to 111.6 ppm in post combustion, zinc from 9.6 ppm to 80.4 ppm, lead from 11.1 ppm to 87.2 ppm, manganese from 18.5 ppm to 65.9 ppm. The concentration of majority the elements has been increased. On the contrary, the concentration of arsenic decreased from 2.6 ppm in pre-combustion to 0.8 ppm in post combustion whereas the concentration of cobalt and mercury did change but static at < 0.1 ppm.

The results show that the heavy metals in summer season have increased from monsoon season due to the heat and dryness observed in the atmosphere and has more dominating capacity which also has more reacting features as the climate supports. But there seems lot of change in the concentration of certain heavy metals between post and pre combustion. The highest change is observed in case of chromium, copper, lead, vanadium, zinc, and cobalt. On the contrary, there is no change in case of mercury which may be due to less use of material containing mercury in the area selected for the study. There is an abnormal increase in copper, manganese, Zinc and vanadium but no change in cadmium, arsenic and mercury from pre combustion to post combustion in summer season. In winter season the concentration of heavy metals of cobalt manganese, lead, zinc and vanadium has increased but there is change in cadmium, arsenic and mercury. Moreover, there is no change in the concentration of these four heavy metals, viz. cadmium, arsenic and zinc from summer to winter season. The heavy metals in monsoon season were at low concentration. But among them, high concentration is observed in manganese, zinc, lead and vanadium in pre combustion agriculture waste. But the concentration remained unchanged in cadmium, arsenic and mercury. The concentration abnormally changed in post combustion in case of cobalt, zinc, manganese, vanadium, lead and copper.

APPLICATIONS

This investigation useful to provide reference information on solid waste management and heavy metal pollution control and variations in concentrations of heavy metals season wise, precombustion and post combustion of agricultural waste.

CONCLUSION

The rapid urbanization, industrialization and increasing economic syndrome produce heaps of solid waste. Waste-To-Energy ("WTE") facilities employ a form of recycling, involving the use of solid waste as a fuel to produce steam which in turn is used to produce electricity. The highest change is observed in case of chromium, copper, lead, vanadium, zinc, and cobalt. On the contrary, there is no change in case of mercury. There is an abnormal increase in copper, manganese, Zinc and vanadium but no change in cadmium, arsenic and mercury from pre combustion to post combustion in summer season. The concentration abnormally changed in post combustion in case of cobalt, zinc, manganese, vanadium, lead and copper.

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